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Insight into the Effect of Oxygen Vacancy Prepared by Different Methods on CuO/Anatase Catalyst for CO Catalytic Oxidation

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Abstract: In this study, CuO loaded on anatase TiO₂ catalysts (CuO/anatase) with oxygen vacancies was synthesized via reduction treatments by NaHB₄ and H₂ (CuO/anatase-B, CuO/anatase-H), respectively. The characterizations suggest that different reduction treatments bring different concentration of oxygen vacancies in the CuO/anatase catalysts, which finally affect the CO catalytic performance. The CuO/anatase-B and CuO/anatase-H exhibit CO conversion of 90% at 182 and 198 °C, respectively, which is lower than what occurred for CuO/anatase (300 °C). The XRD, Raman, and EPR results show that the amount of the oxygen vacancies of the CuO/anatase-H is the largest, indicating a stronger reduction effect of H₂ than NaHB₄ on the anatase surface. The in situ DRIFTS results exhibit that the Cu sites are the adsorption sites of CO, and the oxygen vacancies on the anatase can activate the O₂ molecules into reactive oxygen species. According to the in situ DRIFTS results, it can be concluded that in the CO oxidation reaction, only the CuO/anatase-H catalyst can be carried out by the MvK mechanism, which greatly improves its catalytic efficiency. This study explained the reaction mechanisms of CO oxidation on various anatase surfaces, which offers detailed insights into how to prepare suitable catalysts for low-temperature oxidation reactions.

Keywords: CuO/anatase; H₂ reduction treatment; oxygen vacancies; CO catalytic oxidation; CO reaction mechanism



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1. Introduction

In the past years, carbon monoxide (CO) exhaust from diesel engine vehicles and gasoline-type engines due to incomplete combustion of fuel has been emitted into environment in large amounts [1–3]. It can not only endanger the atmosphere but also the human health [2]. Therefore, how to efficiently remove CO in the atmosphere is an urgent concern of the majority of researchers at present [4]. Previous studies have shown that heterogeneous catalysts, such as platinum-group metal (PGM) materials used in three-way catalysts, can greatly reduce CO emissions from vehicles [5–7]. However, the PGM catalysts are expensive, and resources are limited. It is easy to gather and sinter at high temperature and then be deactivated, which is impractical in industrial applications [8]. Therefore, it is urgent to develop a new type of highly efficient catalyst that can replace the traditional noble metal catalyst.

Transition metal oxide-based catalysts have excellent activities and low cost, becoming one of the best substitutes for PGM catalysts [9–13]. For example, a series of Ce-based catalysts such as ceria-zirconia [9], ceria-praseodymia [9], and ceria-copper [11] catalysts have been synthesized by different methods, and they all show improved CO oxidation activity. In addition, Cu-based catalysts have been used extensively in catalytic oxidations, fine chemical productions, and sterilization processes due to their variable oxidation state of Cu species and surpassing reducibility [14,15]. It is reported that copper species are mainly present as Cu⁺ and Cu²⁺. The redox cycle of Cu⁺ ↔ Cu²⁺ can enhance the redox ability of the catalysts. More importantly, Cu sites have been proved as the adsorption sites

for CO molecules, which is the vital step of catalytic reactions [16–18]. TiO_2 is one of the most popular materials that has been used as support in catalysts due to their low cost and excellent stability. In addition, the interaction between TiO_2 and Cu species can effectively stabilize the Cu species, which can protect the active site [15].

Oxygen vacancies play a crucial role in adjusting the physical and chemical properties of support materials, which is particularly important for the catalytic activity of the catalyst [19–21]. Yang et al. prepared a $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ catalyst with a large amount of oxygen vacancies. This report showed that the oxygen vacancies can be the adsorption site for O_2 and one electron transferred from the oxygen vacancies to O_2 to form a reactive oxygen species O^- , which can react with the CO easily, leading to a better CO conversion [20]. In addition, the in situ electrical conductance measurement had been used to investigate the formation and reaction mechanism of the oxygen vacancies in CO catalytic oxidation on the Au/ TiO_2 catalysts [22]. The results showed that the oxygen vacancies could be generated on the Au/ TiO_2 catalyst and the O_2 molecules were activated on these oxygen vacancies, which were beneficial to the adsorption of CO. In addition to CO oxidation, the role of oxygen vacancies in other oxidation reactions is also crucial. Generally, the methods for preparing oxygen vacancy mainly include hydrogen reduction [23], sodium borohydride reduction [24], electrochemical reduction [25], and so on. Among them, hydrogen reduction and sodium borohydride reduction have lower cost and higher efficiency, which can effectively separate the lattice oxygen on the surface of the catalyst support and form oxygen vacancies [23,24].

Herein, we synthesized a series of CuO/anatase catalysts with different content of oxygen vacancies, which were reduced by NaBH_4 and H_2 (CuO/anatase-B, CuO/anatase-H). The synthesis method used was a wet-impregnation method. Then the samples were characterized by means of XRD, Raman, N_2 adsorption–desorption isotherms, the inductively coupled plasma optical emission spectrometer (ICP-OES), and transmission electron microscopy (TEM) in order to investigate the textural and morphology of the catalysts. The electron paramagnetic resonance (EPR) was derived to detect the oxygen vacancies on the catalyst surface. The in situ diffuse reflectance Fourier transform infrared spectra (DRIFTS) were used to verify the role of the oxygen vacancies and to reveal the role of Cu species in CO catalytic oxidation.

