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Ru-Ti Oxide Based Catalysts for HCl Oxidation: The Favorable Oxygen Species and Influence of Ce Additive

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Abstract: Several Ru-Ti oxide-based catalysts were investigated for the catalytic oxidation of HCl to Cl₂ in this work. The active component RuO₂ was loaded on different titanium-containing supports by a facile wetness impregnation method. The Ru-Ti oxide based catalysts were characterized by XRD, N₂ sorption, SEM, TEM, H₂-TPR, XPS, and Raman, which is correlated with the catalytic tests. Rutile TiO₂ was confirmed as the optimal support even though it has a low specific surface area. In addition to the interfacial epitaxial lattice matching and epitaxy, the extraordinary performance of Ru-Ti rutile oxide could also be attributed to the favorable oxygen species on Ru sites and specific active phase-support interactions. On the other hand, the influence of additive Ce on the RuO₂/TiO₂-rutile was studied. The incorporation of Ce by varied methods resulted in further oxidation of RuO₂ into RuO₂^{δ+} and a modification of the support structure. The amount of favorable oxygen species on the surface was decreased. As a result, the Deacon activity was lowered. It was demonstrated that the surface oxygen species and specific interactions of the Ru-Ti rutile oxide were critical to HCl oxidation.

Keywords: Ru-Ti oxide catalysts; HCl oxidation; oxygen species; Ce incorporation; active phase-support interactions

1. Introduction

The treatment of the huge amount of excess hydrogen chloride byproduct has become a challenging and demanding problem in the chlorine-based chemical industry, as a byproduct HCl is environmentally undesirable and has a very restricted market [1,2]. The method using heterogeneously catalyzed HCl oxidation (Deacon process) to recycle chlorine is regarded as a low energy-consuming and sustainable route for the more efficient Cl₂ industry [1]. The reaction is exothermic and reversible, which is shown as follows.

Ru-based catalysts are commonly considered the most active for this process. RuO₂ supported on rutile TiO₂ and SnO₂ (cassiterite) with an excellent activity and outstanding lifetime have been successively reported by Sumitomo [2] and Bayer [3], respectively. Great attention has been paid to Ru-Ti oxide catalysts in various catalytic reactions besides the Deacon process, including oxidation

of propane [4], N_2O decomposition [5], selective methanation of CO [6], CO oxidation [7], and aqueous-phase ketonization of acetic acid [8,9]. The Ce-based catalysts also exhibit Deacon activity and outstanding stability in the process [10,11]. Related studies have demonstrated that CeO_2 can accelerate the catalyst reoxidation step by supplying oxygen donor/storage sites [10]. Although the single Ce-based or Cu-based catalyst shows a limited activity, the combination of Ce-Cu can boost the overall HCl oxidation performance [12,13]. The build-up of Ce-Ti oxide can also enhance the oxygen storage capacity [14,15]. The $\text{CeO}_2/\text{TiO}_2$ catalyst showed excellent activity for selective catalytic reduction of NO with NH_3 , where the Ce-O-Ti species were confirmed to be the active sites [16–19]. The concentration of surface adsorbed oxygen presented a positive correlation with the catalytic activity in the NH_3 -SCR reaction [16,20]. However, the combination of Ru-Ce-Ti for HCl catalytic oxidation has not been reported to the best of our knowledge.

Despite a number of studies concerning supported Ru-based catalysts for one-step HCl oxidation [21,22], there are only a few research studies about the details of active phase-support interactions in the Ru-Ti oxide-based catalysts [2,23]. Moreover, little attention was paid to the influence of oxygen species in this catalytic process. In addition to the lattice matching and epitaxial growth of RuO_2 on the substrate [2,21], the extraordinary performance of Ru-Ti rutile oxide for the Deacon process still requires a more sufficient interpretation.

