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Review

Gas-solid catalytic reactions over ruthenium-based catalysts

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ABSTRACT

Ruthenium (Ru)-based catalysts are widely employed in several types of gas-solid reactions because of their high catalytic activities. This review provides theoretical research on Ru-based catalysts and an analysis of their basic properties and oxidation behavior. There is particular emphasis on Ru-catalyzed gas-solid catalytic reactions, including the catalytic oxidation of VOCs, preferential oxidation of CO, synthesis of ammonia, oxidation of HCl and partial oxidation of CH₄. Recent literature on catalysis is summarized and compared. Finally, we describe current challenges in the field and propose approaches for future development of Ru-based catalysts.

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1. Introduction

Development and use of catalysts has greatly progressed over past decades and they are used for nearly 80% of all chemical production. It is envisioned that future development of existing catalysts or identification of novel materials for the next generation of catalysts will rely on rational design, which requires an understanding of the complete catalytic reaction system at the atomic scale [1]. A better understanding of the atomic-scale structure of a catalyst requires investigation of model catalysts with simple structures, such as single crystalline films or single crystal surfaces [2]. The mechanisms of real catalytic processes are highly complicated and it is difficult to identify the micro-steps in these reactions. Therefore, analysis

of catalytic performance — including the study of elementary reactions steps, reaction intermediates and related topics — is typically accomplished via a combination of surface science and experimental methods. Such studies have led to an in-depth understanding of catalytic reactions under real-life conditions.

Many catalysts, such as noble metals and transition metal oxides, have been explored for gas-solid reactions. Recently, supported ruthenium (Ru)-based catalysts were employed in many gas-solid reactions because of their excellent activities under low temperature and pressure conditions.

This review describes properties of Ru, the oxidation of Ru metal and the theoretical research on Ru-based catalysts. In addition, we explain the gas-solid reactions catalyzed by Ru-based materials. As shown in Fig. 1, the catalytic applica-

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Fig. 1. Gas-solid reactions promoted by Ru-based catalysts.

tions of these materials include the catalytic oxidation of volatile organic compounds (VOCs) [3–5], preferential oxidation of CO (PROX) [6,7], synthesis of ammonia [8], oxidation of HCl (the Deacon process) [9] and partial oxidation of CH₄ [10–12]. Finally, this review summarizes existing problems as well as future developmental trends for Ru-based catalysts.

2. Ru-based catalysts

2.1. Basic properties

Ru is a rare transition metal belonging to the platinum group in the periodic table. The electronic structure of elemental Ru is $4d^75s^1$ and Ru exhibits a rich variety of oxidation states, including +2, +3, +4, +6 and +8. Ru materials are mainly composed of metallic Ru, RuO₂ and RuO₄. The boiling points of these forms are 4100 °C [13,14], 1400 °C and 100 °C [15,16], respectively. The crystal planes of RuO₂ are illustrated in Fig. 2. In the bulk structure of RuO₂ (rutile structure), the Ru atoms bind to six oxygen atoms, forming a slightly distorted RuO₆ octahedron, while the oxygen atoms are coordinated to three Ru atoms in a planar configuration that is consistent with the sp^2 hybridization of oxygen [1].

Volatility at high temperature is recognized as a serious limitation in applications of Ru-based catalysts. In Ru-based catalysts for gas-solid reactions, metallic Ru and/or RuO₂ have been commonly identified as the active species and the reaction temperatures are usually below 400 °C, much lower than the boiling points of Ru and RuO₂. Hence, volatility of Ru species is not observed in most gas-solid catalytic reactions and there have been no reports of this behavior for such reactions.

2.2. Oxidation behaviors

The transition from oxygen adsorption to oxide formation on Ru is structurally complex because of the various phases of

Fig. 2. The crystal planes of RuO₂.

oxygen on the surface [17]. However, the orientation of the RuO₂ depends on the orientation of the Ru. H. Over *et al.* [18] demonstrated that the active part of this “O-rich” Ru phase is RuO₂, which grows epitaxially with its (110) plane parallel to the Ru (0001) surface at high O₂ partial pressure and elevated temperatures. When the Ru (0001) surface is exposed to molecular oxygen under UHV conditions, a (2×2)-O layer and a (2×1)-O overlayer are formed [19]. At much higher concentrations of oxygen, for example, more than 1 000 L at room temperature, the Ru (0001) surface stabilizes two additional phases of chemisorbed oxygen, namely, (2×2)-3O and (1×1)-O [20]. However, Ru (0001) is oxidized by an autocatalytic process, because of formation of oxide nuclei on the Ru(0001)-(1×1)O surface [17]. The autocatalytic reaction indicates that the surface produces its own ‘catalyst’, thus readily dissociating the oxygen molecules and resulting in self-acceleration of the oxidation process [21]. This complexity is characteristic of oxygen chemistry on many transition metal surfaces, as shown in Fig. 3. The oxidation of Ru occurs only under specific conditions and requires a minimum threshold temperature. Goodman *et al.* [22] discovered that formation of RuO₂ on Ru (0001) required, at a minimum, an O₂/CO pressure ratio of 18/10, a temperature of 360 °C, and a reaction time of 700 s. To generate RuO₂, the oxygen must cover a volume of 4 ML and must have at least two layers of the tri-layer structure [23].

2.3. Theoretical research

Relatively simple reaction structures are usually chosen to represent the atomic-scale structure of the catalyst for study. CO oxidation is one of the most extensively studied reactions because it is relatively simple and includes all basic steps of a heterogeneous process, that is, adsorption, diffusion, dissociation, reaction and desorption [24]. In addition, it is also the most important part of the PROX reaction.