2. Results

2.1. Textural and Morphology of CuO/Anatase Catalysts

First, we have synthesized a series of CuO/anatase catalysts with oxygen vacancies by different methods, and the textural properties of the catalysts were characterized by X-ray diffraction patterns (XRD). As shown in Figure 1, the characteristic diffraction line of the prepared anatase is consistent with the anatase phase (JCPDS Card No. 21-1272) [26]. After the Cu species were loaded on it, no new diffraction lines were observed, indicating that the content of the Cu species is too low [15,27]. Simultaneously, after the reduction treatment by NaBH_4 or H_2 , the characteristic diffraction lines of the catalysts did not change, suggesting that the reduction treatment will not change the crystal structure of the catalyst. Moreover, the intensity of the diffraction line on (101) facet follows the following order: anatase > CuO/anatase > CuO/anatase-B > CuO/anatase-H, indicating that both the Cu incorporation process and the reduction treatment can bring lower crystallinity and the shift of the CuO-anatase samples to lower degrees, which indicates that the Cu species has been doped into the TiO_2 lattice matrix. This result can lead to notable crystal distortion. In addition, compared to the samples without the reduction treatment, the relative intensities between diffraction lines on (105) vs. (211) and (116) vs. (220) were changed, suggesting that the reduction treatment brings different effects on different crystal phases.

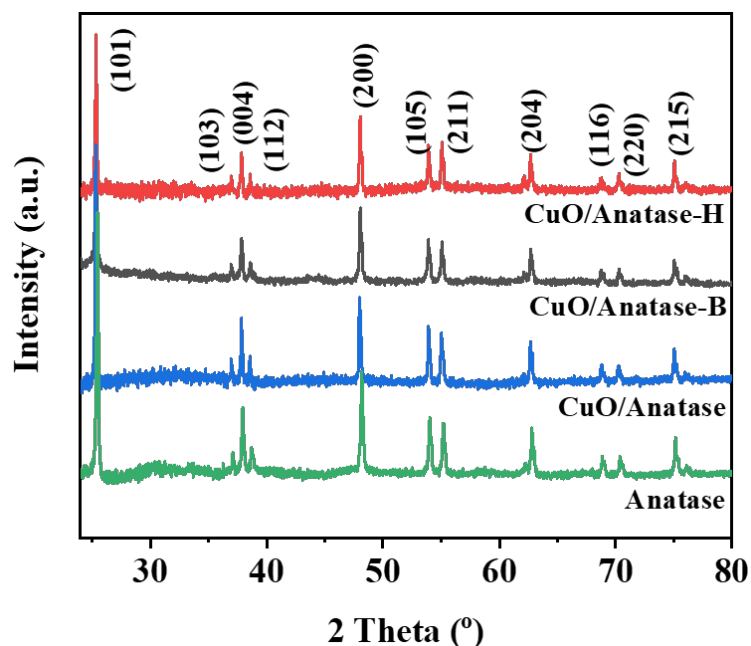


Figure 1. The XRD patterns of anatase, CuO/anatase, CuO/anatase-B and CuO/anatase-H catalysts.

Raman spectra were measured to further confirm the surface crystal structure of the catalysts. As shown in Figure 2, five typical bands, which can be assigned to E_g (141, 196 and 638 cm^{-1}), B_{1g} (395 cm^{-1}) and A_{1g} (515 cm^{-1}) Raman modes of anatase, were observed, which further explained that only pure anatase exists in the four prepared catalysts [28]. This result is consistent with the XRD result. Compared with anatase, a pronounced broadening and weakening mode was observed of the Raman spectra (CuO/anatase, CuO/anatase-B and CuO/anatase-H) at 141 cm^{-1} . Moreover, a significant red shift also occurred at 141 cm^{-1} of the CuO/anatase, CuO/anatase-B, and CuO/anatase-H catalysts. Especially, the CuO/anatase-H catalyst shows the most serious red shift, indicating a significant surface lattice distortion. The above results show that the H_2 reduction treatment is able to create more defects on the anatase surface than NaBH_4 .

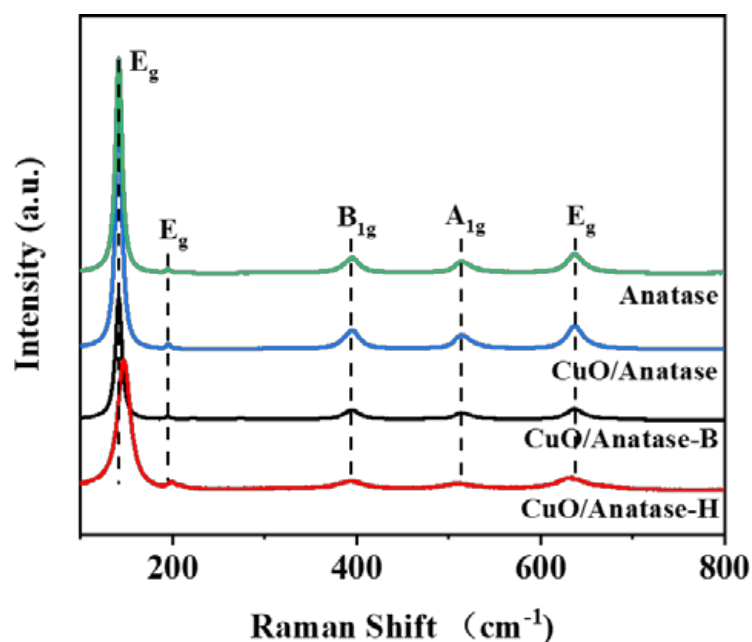


Figure 2. The Raman spectra of anatase, CuO/anatase, CuO/anatase-B and CuO/anatase-H catalysts.

