

Review

Application Prospect of K Used for Catalytic Removal of NO_x, CO_x, and VOCs from Industrial Flue Gas: A Review

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Abstract: NO_x, CO_x, and volatile organic compounds (VOCs) widely exist in motor vehicle exhaust, coke oven flue gas, sintering flue gas, and pelletizing flue gas. Potassium species have an excellent promotion effect on various catalytic reactions for the treatment of these pollutants. This work reviews the promotion effects of potassium species on the reaction processes, including adsorption, desorption, the pathway and selectivity of reaction, recovery of active center, and effects on the properties of catalysts, including basicity, electron donor characteristics, redox property, active center, stability, and strong metal-to support interaction. The suggestions about how to improve the promotion effects of potassium species in various catalytic reactions are put forward, which involve controlling carriers, content, preparation methods and reaction conditions. The promotion effects of different alkali metals are also compared. The article number about commonly used active metals and promotion ways are also analyzed by bibliometric on NO_x, CO_x, and VOCs. The promotion mechanism of potassium species on various reactions is similar; therefore, the application prospect of potassium species for the coupling control of multi-pollutants in industrial flue gas at low-temperature is described.

Keywords: potassium; NO_x; CO_x; VOCs; catalytic removal



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1. Introduction

NO_x, CO, CO₂, and volatile organic compounds (VOCs) are widely present in industrial flue gas and motor vehicle exhaust. Soot is widely present in diesel vehicle exhaust. The typical contents of these pollutants are shown in Table 1. The annual emissions from 2006 to 2015 of these pollutants in China are shown in the Figure 1. In 2015 year, emissions of SO₂, NO_x and soot reached 18.59, 18.51, and 15.38 million tons, respectively. Comparing the total emissions, industrial emissions account for nearly 2/3. And the emission of CO₂ in 2015 was 9.72 billion tons. Furthermore, the emission of CO and nonmethane volatile organic compounds (NMVOCs) reached 188.00 and 28.43 million tons, respectively. These pollutants are harmful to the atmospheric environment and human health. Emission of SO₂ results in acid rain pollution. CO, NO, and VOCs promote the formation of photochemical smog. Soot and VOCs also contribute to haze [1,2]. CO₂, N₂O, and soot will cause global warming. The global warming potential of N₂O is 310 times higher than that of CO₂ [3], and soot is theoretically the second largest global warming factor after CO₂ due to its radiative forcing effect [1,4]. NO_x also causes ozone layer destruction and acid rain [5]. In

addition, NO_x , CO, and VOCs cause human poisoning. Soot and VOCs cause cancer [6,7]. And soot has a greater impact on the human respiratory system.

Table 1. The content of various pollutants in various gases.

Components	Sintering Flue Gas	Pelletizing Flue Gas	Coke Oven Flue Gas	Motor Vehicle Exhaust
NO_x (mg/m^3)	200–400	200–300	300–1000	500–4000
Soot (g/m^3)	1–5	1–10	0.02–0.1	2–6 *
CO (%)	0.3–1	0.6–1	0.04–0.8	1–8
CO_2 (%)	3–7	1–1.5	4–5	6–16
NMVOCs (g/m^3)	0.5–5	6–18	15–20	1–50

* This represents the content of diesel engines.

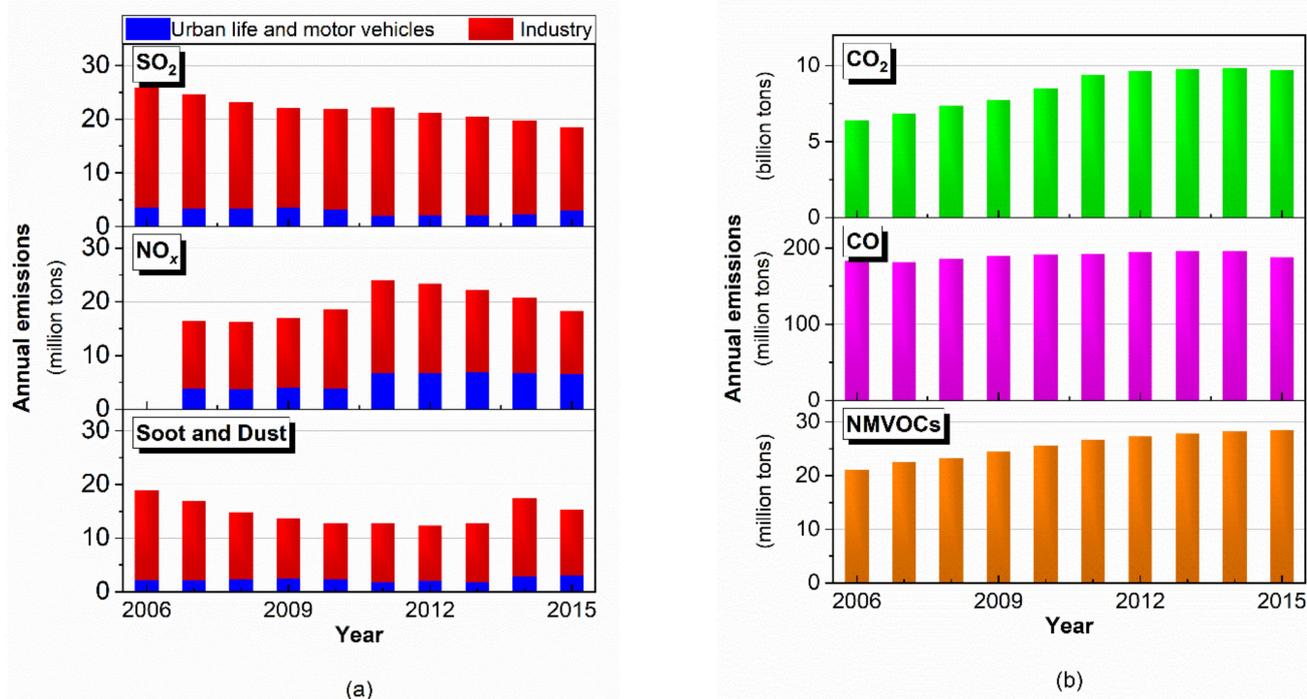


Figure 1. Various pollutant emissions in China from 2006 to 2015 [8–10]. (a) the annual emissions of SO_2 , NO_x and soot in china, and (b) the annual emissions of CO_2 , CO and NMVOCs in china.

There are some ways to remove the above pollutants. Commonly used desulfurization methods include limestone-gypsum technology, rotary spray drying adsorption technology and activated carbon purification technology, which belong to acid-base reaction or adsorption method. However, catalytic reaction is commonly used for the removal of NO_x , CO_x ($x = 0, 1, 2$), and VOCs, such as catalytic decomposition, reduction, and oxidation. The decomposition of NO_x does not require the addition of reducing agents, which is economical and convenient. In particular, the dissociation of N_2O is the most commonly used removal method in the production of adipic acid and nitric acid [3]. Selective catalytic reduction (SCR) of NO_x by NH_3 is widely used in industrial flue gas and motor vehicle exhaust purification. Catalytic oxidation is commonly used to remove multi-pollutants, such as soot, CO, and VOCs, in motor vehicle exhaust and industrial exhaust gas for removal pollutant [11,12]. The preferential oxidation of CO (PROX) is used to purify H_2 for fuel cells [13]. Water-gas shift (WGS), reverse water-gas shift (RWGS), partial oxidation of VOCs and the reforming of VOCs are some effective reuse methods. WGS is an important chemical reaction to produce and purify H_2 , and WGS can adjust the H_2/CO ratio for Fischer-Tropsch synthesis [14]. RWGS uses CO_2 as a raw material to produce CO, and further produce other chemical raw materials through Fischer-Tropsch synthesis [15]. Partial

oxidation of VOCs and reforming of VOCs are the important ways to produce chemical raw materials. For example, partially oxidizing VOCs will produce cyclopropane and hydrogen [16,17]. The CO₂ reforming of methane is considered the most popular way to produce syngas [18]. And the steam reforming of methanol is a recognized H₂ production process [19].

Removal and reuse methods for these pollutants are often applied in separate modular units existing in industrial flue gas and motor vehicle exhaust. Although the role of potassium species (marked as K) has been found in many reactions, systematic summary and analysis are lacking. The use of the difference in the oxidation-reduction properties of pollutants for coupling control has been favored by more and more researchers [20,21]. Systematic summary and analysis are beneficial to provide K with more favorable support in the catalytic control of multiple pollutants, and the research direction can be better discovered.

In this work, the recent research progress of K on the catalytic reaction process and the properties of catalysts related to the removal and reuse of NO_x, CO_x (x = 0, 1, 2), and VOCs are reviewed. Finally, the connections between the commonly used metals and the action mechanism with pollutants are established. The factors affecting the modification process are also summarized. And the future research direction is prospected.

2. The Removal of NO_x

The removal of NO_x has been widely studied, including NO decomposition, NO reduction, NO oxidation, and N₂O decomposition. And NO reduction and N₂O decomposition have been widely applied in industrial flue gas [22].

2.1. N₂O Decomposition

The N₂O decomposition is the process of adsorbing N₂O by catalyst, breaking N–O bond and decomposing N₂O into N₂ and O₂, as shown in Equation (1). This is the most commonly used method for N₂O treatment in adipic acid and nitric acid plants. The commonly used catalysts include Co-based and Cu-based catalysts, and the reaction conditions are shown in Table 2. The reaction consists of four steps, the adsorption of N₂O on the catalyst, the breaking of N–O bond to form N_(ads) and O_(ads), the adjacent N_(ads) and O_(ads) formed on the surface combine with each other to form N₂ and O₂, respectively, and the desorption of N₂ and O₂ from the surface.



2.1.1. Promotion Effects of K on Reaction Process

K has a promotion effect on the N₂O decomposition [23,24]. K promotes the adsorption and dissociation of N₂O. Some researchers have proposed that the electronic actions of alkaline cations enhance the bonds of adsorbates (such as N₂O, NO) to accept metal electrons, and then enhance the adsorption of N₂O on Pt/Al₂O₃ and improve the dissociation activity of N₂O [25]. K also promotes the formation of oxygen vacancies on TiO₂ carrier [26,27]. Moreover, oxygen vacancy on the surface of catalyst is considered to promote N₂O adsorption [3,28]. The effect of K promoter on the N₂O decomposition is also shown in promoting the dissociation of N–O bond, the limiting step of N₂O decomposition [29], through donating electrons [30] and promoting the enrichment of surface electrons [31–33].

The addition of K plays a positive role on the dissociation and desorption of O₂ in the process of N₂O decomposition. Adding K to the Co₃O₄ catalyst promotes the oxidation regeneration of Co²⁺ by oxygen dissociated from N₂O [34], since K promotes the dissociation of O₂. Through temperature-programmed reductions with hydrogen (H₂-TPR) test, it is found that the addition of K to Co–Mn–Al catalyst improves the oxygen migration onto the catalyst surface and the desorption ability of O₂ [35]. In addition, K promotes the desorption of O₂ by improving the reducibility of the catalyst [36–38], such as K, promotes

the transfer of Ir^0 to Ir^+ [39]. The promotion effect of K is also shown in accelerating the recovery of active sites in the redox process, and then the K has a promotion effect on the desorption of O_2 . These two factors together increase the catalytic dissociation activity of N_2O .

2.1.2. Promotion Effects of K on Catalyst Properties

In addition to the reaction process, K affects the electronic properties of the catalyst, such as ionization potential and work function, as well as redox properties. The effect of alkali metals on donated electrons to improve the activity of N_2O decomposition has been found on a variety of catalysts, such as Co_3O_4 [40], $\text{Co}_3\text{O}_4\text{-CeO}_2$ [41], Cu-Co spinels [42], Co-Zn-Ce mixed oxides [43], $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ [44], CoAl hydrotalcites [45], NiO [46], and NiAl hydrotalcites [47]. Among them, the excellent promotion effect of K on the decomposition activity of N_2O on Co-based catalysts has been confirmed by many researchers [48–51]. The promotion effect of K is related to their ionization potential and transferring charge to the catalyst, which leads to the decrease of the binding energy [29]. X-ray photoelectron spectroscopy (XPS) results show that the addition of K increases the electron density of the catalyst and promotes the transition of metal electronic state from high valence state to low valence state on Co-based catalysts [52]. It can also be explained that basic cations (K^+) provide electrons to surrounding oxygen anions (O^{2-}), and further transfer charge to Co, Mn, and Al [34].

It is found that the addition of K_2O reduces the bond energy on Mg/Zn-Ce-Co catalyst, and increases the electron cloud density near Co and promotes the catalytic activity [43]. A large number of studies have shown that the removal activity of N_2O is related to the surface work function [53–56]. Due to its low ionization potential, K significantly reduces the work function of the catalyst by forming a $\text{K}^{n+}\text{-O}^{n-}$ dipole moment [35], provides electrons to the N_2O molecule through the catalyst surface, and activates the adsorption and dissociation of N_2O [41].

K has an effect on the redox properties of the catalyst [57]. On the Co-based catalysts, XPS results show that the addition of K promotes the conversion of Co^{3+} to Co^{2+} , changes the redox characteristics, and thus improves the catalytic activity [43]. The improvement of redox properties of $\text{Co}^{2+}/\text{Co}^{3+}$ by K is also found by other researchers [40]. The dissociation of N_2O is considered to be the redox mechanism [33,58–62], such as the single-site mechanism shown in Figure 2 [34] and the double-sites mechanism shown in Figure 3 [63]. The improvement of reducibility will significantly promote the dissociation of N_2O .

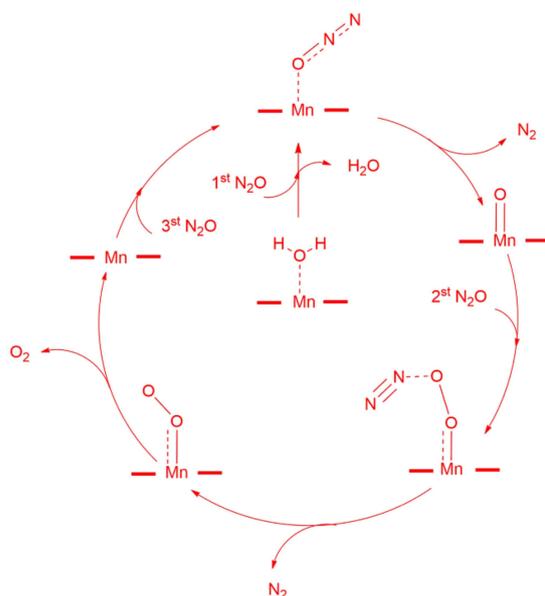


Figure 2. Single-site mechanism of N_2O decomposition [63]. Copyright 2017, Elsevier.

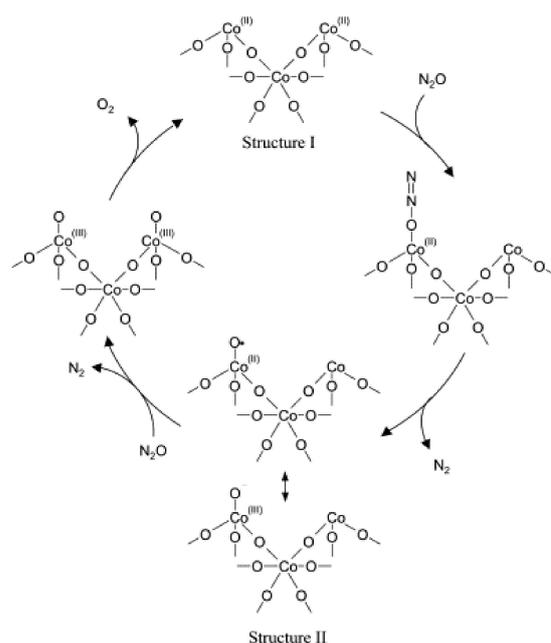


Figure 3. Double-site mechanism of N_2O decomposition [34]. Copyright 2008, Elsevier.