Ru has long been known as an exception in the Pt group metals, in terms of its behavior towards the oxidation of CO. Under UHV conditions, Ru is an extremely poor catalyst for oxidation of CO [25], yet its activity becomes greater than that of the other Pt group metals under high pressure and oxidizing conditions [26–28]. The reaction proceeds through the Langmuir-Hinshelwood (L-H) mechanism which requires the chemisorption of reactants before their recombination [28]. Stampfl

Fig. 3. The rich oxygen chemistry of ruthenium (0001). Reproduced with permission from Ref. [17]. Copyright 2002, the American Association for the Advancement of Science.

et al. [29] found that formation of (1×1)-O overlayer on a Ru (0001) single crystal surface caused the material to become nearly inactive. It was proposed that the “pressure gap” can be bridged by forming RuO₂ on Ru catalysts at elevated reactant pressures [21]. Over *et al.* [2] discussed the complex structure-activity correlation in CO oxidation on Ru, based on results of *in situ* surface X-ray diffraction (SXRD) and on-line mass spectrometry measurements. They discovered that the activity of the catalyst increased when it underwent structural changes, either because it was reduced or because it formed RuO₂(110). According to density-functional theory (DFT) calculations (Fig. 4) reported by Over *et al.* [18], the cus (a coordinative unsaturated site) Ru atom has an exposed dangling bond at the surface, explaining the high reactivity of the RuO₂(110) surface. Gao *et al.* [30] expressed a different view that a chemisorbed oxygen surface is the most thermodynamically stable phase and active phase for CO oxidation. The core-shell structure — with an ultrathin RuO₂ shell coating a metallic Ru core — was identified as the most active and stable state. In contrast, Qadir *et al.* [31] showed that smaller Ru nanoparticles could form a huge bulk of RuO₂ on their surfaces, leading to a lower catalytic activity. They reported that core-shell type RuO₂ became more stable as the size of the nanoparticle increased.

3. Gas-solid catalytic reactions

3.1. Catalytic oxidation of VOCs

VOCs emitted from industrial processes and transportation activities are regarded as major contributors to air pollution and as dangerous to human health. Approaches for removal of VOCs include thermal incineration, catalytic oxidation and adsorption-based techniques. Because of advantages such as high efficiency, low temperature and high selectivity for harmless products, catalytic oxidation is considered a promising path-

way to reduce VOCs emissions and meet the standards of air pollution control regulations.

Various catalysts, such as noble metals (Pt, Pd, and Au) [32–34] and transition metal oxides (Co₃O₄, MnO_x, and V₂O₅) [35–38], have been utilized for complete oxidation of VOCs. However, use of these catalysts often presents problems, including relatively low activity, rapid deactivation by chlorine poisoning or coking, high cost and formation of undesired polychlorinated benzenes. VOCs-oxidation catalyzed by Ru-based materials, compared with by other noble metals, has been much less studied. However, recently, Ru-promoted oxidation of VOCs was broadly reported because of its unique properties, with these reports summarized in Table 1.

Most recently, our group [39] prepared the Ru-based catalysts Ru/TiO₂, Ru/SiO₂, Ru/γ-Al₂O₃ and Ru/ZrO₂ and evaluated their usefulness for CH₃Br oxidation. We found that Ru/TiO₂ performed better catalytically than the other materials. By transmission electron microscopy (TEM) characterization, the Ru species were primarily distributed on the rutile phase of P25 TiO₂. Ru/TiO₂ was also employed in the catalytic oxidation of CO, benzene, methyl acetate and multi-pollutants of a simulated PTA off-gas. Interestingly, when the temperature was below 200 °C, all pollutants had conversions below 10%, results far different from those of single-pollutant tests (Fig. 5). We tentatively propose that the oxygen-rich nature of methyl acetate was the key factor in its being oxidized far more rapidly when in competition with other compounds on the catalyst surface.

Using different types of TiO₂ (anatase, P25 and rutile) as supports, our group [40] synthesized supported-Ru catalysts with homogeneously distributed Ru particles via wet impregnation. All of these catalysts were very active for trichloroethylene oxidation, but we found that Ru oxide species formed during the reaction were very unstable in the anatase phase of TiO₂. In the presence of the rutile phase of TiO₂, which had a similar structure to that of RuO₂, the Ru species tended to distribute on the rutile TiO₂. The Ru/P25 catalyst, with a larger

Fig. 4. Pseudovalence charge density contour plots of the RuO₂(110) surface cut through the cus-Ru atom along the [110] and the [001] directions from DFT calculations. Reproduced with permission from Ref. [18]. Copyright 2000, the American Association for the Advancement of Science.

Table 1

Catalytic oxidation of VOCs over Ru-based catalysts, as reported in recent literature.

