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Article

Ru/FeO_x catalyst performance design: Highly dispersed Ru species for selective carbon dioxide hydrogenation

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ABSTRACT

A series of Ru/FeO_x catalysts were synthesized for the selective hydrogenation of CO₂ to CO. Detailed characterizations of the catalysts through X-ray diffraction, X-ray photoelectron spectroscopy, transmission electron microscopy, and temperature-programmed techniques were performed to directly monitor the surface chemical properties and the catalytic performance to elucidate the reaction mechanism. Highly dispersed Ru species were observed on the surface of FeO_x regardless of the initial Ru loading. Varying the Ru loading resulted in changes to the Ru coverage over the FeO_x surface, which had a significant impact on the interaction between Ru and adsorbed H, and concomitantly, the H₂ activation capacity *via* the ability for H₂ dissociation. FeO_x having 0.01% of Ru loading exhibited 100% selectivity toward CO resulting from the very strong interaction between Ru and adsorbed H, which limits the desorption of the activated H species and hinders over-reduction of CO to CH₄. Further increasing the Ru loading of the catalysts to above 0.01% resulted in the adsorbed H to be easily dissociated, as a result of a weaker interaction with Ru, which allowed excessive CO reduction to produce CH₄. Understanding how to selectively design the catalyst by tuning the initial loading of the active phase has broader implications on the design of supported metal catalysts toward preparing liquid fuels from CO₂.

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1. Introduction

CO₂ emissions are a major environmental problem requiring immediate technological solutions [1,2]. One option, as a practical solution for substantial CO₂ conversion, is the catalytic hydrogenation of CO₂ as a preferential pathway for CO₂ illumination [3], where conversion of CO₂ to CO is an initial key step.

Fischer-Tropsch (FT) synthesis and oxo-synthesis reactions can convert CO₂ into a variety of valuable hydrocarbons [4,5]. However, the continuous conversion of CO₂ to yield a single final product (CO) still remains a great challenge. There is a wealth of scientific research currently focusing on CO₂ hydrogenation *via* thermal and electrochemical catalysis [6,7], by designing highly selective, active and stable catalysts. Numer-

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ous efforts have been devoted to further understand the CO₂ hydrogenation reaction; however, the elucidation of detailed reaction mechanisms is still under debate [8–12].

Supported metal catalysts, especially mixed-oxide metal catalysts, are a highly desirable research field in heterogeneous thermal catalysis owing to their outstanding selectivity to specific products [13–15]. The activation of CO₂ and H₂ is a prerequisite for CO₂ hydrogenation. Researchers have observed that H₂ usually dissociates on metal sites while CO₂ is activated on the oxide support [16]. Only catalysts with such dual “reactive activating” functionalities can effectively catalyze the hydrogenation of CO₂ to CO [17]. A great number of mechanisms have been proposed for the CO₂ hydrogenation reaction, which can be divided into two categories depending on whether or not the CO intermediate is produced: (1) CO₂ dissociates into CO with/without the presence of formate intermediates followed by a CO methanation reaction [18], and (2) CO₂ is directly hydrogenated to bicarbonates, formates, methoxides, and finally methane in the absence of CO intermediates [19]. However, the mechanism is greatly influenced by the nature of the catalyst.

Li *et al.* [15] recently studied the influence of Ir/CeO₂ particle size on the CO₂ hydrogenation reaction. They observed that smaller Ir particles induced a stronger metal-support interaction, which significantly impacted the adsorption and selectivity of CO. Qiao *et al.* [20] detected through Bader charge analysis that single Pt atoms on Pt/FeO_x catalysts carried considerable positive charges, which resulted in a weak CO adsorption, and concomitantly, improvements to anti-poisoning performance for the CO oxidation reaction. All of the above works are devoted to developing well-designed catalysts to explore the adsorption behavior of the CO reactant/intermediate, which can elucidate, to some degree, the reaction path and final selectivity. Previous studies have reported that Ru-based noble metal catalysts are typically more likely to promote the formation of CH₄ in the CO₂ reduction reaction [21,22]. Xu *et al.* [23] explored the influence of pretreatment temperature on Ru/TiO₂ catalysts in CO₂ methanation and suggested that the dissociation of adsorbed CO (CO_{ads}) proceeds *via* a process—assisted by adsorbed H (H_{ads}) species—that results in CO_{ads} to be further reduced to methane. At the same time, Wang *et al.* [24] observed the same CO₂ methanation mechanism in the presence of Ru/Al₂O₃ catalysts, and furthermore, found that the reaction between H_{ads} and CO_{ads}, rather than other steps, is the rate-determining step during the CO₂ methanation reaction. Regardless, controlling the production of CO from CO₂, in the absence of CH₄, is a prerequisite for FT reactions. The catalyst design rationale, by simply tuning the synthesis parameters, is essential when developing efficient catalysts. Although it is well known that catalytic properties are well influenced by metal loading, insights into how the loadings affect the active metal site properties, and importantly the reaction process, are lacking.

In this work, highly dispersed Ru composites were deposited onto FeO_x supports. Analysis of various characterization methods has elucidated the unique structure-property relationship of the Ru/FeO_x catalysts, which obtain 100% CO selectivity. The crystallinity, morphology, as well as the chemical

states and properties were studied by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and temperature-programmed experiments. The interaction between the Ru species and the support, the different H₂ activation and dissociation/desorption behaviors, and how these factors influence product selectivity were studied in detail as a function of Ru surface loading.