The effect of K on increasing the content of active sites and improving the stability of the catalyst is also studied. The researchers proposed that the good redox cycle of K_xO_y to K_xO_{y+1} shows an efficient N_2O catalytic dissociation activity with the K as an active site on activated carbon [64]. The addition of K to Co_3O_4 catalyst promotes the stability of Co^{2+} and the reduction of Co by promoting the desorption of O_2 [34]. Moreover, on Ir/ Al_2O_3 catalyst, K improves the resistance to O_2 poisoning and improves the stability of N_2O decomposition in the presence of O_2 [65]. In addition, K is also found to improve the stability in O_2 and H_2O atmosphere on $\text{Zn}_{0.4}\text{Co}_{2.6}\text{O}_4/\text{Al}_2\text{O}_3$ [45]. This may be attributed to the fact that K promotes the desorption of O_2 and inhibits the adsorption of O_2 on the catalyst surface, thus promoting the stability of the catalyst under aerobic conditions.

2.1.3. Influencing Factors on Promotion Effect

The promotion effect of K on the N_2O decomposition is affected by many factors, such as the type and content of alkali metal, preparation method, precursor, and the calcination temperature and time [57,66]. When alkali metal is added to $\text{Co}_4\text{MnAlO}_x$ catalyst, the catalytic activity of N_2O decomposition increases with the increase of alkali metal ion radius, and the order of promoter activity is $\text{Cs} > \text{Rb} > \text{K} > \text{Na} > \text{Li}$ [29]. The same results were also found on Co-Ce composite oxide catalysts [41], as shown in Figure 4.

The promotion effect of K is related to the doping amount. When the K contents of 0.3–3.1 wt% are doped on Co-Mn-Al catalyst, the promotion effect increases with the increase of K content, and the promotion effect is the best when the K content is 1.8 wt%. After that, the promotion effect is weakened and the activity is inhibited when the K content is up to 3.1 wt% [67]. The volcanic relationship between the promotion effect and the content is also found on other Co-based catalysts [34].

The preparation methods and precursors greatly affect the activity on K-promoted Co_3O_4 [56], especially the reduction degree of Co^{3+} to Co^{2+} at low temperature. In the comparison of various preparation methods of impregnation, homogeneous precipitation, combustion with glycine, gradual oxidation, and hydrothermal, the catalyst prepared by impregnation method obtains the highest reduction degree from Co^{3+} to Co^{2+} and shows the best activity.

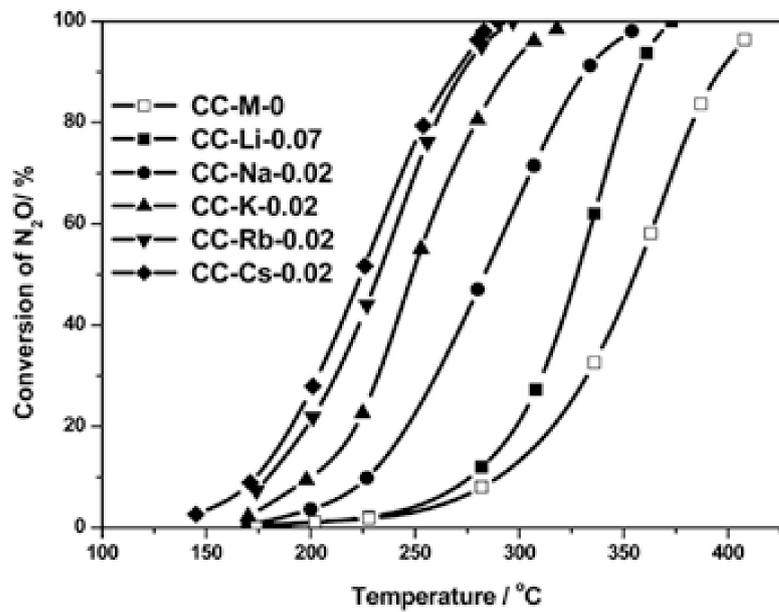


Figure 4. Different alkali metals for N_2O decomposition on cobalt-cerium composite oxide catalysts [41]. Copyright 2009, American Chemical Society.

The precursors of commonly used K include K_2CO_3 , KNO_3 , CH_3COOK , KOH , etc., as shown in Figure 5 [35,68]. The promotion of activity on Co_3O_4 has the following relationship: $K_2CO_3 > KOH > KNO_3 \approx KHCO_3 > CH_3OOK >> K_2SO_4 \approx KCl$. When K_2CO_3 is used as a precursor, the lowest light off temperature and the highest reaction rate are obtained with the lowest work function [69]. The poor performance of K_2SO_4 and KCl is due to the adsorption of SO_4^{2-} and Cl^- on the surface defects, which hinders the decomposition of N_2O .

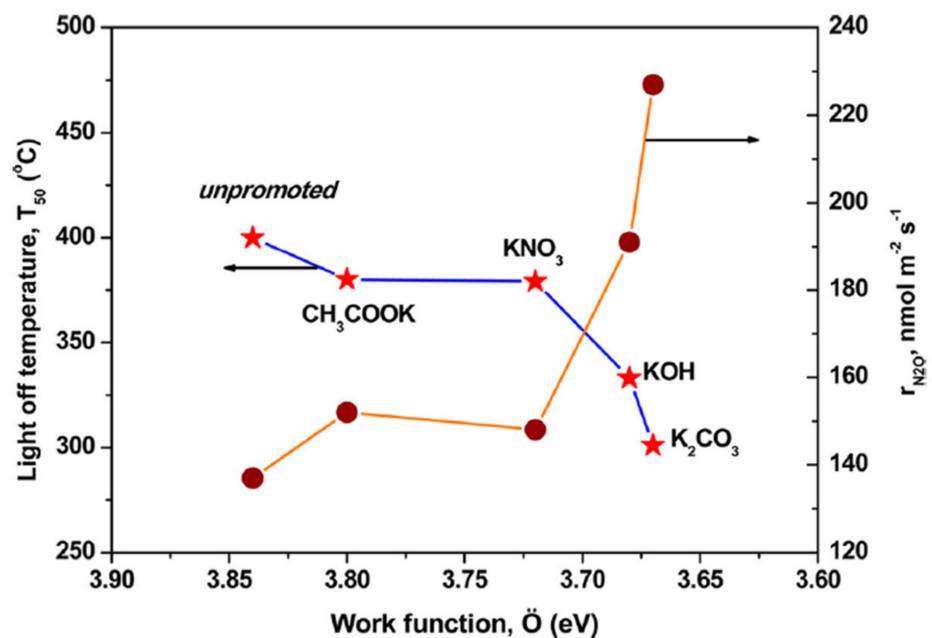


Figure 5. The correlation between precursor and T_{50} , reaction rate, and work function [35]. Copyright 2013, Elsevier.

The promotion effect first increases and then decreases with the increase of calcination temperature from 500 °C and 900 °C on Co-Al catalysts, with the best promotion effect appearing at 700 °C [45]. Moreover, the promotion effect of 4 h calcination is higher than that of 12 h. Too long of a calcination time will cause the sintering of the catalyst and affect the promotion effect.

In summary, K affects the adsorption and dissociation properties of the catalyst and then accelerates the catalytic dissociation process of N₂O. It affects the ionization potential, work function and redox property of the catalyst, and increases the content of active sites to improve the activity. The stability of the catalyst is improved by promoting the desorption of O₂ and stabilizing the active center, similar with the effect on reaction process and the properties of catalyst. The promotion effect of K on N₂O decomposition is mainly found on Co-based catalysts, and other catalysts needs to be more studied.

Table 2. Summary of catalysts and reaction conditions for N₂O decomposition promoted by alkali metals.

Catalysts	Promoter	Content (wt%)	Reaction Conditions						References
			Temperature Range (°C)	T ₅₀ ^a (°C)	N ₂ O (ppm)	O ₂ (%)	H ₂ O (%)	GHSV ^b or WHSV ^c	
Co ₃ O ₄	Li, Na, K, Cs	0.2	200–600	310	1500	3	1	7000 h ⁻¹	[69]
Co ₃ O ₄	K	0.01–0.1 ^d	100–500	160	5000	2	2.5	0.3 g s mL ⁻¹	[34]
Co ₃ O ₄ -CeO ₂	K	2	150–400	215	1000	\	\	0.2 g s mL ⁻¹	[66]
Co ₃ O ₄ -CeO ₂	Li, Na, K, Rb, Cs	0.02–0.07 ^d	150–400	225	1000	\	\	0.2 g s mL ⁻¹	[41]
Co _x Cu _{3-x} O ₄	Na, K	0.005–0.05 ^d	250–650	280	1000	\	\	0.2 g s mL ⁻¹	[44]
CoAl ₂ O ₄	Li, Na, K	0.04 ^d	200–500	290	500	4	2.6	0.12 g s mL ⁻¹	[45]
Co ₃ O ₄	Li, Na, K, Cs	0.015 ^d	450–550	540	0.976%	\	\	2 g s mL ⁻¹	[49]
Co ₃ O ₄	Li, Na, K, Rb, Cs	0.035 ^d	450–700	570	1000	\	\	0.5 g s mL ⁻¹	[52]
Co-Mn-Al	Li, Na, K	0.3–1.8	300–450	330	0.1%	\	\	0.06 g s mL ⁻¹	[50]
Co-Mn-Al	K	0.2–3	300–450	350	0.1%	\	\	40,380 h ⁻¹	[51]
Co ₄ MnAlO _x	Li, Na, K, Rb, Cs	0.2–3.4	300–450	325	0.1%	\	\	0.06 g s mL ⁻¹	[29]
Co ₃ O ₄	K	0.04–0.1 ^d	200–500	260	5000	2	2.5	0.3 g s mL ⁻¹	[56]
Co-Mn-Al	Na, K	0.5–2.5	300–450	330	0.1%	\	\	0.06 g s mL ⁻¹	[70]
Co-Mn-Al	K	0.3–3.1	300–450	340	0.1%	\	\	0.06 g s mL ⁻¹	[67]
Co ₃ O ₄	Cs	0.4–13.7	50–600	110	5%	\	\	7000 h ⁻¹	[68]
Co _{2.6} Zn _{0.4} O ₄ /α-Al ₂ O ₃	K	0.15	100–600	280	5%	\	\	7000 h ⁻¹	[71]
CuO-CeO ₂	Cs	0.6–4.8	350–600	425	1000	2	\	40,000 h ⁻¹	[23]
Cu _{0.8} Co _{0.2} Co ₂ O ₄	Na, K, Cs	0.05 ^d	300–500	340	2%	4	\	0.43 g s mL ⁻¹	[42]
Y ₂ O ₃ -Co ₃ O ₄	K	0.32	200–400	285	1%	2	8.2	12,700 h ⁻¹	[24]
Zn-Ce-Co ₃ O ₄	Na, K	2	200–600	450	3000	\	\	24,000 h ⁻¹	[43]
NiAl mixed oxides	K	0.1	300–500	355	2%	4	8.8	0.43 g s mL ⁻¹	[47]
AC	Na, K	5–20	200–600	280	3000	\	\	0.16 g s mL ⁻¹	[30]
AC	K	5–20	200–600	285	3000	\	\	0.16 g s mL ⁻¹	[64]

^a T₅₀ represents the temperature when the efficiency is 50%. ^b GHSV means gaseous hourly space velocity (h⁻¹). ^c WHSV means weight hourly space velocity (g s mL⁻¹). ^d The molar ratio of alkali metal to active center.

2.2. NO Decomposition

For the NO decomposition, similar with the N₂O decomposition, NO is adsorbed on the catalyst and decomposed into N₂ and O₂ due to the catalytic breaking of N-O bond, as shown in Equation (2). NO decomposition is an economical and convenient method to remove NO without using reducing agent. The catalysts commonly used are Co-based catalysts, and the reaction conditions are shown in Table 3. The reaction includes three steps, the adsorption of NO on the catalyst, breaking of N-O bond in NO to form N₂ and O₂, and the desorption of N₂ and O₂ on the catalyst.



2.2.1. Promotion Effects of K on Reaction Process

K affects reaction process of NO decomposition, such as the adsorption of NO, the reaction pathway, and the desorption of O₂ [72]. The alkaline properties of K affect the NO adsorption and NO_x storage, and promote the catalytic activity of NO decomposition [73]. This is consistent with the mechanism of K in N₂O decomposition reaction. Basic cations enhance the bond strength of adsorbates which can accept metal electrons by electronic interaction [25]. Some researchers also believe that the K regulates the basicity of catalyst surface, thus promoting the adsorption of NO [74,75].

K has an effect on changing the reaction pathway of NO decomposition. On the Co₃O₄ catalyst, it is found that NO is first converted to NO₂⁻ adsorbed on K, then transfers to the interface between K and Co₃O₄, and reacts with adsorbed NO to form N₂ under the catalysis of Co [76]. The K-Co interface formed after doping with K has a higher catalytic activity of NO decomposition [77].

The addition of K also promotes the desorption of O₂. Haneda [77] proposed that the desorption of O₂ is the limiting step of NO decomposition. The redox property of O₂ dissociation is improved by K on Co-Mn-Al catalyst [73]. Moreover, K increases the electron density of Co and weakens the strength of Co-O bond, which is beneficial to promote the desorption of O₂ on Co²⁺ [45,52]. In addition, K improves the dissociation activity of NO under O₂, CO₂ and H₂O atmospheres over Co-Mn-Al catalyst due to the improvement of basicity and reducibility [78].

2.2.2. Promotion Effects of K on Catalyst Properties

K affects the properties of NO decomposition catalysts, including redox properties, basicity, electronic properties and stability. On the K-promoted Co-Mn-Al catalyst, it is found that K increases the reducibility and basicity of the catalyst [73]. Consistent with the role of K in the N₂O decomposition, due to its low ionization potential, K can transfer charge to the transition metal cation, resulting in a dipole that can produce an electric field gradient on the catalyst surface [67]. K increases the specific activity per unit area of Co₃O₄ catalyst [52], and the effect of K on increasing the content of active Co²⁺ sites has also been found by other researchers [49], in spite of weakening the strength of Co-O bond and promoting the formation of low-valent cobalt species [52].

As K loaded on Co-Mn-Al catalyst, the changes well reflect the effect of K on the NO decomposition [73], as shown in Figure 6. K modification makes the surface of catalyst rich in potassium species, which increases the number of basic sites, especially the medium and strong basic sites. K also promotes the formation of active Co²⁺ sites and the adsorption of NO. The increase of catalyst basicity and reducibility further promotes the catalytic dissociation activity of NO and the desorption activity of O₂.

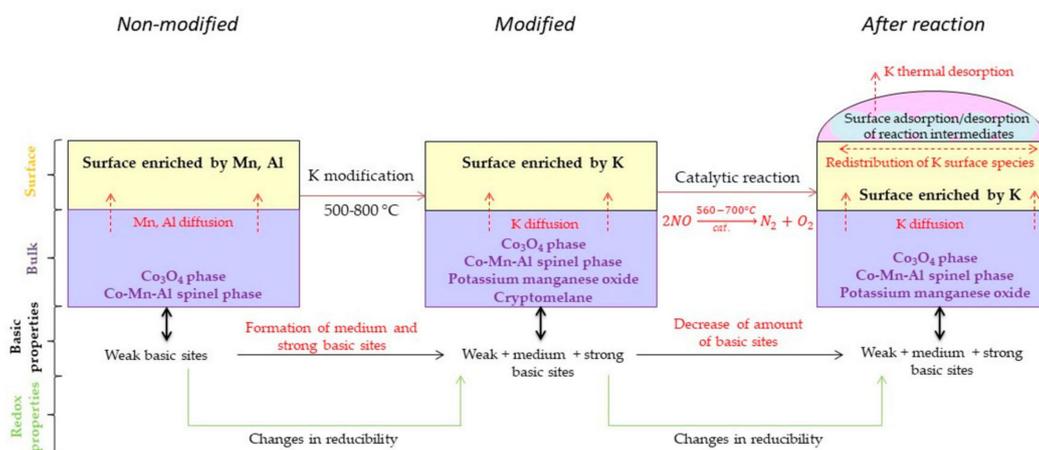


Figure 6. Mechanism of K promoting catalytic dissociation of NO over Co-Mn-Al catalyst [73]. Copyright 2019, MDPI.