Catalyst	VOCs (Concentration)	Conversion of VOCs (%) (T/°C)	Ref.
1%Ru/TiO ₂ (P25)	Methyl bromide (100 ppm)	90 (212)	[39]
1%Ru/TiO ₂ (P25)	Trichloroethylene (500 ppm)	90 (249)	[40]
1%Ru/Co ₃ O ₄ -MOF	Toluene (1000 ppm)	90 (238)	[41]
0.38%Ru/CeO ₂	Chlorobenzene (1000 ppm)	90 (280)	[42]
1%Ru-CeO ₂	Chlorobenzene (550 ppm)	90 (240)	[43]
1%Ru/Ti-CeO ₂	Chlorobenzene (550 ppm)	90 (210)	[44]
4.9%Ru/γ-Al ₂ O ₃	Propane (2000 ppm)	95 (195)	[45]
4.5%Ru/ZnAl ₂ O ₄	Propane (2000 ppm)	50 (198)	[46]
4.6%Ru/γ-Al ₂ O ₃	Butane (2000 ppm)	100 (190)	[47]
1%Ru/CeO ₂	Ethyl acetate (1000 ppm)	90 (190)	[48]
4.6%Ru/γ-Al ₂ O ₃	Propane (2000 ppm)	50 (175)	[49]
1%Ru/CeO ₂	Propylene (6000 ppm)	50 (177)	[52]
0.5%Ru/Al ₂ O ₃	Trichloroethylene (1091 ppm)	50 (326)	[53]
5%RuO ₂ /CeO ₂	Propylene (4000 ppm)	100 (423)	[54]

Fig. 5. (a) Single-pollutant test: CO (■), CH₃Br (●), benzene (▲) and methyl acetate (▼) conversions over Ru/TiO₂ as a function of reaction temperature; (b) Multi-pollutant test: CO (■), CH₃Br (●), benzene (▲) and methyl acetate (▼) conversions over Ru/TiO₂ as a function of reaction temperature. Experiments were performed under the following conditions: pollutant concentrations = 3500, 100, 200 and 500 ppm, respectively; O₂ concentration = 20 vol % and WHSV = 60 000 mL g⁻¹ h⁻¹. Reproduced with permission from Ref. [39]. Copyright 2016, Royal Society of Chemistry.

particle size, showed apparently better catalytic performance than the other two samples. This was tentatively attributed to a size effect, which has been well demonstrated in Pt catalytic systems. The existence of additional water vapor greatly increased HCl formation and reduced the amount of tetrachloroethylene and pentachloroethane as the organic byproducts, whereby catalytic activity was also suppressed, as shown in Fig. 6.

Our group [41] reported Ru/Co₃O₄-metal-organic frame-

work (MOF)-catalyzed toluene oxidation. In the preparation, the Co₃O₄-MOF support was synthesized through a template method for MOF-synthesis and the catalyst was then obtained by the impregnation method. For comparison, the Ru/Co₃O₄-B catalyst was also prepared by the traditional precipitation-impregnation method. We showed that Ru/Co₃O₄-MOF exhibited far better catalytic activity, CO₂ selectivity, stability and anti-moisture properties than other materials. BET, XRD and XPS characterization revealed that Ru/Co₃O₄-MOF had a

Fig. 6. Trichloroethylene conversion and CO_x yields (a,c), distribution of the organic byproducts and fraction of HCl in inorganic chlorine (b,d) as a function of temperature over the Ru₁(WI_{R-450})/P25 catalyst in the absence (a,b) and presence (c,d) of additional water vapor. Reproduced with permission from Ref. [40]. Copyright 2016, Elsevier.

Fig. 7. Toluene conversion as a function of reaction temperature over the catalysts. Reproduced with permission from Ref. [41]. Copyright 2015, Royal Society of Chemistry.

larger surface area than Ru/Co₃O₄-B, and that Ru species were well dispersed on the surface of Ru/Co₃O₄-MOF (Fig. 7).

Huang *et al.* [42] loaded Ru on CeO₂ with different morphological structures, such as nanorods, nanocubes and nanoocto. Their characterization studies revealed that Ru/CeO₂-r exhibited the most abundant Ru⁴⁺, oxygen vacancies and Ru–O–Ce bonds. The investigators concluded that a strong interaction existed between Ru and the CeO₂-r support. Indeed, chlorobenzene oxidation tests showed that Ru/CeO₂-r gave the highest catalytic activity, demonstrating that the activity of Ru/CeO₂ for chlorobenzene was greatly influenced by the shape/crystal plane (Fig. 8).

Dai *et al.* [43] studied the mechanism of CB oxidation over Ru/CeO₂ catalysts and proposed that the C–Cl cleavage would first occur at the Ce³⁺/Ce⁴⁺ active sites, forming Cl₂ through the

Fig. 9. Proposed reaction mechanism for catalytic oxidation of CB over Ru/CeO₂ catalyst. Reproduced with permission from Ref. [43]. Copyright 2012, Elsevier.

Deacon process. The partial C and H of the intermediates would then be oxidized into CO₂ and H₂O by the active oxygen and lattice oxygen on the catalyst surface and the Cl₂ would finally be adsorbed on the active sites, leading to deactivation of the catalyst (Fig. 9).

In their next study, Dai *et al.* [44] doped TiO₂ into 1%Ru/CeO₂ to obtain 1%Ru/Ti-CeO₂, reporting an increased activity of this catalyst for CB oxidation. They further reported that 1%Ru/5%Ti-CeO₂ showed the highest activity. H₂-TPR and TEM results showed that 1%Ru/Ti-CeO₂ exhibited great re-

Fig. 8. (a–c) TEM and HRTEM images of Ru/CeO₂-r; (d–f) TEM and HRTEM images of Ru/CeO₂-c; (g–i) TEM and HRTEM images of Ru/CeO₂-o; (j) Conversion of chlorobenzene (CB) over various CeO₂ and Ru/CeO₂ catalysts; (k) Stability of different Ru/CeO₂ catalysts at 290°C. Reproduced with permission from Ref. [42]. Copyright 2014, Elsevier.