As shown in Figure 3, the nitrogen (N_2) sorption profiles were also recorded to investigate the textural properties of the catalysts. As shown in the N_2 adsorption–desorption isotherms (Figure 3a), the anatase, CuO/anatase, CuO/anatase-B and CuO/anatase-H catalysts all show the typical type-IV isotherms with the type H3 hysteresis loops at a high relative pressure [29–31]. The pore size distributions for different catalysts are displayed in Figure 3b. The pore size of the four catalysts is centered at about 2–40 nm, indicating the existence of a mesopores structure on the catalysts surface [29]. The specific surface area of the four catalysts is summarized in Table 1. The BET surface areas of the anatase, CuO/anatase, CuO/anatase-B and CuO/anatase-H are 34.87, 31.72, 33.51 and 32.97 m^2/g , respectively. After the Cu species were doped on the anatase and the reduction treatment, the BET surface area is almost unchanged, which suggests the structure of the catalysts is stable. In addition, the inductively coupled plasma optical emission spectrometer (ICP–OES) was used to detect the loading of the Cu species on the CuO/anatase, CuO/anatase-B and CuO/anatase-H catalysts. As shown in Table 1, the actual Cu loading was detected to be 4.9, 4.9 and 4.6, which is a little different among the four catalysts.

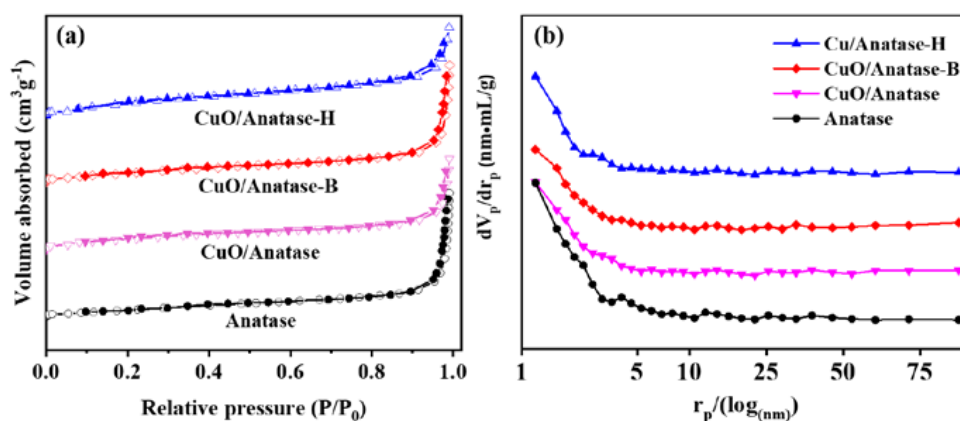


Figure 3. The (a) N_2 adsorption–desorption isotherms and (b) pore size distributions of anatase, CuO/anatase, CuO/anataseB and CuO/anataseH catalysts.

Table 1. ICP-OES results and BET surface area of catalysts.

Samples	Cu Content (wt%)	BET Surface Area ($m^2 g^{-1}$)	Total Pore Volume ($cm^3 g^{-1}$)
Anatase	-	34.9	0.10
CuO/Anatase	4.9	31.7	0.10
CuO/Anatase-B	4.7	33.5	0.13
CuO/Anatase-H	4.6	33.0	0.10

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out to determine the morphology and microstructure of the catalysts. As shown in Figure 4a, anatase is a nanobelt structure with a length of 3–5 μm and a width of 40–90 nm. The HRTEM in Figure 4b shows that the lattice fringes with the interplanar spacings of 0.35 nm were measured, which are indexed to the (101) facet of the anatase phase [19,26]. As shown in Figure 4c, for the CuO/anatase catalyst, the nanobelt structure did not change after the Cu species loaded on the anatase. The interplanar spacings of 0.35 and 0.20 nm were measured, which are consistent with the anatase (101) and CuO (100) facets, respectively [19]. A clear interface between CuO and TiO_2 can be observed in the CuO/anatase catalyst (red circles in Figure 4c,e,g), displaying that CuO exists as isolate nanoparticles on the anatase surface. Similar to these phenomena, the morphology of the nanobelts was maintained in the other two catalysts (CuO/anatase-B and CuO/anatase-H catalysts) after the reduction treatments (Figure 4e,g), which indicates that the reduction treatment will not affect the morphology of the catalyst. Furthermore, the lattice fringes with the interplanar spacings were measured (Figure 4f,h). The CuO/anatase-B and CuO/anatase-H

catalysts present determined interplanar spacings of 0.35 and 0.21 nm, which expose the anatase (101) and CuO (100) facets, respectively. However, as shown in Figure 4f,h, many distortions of the lattice fringes (marked by yellow arrows) have appeared on the surface of the CuO/anatase-B and CuO/anatase-H catalysts, indicating that the catalyst surface becomes uneven after the reduction treatment, which demonstrates that more defects were generated.