2.2.3. Influencing Factors on Promotion Effect

The promotion effect of K on NO decomposition reaction is affected by many factors, such as type and content of alkali metals, calcination, and preparation method. It is found that the order of promotion effect is, $K > Na > Rb > Cs$, by adding Na, K, Rb, and Cs to Co_3O_4 catalysts [76], and K shows an excellent promotion effect on other Co-based catalysts [52]. This is different from the findings in the N_2O decomposition. The promotion effect is affected by the K content. When the Co-based catalyst with Co/Al mole ratio of 3 is supported with K of 0.04–0.12 K/Co molar ratio, the K content of 0.08 shows the best promotion effect [45]. Some researchers have proposed that the catalytic dissociation process of NO on the catalyst surface is related to the surface coverage, crystal phase, and surface defect content [79]. K improves the surface NO adsorption, and increases its coverage and dissociation activity, but too high NO coverage will inhibit the dissociation of NO due to the lack of vacancies to desorb O_2 .

K-modified Co-based catalysts are greatly affected by calcination temperature and calcination time [45,71]. The calcination temperature mainly affects the migration and redistribution of K. The higher the calcination temperature, the more stable K is [73]. However, K volatilizes from transition metal oxides above $500\text{ }^\circ\text{C}$, which may affect the long-term stability of the catalyst [80]. Calcination at high temperature also affects the surface state of K [81]. K migrates from carrier, acting as K reservoir, to spinel nanocrystals and then forms K_xCoO_2 coating at high calcination temperature [82], leading to the disappearance of the strong beneficial effect of K.

The preparation method of K-promoted catalyst has an effect on the activity and stability of NO decomposition. The co-precipitation of metal nitrates by a $Na_2CO_3/NaOH$ and subsequent impregnation KNO_3 leads to a higher activity and stability of the catalyst than the other preparation methods, such as the calcination of corresponding metal nitrates or the impregnation of the calcined Co-Mn-Al precursor with a solution of KNO_3 [80]. In the preparation of K-promoted Co-Mn-Al catalyst, the catalyst prepared by coprecipitation of transition metal nitrate and K_2CO_3/KOH shows a good catalytic activity and stability for the NO decomposition. Addition of K has a positive effect on the stability of the catalyst because K acts as a storage for the catalyst when the K is desorbed from the catalyst surface [72]. Some researchers have also proposed the model shown in Figure 7 for the improvement of the stability of the K-doped catalyst. The more stable $KFeO_2$ is used as the outer layer for the reaction, and $K_2Fe_{22}O_{34}$ is the K reservoir, which constantly supplies the surface K content [81].

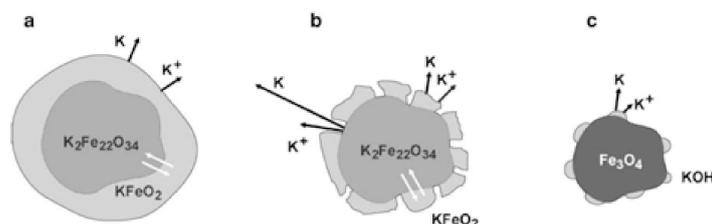


Figure 7. K cladding model [81]. (a) an ideal compact core and shell, (b) a more realistic core and cracked shell, and (c) deactivated catalyst grain morphology. Copyright 2002, Elsevier.

K shows promotion effects on both N_2O decomposition and NO decomposition. On the two types of catalysts, K has the same effect on redox property, increasing the electron density of the active center and weakening the bond energy. Taking the Co-based catalysts commonly used in both reactions as examples, the addition of K promotes the conversion of Co^{3+} to Co^{2+} and the recovery of the active center during the reaction. There are also some different effects of K in the two kinds of reactions. In the N_2O decomposition, the enhanced adsorption of N_2O by K comes from the electron-donating action, while in the NO decomposition, the enhanced adsorption of NO by K comes not only from the electron-donating action, but also from the alkaline action. In addition, K itself can be used

as the active site for N₂O catalytic dissociation on K/AC catalyst in N₂O decomposition, which has not been studied and discovered in NO decomposition. K changes the reaction pathway by forming the NO₂⁻ on K in NO decomposition, which is not discovered in N₂O decomposition. The promotion effect is consistent with the ion radius of the alkali metal in N₂O decomposition, while K shows the best promotion effect in NO decomposition. Furthermore, research on the influence of precursor is lacking.

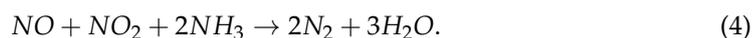
Table 3. Summary of catalysts and reaction conditions for NO decomposition promoted by alkali metals.

Catalysts	Promoter	Content (wt%)	Reaction Conditions			References	
			Temperature Range (°C)	T ₅₀ ^a (°C)	N ₂ O (ppm)		GHSV ^b or WHSV ^c
Co-Mn-Al	K	0.6–18.9	650–700	650	1000	0.6 g s mL ⁻¹	[72]
Co-Mn-Al	K	1–4	560–650	650	1000	0.6 g s mL ⁻¹	[73]
Co ₃ O ₄	Li, Na, K, Rb, Cs	0–0.1 ^d	450–700	580	1000	0.5 g s mL ⁻¹	[52]
Co ₃ O ₄	Na, K, Rb, Cs	0.035 ^d	450–600	600	1000	0.1 g s mL ⁻¹	[76]
Co ₃ O ₄		0.9–3	400–650	<650	9700	2100 h ⁻¹	[83]
Co ₃ O ₄	Na	0–0.091	450–700	620	0.976	2 g s mL ⁻¹	[49]
Co-Mg-Mn-Al	K	2	55–700	660	1000	0.6 g s mL ⁻¹	[84]
Co-Mn-Al	K, Cs	1.5–4	612–650	\	1000	0.6 g s mL ⁻¹	[80]
Ce-Mn	Li, Na, K, Cs	0–10	800	>800	6000	1 g s mL ⁻¹	[85]

^a T₅₀ represents the temperature when the efficiency is 50%. ^b GHSV means gaseous hourly space velocity (h⁻¹). ^c WHSV means weight hourly space velocity (g s mL⁻¹). ^d The molar ratio of alkali metal to active center.

2.3. NO Reduction

NO reduction is generally a process of selective catalytic reduction of NO by NH₃ to form N₂ and H₂O through the catalyst, which is shortly called NH₃-SCR, as shown in Equations (3) and (4). SCR is the most common technology for NO_x removal from industrial flue gas and motor vehicle exhaust. The commonly used catalysts are V-based, Mn-based, and Cu-based catalysts and the reaction conditions are shown in Table 4.



2.3.1. Promotion Effects of K on Reaction Process and Catalyst Properties

The promotion effect of K on the NH₃-SCR has been reported, such as the adsorption and reaction pathway of NO and NH₃. The promotion effect on the basicity, electron donor properties and active center stability of NH₃-SCR catalyst is also found. At present, the widely accepted NH₃-SCR mechanisms are the Langmuir–Hinshelwood (L-H) mechanism and Eley–Rideal (E-R) mechanism. The L-H mechanism is that NH₃ and NO are adsorbed on the catalyst surface, and the adsorbed NH₃ reacts with adsorbed NO to produce N₂ and H₂O. The E-R mechanism is that NH₃ is adsorbed on the catalyst surface and the adsorbed NH₃ reacts with gaseous NO to produce N₂ and H₂O. Different from the traditional mechanism, gaseous NH₃ reacts with adsorbed NO₂ to complete SCR reaction, which is called fast SCR reaction [86]. Some researchers have proposed that K provides alkaline site to adsorb NO₂ in fast SCR. And the doping of K promotes the chemisorption of NO through alkaline and electron donor interaction, and forms a new reaction pathway on the catalyst, thus accelerating the SCR reaction [87]. Moreover, the catalytic dissociation activity of K on N₂O promotes the decomposition of N₂O during SCR reaction to form N₂, which improves the selectivity of N₂. K increases the activity of unsaturated Mn cations in α-MnO₂ catalysts, promoting the chemisorption and activation of NH₃ [88]. Alkali metal cations stabilize the metastable active sites of Fe, Au, etc., thus promoting the catalytic activity [89,90]. K also affects the stability of catalyst. The addition of K on Cu/SAPO-

34 decreases the likelihood of water attack due to the decrease in the density of Si-O(H)-Al bonds, which significantly improves the stability in 3 vol% H₂O atmosphere [91].

Besides NH₃-SCR, selective catalytic reduction by C_xH_y (HC-SCR) or H₂ (H₂-SCR) and the reduction of NO by CO (NO-CO reaction) have also been promoted by K. For the reduction of NO by propene (C₃H₆) on the Pt/γ-Al₂O₃ catalyst, K promotes the adsorption and dissociation of electronegative NO and inhibits the adsorption of electropositive C₃H₆, thus adjusting the adsorption of reactants [92]. Moreover, K strengthens the Pt-NO bond and weakens the N-O bond, thereby increasing the HC-SCR activity [93]. K also shows the same effect in the NO-CO reaction on Pt/γ-Al₂O₃ catalyst [94]. K improves the dispersion of active centers on Pd/K₂O-6TiO [95] and Ag/γ-Al₂O₃ [96] in H₂-SCR. In addition, the content of the intermediate species, Pd⁰-NO, are also increased by K on Pd/K₂O-6TiO₂ [95]. On the CuO/AC catalyst, K promotes the re-oxidation of Cu⁺ to Cu²⁺ and the formation of surface active carbon sites by weakening the C-C bond, which promotes the redox cycle of active sites [97]. K has a promotion effect on the carrier. The modification of K to TiO₂ with loading Au have been found forming K₂Ti₈O₁₇, which promotes the formation of isocyanide (-NCO) [98]. -NCO is an important reaction intermediate, which is considered to be a key to the high activity and selectivity of NO-CO reaction [99].

K also has a promotion effect on selectivity. K promotes the dissociation of NO, increases the content of N_{ads} on the Pt/γ-Al₂O₃, and relatively reduces the content of NO_{ads} [92], thereby promoting the formation of N₂, as shown in Equation (5), and weakening the formation of N₂O, as shown in Equation (6). This effect is also found on Pd-based catalysts [100].



K promotes the stability of the catalyst. Sulfur resistance of catalyst is enhanced by adding alkali metals on Ag/γ-Al₂O₃ catalyst due to the increase of intermediates [96]. The SO₂-TPD results show that the addition of K inhibits the accumulation of sulfur compounds on Ag/Al₂O₃ in HC-SCR, thereby increasing the stability in SO₂ atmosphere [101]. In the reduction of NO by CO and naphthalene reaction on Cu/Ce/TiO₂-SiO₂, K reduces the oxidation of naphthalene, thereby promoting the reduction of NO [102].

2.3.2. Influencing Factors on Promotion Effect

The promotion effect is affected by the type of alkali metal, the content and the reaction temperature. The effects of Li, K, Rb, and Cs in HC-SCR over Pt/γ-Al₂O₃ catalyst are compared [93], and Rb shows the best promotion effect. In the reduction of NO by propene over Pd/Y₂O₃-ZrO₂ catalyst, Na shows the best promotion effect over Li, Na, K, and Cs [100], while Rb shows a better promotion effect than K and Cs in the NO-CO reaction over Pt/γ-Al₂O₃ catalyst, due to the suitable ion size of Rb [94]. There are different optimal types of alkali metals for different active sites in NO reduction.

There is a volcanic relationship between the content of K and the promotion effect. The addition of 4.2 wt% K to Pt/γ-Al₂O₃ catalyst performs the best promotion effect among the content range of 2.6–10.4 wt% in HC-SCR [92]. The alkali metal contents of 0.02–0.1 wt% over Pd/Y₂O₃-ZrO₂ catalyst are studied in HC-SCR and NO-CO reaction [100] with the best promotion effect at 0.02 wt% content. The alkali metal contents of 0.5–2 wt% are studied on Ag/γ-Al₂O₃ catalyst in HC-SCR [96], with the best promotion effect at 1 wt% alkali metal content.

In the H₂-SCR reaction over Pd/K₂O-6TiO₂, the increase of reaction temperature reduces the reaction activity and selectivity due to the promotion in the decomposition of nitrate adsorbed by K to form NO₂ and N₂O [95].

K plays the same role in the both reaction of SCR and NO decomposition for the NO_x removal. Although the catalyst active centers promoted by K in the two reactions are inconsistent, K shows a similar promotion effect. The electron-donating properties of K promote the adsorption of NO, the stability of metastable active sites, activity and stability.

And K has the effect of changing the reaction pathway in both reactions. The effect of the content on the K promotion effect is found to be volcanic in both reactions, indicating that the effects of K are both positive and negative. A proper amount of K promotes the adsorption of NO, while too much K will destroy the adsorption balance and cover the active sites. In the NO reaction, K is found to promote the dispersion of Ag and Pd, which is an undiscovered role on Co-based catalysts in the NO decomposition. There are few researches on factors affecting the promotion of K in NO reduction, especially the precursor. And the research on stability in SO₂ and H₂O on K-promoted catalysts is lacking.

Table 4. Summary of catalysts and reaction conditions for NO reduction promoted by alkali metals.

Catalysts	Promoter	Content (wt%)	Reaction Conditions					References	
			Temperature Range (°C)	T ₅₀ ^a (°C)	NO (ppm)	Reductant	Others		GHSV ^b or WHSV ^c
Pt/γ-Al ₂ O ₃	Li, K, Rb, Cs	1.9–15.5	177–527	300	1000	1000 ppm C ₃ H ₆	\	0.006 g s mL ⁻¹	[103]
Pt/γ-Al ₂ O ₃	Na	2.6–10.4	200–500	300	1000	1000 ppm C ₃ H ₆	\	0.006 g s mL ⁻¹	[92]
Pt/γ-Al ₂ O ₃	K, Rb, Cs	1.9–15.5	100–500	320	1000	1000 ppm CO	\	0.006 g s mL ⁻¹	[94]
Pd/K ₂ O-6TiO ₂	K	\	75–275	95	1000	5000 ppm H ₂	5% O ₂	60000 h ⁻¹	[95]
Pd/Y ₂ O ₃ -ZrO ₂	Na	0.017–0.102	300–450	362	8000	8000 ppm C ₃ H ₆	\	0.00375 g smL ⁻¹	[104]
Pd/γ-Al ₂ O ₃	Na	3.5–7	180–350	275	1000	1067 ppm C ₃ H ₆ 7000 ppm CO	7800 ppm O ₂	0.015 g s mL ⁻¹	[105]
Ag/Al ₂ O ₃	Li, Na, K, Cs	0.5–1	200–500	350	1000	1000 ppm C ₃ H ₆	5% O ₂	0.09 g s mL ⁻¹	[96]
Ag/Al ₂ O ₃	Na, K, Cs	2	450–700	545	500	4000 ppm CH ₄	80 ppm SO ₂	9000 h ⁻¹	[101]
CuO/AC	K	0–10	150–450	317	2000	AC	\	20,000 h ⁻¹	[97]

^a T₅₀ represents the temperature when the efficiency is 50%. ^b GHSV means gaseous hourly space velocity (h⁻¹). ^c WHSV means weight hourly space velocity (g s mL⁻¹).

2.4. NO Oxidation

For the NO oxidation, NO and O₂ are first adsorbed on the catalyst surface and then react to form NO₂, as shown in Equation (7). The commonly used catalysts are Pt-based, Mn-based, and Co-based catalysts and the reaction conditions are shown in Table 5.



2.4.1. Promotion Effects of K on Reaction Process

K promotes reaction process of NO oxidation, such as the adsorption of NO and activation of O₂. K enhances the strength of Pt-NO bond and promotes the formation of adsorbed N species (nitrites/nitrates) [106], which promote the oxidation of NO into NO₂ on Pt/Al₂O₃ [6]. In addition, K provides the adsorption site for NO thereby reduces the competitive adsorption since O₂ is a stronger electron acceptor than NO which is preferentially adsorbed on the Pt site [107]. K has also been found to promote the dissociation of O₂ on the 2D hexagonal boron nitride [108], which is considered to be the limiting step in the oxidation reaction [109].

2.4.2. Promotion Effects of K on Catalyst Properties

K changes the properties of catalysts, such as acid-base properties and redox properties. K reduces the crystallinity of the catalyst, improves the dispersion of surface particles, and changes adsorption characteristics on Mn-CoO_x [110]. In addition, K improves the dispersion and the ratio of Mn⁴⁺/Mn³⁺ and Co²⁺/Co³⁺, and promotes the chemisorption of O₂ and NO. The increasing of the ratio of Co²⁺/Co³⁺ by adding K is also found on Co/K_xTi₂O₅ [103]. Moreover, Fourier transform infrared (FTIR) results show that K in the carrier TiO₂ promotes the formation of chemisorbed species of NO_x on the catalyst surface.