ducibility at low temperatures because of its active oxygen-rich nature and that the strengthened interaction between Ru and CeO₂ was an oxidation, ascribed to the high-energy lattice planes of CeO₂ (110) and (100). Okal *et al.* [45] employed 4.9%Ru/ γ -Al₂O₃ and a H₂-reduced catalyst in propane. The T_{95} values of the former and latter catalysts were 195 and 205 °C, respectively. By TEM characterization, the former exhibited Ru particles with an average size of 1.6 nm, whereas those in the latter had an average size of 6.0 nm. In another study, Okal *et al.* [46] prepared Ru/ZnAl₂O₄ catalysts with different Ru contents (0.5%, 1%, and 4.5%), and employed these catalysts for propane oxidation. The 4.5% Ru/ZnAl₂O₄ showed the highest catalytic efficiency. XRD and HRTEM/SAED results revealed that the Ru species had a small particle size and these were well dispersed on ZnAl₂O₄. The decreased ZnAl₂O₄ particle size facilitated the catalytic efficiency. Mitsui *et al.* [48] compared the catalytic performance of CeO₂-supported noble metals, such as Ru, Pt, Pd and Rh, in the oxidation of ethyl acetate and found that the Ru-containing catalyst demonstrated the highest catalytic activity with a T_{90} = 190 °C. Okal *et al.* [49] reported the preparation of washed 4.6% Ru/ γ -Al₂O₃ and their XPS spectra revealed a very low chlorine content. Catalytic oxidation of propane over unwashed and washed catalysts gave T_{50} = 315 and 175 °C, respectively. It was proposed that chlorine extensively occupied the active sites on the catalyst surface [50,51]. Aouad *et al.* [52] prepared Ru/CeO₂ with different Ru contents of (0.67%, 1%, 3% and 5%). Based on catalytic oxidation of propene, the catalytic efficiency was slightly changed when the Ru content was above 1%. Based on TPR results, the Ru species were saturated on the catalyst surface for 1%Ru/CeO₂. Miranda *et al.* [53] employed 0.5%Ru/Al₂O₃ for trichloroethene oxidation. Compared with the blank test, they found that T_{50} was decreased from 700 to 326 °C. Hosokawa *et al.* [54] loaded Ru on different supports (CeO₂, γ -Al₂O₃, and ZrO₂) and employed these for propene oxidation. RuO₂/CeO₂ exhibited the highest catalytic activity, with T_{100} = 423 °C, and it was proposed that propene molecules were easily influenced by Ru=O.

Currently available studies were primarily focused on the catalytic oxidation of single VOC pollutant and catalytic evaluation and stability test were commonly reported. The detailed oxidation process has been explored far less frequently, though this would inform catalyst development. In addition, reaction conditions closer to those involving real waste gas should be employed in such studies. Hence, mechanistic and kinetic studies and catalytic oxidation of VOCs with multi-pollutants should be strongly encouraged for inclusion in future research.

3.2. Preferential oxidation of CO (PROX)

In recent years, hydrogen-polymer electrolyte membrane fuel cells (H₂-PEMFC) have attracted increasing interest as an environmentally compatible supply of electric energy [55,56]. In these fuel processors, hydrocarbons are transformed into H₂. PROX is an essential step in the fuel processing system for a low temperature H₂-PEMFC and is employed to remove residual CO from an H₂-rich stream. This is done because CO can degrade the electrochemical performance of the PEMFC.

In the PROX system, CO oxidation (Eq. (1)), H₂ oxidation (Eq. (2)), CO methanation (Eq. (3)), CO₂ methanation (Eq. (4)) and the water-gas shift reaction may occur concurrently because all of the reactants (CO, CO₂, H₂, O₂, and H₂O) coexist in the system. Consequently, undesired reactions, such as H₂ oxidation, CO methanation and CO₂ methanation, must be minimized during PROX. For practical applications, PROX catalysts should have a wide temperature window and be able to perform under low temperatures to facilitate complete CO removal. Thus, we concluded that the Ru-based catalysts are suitable for PROX systems, based on recent reports using these agents, as summarized in Table 2.

Kim *et al.* [57] obtained SiO₂ with different surface areas by varying the calcination temperatures for supports and the Ru/SiO₂ catalysts were synthesized through the incipient-wetness impregnation method. These investigators observed that the surface area decreased with increased calcination temperature and the Ru particle size increased with decreased surface area. When the calcination temperature for support was 830 °C, the Ru/SiO₂ was more effective than other materials. In another study [58], a series of Ru-based catalysts, Ru Ru/ α -Al₂O₃ (α = α , κ , γ , η , δ , and θ), were employed in PROX. Ru/ α -Al₂O₃ was the most efficient catalyst, with an average Ru particle size of 2.6 nm and well dispersed Ru particles on the catalyst. H₂-TPR experiments for Ru/ α -Al₂O₃ showed that Ru species could be reduced at a low temperature of 100 °C. Kim *et al.* [59] loaded Ru on different supports (yttria-stabilized zirconia (YSZ), ZrO₂, TiO₂, SiO₂, γ -Al₂O₃) via wetness-impregnation. In the PROX reaction, Ru/YSZ showed an apparently higher catalytic activity than other materials. On TEM images, Ru species were well dispersed on the YSZ support and the average Ru particle size was 1.2 nm. The outlet CO concentration was below 10 ppm, even when CO₂ (17.4 vol%) and H₂O (13.0 vol%) were introduced. Kim *et al.* [60] examined γ -Al₂O₃-supported noble metal catalysts in which the metal content was (5% or 0.5%), at different reaction temperatures, as shown in Fig. 10. They found that the catalytic activity of 5% Ru/ γ -Al₂O₃ was the highest, compared with those of other catalysts. In the absence of H₂O and CO₂, 100% CO conversion could be achieved over 5% Ru/ γ -Al₂O₃ over a wide range of reaction

Table 2
PROX over Ru-based catalysts, as reported in recent literature.