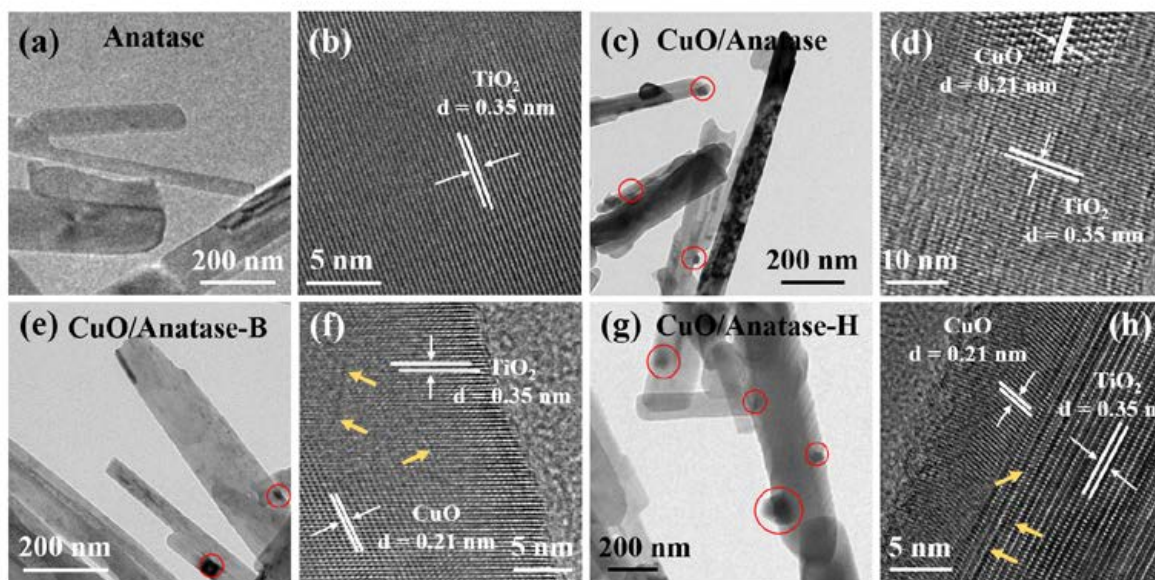


Figure 4. The (a,b) TEM and HRTEM images of anatase, (c,d) TEM and HRTEM images of CuO/anatase, (e,f) TEM and HRTEM images of CuO/anatase-B and (g,h) TEM and HRTEM images of CuO/anatase-H catalyst (red circles: CuO nanoparticles; yellow arrows: distortions of lattice fringes).

2.2. Composition and Surface Chemical State of the Catalysts

The composition and valence of the elements on the catalyst surface were determined by X-ray photoelectron spectrum (XPS) analysis, and the results are shown in Figure 5 and Table 2. As shown in Figure 5a, the XPS profiles of O 1s are deconvoluted by the Gaussian–Lorentz function, and the peak can be fitted into three peaks. The binding energy of the peaks at about 529.7 eV is assigned to the lattice oxygen species (O_{lat}); the peaks at about 531.6 eV are attributed to the surface adsorption oxygen species (O_{ads}), which mainly adsorb on the oxygen vacancies of the catalysts surface; and the peaks at the binding energy of about 533.4 eV correspond to the $-OH$ species (O_{OH}) [30,32]. It is reported that the O_{ads} species are very active in the catalytic oxidation reaction. Therefore, the ratio of $O_{ads}/(O_{ads} + O_{lat} + O_{OH})$ has been listed in Table 2. The CuO/anatase-H catalyst possesses the highest O_{ads} content (32.7%), and the O_{ads} content follows the following order: anatase < CuO/anatase < CuO/anatase-B < CuO/anatase-H. This result shows that after the reduction in the catalyst, a large number of O_{ads} are generated due to the oxygen vacancies on the catalyst surface, which can promote the catalytic reaction, and the H_2 reduction treatment can make more oxygen vacancies form on the catalyst surface.

Ti 2p profiles are shown in Figure 5b. The binding energy of the peaks at 458.5 eV and 464.2 eV is assigned to Ti 2p_{3/2} and Ti 2p_{1/2}, respectively, which suggest the presence of Ti^{4+} [27]. Figure 5c is the Cu 2p XPS spectra of the catalysts. The curves are deconvoluted and are fitted in to the six peaks. The peaks with the binding energy at about 932.4 and 952.4 eV are attributed to the Cu^+ species and the peaks with the binding energy at about 934.6 and 954.8 eV are assigned to the Cu^{2+} species [15,33]. In addition, two satellite peaks that correspond to the Cu^{2+} species are observed. As shown in Table 2, the Cu^+ content follows the following order: CuO/anatase < CuO/anatase-B < CuO/anatase-H, which is consistent with the O_{ads} content order. It is reported that the formation of Cu^+ will be accompanied by the formation of the oxygen vacancies due to the charge imbalance.

Thus, the order of O_{ads} is the same as the Cu^+ content. According to previous reports, the valence state of Cu and the content of the oxygen vacancies are crucial for the CO catalytic oxidation reaction. Generally speaking, because Cu^+ is the active site for CO adsorption and activation, the oxygen vacancies are beneficial to the active of oxygen species. Therefore, the content of Cu^+ and the oxygen vacancies are key factors that affect the catalytic oxidation of CO.