2.4.3. Influencing Factors on Promotion Effect

The promotion of K on NO oxidation is affected by the precursor, content and existing states of K. Among the three kinds of precursors of KOH, K_2CO_3 and KNO_3 on Mn-CoO_x, KOH shows the best activity, which is consistent with the alkalinity. It is found that the catalyst with 10 wt% K in the range of 5–20 wt% K contents shows the best catalytic activity for NO oxidation over Mn-CoO_x catalyst [110], while the Co₃O₄ catalyst with 0.1 wt% K in the range of the 0.05–0.2 wt% K contents shows the best catalytic activity for NO oxidation [111]. On the Co/K_xTi₂O₅ catalysts, 2.15–15.28 wt% K contents are studied [103], and it is found that the NO oxidation activity increases as the increasing of K content. There are different suitable K contents on different catalysts. For the existing states of K, two forms of K are found on Co₃O₄ catalysts, free K and stable K [111]. Free K species, including carbonate and nitrate, have high mobility and easily cover active sites, which is adverse for the oxidation of NO. Stable K species closely relate to the activity serves as electronic and structural modifiers, which is conducive to the formation of O⁻/O²⁻ species, oxygen vacancies, more Co³⁺ sites, and then is conducive to the oxidation of NO.

NO decomposition and NO oxidation are two opposite reaction pathways of NO to form N₂ or NO₂. K promotes the adsorption of NO in the both reactions, but the mechanism is different. In the NO decomposition, K promotes the formation and stability of the low valence metal, while in the NO oxidation, K regulates the ratio of metal valence to favor the reaction, and simultaneously increases the dispersion of the active centers, thus improving the redox performance and the oxidation activity. Especially on Co-based catalysts, the promotion of K on the formation of Co²⁺ or Co³⁺ requires a clearer analysis. Moreover, K plays more promoting roles in NO decomposition than that in the NO oxidation, such as the activation of NO and the increase of the specific surface area of the catalyst. In NO oxidation, the existing states of K are proposed, which is worthy of attention in the research. Moreover, the optimal K precursor is KOH in NO oxidation and K₂CO₃ in N₂O decomposition, showing that different reactions require different catalyst properties.

Table 5. Summary of catalysts and reaction conditions for NO oxidation promoted by alkali metals.

Catalysts	Promoter	Content (wt%)	Reaction Conditions				References	
			Temperature Range (°C)	T ₅₀ ^a (°C)	NO (ppm)	O ₂ (%)		GHSV ^b or WHSV ^c
Co/K _x Ti ₂ O ₅	K	2.15–15.28	200–420	275	700	10	120,000 h ⁻¹	[103]
Co ₃ O ₄	K	0.05–0.2	200–450	240	500	8	0.27 g s mL ⁻¹	[111]
Mn-CoO _x	K	5	50–250	85	500	5	30,000 h ⁻¹	[110]
Ru/K-OMS-2	K	\	27–527	270	1000	8	35,000 h ⁻¹	[112]

^a T₅₀ represents the temperature when the efficiency is 50%. ^b GHSV means gaseous hourly space velocity (h⁻¹). ^c WHSV means weight hourly space velocity (g s mL⁻¹).

3. The Removal and Reuse of CO_x

K has been widely studied for promoting removal and reuse of CO_x (x = 0, 1, 2), such as catalytic oxidation to remove soot and CO, and water-gas shift (WGS) reaction and reverse water-gas shift (RWGS) reaction to reuse CO and CO₂.

3.1. Soot Oxidation

Soot oxidation is oxidizing soot particles by oxidizing species on catalysts to form CO₂, as shown in Equation (8). The oxidation of soot is the most common method for soot removal in motor vehicle exhaust. The commonly used catalysts are Ce-based, Cu-based, Mn-based and Co-based catalysts. The reaction conditions are shown in Table 6. The reaction includes three steps, the adsorption of soot and oxidizing species on the catalyst,

the reaction between soot and oxidizing species to produce CO_2 , and the desorption of CO_2 . The soot also can be oxidized by NO due to its existence in motor vehicle exhaust.



3.1.1. Promotion Effects of K on Reaction Process

K shows a promotion effect in soot oxidation reaction [113], including the adsorption of O_2 , the contact between soot and catalyst, the reaction pathway and the selectivity of CO_2 . The addition of K to Ce-based catalysts promotes the adsorption of O_2 and the formation of surface carbon complexes which can react with soot, thus improving the activity of soot oxidation [114]. Adding K into Mg-Al catalyst shows that surface oxygen on the K active site is reactive oxygen species in the reaction [115]. In addition, K also promotes the dissociation of O_2 . The XPS and in-situ diffuse reflectance infrared Fourier transform (in-situ DRIFTS) results show that K on the catalyst surface reacts with O_2 to form peroxides and superoxide-type substances with high oxygen content which can participate in the soot oxidation process. This is also considered to be the main reason for the increased activity of K promoted catalysts [116]. The low melting point of KNO_3 greatly improves the contact between catalyst and soot on Cu/ CeO_2 [117]. The existence of K also increases the number of structural defects on soot and improves the contact between the catalyst and soot particles, thus increasing the utilization of active sites [118]. The free K species are found on Co_3O_4 , in the forms of carbonates and nitrates with high mobility, which improve the contact state of catalyst-soot and significantly accelerate soot oxidation [111].

The effect of K on the reaction pathway has also been proposed. The process of soot catalytic oxidation could be changed by the molten phase KNO_3 . The molten phase KNO_3 not only promotes solid-liquid contact but also promotes the fragmentation of soot particles and creates a new reaction pathway for soot oxidation, as shown in Figure 8. Soot is oxidized by the oxygen in the molten phase nitrate, and the gaseous O_2 is used to supply the oxygen consumed in the molten phase nitrate [119]. The oxidation pathway of soot changes from the direct oxidation by gaseous O_2 to the indirect oxidation, so soot oxidation can be transferred from high temperature to low temperature. On the K/MgAlO catalyst, active oxygen is formed on K to participate in the oxidation process and the oxidation of soot follows the oxygen overflow mechanism [120]. The active oxygen existing at the K site overflows to the surface of soot particles, reacts with the free carbon to form an intermediate ketene with a $\text{C}=\text{C}=\text{O}$ structure, and then the active oxygen species at the K site are continuously supplemented by gaseous O_2 and lattice oxygen, and ketene is further oxidized to CO_2 , as shown in Figure 9.

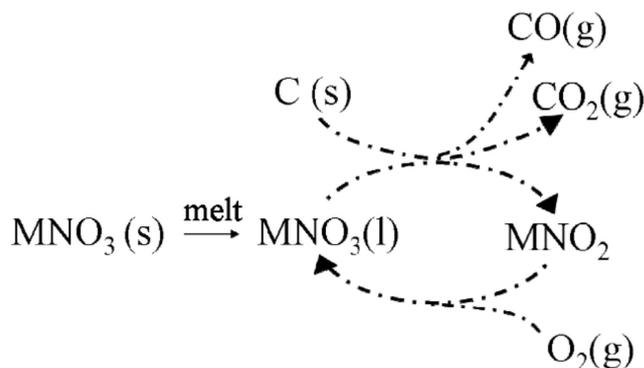


Figure 8. The mechanism of soot oxidation on molten salt [119]. Copyright 2008, WIT Press.

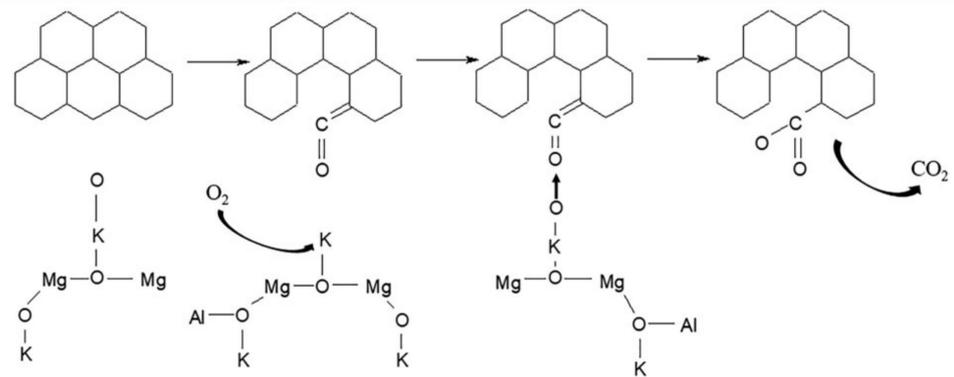


Figure 9. The oxygen overflow mechanism of soot oxidation [120]. Copyright 2019, Elsevier.

In the oxidation of soot by NO and O₂ on Mg-Al catalyst, it is found that K provides new active oxygen species and changes the reaction pathway for the oxidation of soot by NO [115]. As shown in Figure 10, NO is first oxidized to nitrites by the active oxygen at the K site. Then the nitrites react with the C on the soot to form the ketene group. Finally, the ketene group is further oxidized to CO₂. The same effect is also found on K-modified Co₃O₄ nanowires monolithic catalysts (KCo-NW), as shown in Figure 11 [121]. K promotes the chemical adsorption of NO and forms chemisorbed NO_x species on the surface. Among 200–250 °C, the chemisorbed NO_x species on the catalyst surface participate in the soot oxidation reaction. Among 250–330 °C, the surface chemically adsorbed NO_x species begin to decompose, and the produced NO₂ participates in the soot oxidation reaction. Above 330 °C, soot is oxidized by gaseous NO₂ and O₂. The addition of K forms new reactive oxygen species, which causes soot oxidation to occur at lower temperature. Moreover, on the CeO₂ catalysts, K increases the possibility of multiple reaction pathways by acting as a reaction site, thus improving the oxidation activity of soot, as shown in Figure 12 [118]. After adding K salts, soot oxidation mechanism is no longer merely oxygen transfer mechanism, but also electron transfer mechanism [122]. The effect of K on CO₂ adsorption, promoting the formation of CO₂ and improving selectivity, is also found on CaO-MgO [123,124].

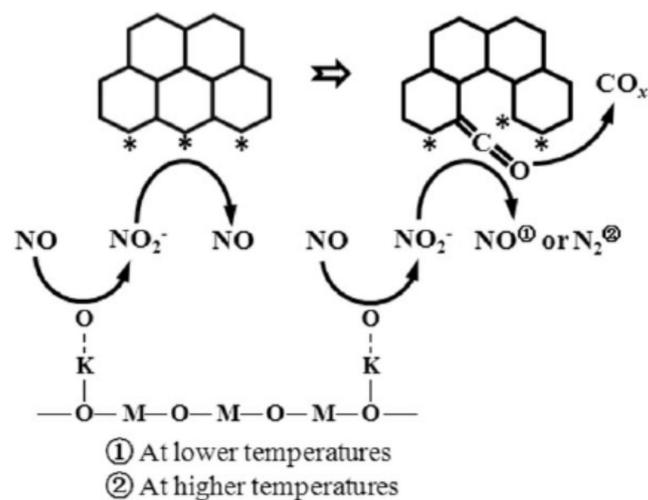


Figure 10. A nitrite-ketene mechanism for soot oxidation by NO [115]. M stands for metal and “*” stands for the free carbon sites on soot. Copyright 2011, Wiley Online Library.

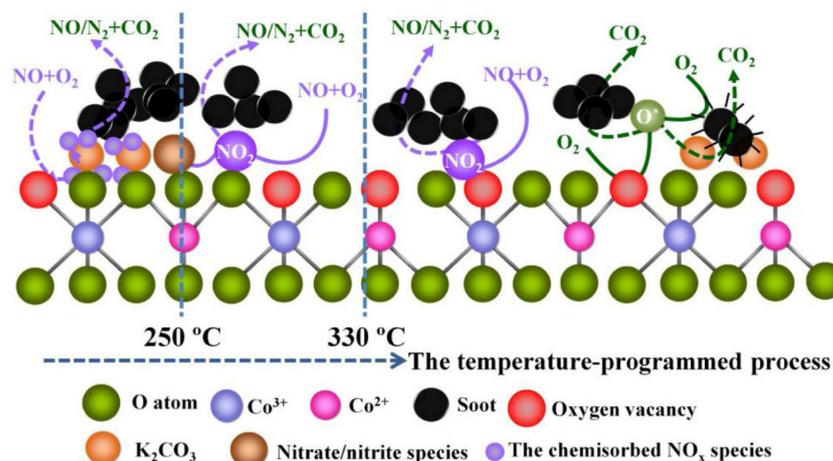


Figure 11. Reaction mechanism for soot oxidation on KCo-NW catalysts under NO/O₂ atmosphere [121]. Copyright 2017, Elsevier.

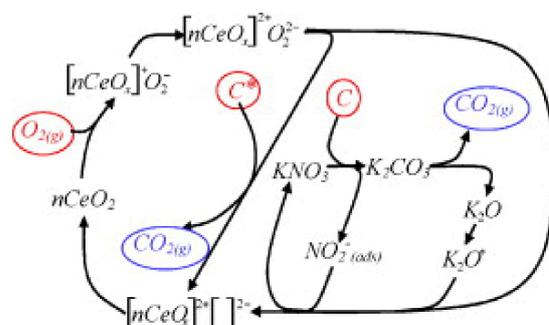


Figure 12. Reaction network for soot oxidation on K/CeO₂ catalysts [118]. Copyright 2009, Elsevier.

3.1.2. Promotion Effects of K on Catalyst Properties

Researchers have found that alkali metal additives can be directly used as active centers. K⁺ is considered to be the active site of soot oxidation on KNbO₃ catalyst [125]. K on the KNO₃ catalyst in the molten phase is also directly used as the active centers for soot catalytic oxidation [119]. Moreover, the potassium oxides and peroxides are considered to be active species for the reaction of C with O₂ [126].

K affects the redox properties of the catalyst. The addition of K enhances the reducibility on CaO-MgO catalyst [116], promotes the formation of large oxygen-containing surface substances on MgO [127], forms new reactive oxygen species, K-Co-O, on Co-MgAlO catalyst [128] and increases the number of oxygen vacancy on Mg-Al catalyst [120], which significantly improves the oxidation activity of soot.

K also promotes the stability of the catalyst. It is found that the sulfur resistance of the MnO_x-CeO₂ and Cu/CeO₂ catalyst is improved by impregnating KNO₃ [117,129], which is attributed to the protection of the active center by the basicity of K. The addition of K to the CaO-MgO catalyst reduces the content and stability of carbonates formed on the surface, while the carbonate groups invalidate the active sites and prevent the adsorption and dissociation of O₂ [116]. K reduces decomposition temperatures of carbonate on catalyst surfaces is also found [130].

3.1.3. Influencing Factors on Promotion Effect

The promotion effect of K on soot oxidation catalyst is affected by the type of alkali metal, the content and the calcination temperature. In a series of MNbO₃ catalysts (M = alkali metal), the promotion effect has the following relationship: KNbO₃ > NaNbO₃ > RbNbO₃ > LiNbO₃ [125]. Some researchers found that promotion effect of alkali metals increases with the increase of atomic number, that is, K > Na > Li [131–136]. The linear

relationship between promotion effect and the content is found on Cu/CeO₂ in molar ratio of K/Cu from 0.4 to 2.5 [117] and on Co-MgAlO catalysts among 1.5–10% K [128]. However, the volcanic relationship between promotion effect and the content is found on Ce-based catalysts among 3–13.5% K [114].

The XRD results show that the appropriate increase of calcination temperature increases the crystallinity of KNbO₃ catalyst, but too high calcination temperature reduces the specific surface area, and the calcination temperature at 650 °C shows the best activity [125]. The promotion effect is affected by calcination temperature due to the type of salts. K forms KNO₃ species at low calcination temperatures (450 °C) and forms K₂O species at high calcination temperatures (650 °C) on the Fe/Al₂O₃ catalysts [6]. Different existing states of K have different effect on activity. KNO₃ plays a promoting role in the reaction, while K₂O will combine with the product CO₂ to form K₂CO₃ and further decompose to produce basic O²⁻, which covers the active sites, thereby reducing the soot oxidation activity.