In this article, the performance of different shaped Ru-Ti oxide based catalysts, resembling the forms of the industrial reality, are compared in the Deacon process. Detailed characterizations are performed to investigate the special oxygen species and interactions of the catalysts. The favorable oxygen species and specific active phase-support interactions ensure high Deacon activity of $\text{RuO}_2/\text{TiO}_2$ -rutile. The role of Ce in the Ru-Ti rutile oxide system was also investigated. The addition of Ce decreased favorable oxygen species and affected the active phase-support interactions between RuO_2 and TiO_2 , by evolving the Ru-O-Ce structure and enhancing the positive charge density of Ru sites. The Deacon activity was lowered as a result. It can be deduced that the electronic interactions between RuO_2 and rutile TiO_2 are critical for the gas-phase oxidation of HCl to Cl_2 . The findings in this work may be a reference value for the design and tailor of Ru-Ti oxide based catalysts toward better Deacon activity.

2. Results and Discussion

2.1. Morphology and Phase Structure

The crystal structures of the catalysts were analyzed by X-ray diffraction (XRD). The XRD patterns of the supported catalysts only exhibit characteristic diffraction peaks of the TiO_2 supports (Figure 1). Due to the low loading and high dispersion of the Ru species, the RuO_2 phase were logically not detected. In the XRD pattern of $\text{RuO}_2/\text{TiO}(\text{OH})_2$, much broader peaks can be observed than those of $\text{RuO}_2/\text{TiO}_2$ -a, which implies that the support that originated from the $\text{TiO}(\text{OH})_2$ precursor has a much lower crystallinity as well as average crystallite size.

Figure 1. XRD patterns of the $\text{RuO}_2/\text{TiO}_2$ catalysts with the supports of: TiO_2 -rutile, TiO_2 -anatase, and $\text{TiO}(\text{OH})_2$ (as the precursor).

The SEM micrographs in Figure 2 show that the anatase TiO_2 and the corresponding catalysts (35 to 50 nm) have a smaller particle size than the rutile of 45 to 60 nm. The particle size of rutile TiO_2 has not changed much after loading RuO_2 (Figures 2a and 2c), while some coagulation can be observed on anatase TiO_2 and the average size has increased from 40.3 nm to 48.5 nm (Figures 2b and 2d). The supported catalysts were also scrutinized by TEM. As displayed in Figure 3a, some dark edges and layers were observed on the substrate of $\text{RuO}_2/\text{TiO}_2$ -r. They were presumed to be the dispersed RuO_2 phase, which was consistent with the literature [2,4]. On the other hand, some aggregation can be observed in $\text{RuO}_2/\text{TiO}_2$ -a (Figure 3b). The EDX elemental mapping proves the existence of highly dispersed Ru species on the TiO_2 -r support (Figure 4).

Figure 2. SEM micrographs of the rutile (a) and anatase TiO_2 supports (b) used in this study, $\text{RuO}_2/\text{TiO}_2$ -r (c), $\text{RuO}_2/\text{TiO}_2$ -a (d).

Figure 3. TEM images of RuO₂/TiO₂-r (a) and RuO₂/TiO₂-a (b).

Figure 4. TEM-EDX elemental mapping of RuO₂/TiO₂-r: (a) representative TEM image, (b) Ti (Kα1) green color, (c) O (Kα1) blue color, (d) Ru (Lα1) pink color, and (e) EDX (Energy-dispersive X-ray) result of the selected area.

2.2. Characterization of Oxygen Species and Interfacial Interactions

2.2.1. H₂-TPR Analysis

Temperature programmed reduction (TPR) by H₂ was employed in this study to distinguish specific oxygen species and estimate the oxygen storage capacity [11,14]. The H₂-TPR profiles of the bulk RuO₂ and supported catalysts are shown in Figure 5. In this scenario, all the supported catalysts were loaded with an Ru content of 0.5 wt%. The bulk RuO₂ sample was reduced in the range of 130 to 230 °C. It should be noted that the RuO₂ sample used in characterization was obtained from RuCl₃·3H₂O calcined at 350 °C for 8 h, the phase of which was verified by XRD (see Figure S1). The RuO₂ phase prepared by this method has a preferential (1 0 1) plane rather than (1 1 0) (PDF #65-2824). It may be the origin of different reduction temperatures as discussed in the previous study [21]. The H₂-TPR profile of RuO₂/TiO₂-r contains three peaks in the range of 90 to 200 °C and one peak from 330 to 450 °C. The former three peaks are assigned to the reduction of RuO₂, while the last one is attributed to the partial reduction of the TiO₂ surface [24]. Ru-Ce/TiO₂-r and RuO₂/TiO₂-a exhibit a similar reduction peak of titania, except that the peak shifts to a higher temperature were similar to RuO₂/TiO₂-r. Note the peak in the range 370 to 500 °C of Ru-Ce/TiO₂-r includes the reduction of ceria. The H₂-TPR profiles of pure TiO₂ in rutile and anatase phase are shown in Figure S2, which confirms the partial reduction of TiO₂ support.