Catalyst	CO concentration (vol%)	Conversion of CO (%)	$T/^\circ\text{C}$	Ref.
1.08%Ru/SiO ₂	1	95	400	[57]
0.696%Ru/ α -Al ₂ O ₃	1	98	390	[58]
0.64%Ru/YSZ	1	80	380	[59]
5.0%Ru/ γ -Al ₂ O ₃	1	100	333	[60]
3.8%Ru/Al ₂ O ₃	0.3	99.8	150	[61]
1.0%Ru/ θ -Al ₂ O ₃	0.5	99	140	[62]
5.0%Ru/ZrO ₂	1	96	310	[63]
5.0%Ru/ γ -Al ₂ O ₃	1	96	75	[64]

Fig. 10. (a) Temperature-dependence of CO conversion and CH₄ yield for PROX over 5% noble metal catalysts supported on γ -Al₂O₃; (b) CO conversion and CH₄ yield for PROX over 0.5% noble metal catalysts supported on γ -Al₂O₃ with increasing temperature. All catalysts were reduced in H₂ at 300 °C before the reaction. Reproduced with permission from Ref. [60]. Copyright 2009, Elsevier.

temperatures, from 60 to 200 °C. Though 0.5 wt% Ru/ γ -Al₂O₃ and 5 wt% Ru/ γ -Al₂O₃ had similar particle size distributions by TEM analysis, the latter catalyst, with a smaller amount of chemisorbed CO and O₂ per Ru atom, showed much better PROX activity.

Hidenobu *et al.* [61] studied the influence of NH₃ on Ru/Al₂O₃-catalyzed selective CO oxidation and found that the catalyst showed lower activity in the presence of NH₃ at a high ratio of [O₂]/[CO]. It was suggested that high O₂-concentration facilitated oxidation of NH₃ and generation of nitrosyl, which led to the deactivation of the catalyst. Similarly, the presence of NO or NO₂ also resulted in nitrosyl-induced deactivation (Fig. 11). Chin *et al.* [62] examined the influence of Ru precursors, H₂O and CO₂ on the Ru/Al₂O₃-catalyzed PROX reaction. The

activity of the catalyst made from nitrate precursors (Ru(NO)(NO₃)₃·xH₂O) was apparently higher than those made from chloride hydroxyl precursors (RuCl₃·xH₂O, Ru₃(CO)₁₂). 99% CO conversion was achieved at 140 °C with the catalyst using Ru(NO)(NO₃)₃·xH₂O as a precursor. The high turnover frequency (TOF) was ascribed to the homogeneous dispersal of Ru species, as seen from HRTEM images. The introduction of 10% H₂O had a significant inhibitory effect when the reaction temperature was below 180 °C and a promotional effect was demonstrated clearly when the temperature was above 200 °C. Moreover, 15% CO₂ severely inhibited CO oxidation. Han *et al.* [64] employed Ru/ γ -Al₂O₃ to remove CO from fuel gas and the CO conversion reached 96% at 75 °C. In this study, TEM images showed a Ru particle size of 2.5 nm.

Simply stated, the key to the application of PROX is to develop a highly active and selective catalyst that could be employed over a wide temperature range and that exhibits good resistance to CO₂ and H₂O. Introduction of the second transition metal component to form a bimetallic catalyst [6] or core-shell structure [31] may be a useful approach to enhance low temperature activity for PROX.

3.3. Ammonia synthesis

Ammonia and its processed products play significant roles in the pharmaceutical, metallurgy and environmental protection industries. However, ammonia synthesis is highly energy consuming. The primary difficulty in ammonia synthesis originates from the character of the N≡N bond, which is the strongest bond among diatomic molecules. The role of the catalyst is to lower the dissociation energy of the N≡N bond [65]. To decrease the energy required for this reaction, significant effort has focused on the search for efficient catalysts for ammonia synthesis at low temperature and low pressure.

Iron (Fe)-based materials are well established as first-generation ammonia synthesis catalysts. Yet, the requirements of high temperature and pressure directly lead to high costs and energy consumption. In the seventies, Aika *et al.* [66] found that

Fig. 11. Deactivation and reactivation models over a Ru/Al₂O₃ catalyst. Reproduced with permission from Ref. [61]. Copyright 2007, American Chemical Society.

Ru-K/AC was very efficient for ammonia synthesis, 10 times more than was the Fe-based catalyst at 250 °C, under ordinary pressure. This report received considerable attention from researchers worldwide. Compared with the traditional Fe catalyst, the supported-Ru catalyst was more reactive at lower temperatures under lower pressures [67,68]. Additionally, the Ru catalyst is insensitive to H₂O, CO_x and NH₃ concentrations and, thus, is regarded as the ideal second-generation ammonia synthesis catalyst. Many studies proved that the catalytic performance of Ru-based catalysts for ammonia synthesis depended on the nature of the supports. It was proposed that strong interactions between Ru and the support led to rapid electron transfer from the support to Ru particle surface. Doping of other elements might provide more oxygen vacancies and effectively prevent catalyst agglomeration from high temperatures calcination. The results of recent studies on Ru-catalyzed ammonia synthesis are summarized in Table 3.