K can act as an active center in soot oxidation, which changes the reaction pathway. This is not found in the NO_x removal. The researchers discovered the deep meaning of the influence of calcination temperature, which changed the existing states of K on the surface. However, there are some contradictions in soot oxidation and NO_x removal. Although K can promote the adsorption of reactants in both reactions, it is a new discovery in the soot oxidation reaction to promote soot adsorption by constructing defect sites. It is found that K promotes the desorption of O₂ on the Co-based catalyst during NO_x decomposition, while K promotes the adsorption of O₂ on CeO₂ during soot oxidation. K promotes the formation of active oxygen species on the catalyst surface in soot oxidation, which is also different from the findings in NO_x removal. The difference of K in soot oxidation and NO_x removal may be due to the nature of the active center and the atmosphere conditions, and more in-depth research is needed.

Table 6. Summary of catalysts and reaction conditions for soot oxidation catalysts promoted by alkali metals.

Catalysts	Promoter	Content (wt%)	Reaction Conditions							References	
			Temperature Range (°C)	T _m ^a (°C)	Soot (g Soot/g Catalyst)	O ₂ (%)	H ₂ O (%)	NO (ppm)	Others		GHSV ^b or WHSV ^c
MnO _x -CeO ₂	K	0.08–0.67 ^d	300–700	440	0.05	10	3	1000	\	0.043 g s mL ⁻¹	[129]
CeO ₂	K	4–14	300–650	350	0.05	6	\	\	\	0.024 g s mL ⁻¹	[118]
CeO ₂	K	3–13.5	300–500	360	0.05	6	\	\	\	0.00375 g s mL ⁻¹	[114]
CeO ₂ -ZrO ₂	K	8	400–650	430	0.1	10	\	\	1000ppm NO	0.0132 g s mL ⁻¹	[137]
Cu/CeO ₂	K	2–5	300–500	315	0.1	10	\	1000	\	0.0132 g s mL ⁻¹	[117]
Cu/Al	K	0.5–1 ^d	250–650	550	0.2	5	\	500	\	≈1270 h ⁻¹	[113]
Co/Al											
V/Al	K	1.5–10	50–300	348	0.05	air			\		[128]
Co-MgAlO	Li, Na, K	5.4	250–750	430	0.25	air	air	air	air	0.0025 g s mL ⁻¹	[116]
MgO											
MgO	K	2.3	350–700	421	0.25	air	air	air	air	0.0025 g s mL ⁻¹	[127]
MgAlO	K	0.14	50–500	217 ^e	\	10	\	0.1%	0.05% CO, C ₃ H ₆	20,000 h ⁻¹	[120]
MgAlO	K	≈1.9–3.9	376–750	410	0.11	air	air	air	\	\	[138]
Alkaline salts	Li, Na, K	\	250–500	350	0.5	10	\	\	\	0.138 g s mL ⁻¹	[119]
alkaline niobates	Li, Na, K, Rb	\	400–700	470	0.25	12	\	\	\	0.0025 g s mL ⁻¹	[125]

^a T_m represents the temperature when the efficiency is maximum. ^b GHSV means gaseous hourly space velocity (h⁻¹). ^c WHSV means weight hourly space velocity (g s mL⁻¹). ^d The molar ratio of alkali metal to active center. ^e This temperature represents ignition temperature.

3.2. CO Oxidation

CO oxidation is that adsorbed CO is oxidized by O₂ to generate CO₂, as shown in Equation (9). This is one of most effective ways to reduce CO emissions in industrial flue gas and motor vehicle exhaust. The commonly used catalysts are Pt-based, Cu-based, Au-based, and Rh-based catalysts. The reaction conditions are shown in Table 7. The reaction goes through three steps, the adsorption of CO and O₂ on the catalyst, the reaction of adsorbed CO with active oxygen species to form CO₂, and the desorption of CO₂. This is similar to the catalytic oxidation of soot. In addition, high preferential oxidation activity of CO in H₂ is beneficial to the acquisition of high purity hydrogen fuel, which is very important for fuel cells.



3.2.1. Promotion Effects of K on Reaction Process

K favors the adsorption O₂, changes the reaction pathway and improves the selectivity of CO₂ [1,13,122,139]. K affects the adsorption of CO and O₂. On the one hand, K weakens the adsorption of CO and promotes the adsorption of O₂. On Pt-based catalysts, the addition of K weakens the interaction between CO and surface Pt atoms, reduces the coverage of CO, and thus improves the chemical adsorption of competitive O₂ on Pt atoms [140]. This weakening effect is related to the electronic action of K [141]. The FTIR results on Pt/Al₂O₃ catalyst also show that the K weakens the relationship between CO and Pt, and changes the adsorption site of CO [142]. And the interaction between CO and Pt becomes weaker with the increase of K content [143]. According to the kinetic study, K decreases the adsorption equilibrium constant of CO and reduces the chemisorption of CO, which promotes the chemisorption of O₂ and significantly reduces the reaction barrier between chemisorbed CO and O₂ [140]. The doping of K on Ru-based catalysts also inhibits the adsorption of CO, thus promotes the adsorption of O₂ through competitive adsorption at lower temperatures [144]. Some researchers have also proposed that the K promotes the adsorption of O₂ by changing the binding energy [145,146]. In addition, with the addition of K, the formed K₂O provides a site for the adsorption of O₂ to promote the adsorption of O₂ [147]. The role of K in promoting the dissociation and adsorption of O₂ is also found on Ce_{0.8}Zr_{0.2}O₂ catalysts [114].

On the other hand, the addition of K to Pt-based catalysts has promoting effect on strong adsorption of CO. Although K reduces the overall CO adsorption content on Pt-based catalysts, the formed K-O-Pt species have strong adsorption to CO and reduces the reaction barrier, thus obtaining higher activity [140]. Moreover, K also improves the adsorption properties of CO and O₂ [145,146,148]. The addition of K on Rh/ultra-stable Y zeolite (USY) promotes the adsorption of CO by increasing the formation of linear CO and bridged CO [149], which is consistent with the results observed on Rh/Al₂O₃ [150]. The addition of K on Au/TiO₂ catalyst also promotes the adsorption of CO, and K is considered as serve as anchor sites for adsorbates [151].

The opposite effects of K on the adsorption of CO are worth noting. K promotes the adsorption of CO on the Rh-based and Au-based catalysts by increasing the CO adsorption species, acting as the CO adsorption anchor, forming new species and generating electrostatic interaction between K^{δ+} and O^{δ-}. The difference is that, on the Pt-based and Ru-based catalysts, K weakens the strength of the Pt-C bond by increasing the electron density near the Pt site, thus inhibiting the adsorption of CO. The role of K on Pt-based catalysts is special. The addition of K reduces the adsorption equilibrium constant of CO and improves that of O₂. But the new species, K-O-Pt, have higher CO adsorption activity, reduce the energy barrier of CO oxidation reaction, and promote the reaction rate.

K changes the reaction pathway of CO oxidation in the catalytic process. The formed K₂O provides a site for the adsorption of O₂ on the Pt/Al₂O₃ [147]. The O₂ adsorbed on K₂O reacts with the CO adsorbed on the adjacent Pt site to complete the oxidation of CO, and then the reaction pathway between CO and O₂ is changed from the competitive adsorption reaction on single active site to the non-competitive adsorption reaction on

double active sites. The addition of K on Pt-based [140], Ir-based [152], and Au-based catalysts [151] has been found to change the reaction pathway which significantly reduces the reaction barrier and the disproportionation reaction of CO occurs on Au/TiO₂, as shown in Equation (10).



K also improves the selectivity of CO₂ in the reaction process. On both Pt/Al₂O₃ and Rh-based catalysts, the addition of K improves the selectivity of CO₂ [153,154]. On Ni-based catalysts, as shown in Figure 13, Alkali metals inhibit the formation of carbonyl nickel on the surface, prevent the occur of methanation, and improve the selectivity [155].

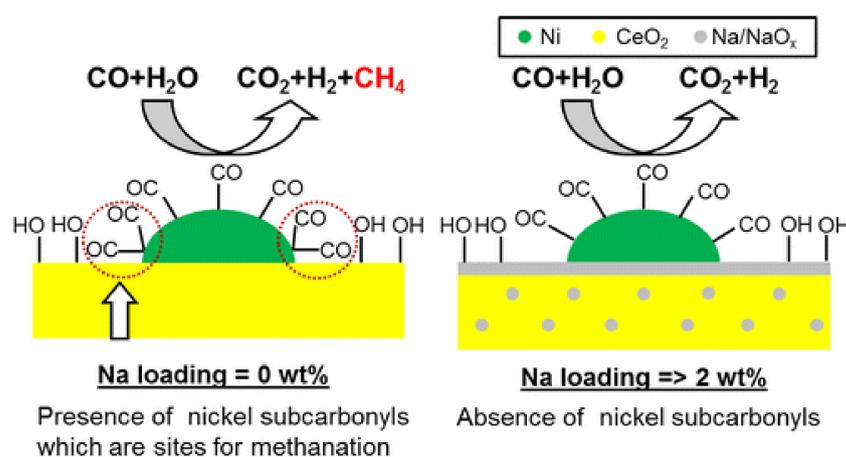


Figure 13. Mechanism of improvement of CO₂ selectivity over Ni-based catalysts [155]. Copyright 2014, ACS Publications.

3.2.2. Promotion Effects of K on Catalyst Properties

K affects the properties of CO oxidation catalysts, such as promoting the stability of active centers, increasing the number and activity of active centers, improving redox properties, and affecting surface active oxygen. K stabilizes the structure of Au on Au-based catalysts [156] and the metal state of Rh particles by the interaction between K and acidic sites on USY zeolite [157], thereby increasing the CO oxidation activity. K weakens the interaction between Ru and carrier silica, reduces the reduction stability of Ru, and keeps Ru in the state of metal Ru on Ru/SiO₂ [144] and stabilizes Cu⁺ on Cu-based catalysts [158] through the characteristics of electron donor.

K improves the dispersion, quantity and activity of active centers. K is considered to be served as anchor sites for Au on Au/TiO₂ catalyst [159]. K can improve the dispersion of Rh on Rh/SiO₂ [154], increase the percentage of surface active center Ru⁰ on Ru/SiO₂ [144] and change the surface Rh species to form more active sites on Rh/USY [157]. K also affects the redox property of the active center. The H₂-TPR result shows that the addition of K to CuO-CeO₂ catalyst decreases the reduction temperature of metal oxides [155], and XPS characterization reveals that the content of Ce³⁺ significantly increases [18].

K affects the surface reactive oxygen species and promotes the oxidation performance of the catalyst. The addition of K to the Pt/TiO₂ [26] and CuO/CeO₂ [160] promotes the formation of oxygen vacancy, which enhances the oxygen storage capacity, and increases the number of surface active oxygen species. K increases the proportion of reactive oxygen species, the peroxide and superoxide formed, in the process of O₂ adsorption on the surface of Ce_{0.8}Zr_{0.2}O₂ [161]. K transfers electrons to the Ce-O bond on Ce-based catalysts, thus increases the reactivity of oxygen, and prevents the reduction of oxygen capacity [137]. K enhances the synergism between Cu and CeO₂ on CuO-CeO₂ [160]. K also participates in the redox cycle of Ce [114]. The alkalinity of K has a positive effect on catalyst. K can interact with the catalyst on the Pt/Al₂O₃ and improve the coverage of OH groups on the surface, which participates in the catalytic oxidation of CO [162].

The doping of K promotes the stability of the catalyst. K improves the resistance of CO₂ and H₂O on Ru/SiO₂ [157]. In addition, K prevents carbon deposition on Ni-based catalysts, thus promoting the stability of the catalyst [18].

The preferential catalytic oxidation of CO in H₂ atmosphere has also been widely studied. K shows a unique promotion effect on PROX, in other words, K makes H₂ in the atmosphere no longer inhibit or even promote the oxidation activity of CO, since K suppresses the competition of H₂ on the catalysts. On Rh/USY catalyst, the CO oxidation activity of unmodified catalyst decreases significantly in H₂-rich atmosphere, while the activity of K-modified catalyst is not affected by the partial pressure of H₂ [157] because K inhibits the oxidation of H₂ [163]. The in-situ DRIFT result shows that K enhances the adsorption of bridged CO, so it is difficult to activate H₂ on Rh/USY, which leads to the high PROX activity. Similarly, with the addition of K on Rh-based catalysts, the electron donor effect of K increases the electron density of Ru, weakens the adsorption of H₂ on Ru and makes H₂ not be activated, so the reaction selectivity of PROX has been improved [144]. It is worth noting that the presence of H₂ in the atmosphere decreases the oxidation activity of CO on the Rh/SiO₂ catalyst, but promotes the oxidation activity of CO with the addition of K promoter [164]. The same phenomenon is also found on Pt-based catalysts [162]. K reduces the adsorption of CO in the PROX process on Pt/Al₂O₃ catalyst, the adsorption species of H₂ and O₂ (such as OH species) are formed on the surface, and the OH species participate in the oxidation of CO, so that the presence of H₂ in the atmosphere promotes the oxidation of CO [142].

3.2.3. Influencing Factors on Promotion Effect

The promotion effect of K is affected by the type and content of alkali metal, preparation method and carrier. The interaction between surface OH groups and alkali metal ions largely depends on the alkalinity, while K performs best promotion effect on Pt/Al₂O₃ due to its moderately alkaline [162].

The content of K also affects the promotion effect. The volcanic efficiency is well reflected in the content and the promotion effect on CO catalytic oxidation catalyst [165]. On Pt/TiO₂, the promotion effect is not obvious when K content is 0.1 wt%, but it is obviously promoted when K content is 0.3 wt%, while the activity decreases when K content increases to 0.5 wt% [26]. This is because an appropriate amount of K increases the dispersion of Pt, while an excessive amount of K reduces the dispersion of Pt. The catalyst shows the best activity as K/Rh = 3 on Rh/SiO₂. At a low K content, a strong interaction between K and Rh is obtained, while, at a high K content, too much K will cover the active sites, resulting in the decrease of the number of active sites [164]. On Pt/Al₂O₃ catalyst, at an alkali metal content of M/Pt < 3, all alkali metal ions except Li show promotion effect. At M/Pt > 3, Na and K continue to show promotion effect, but Rb and Cs show inhibitory effect [162].

The preparation method also has an effect on the promotion effect. The K-modified Ru/SiO₂ catalysts prepared by co-impregnation, sequential impregnation and sequential calcination are compared, and the catalysts prepared by sequential impregnation show the best activity [164]. A suitable preparation method is suggested to improve the dispersion of Rh and the interaction between Rh and K₂CO₃ [164].

For the same active center metal, K performs different promotion effect on different carriers. For Rh-based catalysts, K promotes the PROX activity on Rh/SiO₂ and Rh/USY catalysts, but the promotion mechanism is different. On the Rh/SiO₂ catalyst, K improves the dispersion of Rh with turnover frequency (TOF) not change, while on the Rh/USY catalyst, K improves the TOF with the dispersion of Rh unchanged [154]. Compared with the CuO-CeO₂ catalysts supported on CNT and reduced graphene oxide, it is found that K plays a better promotion effect on CNT, which is attributed to the fact that CNT has a better electron transfer effect than reduced graphene oxide [160].

In the two similar reactions of soot oxidation and CO oxidation, the promotion effect of K is consistent to a certain extent. K promotes the adsorption and dissociation of O₂,

and changes the reaction pathway. In addition, K increases the content of active center, improves the reducibility of active center, promotes the formation of active oxygen species, and improves the selectivity of CO₂ and the stability of the catalyst for the two kinds of oxidation catalysts. This provides a meaningful guidance for the application of K in oxidation catalysts. However, there is a lack of research on the state of K on the catalyst surface in CO oxidation. In different catalysts, especially different active centers, K shows opposite effects on the adsorption of CO and O₂. This reflects that different forms of K on the catalyst surface play different roles. More in-depth characterization and analysis of the existing state of K should be carried out.

Table 7. Summary of catalysts and reaction conditions for CO oxidation catalysts promoted by alkali metals.