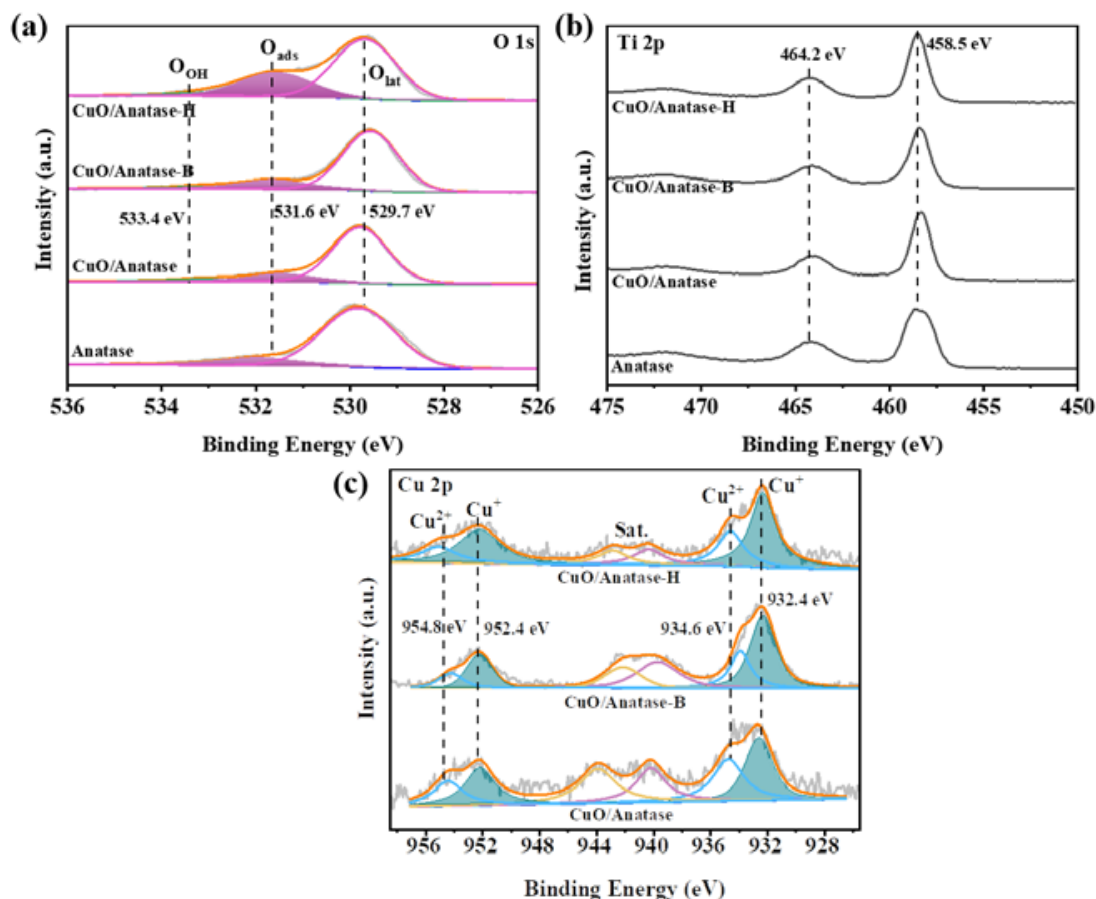


Figure 5. XPS of (a) O 1s, (b) Ti 3p and (c) Cu 2p of anatase, CuO/anatase, CuO/anatase-B and CuO/anatase-H catalysts.

Table 2. Surface compositions of the catalysts.

Catalysts	$O_{ads}/(O_{ads} + O_{lat} + O_{OH})$	$Cu^+/(Cu^+ + Cu^{2+})$
Anatase	18.3%	-
CuO/Anatase	19.0%	37.9%
CuO/Anatase-B	20.8%	46.8%
CuO/Anatase-H	32.7%	57.1%

2.3. Characterization of Oxygen Vacancy

The electron paramagnetic resonance (EPR) was derived to detect the oxygen vacancies on the catalyst surface and the hyperfine structure of the copper species, and the results are shown in Figure 6. It can be seen from Figure 6a that there appears a signal of oxygen vacancy at $g = 2.00$ of the CuO/anatase, CuO/anatase-B and CuO/anatase-H catalysts [20]. Compared with the CuO/anatase, the oxygen vacancy signal of the catalyst after reduction is significantly increased (CuO/anatase-B and CuO/anatase-H catalysts). Compared with the CuO/anatase-B catalyst, the oxygen vacancy signal intensity of the CuO/anatase-H catalyst is larger, which suggests that the H_2 reduction treatments are much easier for generating oxygen vacancies on the anatase surface. As shown in Figure 6b, for the

CuO/anatase, CuO/anatase-B and CuO/anatase-H catalysts, there are fine structure signals with a parallel component of $g_{\parallel} = 2.37$ and a vertical component of $g_{\perp} = 2.08$ in the spectral line, which are attributed to the signal of the Cu^{2+} species. In addition, there are no lone pair electrons in the Cu^+ orbital, so there is no signal of Cu^+ that appears [34].

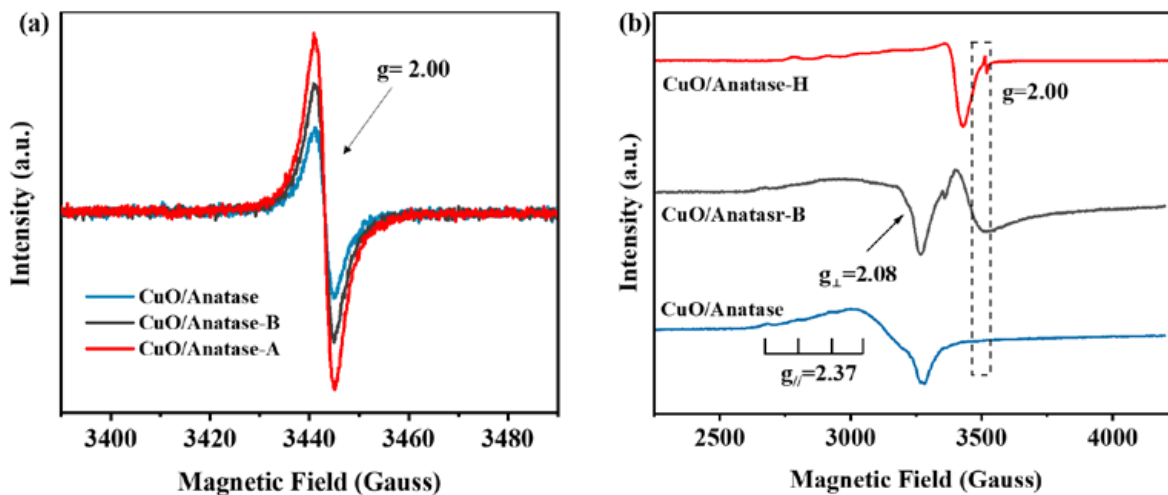


Figure 6. EPR of CuO/anatase, CuO/anatase-B and CuO/anatase-H catalysts. (a) EPR signal of oxygen vacancy; (b) EPR signal of Cu species and oxygen vacancy.