Figure 5. H₂-TPR profiles of the bulk and supported RuO₂ catalysts.

In the range of 50 to 200 °C, the oxygen species of RuO₂ were subjected to reduction. Generally, the reduction temperature of the same phase is related with the particle size. In fact, oxygen species with different reducibility can be a more essential perspective. We know that smaller particles expose more surface species. For our catalysts, RuO₂ phase is mainly distributed on the surface of TiO₂ support and more surface species mean more surface oxygen species. Among these oxygen species, it is quite probable that species with more coordination numbers are more difficult to reduce.

For sample RuO₂/TiO₂-r, the peaks (from 90 to 200 °C) are evidently distinguished from the other two catalyst samples. We deduce that the three peaks are assigned to the reduction of top oxygen, bridge oxygen, and bulk oxygen of RuO₂ with H₂, from a low to a high reduction temperature. These three types of oxygen are coordinated to 1, 2, 3 Ru atoms, respectively. The former two oxygen species are located at the surface and are significant to the Deacon process [21,25,26]. For sample RuO₂/TiO₂-a, only one reduction peak was detected in the range from 90 to 200 °C, which was

attributed to the elimination of bulk oxygen. It could be rationalized in the following way. RuO_2 could not grow epitaxially on TiO_2 -a due to a huge difference of lattice matching. Thus, the RuO_2 active phase mainly exists as bigger particles on TiO_2 -a rather than films in $\text{RuO}_2/\text{TiO}_2$ -r [2]. In this case, the bulk oxygen species of RuO_2 prevailed, which was coordinated to 3 Ru atoms and was the most difficult to reduce. From Figure 5, it can be observed that $\text{Ru-Ce}/\text{TiO}_2$ -r and $\text{RuO}_2/\text{TiO}_2$ -a have a better oxygen storage capacity than $\text{RuO}_2/\text{TiO}_2$ -r, especially in the high temperature range.

2.2.2. XPS Analysis

XPS analysis was performed to study the surface species and electronic structure of the catalyst samples. The survey spectra verified the complete removal of chlorine in all the catalysts (not shown). The XPS peaks of O 1s were deconvoluted to analyze the different types of O species in the supported catalysts (Figure 6). The O 1s peaks were mainly composed of signals corresponding to the chemisorbed oxygen (O_α) and the lattice oxygen (O_{β_1} , O_{β_2}) [27–29]. XPS data of chemisorbed oxygen are listed in Table 1. The proportion of chemisorbed oxygen (O_α) on the surface exhibited a dependence on Ru loading (Figure 6a–c). $\text{RuO}_2/\text{TiO}_2$ -r exhibited a higher amount of chemisorbed oxygen with the increase of Ru loading, while a much lower content of chemisorbed oxygen was detected in $\text{RuO}_2/\text{TiO}_2$ -a (Figure 6d, Table 1). The Ti 2p core-level spectra of $\text{RuO}_2/\text{TiO}_2$ -r also show a relevance with the Ru content (Figure S3), where the XPS peaks are broadened and shifted to a lower binding energy with the increase of ruthenium. The chemical environment change of the Ti sites can be ascribed to the interactions and electronic effects among Ti, Ru, and O atoms. A slight interfacial charge transfer from RuO_2 to TiO_2 -r may lead to the binding energy shift of the Ti 2p peaks [30,31].

Figure 6. XPS profiles and fitting curves of O 1s peaks: $\text{RuO}_2/\text{TiO}_2$ -r of (a) 0.3, (b) 0.5, (c) 1.0 wt% Ru, $\text{RuO}_2/\text{TiO}_2$ -a of (d) 0.5 wt% Ru.

Table 1. Chemisorbed oxygen (O_α) in the RuO_2/TiO_2 catalysts.