Catalysts	Promoter	Content (wt%)	Reaction Conditions						References	
			Temperature Range (°C)	T ₅₀ ^a (°C)	CO (%)	O ₂ (%)	H ₂ (%)	Others		GHSV ^b or WHSV ^c
Pt/Al ₂ O ₃	K	0.02–0.42	120–280	165	1	1	\	\	9600 h ⁻¹	[140]
Pt/Al ₂ O ₃	K	10 ^d	50–200	80	0.2	0.2	75	\	30,000 h ⁻¹	[142]
Pt/Al ₂ O ₃	K	10–20 ^d	100–200	<100	0.45	0.45	50.25	0.34% CH ₄ , 16.55% CO ₂	12,000 h ⁻¹	[147]
Pt/Al ₂ O ₃	K	1–20 ^d	100	<100	0.2	0.2	75	\	30,000 h ⁻¹	[162]
Pt/Al ₂ O ₃	K	5–20 ^d	50–180	70	0.2	0.2	75	\	30,000 h ⁻¹	[153]
Rh/SiO ₂	K	3	50–150	100	0.2	0.2	75	\	0.015 g s mL ⁻¹	[154]
Rh/USY	K	1–10 ^d	80–150	100	0.2	0.2	75	\	0.015 g s mL ⁻¹	[157]
Au/Al ₂ O ₃	Li, Rb	1–30 ^e	50–300	<50	2.67	1.33	\	\	2500 h ⁻¹	[156]
Rh/SiO ₂	K	1–10 ^d	50–200	120	0.2	0.2	75	\	0.015 g s mL ⁻¹	[164]
CuO-CeO ₂ /CNT	K	0.5–2	50–200	110	1	1	50	\	0.03 g s mL ⁻¹	[160]
CuO-CeO ₂ /graphene	K	0.17–0.71 ^d	80–220	<80	1	1	50	\	0.15 g s mL ⁻¹	[144]

^a T₅₀ represents the temperature when the efficiency is 50%. ^b GHSV means gaseous hourly space velocity (h⁻¹). ^c WHSV means weight hourly space velocity (g s mL⁻¹). ^d The molar ratio of alkali metal to active center. ^e The atomic ratio of alkali metal to Al.

3.3. WGS

Water-gas shift reaction is the reaction of CO with H₂O to form CO₂ and H₂, as shown in Equation (11). This is an important reaction to produce and purify H₂. The commonly used catalysts are Cu-based, Pt-based and Co-based catalysts. The reaction conditions are shown in Table 8. The WGS reaction is divided into three processes, the adsorption of CO and H₂O, the reaction of CO with H₂O on the catalyst to form CO₂ and H₂, and the desorption of CO₂ and H₂.



3.3.1. Promotion Effects of K on Reaction Process

The promotion effect of K on WGS reaction has been widely found. K promotes the adsorption and dissociation of reactants, the production and decomposition of intermediates and the selectivity of CO₂ products. K promotes the adsorption of CO gas molecules by adsorbing CO to bridge CO₃²⁻ on Ni/CeO₂ [18]. On Mo₂C catalysts, the results of high resolution electron energy loss spectroscopy (HREELS), Auger Electron Spectroscopy (AES) and TPD show that K stabilizes and activates the adsorbed CO, so that most of the CO is dissociated rather than desorbed among 77–277 °C [166]. K also promotes the adsorption of CO through the electrostatic interaction between K^{δ+} and O^{δ-} [27]. Another effect is altering the adsorption of reactants. When K₂CO₃ is used to modify the Ru/C catalyst, a large amount of water is adsorbed around the active site, which reduces the

strong adsorption of CO and balances the adsorption of H₂O and CO on the active site, thus increasing the WGS activity [167].

K promotes the dissociation of H₂O and decomposition of intermediates [14]. The H¹⁸O-adsorbed TPD characterization shows that the addition of K to Co-based catalysts obviously promotes the dissociation of H₂O, thus increasing the activity of WGS [168]. The promotion on the dissociation of H₂O, the limited process of WGS, can reduce the apparent activation energy and increase the catalytic activity [27]. In addition, K favors the thermochemistry for water dissociation on Cu/TiO₂ with the cleavage of an O-H bond occurring at room temperature [169]. The addition of K on Pt-based catalysts weakens the strength of C-H bond in intermediate formate and promotes the decomposition of intermediate products [170].

K also improves the selectivity in the reaction process, and the mechanism of improving the selectivity on Ni-based catalysts is shown in Figure 14 [171]. On the non-K catalyst, methanation reaction occurs between CO₂ adsorbed on the carrier and H adsorbed on Ni; on the K-modified catalyst, the K locates near Ni, adsorbs OH groups, and then inhibits the methanation reaction. The Pt-based catalysts modified by KOH has also been found to improve the selectivity of CO₂ [172].

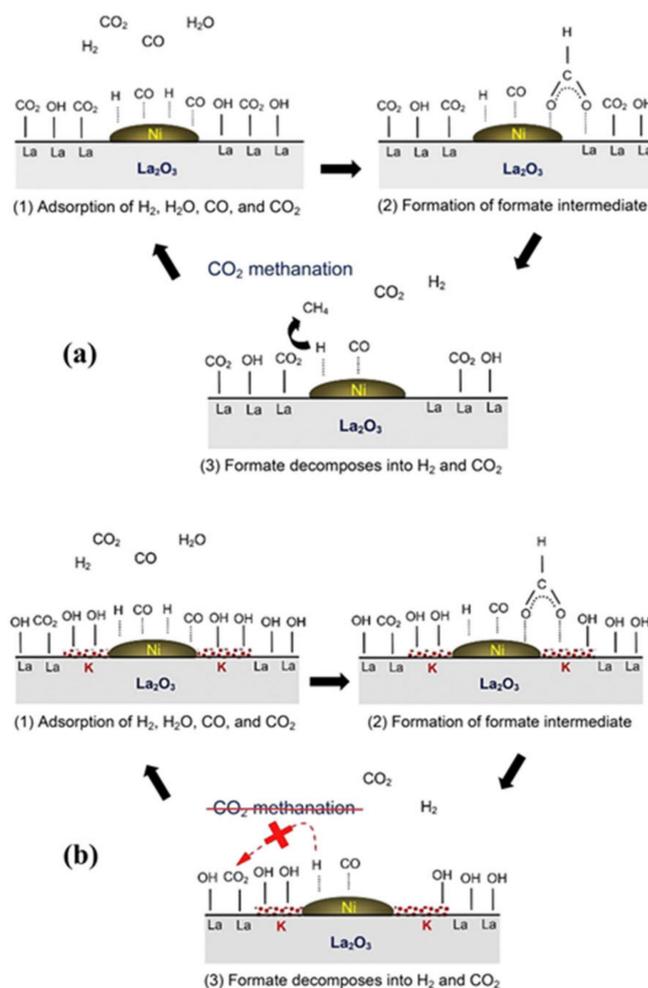


Figure 14. The mechanism of alkali metals improving the selectivity of water-gas shift (WGS) [171]. (a) the reduced LaNiO₃ perovskite catalyst and (b) the reduced K-doped LaNiO₃ perovskite catalyst. Copyright 2017, Elsevier.

3.3.2. Promotion Effects of K on Catalyst Properties

K has a significant effect on the properties of WGS catalyst, such as the stability, type, and dispersion of active sites, as well as surface reactive oxygen species. The addition of K promoter to cobalt carbide catalysts maintains the carbonized phase of Co and stabilizes the active center [14]. In addition, the promotion effect of K lies in the formation of active centers. The key steps of WGS on Pt-based catalysts are CO adsorption and H₂O activation, both of which occur at the oxidized Pt site. New active species with higher activity at low temperature can be formed by adding K, especially on Pt-based and Au-based catalysts. And the new active sites can be summarized as Pt-alkali-O_x(OH)_y [173] and AuO_y(OH)_z(K)_x [90]. Based on the results of density functional theory (DFT), PtK₆O₄(OH)₂ is considered to be the most promising candidate [173].

There are many sources of the promotion effect of K on the surface active center. After the addition of K to cobalt molybdenum carbide catalysts, the activity of WGS reaction has been increased, in that the electron donor of K promotes the electronic properties of active sites [168]. K stabilizes the dispersion of Pt atoms on Pt/SiO₂ and Pt/CeO₂ [174,175]. K increases the reducible oxygen on the surface of Pt/SiO₂ and Pt/Al₂O₃, thus improving the activity [173]. This is similar to that K weakens the bond between oxygen and the surface of Al₂O₃ [175]. In addition to the active center, the promotion effect of K on the carrier is also proposed. K modifies the properties of Al₂O₃ and TiO₂ on Pt/Al₂O₃ and Pt/TiO₂ resulting increasing the catalytic activity, but remaining the rate per mole of surface Pt and the WGS kinetics [176].

K also improves the stability of the catalyst for WGS reaction. Comparing the changes of C/(Co + Mo) and O/(Co + Mo) before and after the reaction, it is found that the addition of K on cobalt molybdenum carbide catalysts significantly reduces carbon deposition and promotes the formation of CO₂ [168].

3.3.3. Influencing Factors on Promotion Effect

The promotion effect of K on WGS reaction catalyst is affected by the type and content of alkali metal, precursor, and temperature. On Co-Mo/Al₂O₃ catalyst, K is one of the best promoters for WGS reaction, and for the precursor of K, K₂CO₃ is found to be the most stable source [177]. The promotion effect of alkali metal species on Co₃O₄ catalyst in WGS reaction follows the order of K > Na > Rb > Cs, and K also shows the best promotion effect [14,178]. However, the order of alkali metal promotion effect is different on Cu(111) and Cu(110), following the order of Cs > Rb > K > Na. And the promotion effect of K is related to work function and surface dipole moment [27]. The lower work function and the higher surface dipole moment can lead to an obvious promotion effect.

There is a volcanic relationship between promotion effect and the content. Adding 0.20–5.89 wt% of K to the Co₃O₄ catalyst, the promotion effect gradually increases with the increase of K content. The best promotion effect is obtained when the K content is 3.93 wt%, and then the promotion effect gradually decreases with the increase of K content [178]. The same trend is also found on Ni-based catalysts among the content of K from 1 to 10 [18]. In addition, the temperature has a great effect on the catalytic activity of the K-modified catalyst. This is due to the weak binding force of K, which is easily lost at high temperature, resulting in poor stability of the catalyst [179].

In the WGS reaction, the promotion effect of K is mainly attributed to the promoting the adsorption of CO, balancing the adsorption of CO and H₂O, changing the reaction pathway, improving the selectivity of CO₂, stabilizing the active center, and improving stability. The important finding is that K combines with the active center metal to form a new active center, which is rarely found in other reaction. K can reduce carbon deposition and promote the formation of CO, which provides a choice for K in the chemical industry to improve catalyst stability. There is a lack of research on the influence of precursors. Only the influence of alkali metal type is studied, but the optimal alkali metal type is different under different systems.

Table 8. Summary of catalysts and reaction conditions for WGS catalysts promoted by alkali metals.

Catalysts	Promoter	Content (wt%)	Reaction Conditions						References
			Temperature Range (°C)	T ₅₀ ^a (°C)	CO (%)	H ₂ O (%)	Others	GHSV ^b or WHSV ^c	
Co ₃ O ₄	K	0.2–5.89	300	<300	3.22	16.13	22.58% H ₂	0.0077 g s mL ⁻¹	[178]
Co ₃ O ₄	Li, Na, K, Rb, Cs	0.02–0.05 ^d	180–300	215	3	26.1	29.9% H ₂	2.4 g s mL ⁻¹	[14]
cobalt molybdenum carbide	K	2	180	<180	10.5	21	20% H ₂	0.2 g s mL ⁻¹	[168]
Pt/ceria	Li, Na, K, Rb, Cs	0.15–2.9	225–275	250	2.8	46.7	50.5% H ₂	0.018 g s mL ⁻¹	[170]
Pt/SiO ₂	Na	1–3	150–350	220	2	10	\	0.09 g s mL ⁻¹	[173]
Pt/Al ₂ O ₃	Li, Na, K	7–125 ^d	230–250	\	6.8	21.9	8.5% CO ₂ , 37.4% H ₂	0.796 g s mL ⁻¹	[176]
Pt/TiO ₂	Na	1–10	200–300	\	2.83	5.66	37.74% H ₂	0.012–0.2 g s mL ⁻¹	[180]
Ni/CeO ₂	K	1–10	300–600	320	5 mol.%	25 mol.%	\	68,000 h ⁻¹	[18]
LaNiO ₃	K	2.5–10	350–550	<350	5	25	\	0.06 g s mL ⁻¹	[171]
Ru/C	K	2–10	200–325	295	10	20	\	0.3 g s mL ⁻¹	[167]

^a T₅₀ represents the temperature when the efficiency is 50%. ^b GHSV means gaseous hourly space velocity (h⁻¹). ^c WHSV means weight hourly space velocity (g s mL⁻¹). ^d The molar ratio of alkali metal to active center.

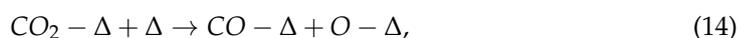
3.4. RWGS

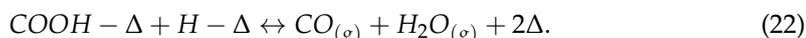
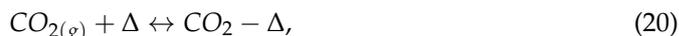
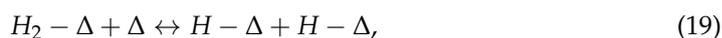
Reverse water-gas shift reaction is the reverse reaction of WGS, used to convert CO₂ into CO, which is an important raw material for chemical production. The reaction is shown in Equation (12). The commonly used catalysts are Fe-based, Pt-based, and Ni-based catalysts, and the reaction conditions are shown in Table 9.



3.4.1. Promotion Effects of K on Reaction Process

K shows a promotion effect on RWGS reaction [181], which is embodied in the adsorption of reactants, the change of reaction pathway and the selectivity of product CO. The alkalinity of K promotes the adsorption of acidic reactants CO₂ [182,183]. As an electron promoter, K promotes electron transfer and enhances the electrostatic interaction between the catalyst and reaction molecules [184]. It is found that the stable intermediates additionally appear after adding K with the reaction pathway changed on Fe/Al₂O₃ [185]. For the Fe-based catalysts, RWGS follows the redox mechanism before modification, as shown in Equations (13)–(17), and an associative pathway completes the reaction after adding K, as shown in Equations (18)–(22) [185]. The Δ in equation represents the active site. On Pt-based catalysts, K weakens the adsorption strength of CO on Pt through electronic properties, resulting in a weak interaction between CO and Pt which promotes the formation of formic acid intermediates [186]. K improves the selectivity of CO in the reaction process [187]. It is found that K increases the binding energy, improves the reaction activity of CO₂, and promotes the cleavage of C = O bond and the formation of CO on Mo₂C [188].





3.4.2. Promotion Effects of K on Catalyst Properties

K has an important influence on the dispersion, stability and activity of the active center. K improves the dispersion of Ni on Ni/Al₂O₃ [181]. And K can keep the active center Mo in the reduced state and active state on Mo-based catalysts [182]. K forms new active sites at the interface of Cu-K on Cu/SiO₂. Moreover, the addition of K can form K₂O, which is considered to be the active site for the decomposition of formates [189]. H₂-TPR and XPS results show that a strong interaction between K and Pt stabilizes Pt in a high oxidation state on Pt-based catalysts [186]. The new interface between KO_x and Pt formed by adding K is considered as the active site for the decomposition of formic acid to produce CO [186]. Consistent with the WGS reaction, XANES and XPS results show that the addition of K promotes the formation of Pt-O(OH)-K, and in-situ DRIFT spectroscopy and microcalorimetry measurements determine that the Pt-O(OH)-K interface is the main active site to adsorb CO₂ and produce bridge-bonded formate intermediates [190].

3.4.3. Influencing Factors on Promotion Effect

The promotion effect of K on RWGS reaction is affected by the content of K. The atomic ratio of K/Pt from 5 to 200 is studied on Pt-based catalysts, and the promotion effect is the best when the atomic ratio of K/Pt is 80, and too much K will have a blocking effect, thereby weakening the promotion effect [190].

K shows promotion effect on the two reverse reactions of WGS and RWGS, but there are similarities, as well as differences, between the two kinds of reactions. The similar influence of K is forming active centers. Taking the Pt-based catalysts as an example, K forms the Pt-O(OH)-K active species and promotes the formation of the reaction intermediate formate species. Interestingly, the formed Pt-O(OH)-K species can promote both WGS and RWGS. The difference lies in the catalytic temperature, as shown in Tables 8 and 9. The promotion of K for WGS is shown at low temperature (<400 °C), while, for RWGS at high temperature, (>400 °C). In addition, K shows the ability to weaken the C-H bond in WGS reaction, while shows the ability to weaken the C = O bond in RWGS reaction. The promotion effect of K for WGS and RWGS both originates in the formation of intermediate formate species. However, there is a lack of research on the influence of type of alkali metals and precursors.