2.4. CO Catalytic Oxidation Performance

In order to verify the influence of the oxygen vacancies constructed by different methods on CO catalytic oxidation performance, we evaluated the catalytic oxidation activity of the anatase, CuO/anatase, CuO/anatase-B and CuO/anatase-H catalysts. Figure 7a shows the light-off curves of anatase, CuO/anatase, CuO/anatase-B and CuO/anatase-H catalysts for the CO oxidation. The results show that when the test temperature is close to 400 °C, the catalytic activity of the anatase catalyst is still less than 5%. However, with the incorporation of CuO, the catalytic activity of the CuO/anatase catalyst was significantly improved ($T_{90} = 300$ °C), indicating the main active site should be assigned to the Cu species. Furthermore, compared with the CuO/anatase catalyst, the catalytic activity of the CuO/anatase-H and CuO/anatase-B catalysts is greatly improved, which can be attributed to the generation of the oxygen vacancies. In addition, from Figure 7a, the CuO/anatase-H catalyst has better CO catalytic activity than the CuO/anatase-B catalyst, which indicates that the greater the surface oxygen vacancy content, the better the CO catalytic performance. It also indicates that the H_2 reduction is more effective than the NaBH_4 reduction on the anatase surface. The performance of these catalysts is comparable to other Cu-based catalysts (Table S1). Then, the intrinsic activity of the CuO/anatase-B and CuO/anatase-H catalysts was investigated by steady-state kinetics study, and the apparent activation energies (E_a) are shown in Figure 7b. As shown in Figure 7b, the E_a for the CuO/anatase-H catalyst is 40.81 KJ/mol, which is much lower than that of the CuO/anatase-B catalyst (66.98 KJ/mol), which is in accordance with the CO catalytic performance. As shown in Figure 7c, with the increase in O_2 in the fed gas, the CO conversion of the CuO/anatase-H also increases. This result indicates that more oxygen fill into the oxygen vacancies can promote the CO oxidation, which occurs through the MvK pathway. As shown in Figure S1, after three rounds of the CO catalytic oxidation performance test, the activities of all catalysts are almost the same as round 1, indicating that the catalysts are stable after several cycles.

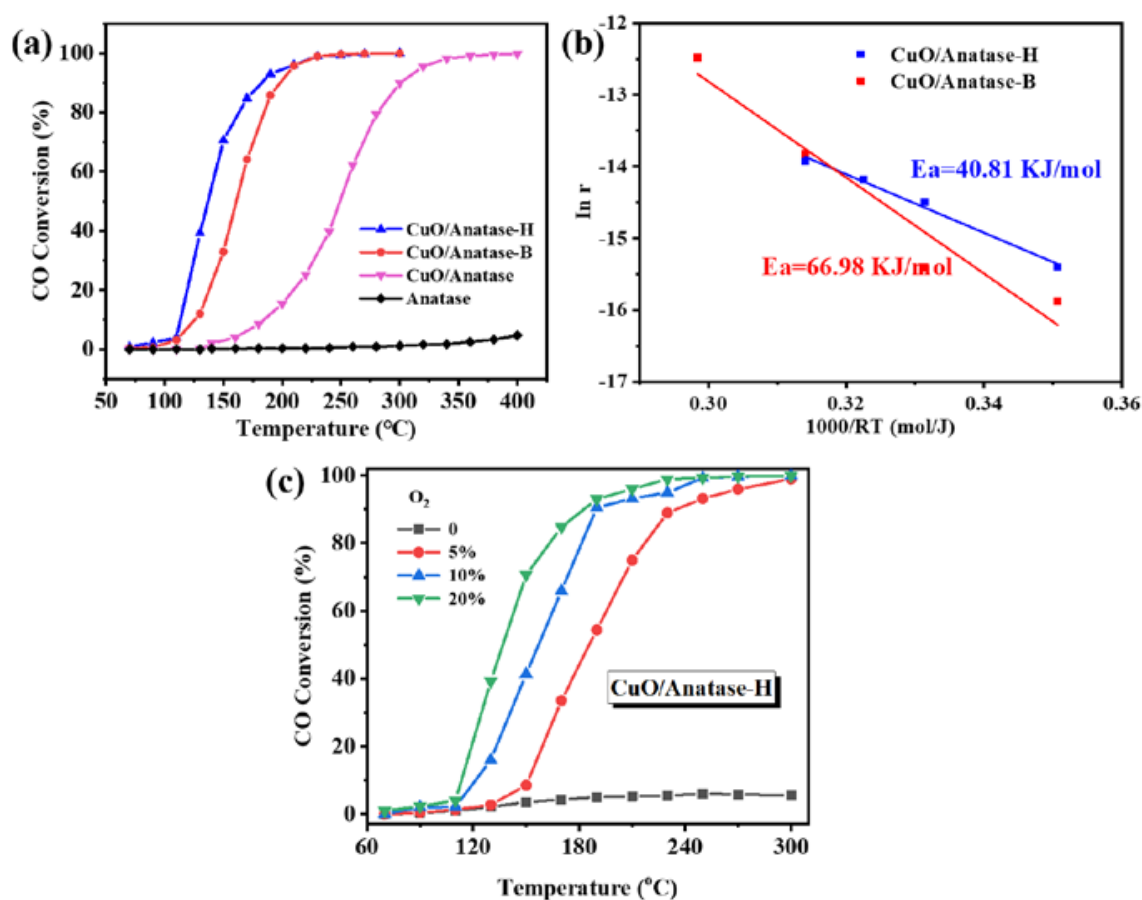


Figure 7. (a) Light-off curves for catalytic CO oxidation of anatase, CuO/anatase, CuO/anatase-B and CuO/anatase-H catalysts. (b) Apparent activation energies of CuO/anatase-B and CuO/anatase-H catalysts. (c) The CO conversion of CuO/anatase under different content of O₂. Reaction conditions: 1% CO, 20% O₂ and balanced with N₂, GHSV = 60,000 mL·g^{−1}·h^{−1}.