Sample	E_b of O_α (eV)	O_α/O_T (%)
0.3 wt%- RuO_2/TiO_2 -r	532.11	18.29
0.5 wt%- RuO_2/TiO_2 -r	532.27	20.12
1.0 wt%- RuO_2/TiO_2 -r	532.57	23.70
0.5 wt%- RuO_2/TiO_2 -a	532.36	16.51

The Ru 3d spectra for RuO_2-CeO_2/TiO_2 -r catalysts are presented in Figure 7. The signal of Ru 3d_{5/2} core-level, attributed to RuO_2 or $RuO_2^{\delta+}$, was detected in the region of 281.2–282.9 eV. Meanwhile, the peaks around 280.5 eV appeared for Ru-2Ce/ TiO_2 -r and Ru-2Ce-C/ TiO_2 -r, which were assigned to Ru^0 [3]. The peaks of C 1s and Ru 3d_{3/2} appeared to overlap [32,33]. The Ru 3d_{5/2} peaks shifted toward a higher binding energy when the preparation methods were altered. In the spectra of Ce 3d, an overall shift towards lower binding energies was observed in the similar sequence of Ru-2Ce-R/ TiO_2 -r, Ru-2Ce/ TiO_2 -r, and Ru-2Ce-C/ TiO_2 -r (Figure S4). It can be inferred that electrons are transferred from RuO_2 to CeO_2 , which results in the further oxidation of RuO_2 into $RuO_2^{\delta+}$. As shown in Figure 5, the reduction peaks of Ru-Ce/ TiO_2 -r in the low temperature range (90 to 200 °C) are one fewer than those of RuO_2/TiO_2 -r, which is ascribed to the elimination of top oxygen on the RuO_2 surface (vide supra). The existence of top oxygen is critical to the Deacon reaction with Ru-based catalysts [25,26]. In RuO_2-CeO_2/TiO_2 -r, Ru-O-Ce linkage was likely formed, which induced the decrease of the active sites in the Ru-Ti rutile oxide system. The generation of Ru^0 in Ru-2Ce/ TiO_2 -r and Ru-2Ce-C/ TiO_2 -r also indicated the decrease of the active sites for HCl oxidation. The decline of chemisorbed oxygen from XPS data is also consistent with the deduction above (see Figure S5, Table S1).

Figure 7. XPS spectra and peak fitting curves of Ru 3d of the supported RuO_2 and Ru-Ce/Ti oxide catalysts.

2.2.3. Raman Analysis

The active phase-support interactions were further confirmed by Raman characterization. As shown in Figure 8a, the characteristic bands of rutile TiO_2 are observed at 234, 441, and 606 cm^{-1} , which can be assigned to the multiple photon scattering process, the E_g (planar O-O vibration), and A_{1g} (Ti-O stretch) Raman-active modes, respectively [32,34,35]. Since the RuO_2 Raman bands overlapped with those of TiO_2 -r, only the E_g mode of RuO_2 at 515 cm^{-1} could be distinguished [5], which indicates the existence of the RuO_2 phase in the catalyst. The declination of Raman signals of TiO_2 -r was

ascribed to the decreased amount of Ti-O-Ti structure, which resulted from the formation of Ru-O-Ti structure with the increase of Ru loading. The relative intensity of the RuO₂ Raman signal at 515 cm⁻¹ was enhanced at the same time, which coincided with the change of the active component loading. Moreover, the RuO₂ Raman bands shifted from 515 to 507 cm⁻¹ with the increase of Ru loading, while a clear blue-shift towards higher wavenumbers (from 234 cm⁻¹ to 258 cm⁻¹) was observed in the spectrum of the support (Figures 8b and 8c). The Raman shifts suggest that the rutile structure of the TiO₂ support was modified according to the changed RuO₂ crystal size and interfacial interactions, substantially as a result of the mechanical strains generated from the differences between the rutile phase of RuO₂ and TiO₂ support [6]. The formation of Ru-O-Ti linkage corresponded with the results from XPS analysis. The interactions between Ce and Ti were also confirmed by Raman characterization on the set of Ce-containing RuO₂/TiO₂-r catalysts. The characteristic bands of planar Ti-O vibration and O-O stretch for TiO₂-r exhibited a slight blue shift (see Figure S6) in accordance with the binding energy shift of the Ru 3d_{5/2} core-level peak. It indicated that the chemical environment of the rutile support was also affected by Ce addition.