Table 9. Summary of catalysts and reaction conditions for reverse water-gas shift (RWGS) catalysts promoted by alkali metals.

Catalysts	Promoter	Content (wt%)	Reaction Conditions				References	
			Temperature Range (°C)	T ₂₀ ^a (°C)	CO ₂ (%)	H ₂ (%)		GHSV ^b or WHSV ^c
Fe/Al ₂ O ₃	K	1–4	480	\	15/60	60/15	0.018–0.036 g s mL ⁻¹	[185]
Fe/Al ₂ O ₃	Cs	0–5	400–800	<400	CO ₂ :H ₂ = 1:4		0.3 g s mL ⁻¹	[191]
Ni/Al ₂ O ₃	K	2	400–700	400	50	50	0.24 g s mL ⁻¹	[181]
Pt/zeolite	K	5–200 ^d	200–500	450	45	45	0.12 g s mL ⁻¹	[190]
Mo ₂ C/γ-Al ₂ O ₃	K	1–3	300	<300	CO ₂ :H ₂ = 1:3		0.24–1.2 g s mL ⁻¹	[182]
WC/γ-Al ₂ O ₃	Na, K	0.25 ^d	350	350	CO ₂ :H ₂ = 1:3		0.4–4 g s mL ⁻¹	[187]
Co-CeO ₂	K	1	400–600	425	CO ₂ :H ₂ = 1:1		0.012 g s mL ⁻¹	[192]
Cu/SiO ₂	K	0.52–5.2	200–600	>600	50	50	\	[189]

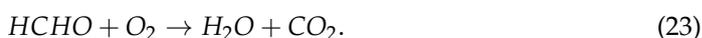
^a T₂₀ represents the temperature when the efficiency is 20%. ^b GHSV means gaseous hourly space velocity (h⁻¹). ^c WHSV means weight hourly space velocity (g s mL⁻¹). ^d The molar ratio of alkali metal to active center.

4. Removal and Reuse of VOCs

VOCs produced by industrial production has a serious impact on the environment and human body. Some of them are toxic and carcinogenic. VOCs is also a contributing factor to haze and photochemical smog. The methods of removal and reuse of VOCs include catalytic oxidation and reforming reaction.

4.1. VOCs Oxidation

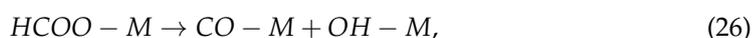
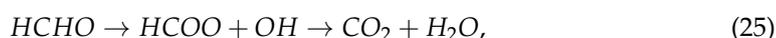
VOCs catalytic oxidation is that VOCs are oxidized to small molecules, such as CO₂ and H₂O, and may simultaneously produce by-products, such as CH₄ and CO. Taking formaldehyde as an example, the reaction process is shown in Equation (23). Catalytic oxidation is commonly used to remove VOCs in motor vehicle exhaust and industrial flue gas. And partial oxidation of VOCs is the important way to produce chemical raw materials. The commonly used catalysts are Pt-based, Cu-based, Ni-based, and Co-based catalysts, and the reaction conditions are shown in Table 10.



4.1.1. Promotion Effects of K on Reaction Process

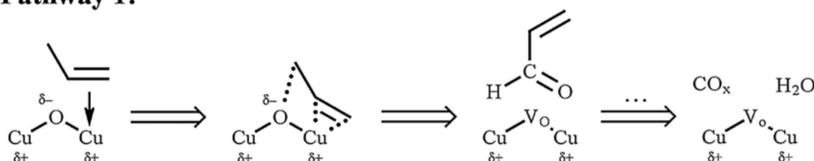
The promotion effect of K on the catalytic oxidation of VOCs has been widely studied [193–195]. These includes the promotion of the affinity of oxygen species, the decomposition of reaction intermediates, the influence of reaction pathway, and the promotion of product selectivity. The in-situ DRIFT results show that the addition of K enhances the decomposition of intermediate formate on Pt/Al₂O₃ catalysts [196]. The addition of K to Pt-based catalysts promotes the decomposition of intermediate formaldehyde in the dichloromethane oxidation reaction [170,197], in that the formation of Pt-O(OH)_x-K species changes the reaction pathway of formaldehyde and the reaction equilibrium, thus accelerates the decomposition of formaldehyde to form CO [198]. For the oxidation of benzyl alcohol on Cu/NaY, K increases the type of adsorbed oxygen and provides greater affinity of oxygen [199].

K opens up a new reaction pathway for the catalytic oxidation of VOCs. In the catalytic oxidation of formaldehyde over Pt/TiO₂ catalyst, K stabilizes the dispersed Pt-O(OH)_x-alkali metal species on the surface, significantly improves the activity of formaldehyde oxidation by activating H₂O and catalyzing the reaction of surface OH groups with formates [198]. On the non-K catalyst, the results of in-situ DRIFT show that the oxidation of HCHO follows the formate decomposition route, as shown in Equation (24). However, a new reaction pathway appears on the K-modified catalysts, the direct oxidation pathway of formate is shown in Equation (25). The reaction between surface hydroxyl group and formate is prior to the decomposition of formate into CO, and then oxidation of CO [200]. The kinetic results show that K obviously increases the reaction rate due to the new formation of OH group, which also confirms that the reaction pathway has changed [198]. The existence of OH group inhibits the direct decomposition of formate, as shown in Equation (26), and promotes the direct oxidation process of formate, as shown in Equation (27). Moreover, the existence of K continuously supplements the OH group by activating H₂O. The effect of K on weakening the C-H bonds also be found on H-Zeolite Socony Mobil-5-supported Pd catalysts (Pd/H-ZSM-5) [201], similar to the finding in WGS. Similarly, the C-H bond is weakened by K observed at low temperature (<400 °C).



K promotes the selectivity of VOCs oxidation. K improves the oxidation selectivity by reducing the reactivity of lattice oxygen on Fe-based catalysts in propylene epoxidation [202] and reduces the by-product acetaldehyde production on the Co-Mn-Al catalyst in ethanol oxidation [203]. For the propylene partial oxidation over $\text{CuO}_x/\text{SiO}_2$ catalysts, K decreases the nucleophilic strength of oxygen in CuO_x by attracting its electrons, accompanied by a notable shift in selectivity from acrolein towards propylene oxide, as shown in Figure 15 [16].

Pathway 1:



Pathway 2:

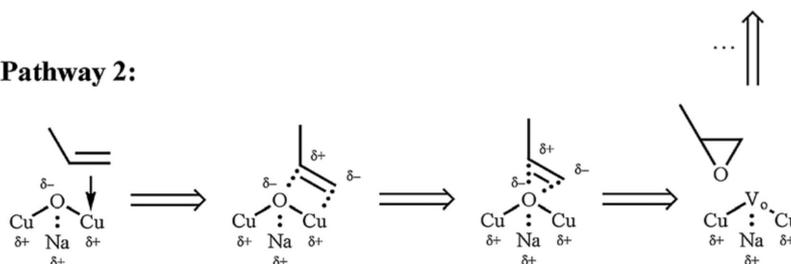


Figure 15. Effect of alkali metals on selectivity of propylene oxidation over $\text{CuO}_x/\text{SiO}_2$ [16]. Copyright 2018, Elsevier.

4.1.2. Promotion Effects of K on Catalyst Properties

K has an effect on the active center of VOCs oxidation catalyst, such as increasing the surface active species, improving the dispersion of active center, and reducing the size of metal cluster, increasing the specific surface area, improving the basicity and redox properties, and improving the stability of the catalyst. K can form a new species Pt-O-K_x on the surface to enhance the reducibility of the catalyst on $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst in dichloromethane oxidation [173]. It is further found that the washing process has no effect on the activity, indicating that K plays a role by connecting with the catalyst, which indirectly proves the formation of new species Pt-O-K_x [198].

K has an effect on the properties of the active center of VOCs oxidation catalyst. The addition of KCl changes the local coordination of Fe through electronic interaction on $\text{FeO}_x/\text{SBA-15}$, resulting in the formation of tetrahedral configuration of Fe [202]. K also improves the dispersion of active center on Fe-based catalysts [202], Au-based catalysts [204], and Pd-based catalysts [201]. And the EXAFS results show that K reduces the particle size of Pt on Pt/TiO_2 [198]. K also increases the specific surface area and basicity on NiCo_2O_4 catalyst [205] and Co-Mn-Al catalyst [203].

The electron supply of K improves the reactivity of O in M-O bond, so the catalytic oxidation activity can be promoted [137]. Moreover, the effect of K on the increase of valence state of active center has been widely found on Co-Mn-Al [203], Co/NaY [206], Co/NaUSY [207], and $\text{Pt}/\text{Al}_2\text{O}_3$ [196]. And K can increase the oxidation performance by increasing the electrophilic oxygen species [205] and forming hydroxyl species [173,180] on the surface. In addition, K also improves the stability of the catalyst. Compared with catalysts without K, the hydroxyl species appear near Pt stabilized by K. The addition of K to the Pt/TiO_2 catalyst used in the oxidation reaction of formaldehyde improves the stability in humid atmosphere [198].

4.1.3. Influencing Factors on Promotion Effect

The effect of K on the catalytic oxidation of VOCs is affected by the type, precursor, the content and atmosphere. The K performs the best promotion effect on FeO_x/SBA-15 than Na, Rb, and Cs [202]. And KCl is the suitable precursor than K₂CO₃, KNO₃ and KBr. The content corresponding to the best effect is different in different types of VOCs oxidation. The effect of 0–3 wt% content K on Co-Mn-Al catalyst is studied. The K content of 1 wt% shows the best activity in toluene oxidation, while the activity increases with the increase of K content in ethanol oxidation [203]. The volcanic relationship between promotion effect and the content is found on Pt-based catalysts among the ratio of K/Al from 0.02 to 0.1 [208]. The inhibition of excessive K is attributed to the hindrance of the formation of a large number of three-dimensional crystallites on the surface [209].

The ratio of reactants to O₂ in the atmosphere affects the promotion effect of K. On the Pt/Y₂O₃-ZrO₂ catalyst, under the condition of C₃H₆/O₂ near to the stoichiometric ratio, K shows a strong promotion effect [210]. However, when O₂ is in large excess, K loses its promotion effect, or even performs an inhibitory effect [211], while K shows a strong promotion effect on Pt/β-Al₂O₃ catalyst under stoichiometric ratio and oxygen-rich conditions [212].

The promotion effect of K on VOCs oxidation is similar to that of soot oxidation and CO oxidation. Among them, K affects the reaction pathway, product selectivity, redox properties of catalysts, and the formation of active oxygen species. Different from soot oxidation and CO oxidation, the addition of K to catalysts for the VOCs oxidation plays a role in promoting the dissociation of intermediate species, thus promoting the activity of the reaction. The weakening of C-H bond is also found at low temperature (<400 °C). In VOCs oxidation, new species of K formed on Pt-based catalysts are also commonly found. However, it is found that K can increase the metal valence in VOCs oxidation, which is inconsistent with the results in the N₂O and NO decomposition, and further research is needed. Due to the different target reactants of VOC oxidation, the promotion effect of K content shows inconsistency. It is worth noting that the application of K-modified catalyst to VOCs oxidation in industrial flue gas needs to consider the effect of atmosphere on K promoter in detail.

Table 10. Summary of catalysts and reaction conditions for volatile organic compounds (VOCs) oxidation catalysts promoted by alkali metals.

Catalysts	Promoter	Content (wt%)	Reaction Conditions						References
			Temperature Range (°C)	T ₅₀ ^a (°C)	VOCs	O ₂ (%)	Others	GHSV ^b or WHSV ^c	
Pt/Al ₂ O ₃	K	0.02–0.05	225–500	275	3000 ppm Dichloromethane	\	air	15,000 h ⁻¹	[196]
Pt/TiO ₂	Na	1–2	15–200	<15	600 ppm Formaldehyde	20	50% Relative humidity	120,000 h ⁻¹	[198]
Pt/Al ₂ O ₃	K	0.02–0.1 ^f	100–350	200	500 ppm ethanol	\	air	0.072 g s mL ⁻¹	[208]
Co/NaY Co/SiO ₂	Li, Na, K, Rb, Cs	2–16	350	>350	2.78% benzyl alcohol	8.33	N ₂	520 g s mol ⁻¹	[207]
Co/NaY Co/NaUSY	K	0–25 ^d	350	>350	2.78% benzyl alcohol	8.33	N ₂	520 g s mol ⁻¹	[206]
Co-Mn-Al	K	0–3	100–400	145	1 g/m ³ toluene and ethanol	\	air	0.36 g s mL ⁻¹	[203]
Co _{0.1} /ZrO ₂	Cs	0.15	\	296	1000 ppm toluene	10	N ₂	10,500 h ^{-1e}	[213]
NiCo ₂ O ₄	K	2	220–400	330(T ₉₈)	Toluene; acetone; alcohol; acetic ether	\	air	5000 h ⁻¹	[205]

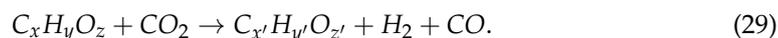
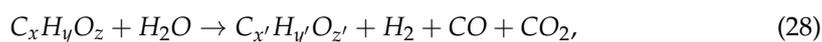
Table 10. Cont.

Catalysts	Promoter	Content (wt%)	Reaction Conditions						References
			Temperature Range (°C)	T ₅₀ ^a (°C)	VOCs	O ₂ (%)	Others	GHSV ^b or WHSV ^c	
Cu-Mg-Al	K	0.9	250–600	415	0.5% Methane	4.5	He	\	[214]
Cu/ZrO ₂	Cs	0.15	250–500	480	1000 ppm toluene	10	N ₂	10,500 h ⁻¹ ^e	[215]
Fe/SBA-15	Li, Na, K, Rb, Cs	5 ^d	320	>320	2.5% Propylene	\	25% N ₂ O	0.2 g s mL ⁻¹	[202]
Natural manganese ore	K	0.07	200–330	225	550 ppm o-xylene	20%	N ₂	0.6 g s mL ⁻¹	[216]

^a T₅₀ represents the temperature when the efficiency is 50%. ^b GHSV means gaseous hourly space velocity (h⁻¹). ^c WHSV means weight hourly space velocity (g s mL⁻¹). ^d The molar ratio of alkali metal to active center. ^e This represents a liquid hourly space velocity (LHSV). ^f The represents the ratio of K and Al.

4.2. Reforming Reaction

The reforming reaction is the reorganization of organic molecules into gaseous small molecules, such as CO, H₂, etc. The steam reforming and CO₂ reforming are shown in Equations (28) and (29). The reforming reaction is the important way to produce chemical raw materials. The commonly used catalysts are Pt-based catalysts and Ni-based catalysts. The reaction conditions are shown in Table 11.



4.2.1. Promotion Effects of K on Reaction Process

K plays an important role in the reforming reaction, such as the adsorption of reactants, the selectivity of products, and reaction pathway. The addition of K can promote the chemisorption of CO on the surface of Mo carbide and Mo(100) [166]. Because of its alkalinity, K also promotes the adsorption of CO₂ [217]. The addition of K can promote the activity and stability of the reforming of methanol, and K is a good promoter to increase the production of CO₂ on the Ni/Al catalyst [19]. The promotion effect of K on selectivity is also found on Mo₂C [218] and Pt/Al₂O₃ [219]. The acidic sites of alumina catalyze the dehydration of ethanol, and the addition of K neutralizes these acidic sites thus inhibits the formation of ethylene, which is beneficial to improve the selectivity of the reforming of methanol [208]. Through TPD, it is found that K reduces the stability of surface acetate species, so that they can be decomposed at lower temperatures to produce the CO₂ and CH₄, favoring to improve the selectivity [219]. K changes the ethanol adsorption from bridged form acetate to monodentate form acetate on the Co/α-Al₂O₃, thereby increasing selectivity of ethanol to H₂ [220]. The surface acetate can inhibit the steam reforming activity of Pt-based catalysts and lead to a significant decrease in the number of products, but also promote the formation of ethylene. The promotion effect of K on the decomposition of acetate significantly enhances the selectivity of the target products (H₂ and CH₄) of steam recombination [219]. On K-promoted Pt-hydroxalcalite catalysts (K-Pt-HT) for reforming of glycerol to the production of H₂, K changes the reaction pathway and reduces the formation of by-products, thereby increasing the selectivity of H₂, as shown in Figure 16 [221].