2.5. Mechanism of CO Catalytic Oxidation

As shown in Figure 8, the in situ diffuse reflectance Fourier transform infrared spectra (DRIFTS) were recorded to verify the role of the oxygen vacancies constructed by different methods and the role of Cu species in CO catalytic oxidation. As shown in Figure 8a, after the CO atmosphere (black curve) was introduced into the reaction cell, bands at 2175 and 2110 cm^{−1} appeared on the CuO/anatase-H catalyst surface, which are attributed to the CO adsorbed on Cu²⁺ and Cu⁺, respectively [33]. The bands at 1590, 1427 and 1337 cm^{−1} are assigned to the carbonate intermediates, which indicate that CO can react with the surface oxygen species on the CuO/anatase-H catalyst even without gas phase O₂ [15]. The CO oxidation on the CuO/anatase-H catalyst can follow the MvK pathway. Subsequently, the catalyst surface was purged by N₂ and the O₂ (pink curve, Figure 8a). The intensity of the band at 1590 and 1427 cm^{−1} was strengthened evidently, indicating that the CO adsorbed on the catalyst surface can also react with oxygen molecules.

As shown in Figure 8b, the bands appearing on the CuO/anatase-B surface are different from the ones on the CuO/anatase-H catalyst surface. Only two bands at 2173 and 2110 cm^{−1} are observed, which correspond to CO–Cu²⁺ and CO–Cu⁺. No bands belonging to the intermediates can be noticed, indicating that the oxygen species on the CuO/anatase-B surface has trouble participating in the CO oxidation reaction. However, when the oxygen atmosphere was introduced, two bands at 1585 and 1423 cm^{−1} appear, which are assigned to the carbonate species. This result indicates that the CO oxidation reaction of the CuO/anatase-B catalyst cannot follow the MvK pathway but may be only carried out through the L–H or E–R pathway. According to the above results, with the

NaBH_4 or H_2 reduction, the anatase surface can be activated with different content. The type and concentration of the oxygen vacancies on these two reduced surfaces may be disparate, resulting in the different reaction pathway of the catalysts. The detailed properties of the oxygen vacancies on these two reduced surfaces will be studied in future research.

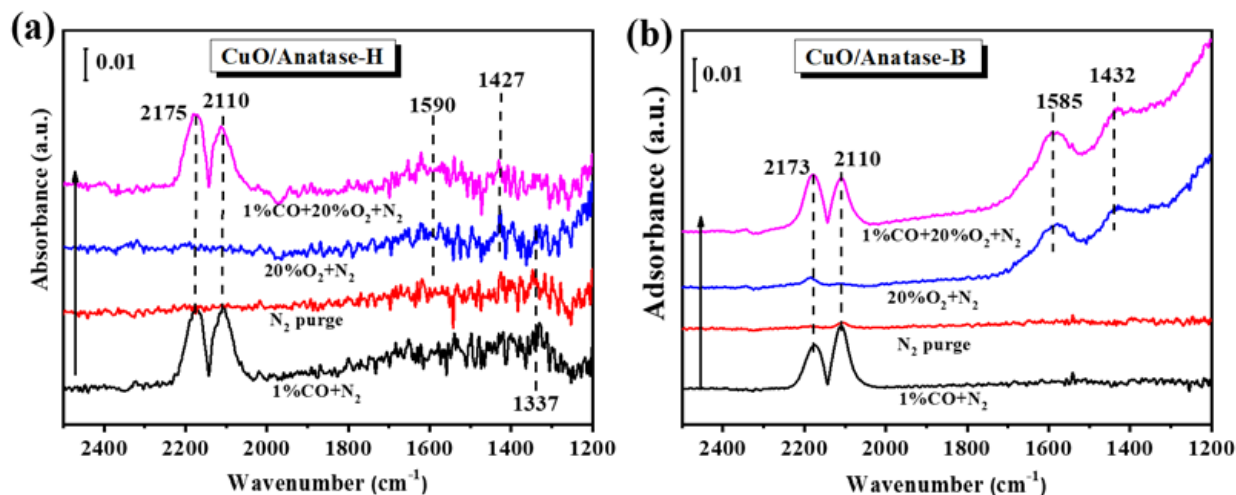


Figure 8. DRIFTS spectra recorded in streams of 1% CO, 5% O_2 balanced by N_2 with a total flow rate of 100 mL/min for (a) CuO/anatase-H and (b) CuO/anatase-B catalysts at 150 °C. Black arrows stand for the actual order of added atmosphere during DRIFTS experimental process.

3. Materials and Methods

3.1. Materials

Commercial anatase (99.8%), NaOH (AR), HCl (36–38%), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99%), butanol (AR), NaBH_4 (97%), and ethanol (AR) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China).

3.1.1. Preparation of Anatase TiO_2

The anatase TiO_2 (labeled as anatase) was synthesized by one-step hydrothermal synthesis using commercial anatase as a precursor [35]. The specific experimental steps are as follows: 60 g of NaOH and 150 mL H_2O were mixed under stirring, and 75 mL of the above solution and 1.05 g commercial anatase were transferred to a teflon reactor and stirred for 30 min. Then, the above mixture was put into the oven at 200 °C for 24 h. The obtained samples were washed with water and then were centrifuged with HCl, and washed with deionized water. Finally, the sample was calcinated at 750 °C for 30 min to obtain anatase TiO_2 powder named anatase.