Wang *et al.* [69] prepared Ru/BaTiO₃ with the impregnation method and observed that the catalyst exhibited higher efficiency for ammonia synthesis than Ru/TiO₂, Ru/MgO or Ru/CeO₂. They proposed that strong interactions between Ru and the support led to rapid electron transfer from the support to the Ru particle surface. This would greatly promote the cleavage of N≡N and improve the catalytic activity for ammonia synthesis. Zhou *et al.* [70] modified mesoporous carbon (MC) by doping SiO₂ to change its surface area and pore size and prepared Ba-Ru-K/MC, using modified MC as the support. They found that the particle size of SiO₂ and the ratio of SiO₂ to MC greatly affected the surface area and the pore size of the modified MC. The catalytic activity for ammonia synthesis increased with the improved surface area found in the modified MC. Lin *et al.* [71] employed K-Ru/Ba-ZrO₂ for ammonia synthesis at high temperatures and found that formation of BaZrO₃ and introduction of K⁺ improved electronic conductivity and basicity. Zhang *et al.* [72] loaded Ru on CeO₂ doped with Sm (0, 2, 5, 7 and 10 wt%) and showed that the resultant Ru/Sm₂O₃-CeO₂ was most efficient when the Sm content was 7 wt%. The introduction of Sm³⁺ prevented sintering of the catalyst, preserved its morphology by generating more oxygen vacancies and facilitated CeO₂ reduction. Pan *et al.* [73] investigated Fe-Ru/AC-catalyzed ammonia synthesis under various conditions (temperature, space velocity, pressure and H₂/N₂

ratio) and also conducted tests with Fe/AC and Ru/AC for comparison. Yang *et al.* [74] discovered that Ru/BaCeO₃ yielded higher catalytic activity than Ru/γ-Al₂O₃, Ru/MgO, or Ru/CeO₂. XRD, HRTEM, XPS, and H₂-TPR data confirmed that strong interactions between Ru and the support facilitated the electron transfer process and that Ce³⁺ was crucial to the reduction of the Ru species. Luo *et al.* [75] applied Ru/CeO₂-La₂O₃ to ammonia synthesis. At 188 °C and 10 MPa, with a La₂O₃ content of 10% and an NH₃ concentration of 13.9%, the catalytic activity of Ru/CeO₂-La₂O₃ was apparently higher than that of Ru/CeO₂. These investigators concluded that introduction of La₂O₃ facilitated oxygen reduction on the catalyst surface and enhanced stability of the catalyst. Lin *et al.* [76] prepared Cl-depleted Ru/γ-Al₂O₃ through hydrazine reduction and observed that the chlorine content was lowest when the mole ratio of hydrazine to Ru was 3 and the corresponding catalyst had the highest activity. Saito *et al.* [77] synthesized a MgO-CeO₂ support through a co-precipitation method and found that its surface area decreased with increasing CeO₂ content. The modified Ru particle distribution was attributed to isolation of CeO₂ by amorphous MgO, formed after loading Ru. The partially reduced CeO_{2-δ} (0 ≤ δ ≤ 1) would facilitate the electron transfer to Ru and thus promote cleavage of N≡N, whereby the catalytic activity for ammonia synthesis was improved. For example, when CeO₂ content was 50 mol%, the rate of ammonia synthesis in the presence of Ru/(MgO-CeO₂) was 8 times higher than that in the presence of Ru/MgO. Xu *et al.* [78] prepared K-Ru/CNTs-K-Ru/MgO by mixing K-Ru/MgO and K-Ru/CNTs (carbon nanotubes) in acetone. They found that this catalyst did not have the drawbacks of MgO, including low basicity of CNTs and poor electron transfer ability, and the activity of the composite catalyst was substantially higher than those of catalysts with single supports (Fig. 12).

3.4. HCl oxidation (the Deacon process)

Recycling elemental chlorine is important to reduce HCl emissions and to meet the increasing demand for Cl₂. An attractive route for chlorine recovery is the gas-solid catalytic oxidation of HCl with air or oxygen, the Deacon reaction. Supported CuCl₂ catalysts are the preferred catalysts for the Deacon process, even though they still exhibit serious drawbacks when

Table 3

Ammonia synthesis over Ru-based catalysts, as reported in recent literature.

Catalyst	NH ₃ concentration (vol%)	T/°C	Ref.
4.0%Ru/BaTiO ₃	6.96	425	[69]
Ba-4.0%Ru-K/MC15	16.4	152	[70]
K-4.0%Ru/Ba-ZrO ₂	9.24	152	[71]
4.0%Ru/Sm ₂ O ₃ -CeO ₂	13.4	152	[72]
Fe-4.0%Ru/AC	24.4	102	[73]
5.0%Ru/BaCeO ₃	3.2	350	[74]
4.0%Ru/CeO ₂ -La ₂ O ₃	13.9	177	[75]
Sm-5.0%Ru/γ-Al ₂ O ₃ (h3)	7.4	475	[76]
5.0%Ru/(MgO-CeO ₂)	12.6	375	[77]
K-5.0%Ru/CNTs-K-5.0%Ru/MgO	24.3	400	[78]

Fig. 12. TEM image of K-Ru/MgO + K-Ru/CNTs. Reproduced with permission from Ref. [78]. Copyright 2006, Elsevier.

used at 430–500 °C. These include limited activity, rapid deactivation due to volatilization of CuCl_2 above 400 °C and corrosion caused by unreacted HCl and the product H_2O .