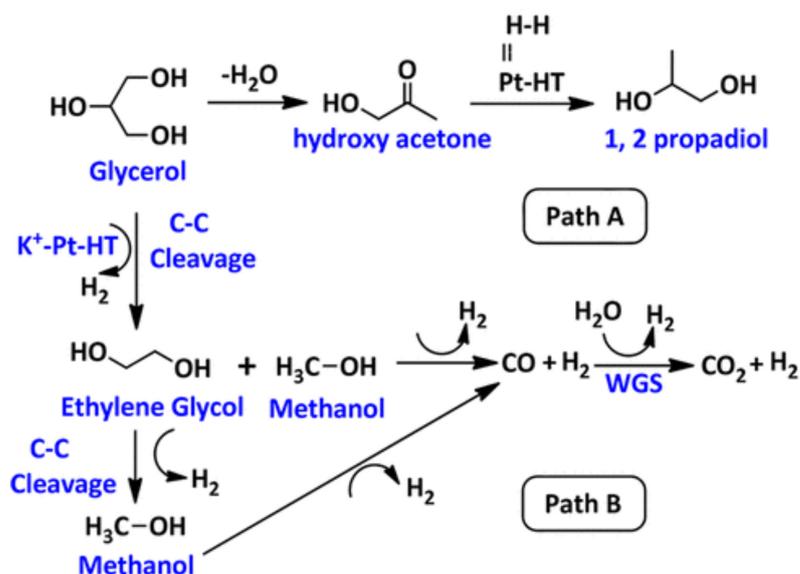


Figure 16. Reaction pathway of H₂ formation in glycerol reforming promoted by K [221]. Copyright 2017, American Chemical Society.

4.2.2. Promotion Effects of K on Catalyst Properties

More and more attention has been paid to the effect of K on the active center of the reforming catalyst. It is embodied in the generation of metal-carrier interaction, the change of redox, the increase of the content of active sites and the improvement of stability. It has been discovered that K leads to strong metal to support interaction (SMSI), especially on Ni/Al₂O₃ [222,223]. The H₂-TPR results show that K shifts the reduction peak of the catalyst to high temperature, which means that the interaction between the active center and the carrier becomes stronger. And adding K can increase the number of active Ni sites and realize a higher activity on the Ni/Al₂O₃ catalyst [224].

K also significantly improves the stability of the catalyst for the reforming reaction. The role of K in preventing the occurrence of coking on the catalyst surface is widely recognized [225]. It can be attributed to the ability of K to divide the surface into small parts [226], promote CO₂ adsorption and strengthen carbon gasification [217,224], strengthen the boudouard reaction [227] which C reacts with CO₂ to produce CO, reduce acid sites on the carrier surface [228] and depress the metal sintering [229].

4.2.3. Influencing Factors on Promotion Effect

The promotion effect of K on the catalysts for reforming reaction is affected by the type and the content of K. It is found that K shows the best promotion effect than other alkali metals on Ni-based catalysts [230]. Moreover, K shows a low coke deposition and a high catalytic activity on Ni/γ-Al₂O₃ catalyst [223]. The addition of K with 1, 5, 10 wt% content to the Ni/Al₂O₃ catalysts for methane reforming shows that the K content with 1 wt% and 5 wt% shows promotion on activity, while the K content with 10 wt% shows inhibition on activity [226].

The role of K in the reforming reaction is similar to that in WGS and RWGS reactions. All of them can promote the adsorption of reactants and the formation of reaction intermediates, and improve the selectivity of products. In the removal and reuse of VOCs, the promotion effect of K has been well found in the formation of new active centers, the decomposition of intermediates, and the generation of new reaction pathways. Due to the wide variety of VOCs, the promotion effect of K on the change of reaction pathway will be changeable. DFT is an advantageous method to clarify the specific role of K in reaction pathway and the change of the existing state of K. In the reforming reaction, the discovery that K leads to SMSI is noteworthy, especially on Ni-based catalysts. In addition, there is

lack of research on the influence of the precursors. The wide variety of VOCs makes the research on the type of alkali metals and precursors become more important.

Table 11. Summary of catalysts and reaction conditions for reforming catalysts promoted by alkali metals.

Catalysts	Promoter	Content (wt%)	Reaction Conditions						References
			Temperature range (°C)	T ₉₀ ^a (°C)	VOCs	CO ₂ (%)	H ₂ O (%)	GHSV ^b or WHSV ^c	
Ni/Al ₂ O ₃	K	0.04–0.69 ^d	700	>700	50% Methane	50	\	22,500 h ⁻¹	[223]
Ni/Al ₂ O ₃	Na, K	0–18	350–600	400	6–7.5 ^f Acetic acid, ethanol, 1-propanol, propanoic acid			12.1 h ⁻¹ g	[224]
Ni/Al ₂ O ₃	K	0.5–2.9	800	<800	Methane: CO ₂ = 1:1			1.26 g s mL ⁻¹	[231]
Ni/MgO	Li, Na, K	1	650	<650	8% Ethanol	\	8	40,000 h ⁻¹	[232]
Ni-La/cordierite	K	5 ^e	500–700	650	3.5 ^f kerosene			2300 h ⁻¹	[228]
Ni incorporated mesoporous smectite	Li, Na, K, Rb, Cs	1	450	<450	3.3 ^f Acetic acid	\	27	0.005 g s mL ⁻¹	[230]
Pt/Al ₂ O ₃	K	0.04–0.4	450	<450	Ethanol : H ₂ O = 1:3			0.05 g s mL ⁻¹	[219]

^a T₉₀ represents the temperature when the efficiency is 90%. ^b GHSV means gaseous hourly space velocity (h⁻¹). ^c WHSV means weight hourly space velocity (g s mL⁻¹). ^d The molar ratio of alkali metal to active center. ^e The weight content percentage (wt%) of K₂O. ^f This represents a given steam to carbon ratio. ^g This represents a liquid hourly space velocity (LHSV).

5. Summary

To summarize, K shows promotion effect in many kinds of reactions, and plays an important role in the removal and reuse of NO_x, CO_x (x = 0, 1, 2), and VOCs. The promotion effect of K on the catalytic reaction is mainly reflected in three aspects: the reaction process, structural properties and chemical properties of catalysts. The promotion effects on the reaction process include the adsorption of reactants, desorption of products, reaction pathway, recovery of active center, and selectivity. The promotion effects on the catalyst properties involve improving basicity, increasing the content of active centers, improving stability, improving the electron donor characteristics, changing the redox property, increasing the surface area and promoting SMSI. The bibliometrics is an effective method to analyze and reflect the relationship between different factors [233]. The correlation results of the promotion effect of K on the commonly used active centers and types of promotion effect for different pollutants are shown in Figure 17. It can be clearly seen that, on Co-based, Mn-based, and Pt-based catalysts, K shows the promotion effect of the removal and reuse of the all types of pollutants. In addition, on Fe-based, Cu-based, Mo-based, and Ni-based catalysts, there are more research on the promotion effect of K in the removal and reuse of CO_x and VOCs. For the types of metals, the research of transition metals is significantly more than that of alkaline earth metals and noble metals. The correlation between the types of promotion effect and pollutants can reflect the importance of specific promotion effect for a certain pollutant. The promotion effects on reactant, pathway, stability and active center are important for all three pollutants. Additionally, the promotion effects on electronic properties are important for NO_x, surface area, and basicity are important for CO_x, and basicity and redox properties are important for VOCs.

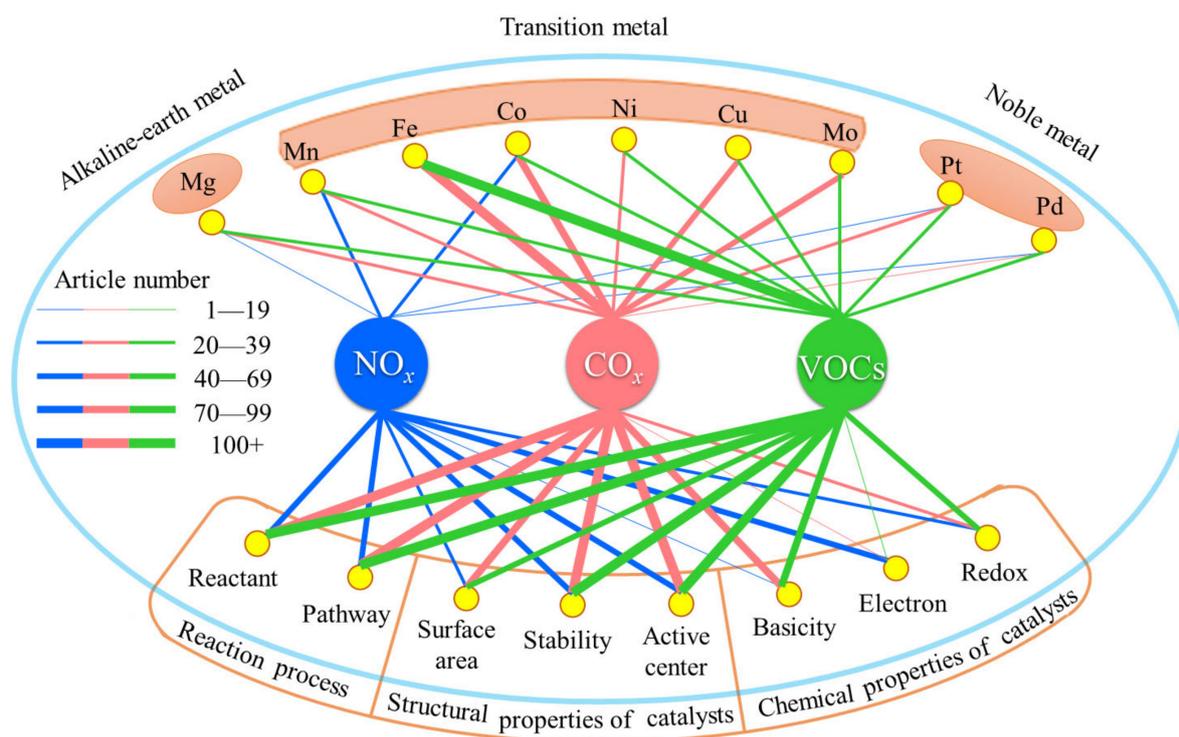


Figure 17. The correlation of the promotion effect of K on the commonly used active centers and types of promotion effect for NO_x , CO_x , and VOCs.

The promotion effect of K is affected by many factors. These factors in different reactions are summarized in Table 12. All investigations focus on the effects of content, some of the investigations involve in the types of alkali metals and precursors. However, the effects of temperature, calcination time, preparation, carrier, and atmosphere, such as H_2O , SO_2 , and As, have not been studied enough. According to current studies, K exhibits an excellent promotion effect and precursor K_2CO_3 has a better effect. The best promotion effect can be obtained by controlling the load content and calcination temperature reasonably. In most cases, the promotion effect and the content show a volcanic relationship, and lower temperature favors the stability and promotion effect of K.

Table 12. Summary of the factors affecting the promotion effect of alkali metals.

	Type	Content	Preparation	Precursor	Calcination Temperature	Calcination time	Carrier	Reaction Temperature	Atmosphere
N_2O decomposition	↑	▲	Impregnation	K_2CO_3	-	-	-	-	-
NO decomposition	-	▲	co-precipitation	-	▲	↓	-	-	-
Soot oxidation	K	↑	-	-	▲	-	-	-	-
CO oxidation	K	▲	Sequential impregnation	-	-	-	electron transfer effect	-	-
WGS	K	▲	-	K_2CO_3	-	-	-	Not too high	-
RWGS	-	▲	-	-	-	-	-	-	-
VOCs oxidation	K	▲	-	KCl	-	-	-	-	stoichiometric ratio
Reforming	-	↓	-	-	-	-	-	-	-

↑ This symbol represents a positive correlation between activity and factor. ↓ This symbol represents a negative correlation between activity and factor. ▲ This symbol represents a volcanic type relationship between activity and factor.

The effect of K on CO adsorption and metal valence is determined by conditions. The addition of K to Rh-based, Au-based, Ni-based, and Mo-based catalysts promotes the adsorption of CO which accepts electrons on the catalyst surface, attributed to the electron-donating properties. However, the addition of K to Pt-based and Ru-based catalysts weakens the strong adsorption of CO, and relatively increases the adsorption of O₂ and H₂O and the cover of surface -OH species, through the electronic modification of the active center, accompanied by the weakening the metal-C bond and promoting the desorption of CO, particularly for Pt-based catalysts. However, it has also been found that the Pt-O-K_x species formed on the Pt-based catalyst can enhance the adsorption strength of CO, which reduces the energy barrier of CO oxidation and increase the reaction rate. K shows an excellent effect in regulating the active center of the catalyst. On the one hand, K supplies electrons to the metal, increases the electron density of the metal, weakens the metal-O bond, and makes the metal transfer to the low valence state. On the other hand, K increases the affinity of active sites for oxygen [207] and promotes the formation of high valence metals. The effect of K on adsorption of CO and valence state of active center needs to be studied in different catalytic systems and atmospheres. The different performances of promotion effect of K should be clearly considered in the application of industrial flue gas.

6. Potential

Although K shows excellent promotion effects in many reactions, some disadvantages need to be paid special attention in the industrial application. K volatiles above 500 °C, so high temperature windows should be avoided. In addition, K also exhibits poisoning effects, especially on V-based catalysts in SCR. Therefore, it is also necessary to consider the negative effects of K on the catalyst. In addition, most of the researches on K promoters focus on finding the relationship between the catalyst properties and activity. There are relatively few studies on the effects of K in the intermediates and the existing states of K. Clarification of the role of K in the catalytic process can better provide theoretical basis and guidance for the use of K.

The promotion effect of K on various reactions provides an idea for the synergistic removal of multiple pollutants. Most of researches are based on the promotion effect of K for a single pollutant removal reaction, but there are many gas components coexist in the industrial flue gas which perform the oxidation properties, such as O₂ and VOCs, or the reduction properties, such as NO and CO. Injecting NH₃ into the flue gas provides atmospheres for NH₃-SCR, CO oxidation, VOCs oxidation, and NO-CO reaction. K has a potential promotion effect on the above reactions. In the aspect of synergistic removal of CO, NO, and VOCs, the addition of K can improve the removal efficiency of multi-pollutants. For the CO oxidation, SCR and VOCs oxidation, the three types of reactions have the same temperature range of 100–200 °C, so it is possible for K to promote catalysts to synergistically remove multi-pollutants. The temperature range also ensures the application of carbon-based catalysts. And activated carbon itself also has the ability to remove multi-pollutants [234–236], such as SO₂, NO_x, and VOCs. The promotion effect of K provides support for the coupling control of multi-pollutants in industrial flue gas, and provides a new idea for more economical and convenient removal of industrial flue gas pollutants.

7. Conclusions

By summarizing the promotion effect of K on the removal and reuse of NO_x, CO_x, and VOCs, it is found that K has an important influence on reactants, intermediates and catalyst active centers based on its two important properties, basicity and electronic properties. Thus, it has a positive effect on the reaction activity, selectivity and stability of the catalyst. The effect on the reactants is mainly to promote the adsorption, which is achieved through alkalinity, increasing the adsorption sites, changing the adsorption type, and generating electrostatic interaction between K^{δ+} and O^{δ-}. The effect on intermediates is achieved by promoting the formation of intermediates, accelerating the decomposition of intermediates

and changing the type of intermediates. The effect on the active center is achieved by changing the electronic and acid-base characteristics, increasing the number of active centers, improving the dispersion, changing the valence state, forming new active centers, and recovering the active centers. The existence and combination of K are important information for promotion effect, and it is worthy of more in-depth research by DFT and EXAFS. K has a better promotion effect than other alkali metals in most cases. However, the existence of K has positive and negative effects, along with the promotion effect and content of K showing a volcanic relationship in most reactions. The application of K in industrial flue gas conditions also requires in-depth consideration of the influence of the atmosphere, which is lacking in the current research, especially for the resistance to H₂O, SO₂, and As. Nevertheless, K still has good prospects for applications in the removal of multiple pollutants from industrial flue gas, especially CO, NO_x, and VOCs.

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Conflicts of Interest: The authors declare no conflict of interest.

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