Figure 8. Raman spectra of TiO₂-r and RuO₂/TiO₂-r with 0.1, 0.3, 0.5, and 1.0 wt% Ru loading (a) and partial enlarged views of TiO₂-r (b) and RuO₂ (c).

2.3. Catalytic Performance of Ru-Ti Oxide Based Catalysts

2.3.1. Catalytic Activity of RuO₂/TiO₂-r Catalyst

The influence of Ru loading on HCl conversion is depicted in Figure 9a. It can be noted that the increase of Ru loading contributes to the reaction conversion to a certain extent. The catalysts with 0.5 wt% and 1.0 wt% Ru loadings achieved similar conversion. As presented in Figure 9b, the ratio of O₂/HCl also plays a critical role in the reaction, especially when the value is less than 1.0 vol./vol. Since oxygen re-adsorption is recognized as the rate-determining step under lean oxygen condition, a higher O₂ partial pressure has been proven to be beneficial for Cl₂ production [26].

Figure 9. The influence of Ru loading at 350 °C (a) and feed O₂/HCl ratio at 320 °C (b) on HCl conversion. Note volumetric flowrate HCl/O₂ = 1:2 for (a).

Figure 10 shows HCl conversion at different reaction temperatures on catalysts with 0.5 wt% and 1.0 wt% Ru loading. For both catalysts, the conversion was improved with the elevation of the reaction temperature. When comparing the two catalysts with different Ru loadings over 300 °C, we found that the conversion was not proportional to the loading amount of the active component. It implied that the Ru-specific activity declined with the increasing loading. As indicated by Figure S3, a slight interfacial charge transfer from RuO₂ to TiO₂-r shows up with the increase of Ru content. This charge transfer was deduced not to be beneficial to Ru-specific activity.

Figure 10. HCl conversion on different reaction temperatures and Ru loading.

2.3.2. Comparison of Ru-Ti Oxide Based Catalysts

The catalytic activities for HCl oxidation over Ru-Ti oxide based catalysts using different supports are compared in Table 2. Although RuO₂/TiO₂-r has the smallest surface area (28 m²·g^{−1}) among all the Ru-Ti oxide based catalysts, its catalytic activity turned out to be the best. Notably, the specific surface area of the supports seemed to be less critical in the RuO₂/TiO₂-based catalytic system. The performances of catalysts differed significantly when the support was changed, even though the supports were all based on the Ti-O structure.

Table 2. Characterization and catalytic activity data.

Reaction Temperature	No.	Catalyst ^a	BET Surface Area ^c (m ² ·g ^{−1})	HCl Conversion (%)	STY ^d (g _{Cl₂} ·g _{Ru} ^{−1} ·h ^{−1})	TOF (h ^{−1}) ^g
350 °C	1	RuO ₂ /TiO ₂ -r	28 (28)	93.5	57.3	163.2
	2	RuO ₂ /TiO ₂ -a	44 (79)	53.6	32.8	93.4
	3	RuO ₂ /TiO(OH) ₂ ^b	193 (309)	21.1	12.9	36.7
320 °C	4	RuO ₂ /TiO ₂ -r	28	81.0	49.6	141.3
	5	Ru-Ce/TiO ₂ -r ^e	27	74.3	45.5	129.6
	6	Ru-2Ce-R/TiO ₂ -r ^f	26	73.2	44.8	127.6
	7	Ru-2Ce/TiO ₂ -r	27	66.3	40.6	115.6
	8	Ru-2Ce-C/TiO ₂ -r	27	61.8	37.9	107.9

^a 0.5 wt% Ru loading based on the support or support precursor. ^b The precursor of support is TiO(OH)₂.

^c Determined by N₂ adsorption, surface area of the support in brackets. ^d The space time yield defined as the gram of Cl₂ produced per gram of Ru per hour. ^e The molar ratio of Ru/Ce is 1 and 0.5, denoted as Ru-Ce and Ru-2Ce respectively. ^f The catalysts prepared by different methods are distinguished by suffixes -R and -C, which

refer to the impregnation of TiO₂-r support with Ru first and Ce first, respectively. The catalysts without suffixes above are prepared by co-impregnation with Ru and Ce. ^g Calculated based on the mole of HCl reacted per hour per mole of Ru.