In 2003, Sumitomo Corporation [79,80] reported novel Ru-based catalysts and applied them in industrial plants. In these catalysts, TiO_2 , ZrO_2 , Al_2O_3 or zeolite were used as supports and the TiO_2 supported material showed the highest efficiency. Ru content was within the range of (2–6) wt%. In addition, some dopants such as Pd, Cu, Cr, V, rare earth compounds or alkali metal compounds were added to the catalysts to enhance their catalytic performance. At standard pressure, a space velocity of 20–1000 h^{-1} and a temperature of 200–380 °C, the HCl conversion reached 95.9% and the lifetime exceeded 16000 h. Nonetheless, the catalytic activity decreased with time and irreversible deactivation usually occurred as a result of the impurities in the HCl gas or because of errors in technical operation. BASF Corporation [81] used RuO_2 , RuCl_3 , or other Ru precursors to synthesize Ru catalysts loaded on SiO_2 , Al_2O_3 , TiO_2 or ZrO_2 . In HCl oxidation, these investigators observed that the per-pass conversion of HCl reached (40–90)%. López *et al.* [82] studied the mechanism of HCl oxidation over $\text{RuO}_2/\text{TiO}_2$ and their DFT studies revealed that the reaction mechanism was consistent with the Mars-van-Krevelen mechanism in 5 steps. These steps were hydrogen abstraction from HCl (6), recombination of atomic chlorine (7), hydroxyl recombination (8), water desorption (9) and dissociative oxygen adsorption (10).

It was also discovered that Cl_2 conversion increased with an increased ratio of O_2 to HCl. This change was attributed to the increased O concentration on the catalyst surface and the decreased binding energy of Cl. Seitsonen *et al.* [83] also studied the mechanism of HCl oxidation over $\text{RuO}_2(110)/\text{TiO}_2(110)$ using DFT studies. As shown in Fig. 13, a calculated 1 ML (monolayer) s- RuO_2 was loaded on TiO_2 , affording a well-defined s- $\text{RuO}_2@/\text{TiO}_2$ catalyst model.

When $1/2\text{O}_2$ was introduced, O_{ot} was formed at the 1f-cus (the one-fold under coordinated metal site) site. Some O_{ot} sites adsorbed HCl, forming $\text{O}_{\text{ot}}\text{H}$ and Cl_{ot} . In addition, other surface HCl's were adsorbed, forming $\text{O}_{\text{ot}}\text{H}_2$ and 2Cl_{ot} and, finally, H_2O and Cl_2 were desorbed and released. Recently, scientists from Tsinghua University [84] reported a series of monolithic catalysts, composed of FeCrAl alloy or cordierite as the skeleton, (7–12) wt% supports and (1–3) wt% active species $\text{RuO}_2(110)$. In HCl oxidation, 87.3% HCl conversion was achieved at a low temperature of 280 °C. Over [85] compared activities of several types of RuO_2 -based catalysts for HCl oxidation, reporting that the catalytic activity of RuO_2 -rutile- TiO_2 was significantly higher than that of RuO_2 -anatase- TiO_2 and other catalysts (Fig. 14).

In fact, the actual reaction process is more complicated because of differences in properties of the oxygen species on the surface and in oxygen and chlorine coverage. For instance, O^* in

Fig. 13. The catalytic cycle of HCl oxidation over 1 ML of $\text{RuO}_2(110)$ supported on $\text{TiO}_2(110)$, starting with a selective and self-limiting replacement of the bridging O atoms of s- $(\text{RuO}_2)_1@/\text{TiO}_2$ by bridging chlorine, forming c- $(\text{RuO}_2)_1@/\text{TiO}_2$. The activation energies E_{act} are given in kJ/mol. The rate-determining step was identified as association of two neighboring Cl atoms to form Cl_2 . Reproduced with permission from Ref [83]. Copyright 2010, American Chemical Society.

Eqs. (6) and (8) can be either O_{cus} or O_{b} and each should be simulated separately. The lattice oxygen O_{b} plays an extremely important role in the process of hydrogen abstraction from HCl and hydroxyl recombination in water formation. However, the structural oxygen in ruthenium oxide (O_{b}) cannot be removed as water ($\text{H}_2\text{O}_{\text{b}}$). In contrast, O_{cus} is crucial to formation of hydroxyl groups on the surface and water molecules and the binding energy of the latter is sufficiently low under reaction conditions [82]. Therefore, the Ru-based catalyst must be able to supply enough oxygen species and oxygen vacancies under actual reaction conditions and to prevent catalyst deactivation because of the existence of the Cl element.

3.5. Partial oxidation of CH_4

The conversion of methane to syngas is commonly classified into three methods: steam reforming, partial oxidation of CH_4 and CO_2 reforming. Among those approaches, partial oxidation of CH_4 has been recognized as the most efficient method because of its low energy cost, high reaction rate and the conven-

Fig. 14. Relative activities of RuO_2 -based catalysts for HCl oxidation, depending on the chosen support. The inset shows 1 ML of $\text{RuO}_2(110)$ coated on $\text{TiO}_2(110)$. Reproduced with permission from Ref. [85]. Copyright 2012, American Chemical Society.

ient synthesis of methanol. The partial oxidation of CH₄ is often performed on Ni-based catalysts. However, the reaction must be conducted at high temperatures to activate the metal nickel, which causes catalyst deactivation by sintering and carbon deposition [86,87]. This is the motivation for developing stable and active catalysts that can operate at the low temperatures. Nishimoto *et al.* [88] prepared 0.5%Ru/Y₂O₃ and employed it for partial oxidation of CH₄ at 600 °C, with CH₄/O₂ ratio = 5. The CH₄ conversion was 27% with $n(\text{CO})/n(\text{H}_2) = 0.5$ and the selectivity was 75%. No carbon deposit was observed on the catalyst surface after 10 h of stream reaction. Figen *et al.* [89] found that complete oxidation was the dominant process within the temperature range of 600–650 °C and partial oxidation was dominant when the temperature was above 700 °C. Cordierite-supported Co, Co-Ni, Co-Ru, Co-Ni-Ru and Ni catalysts were prepared through the impregnation method and used for partial oxidation of CH₄. TG-FTIR results illustrated that Co-Ni-Ru exhibited less carbon deposits than did other materials, primarily because of the catalytic efficiency and stability imparted by Ru. The conversion of CH₄ was 93.96% at 800 °C and the selectivity to H₂ and CO was 91.81% and 90.85%, respectively.