3.1.2. Preparation of CuO/Anatase Catalysts

CuO/anatase sample was prepared by the impregnation method using the anatase synthesized above as support. In all, 20 mL of n-butanol and 121 mg of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were mixed and stirred at room temperature. Then 800 mg anatase were put into the precursor solution of the above. The content of Cu was 5 wt%. The above solution was dried overnight in a blast oven at 80 °C, and the sample was calcinated at 450 °C for 240 min. The sample named as CuO/anatase.

3.1.3. Preparation of CuO/Anatase-H Catalyst

In all, 200 mg of CuO/ TiO_2 -A prepared as above were put into a quartz tube, then 100 mL/min of H_2 gas (10%) were passed, and it was kept at 600 °C for 10 h to obtain a dark blue powdery solid labeled as CuO/anatase-H.

3.1.4. Preparation of CuO/Anatase-B Catalyst

Typically, 0.01 mol/L NaOH solution was put into the ice bath. Then 1.9 g NaBH₄ were added into the NaOH solution and stirred for 30 min. After the NaBH₄ was completely dissolved, 300 mg CuO/anatase were added and the dispersed slurry was mixed for 30 min. Then obtained sample was washed and filtered with water till the pH of filtrate was 7 to ensure that no Na ions were left, and then it was placed in a vacuum drying oven at 60 °C to obtain gray powder, which was marked as CuO/anatase-B.

3.2. Characterization

The X-ray diffraction patterns (XRD) were measured by Bruker D8 advance instrument with the Cu K α as the X-ray source (Billerica, MA, USA). The scanning angle range of the catalysts is 20–40°. Raman spectra were obtained on the Lab RAMHR Evolution laser Raman spectrometer produced by Japanese HORIBA Company (Kyoto, Japan). The content of the Cu species was recorded by the inductively coupled plasma optical emission spectrometer (ICP-OES) (Agilent, Palo Alto, CA, USA). The nitrogen adsorption and desorption (N₂-Ads/Des) experiment was measured by ASP-2020M porosity analyzer (Microtrac MRB, Osaka, Japan). Before this analysis, a purification process of the sample was performed at 300 °C under vacuum. The pore size distributions were evaluated by the BJH method. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were carried out on Titan G2 60–300 transmission electron microscope (Thermo Fisher Scientific, Waltham, MA, USA). The electron paramagnetic resonance (EPR) was derived to detect the oxygen vacancies on the catalyst surface (Billerica, MA, USA).

In situ diffuse reflection infrared spectroscopy (DRIFTS) were recorded on a Nicolet is50 FTIR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The samples were pretreated for 1 h under N₂ (50 mL/min) at 300 °C. The background spectra were collected at 150 °C under N₂ atmosphere. The order of different reaction atmospheres was as follows: 1% CO and N₂ → N₂ purge → 20% O₂ and N₂ → 1% CO, 20% O₂ and N₂. The total gas flow rate during the test was 50 mL/min.

3.3. Evaluation of Catalytic Performance

In all, 50 mg of samples in 40–60 mesh were packed into the quartz tube. The gas mixture was composed of 1% CO, 20% O₂ and N₂, and the total flow rate was 50 mL/min to make the GHSV be 60,000 mL g^{−1}h^{−1}. The CO conversion can be obtained according to the concentration difference of CO before and after the reaction. The gas in the outlet was analyzed with an online gas chromatograph (GC–9790, Taizhou). The specific calculation formula is as follows:

$$X_{\text{CO}} (\%) = \frac{[\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100\%$$

where [CO]_{in} and [CO]_{out} are the concentration of CO in the inlet and outlet gas, respectively.

$$r = (X \times F) / S \times W,$$

X is the CO conversion, which is below 15%, F is the flow of the feed gas (mol/s), S is the surface area of the catalysts (m²/g) and the W is the weight of the catalysts (g). The apparent activation energy (E_a) can be expressed by the Arrhenius law ($r = A \exp(-E_a/RT)[\text{CO}]^a[\text{O}_2]^b$).

4. Conclusions

In this work, H₂ and NaBH₄ were used to generate oxygen vacancies on the CuO/anatase catalyst to study the different effect of oxygen vacancy prepared by different methods. The experimental results demonstrated that the oxygen vacancies and Cu⁺ may form after the reduction treatment. More oxygen vacancies were generated on catalysts surface by the H₂ reduction treatment (CuO/anatase-H), leading to a high CO oxidation activity (T₉₀ = 182 °C). Both reductive catalysts show better CO conversion than the catalyst with-

out the reduction treatment (CuO/anatase, $T_{90} = 300\text{ }^{\circ}\text{C}$). The Cu sites (Cu^{2+} and Cu^{+}) are the adsorption sites of CO, and the oxygen vacancies may transform the active O_2 molecules into active oxygen species. The synergy effect of them can promote the CO reaction efficiency obviously. Additionally, the in situ DRIFTS of the CO oxidation indicates that only the CuO/anatase-H can be carried out by the MvK mechanism. This study unveils the different behavior of various anatase surfaces in the CO oxidation reaction, which facilitates the efficient preparation of active catalysts for low-temperature oxidation.

In future work, the reaction mechanism will be further explained from the atomic level in combination with the DFT calculation to understand the influence of catalyst structure on performance.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13010070/s1>, Figure S1: The CO oxidation performance of catalysts; Table S1: Comparison of the catalytic performance between the CuO/anatase catalyst and the present catalysts [36–39].

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