Herein, we attempt to explicate the influence of favorable oxygen species and interfacial interactions of the Ru-Ti oxide system on the Deacon process, by correlating the characterization results with catalytic performances. With the increase of Ru loading, the linkage of Ru-O-Ti appeared to be more abundant, which was confirmed by the results from XPS and Raman spectra. Subsequently, the amount of chemisorbed oxygen species increased. The chemisorbed oxygen is intimately related with coordinatively unsaturated ruthenium atoms [26], which provide critical active sites and promote oxygen activation. It can partially explain the higher activity of RuO₂ when loaded on TiO₂-r. Since RuO₂ can grow epitaxially on the rutile titania, the exposure of more active sites is favored.

A series of Ru-Ce-Ti oxide catalysts were prepared by different methods, as described in the experiment. From Table 2, it can be affirmed that the incorporation of Ce reduced the activity of Ru-Ti rutile oxide catalysts. The catalytic activity declined with the increase of Ce loading by comparing the results of No. 4, 5, and 7 in Table 2. When exchanging the impregnation sequence of Ru and Ce, it was found that performing Ru impregnation in the first place was beneficial for improving the catalytic performance to some extent (see No. 6, 7, and 8).

2.3.3. The Influence of Ce on the Ru-Ti Rutile Oxide System

The characterizations and catalytic performances of Ce-containing RuO₂/TiO₂-r catalysts further confirmed the significance of the active phase-support interactions for the RuO₂/TiO₂-r system. When Ce was introduced to the TiO₂-r support prior to Ru, a greater change of the RuO₂ and TiO₂-r structure was incurred. The formation of Ti-O-Ce and Ru-O-Ce linkages remarkably affected the interfacial interactions and electronic structure of the RuO₂/TiO₂-r system, which was corroborated by XPS and Raman characterizations. The new linkages restricted the active sites of coordinatively unsaturated ruthenium and the transport of oxygen species. The amount of chemisorbed oxygen evidently decreased when improving the priority of the introduction of Ce (Figure S4, Table S1). The correlated catalytic activity declined, as presented in Table 2 (No. 4, 6, 7, and 8).

The introduction of Ce triggered further oxidation of RuO_2 into $\text{RuO}_2^{\delta+}$ and could be unfavorable for H_2O desorption and Cl recombination. Higher positive charge density of Ru sites induced easier adsorption of the reactants. Therefore, the active-phase surface was more likely to be poisoned by adsorbates. Since HCl oxidation proceeds on RuO_2 via a Langmuir-Hinshelwood reaction mechanism, adsorbed HCl dehydrogenates through a hydrogen transfer to produce Cl and OH species in on-top positions [26]. The recombination of neighboring on-top Cl atoms to form the desired Cl_2 product is regarded as the rate-determining step. Nevertheless, the existence of Ce strengthened the dissociative adsorption of HCl so that the liberation of Cl_2 restricted the activity, which was also observed on the $\text{IrO}_2(110)$ surface [36,37]. Although Ce-based catalysts showed Deacon activity themselves, the active temperature for the Deacon process was generally reaching 430 °C or more, considering the higher energy requirements for Cl activation and recombination [10,11]. Therefore, ceria itself contributed to little Deacon activity for $\text{RuO}_2/\text{TiO}_2\text{-r}$ below 350 °C in this study.

On the other hand, although Ce provided more reducible oxygen species (Figure 5), it seemed that the oxygen species with a high reduction temperature were not crucial for the Deacon reaction. The oxygen species of support with a lower reduction temperature (330 to 350 °C) in $\text{RuO}_2/\text{TiO}_2\text{-r}$, as a result of interfacial interactions between the phases, was speculated to be beneficial for facilitating activation and transport of oxygen species for the active phase. Moreover, compared to $\text{RuO}_2/\text{TiO}_2\text{-r}$, the most readily reducible oxygen species (90 to 100 °C) in $\text{Ru-Ce}/\text{TiO}_2\text{-r}$ disappeared. The on-top oxygen occupying the coordinatively unsaturated ruthenium sites are mentioned in the discussion of the H_2 -TPR results. The introduction of Ce enhanced the positive charge density of Ru sites, which might cause the easier formation of the bridge and bulk oxygen of RuO_2 other than the on-top oxygen. Because of the higher positive charge density of Ru sites, O was more inclined to bond to Ru atoms and the coordination number of O with Ru on the RuO_2 surface likely increased. More evidence may be provided by further characterizations on fine structure and corresponding computational studies.