4. Conclusions

Ru-based catalysts have attracted considerable attention as models for surface science and computational studies. Ru-based catalysts have been well established in various gas-solid catalytic reactions, such as the catalytic oxidation of VOCs, PROX, ammonia synthesis, the Deacon process and partial oxidation of CH₄, because of their advantages including high activity, great stability and low yield of byproducts. Catalytic performance is greatly influenced by the physicochemical properties of the catalysts. Morphology and size effects have been well demonstrated in catalytic oxidation of VOCs and PROX and in partial oxidation of CH₄. For ammonia synthesis, it is crucial to ensure rapid electron transfer, and this is attributed to strong interactions between Ru and the support. In the Deacon process, active oxygen species and oxygen vacancies play important roles.

However, challenges still exist in the field of catalytic systems and novel catalysts and, also, their reaction mechanisms should be explored in future research. For example, more formidable catalysts are needed for oxidation of VOCs with multi-pollutants. Many studies have proven that the catalytic performance of Ru-based catalysts for ammonia synthesis is influenced by the nature of the supports. A promising support would show high conductivity and electron-donating ability. It is critical to avoid side reactions and byproducts in PROX and partial oxidation of CH₄. Based on the needs we have summarized here, we believe that this review will be beneficial to those addressing future development and application of Ru-based catalysts.

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Graphical Abstract

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Gas-solid catalytic reactions over ruthenium-based catalysts

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The activity of Ru/RuO₂ has been illuminated on the atomic scale by the method of combining experiment and theory. Due to their high catalytic activity, Ru-based catalysts are widely used in all kinds of gas-solid reactions including catalytic oxidation of VOCs, preferential CO oxidation, ammonia synthesis, HCl oxidation and CH₄ partial oxidation. The basic properties, oxidation behavior, and theoretical research are also summarized.

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钌基催化剂催化的气固相反应

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摘要: 催化剂被广泛应用于各种化学品的生产, 从原子尺度了解整个催化反应体系有利于合理设计新型催化剂. 参与气固相反应的催化剂主要有贵金属催化剂和过渡金属催化剂. 近年来, Ru 基催化剂由于在低温低压下表现出良好的催化活性而广泛应用于一些气固相反应. 本文对 Ru 的基本性质、氧化行为以及 Ru 基催化剂的理论研究进行综述. 介绍了钌基催化剂参与的气固相反应, 包括挥发性有机物的催化氧化、一氧化碳优先氧化(PROX)、氨合成、氯化氢氧化以及甲烷部分氧化, 分析了催化性能与理化性质之间的构效关系, 提出了钌基催化剂在相关反应中存在的问题以及未来发展趋势.

Ru 具有多种氧化态, 在 Ru 基催化剂参与的气固相反应中, 金属 Ru 和/或 RuO₂ 被认为是活性物种, 通常反应温度在 400 °C 以下. Ru (0001) 晶面在 O₂ 存在条件下, 随着氧气含量的不同会从中间态过渡到氧化态, 实验证明该晶面属于 RuO₂. 理论研究证实了在反应过程中 RuO₂ 的存在, 并提出了核壳结构, 对于其它气固相反应的机理研究有一定启发.

挥发性有机物(VOC)的催化氧化主要集中烷烃、烯烃、芳烃以及卤代烃的催化氧化, 催化剂的理化性质包括颗粒粒径、价态和晶体结构等对催化活性有很大影响, 并且 Ru 基催化剂对卤代烃的催化氧化表现出良好的抗卤性, 同时多卤代副产物低于其它贵金属体系. Ru 基催化剂在低温条件下对 PROX 具有高的活性和选择性, 并且可以有效抑制 H₂ 氧化、CO 甲烷化和 CO₂ 甲烷化等副反应发生. 氨合成的难点在于 N≡N 具有很强的解离能, 许多研究表明, 氨合成使用的 Ru 基催化剂的催化性能与载体性质密切相关, Ru 与载体之间强的相互作用使得电子可以迅速地从载体转移到 Ru 颗粒上, 掺杂其它有效元素可能会提供更多的氧空位和有效防止高温焙烧导致催化剂烧结. 对于 HCl 氧化虽然研究较少, 但是 Over 等人对 HCl 氧化机理进行了深入研究, 并且日本住友化工设计的 Ru 基催化剂已经商业化. Ru 基催化剂可以有效降低甲烷部分氧化的反应温度和压力, 并具有高的选择性和稳定性, 避免副产物生成.

现有催化系统以及新型催化剂开发仍面临诸多挑战, 例如: 对于单一 VOC 氧化过程和多元 VOCs 催化氧化的机理和动力学需要进一步研究; 对于氨合成需要寻求具有高电导率的载体, 从而将电子快速转移到 Ru 颗粒表面, 使得氨合成在更低温度下进行; 为了避免副产物生成, 需确保新型 Ru 基催化剂上 PROX 和甲烷部分氧化在低温低压条件下进行; Ru 基催化剂理化性质对活性的影响以及失活等问题需要进一步研究.

关键词: 气固相反应; 钌; 挥发性有机物; 催化氧化; 一氧化碳优先氧化; 氯化氢氧化

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