3. Materials and Methods

3.1. Preparation of Catalysts

All the reagents were of an analytical grade, supplied by Aladdin (Shanghai, China), and used as received without further purification, except for $\text{TiO}(\text{OH})_2$ from Tuoboda Titanium Dioxide Products Co. (Wuxi, China). Ru-Ti oxide based catalysts were prepared by a facile wetness impregnation method as follows. First, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was dissolved in a mixed solution with an equal volume of water and ethanol. After 3 min of ultrasonic mixing, support or the support precursor was added and the suspension was stirred for 16 h at room temperature. Then the mixture was evaporated under vacuum in a rotary evaporator. The obtained powder was dried at 120 °C for 12 h and was then tableted into cylinders with a diameter of 5 mm. Lastly, the sample were calcined at 350 °C in static air for 8 h. The nominal loading of Ru was 0.1, 0.3, 0.5, and 1.0 wt% on the support basis. The supports and support precursors included rutile and anatase TiO_2 and $\text{TiO}(\text{OH})_2$. Henceforth, the rutile and anatase TiO_2 polymorphs are abbreviated as $\text{TiO}_2\text{-r}$ and $\text{TiO}_2\text{-a}$, respectively. The $\text{RuO}_2\text{-CeO}_2/\text{TiO}_2\text{-r}$ catalysts were all loaded with 0.5 wt% Ru on the rutile TiO_2 basis. They were prepared by almost the same method as $\text{RuO}_2/\text{TiO}_2$ except that $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ was introduced to the solution when dissolving $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$. The molar ratios of Ru/Ce were 1.0 and 0.5, which were denoted as $\text{Ru-Ce}/\text{TiO}_2\text{-r}$ and $\text{Ru-2Ce}/\text{TiO}_2\text{-r}$, respectively.

In order to investigate the effect of Ce on the Ru-Ti oxide system, the $\text{RuO}_2\text{-CeO}_2/\text{TiO}_2\text{-r}$ catalysts were also prepared by changing the sequence of Ce introduction, where the molar ratios of Ru/Ce were 0.5. The powder from the rotary evaporator (vide supra) was added to the solution of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. Then the suspension was stirred, evaporated, dried, tableted, and calcined as described before. The impregnation sequence of Ru and Ce was also exchanged for obtaining another catalyst. These two catalysts were distinguished by suffixes -R and -C, namely $\text{Ru-2Ce-R}/\text{TiO}_2\text{-r}$ and $\text{Ru-2Ce-C}/\text{TiO}_2\text{-r}$. The catalysts without the suffixes were prepared by co-impregnation with Ru and Ce.

3.2. Characterization of Catalysts

Powder X-ray diffraction (XRD) patterns were recorded with an Empyrean, PANalytical X-ray diffractometer (Almelo, The Netherlands), with Cu K α radiation ($\lambda = 0.154056$ nm) at 40 kV and 40 mA. The diffraction patterns were taken in the 2θ range of 5 to 90° with a step size of 0.02°. Specific surface areas of the samples were measured by N₂ physisorption at 77 K using a Micromeritics ASAP 2020 instrument (Norcross, GA, USA). The surface area was determined by the Brunauer-Emmett-Teller (BET) method. The morphology and particle size of prepared catalysts and supports were studied by a scanning electron microscope (SEM, FEI Quanta 600FEG, operated at 20 kV, Hillsboro, OR, USA) and a transmission electron microscope (TEM, FEI Tecnai G2 F20, operated on 200 kV, Hillsboro, OR, USA). The energy-dispersive X-ray spectroscopy (EDX, Oxford INCA Energy IE350, Oxford, UK) mapping method was applied to determine the elemental distributions of different components in the catalysts.

Temperature programmed reduction of hydrogen (H₂-TPR) was performed at an AutoChem II 2950 instrument (Micromeritics, Norcross, GA, USA) equipped with a thermal conductivity detector (TCD). Furthermore, 100 mg catalyst was heated and programmed from 50 °C to 550 °C (or 800 °C for the pure support) at a rate of 10 °C·min⁻¹ in a gas flow of 5 vol.% H₂/Ar of 50 cm³ STP min⁻¹. Raman spectra were collected on a confocal Raman microscope (inVia Raman Microscope, Renishaw plc, Wotton-under-Edge, UK) with a 785 nm laser diode (Renishaw plc, Wotton-under-Edge, UK). X-ray photoelectron spectra (XPS) were recorded on a Thermo ESCALAB 250 spectrometer (Waltham, MA, USA) with a monochromatized Al K α (1486.6 eV) radiation and a passing energy of 50 eV. The binding energies were calibrated by the C 1s signal of adventitious carbon at 284.8 eV.

All the characterizations were performed on catalyst samples with a 0.5% Ru loading unless otherwise specified.

3.3. Catalytic Tests

The catalytic oxidation of HCl to Cl₂ was investigated in a Hastelloy alloy (HC-276®) fixed-bed reactor with a diameter of 30 mm at an ambient pressure. The upstream lines of the set-up were also made from Hastelloy alloy (HC-276®) in order to prevent the corrosion of the reactor, while the downstream lines were made from Teflon® to improve corrosion resistance. In addition, a 25-g shaped cylinder catalyst was loaded into the reactor. Thereafter, the reaction feed (HCl flow = 80 cm³ STP min⁻¹ and volumetric flowrate HCl/O₂ = 1:2, unless otherwise specified) was continuously introduced. The reaction temperature was controlled in the range of 330 to 430 °C (± 1.0 °C). The data obtained by each test were the average of at least three steady-state measurements. The total chlorine balance was confirmed with an accuracy of $\pm 2\%$. Blank support without a loading active component showed negligible activity under the corresponding reaction condition. The reaction effluent was absorbed by excessive potassium iodide solution and analyzed by iodometry and acid-base titration to measure the generated Cl₂ and unreacted HCl. The conversion of HCl was calculated based on the detected results.

4. Conclusions

A series of Ru-Ti oxide based catalysts have been investigated for HCl oxidation in this research. It was clarified that the special oxygen species and active phase-support interactions of RuO₂/TiO₂ were significant for the Deacon process. RuO₂ film grows epitaxially on rutile TiO₂. This produces more active sites and oxygen species on the catalyst surface. More importantly, the assembly of RuO₂ and rutile TiO₂ generates coordinatively unsaturated ruthenium sites and bridge oxygen, which are efficient for the Deacon reaction. The interactions of Ru-Ti were confirmed by characterizations and correlated to the amount of the active component. The reducible oxygen species of the rutile TiO₂ may facilitate activation and transport of oxygen species during the active phase. It is inferred that the rutile support is likely involved in the catalytic reaction rather than merely acting as an inert support. On the other hand, the incorporation of Ce altered the electronic structure of the RuO₂/TiO₂-r system. The formation of Ru-O-Ce linkage decreased the amount of favorable oxygen species and

increased the positive charge of Ru sites, which restricted the recombination of Cl atoms and Cl₂ elimination. To achieve a better catalytic performance, a more delicate tuning of the RuO₂/TiO₂-r system by considering moderate positive charge density of Ru sites is required.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/9/2/108/s1>, Figure S1: XRD patterns of the self-made RuO₂ and the corresponding intensity line in red from PDF 65-2824, Figure S2: H₂-TPR profiles of the pure TiO₂ in rutile and anatase, Figure S3: XPS profiles of Ti 2p for RuO₂/TiO₂-r with 0.3, 0.5, and 1.0 wt% Ru, Figure S4: XPS spectra of Ce 3d for Ru-Ce/Ti oxide catalysts, Figure S5: XPS spectra of O 1s for the supported RuO₂ and Ru-Ce/Ti oxide catalysts, Table S1: Chemisorbed oxygen (O_α) in the supported RuO₂ and Ru-Ce/Ti oxide catalysts, Figure S6: Raman spectra of the supported RuO₂ and Ru-Ce/Ti oxide catalysts.

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