2. Experimental

2.1. Preparation of supported ruthenium catalysts

All chemicals used in this experiment were of analytical grade and used without further purification. RuCl₃·xH₂O was purchased from Aladdin. Other chemicals including NaOH and Fe(NO₃)₃·9H₂O were purchased from Chengdu Kelong Chemical Co., Ltd., China, and deionized water was used in all the experimental processes. All catalysts were prepared *via* co-precipitation methods [25]. A mixed solution of RuCl₃·xH₂O and Fe(NO₃)₃·9H₂O in desired proportions was added dropwise into 0.4 mol L⁻¹ NaOH at 80 °C with vigorous stirring. After the co-precipitation, the slurry was maintained at pH = 8.0 by NaOH. The slurry was stirred continuously at 80 °C for 3 h, and then aged at the same temperature for 1 h. The precipitate was washed with deionized water before drying at 60 °C for 15 h without any further heat treatment. The catalyst was denoted as *m*%Ru/FeO_x with *m*% as the Ru loading. At the same time, a reference support, denoted as FeO_x, was synthesized by the same method only in the absence of Ru.

2.2. Catalyst characterization

XRD diffractograms were recorded on a DX-2700 diffractometer with Cu K_α radiation (40 kV, 30 mA). The 2θ scanning range was 10°–90° with a scan step of 0.03° s⁻¹. Specific surface area, total pore volume and average pore diameter of the samples were measured from N₂ adsorption-desorption isotherms at -196 °C (Quantachrome Nova 1000e apparatus). The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) equation, and the pore size distribution and average pore diameter were determined from the desorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) model. The *m*%Ru/FeO_x samples were outgassed to 0.1 Pa at 110 °C to ensure structural integrity of the support. TEM was performed using an FEI Tecnai G2 microscope equipped with high angle annular dark field (HAADF) and energy-dispersive X-ray (EDX) analysis detectors at 200 keV. Temperature-programmed reduction with hydrogen (H₂-TPR) was performed using a Tian Jin TP-5080 catalyst characterization system. First, 50 mg of catalyst was loaded into a fixed-bed reactor and purged with N₂ at 120 °C for 2 h to remove absorbed carbonates and hydrates. After cooling to 30 °C, the purge gas was switched to a 10 vol% H₂/N₂ reduction gas composition at a flow rate of 30 mL min⁻¹. The temperature of the catalyst was raised from 30 to 900 °C at a rate of 10 °C min⁻¹. Hydrogen temperature-programmed desorption (H₂-TPD) was performed on a Tian Jin TP-5080 catalyst characterization system. 200 mg of catalyst was first pre-

treated at 200 °C under a hydrogen flow (20 mL min⁻¹) for 45 min at a heating rate of 10 °C min⁻¹. After cooling to 30 °C, the sample was purged with N₂ for 90 min to remove weakly adsorbed H₂. Thereafter, the sample was heated from 30 to 500 °C at a ramp rate of 10 °C min⁻¹ with the desorbed H₂ detected on-line. *In situ* temperature-programmed surface reaction (TPSR) experiments for the CO₂ hydrogenation reaction were analyzed on-line by a British Hidden QIC-20 mass spectrometer. Prior to performing the TPSR experiments, the catalyst was placed in a fixed-bed quartz reactor having an internal diameter of 6 mm. The reactor was heated within a tube furnace equipped with a temperature controller, and all gases were monitored by calibrated mass flow controllers. Prior to the experiment test, 200 mg of the catalyst was first pretreated under a 20 mL min⁻¹ hydrogen flow for 2 h at 200 °C at a heating rate of 5 °C min⁻¹. Upon cooling to 100 °C under flowing Ar, a mixture of H₂, CO₂ and Ar, having a molar composition of: 3 H₂ : 3 CO₂ : 40 Ar was introduced into the reactor having a total gas flow of 46 mL min⁻¹. The gas hourly space velocity (GHSV) was maintained at 1800 mL g⁻¹ h⁻¹ under atmospheric pressure. After the baseline was stable, the temperature of the reactor was raised to 500 °C at a uniform rate of 10 °C min⁻¹. The gas composition of the reverse water gas shift (RWGS) reaction was analyzed on-line by a QIC-20 mass spectrometer during the heating process.

2.3. Conventional catalytic activity test (micro fixed-bed reactor)

Conventional catalytic evaluation of the RWGS reaction was performed under atmospheric pressure on a micro fixed-bed tubular quartz reactor having an internal diameter of 6 mm. Typically, 300 mg of catalyst was loaded and reduced *in situ* with pure H₂ at 200 °C for 1 h at a gas flow of 30 mL min⁻¹. The catalyst was subjected to an operating temperature of 240 °C and purged with the reaction gas having a molar composition of: 1 H₂ : 1 CO₂ with a GHSV of 1200 mL g⁻¹ h⁻¹. The effluent gases from the reactor were analyzed on-line using a SP-7890 model gas chromatograph equipped with a TDX-01 column and a thermal conductivity detector (TCD), using Ar as the carrier gas. Activity was evaluated every 10 °C over the temperature range of 240–360 °C. Catalytic performance was evaluated by the conversion of CO₂ based on the concentration difference between the inlet and outlet, which is defined as:

$$X(\text{CO}_2) = (F(\text{CO}_{2,\text{in}}) - F(\text{CO}_{2,\text{out}})) / F(\text{CO}_{2,\text{in}}) \times 100\%$$

CO and CH₄ selectivity is defined as follows:

$$S(\text{CO}) = F(\text{CO}, \text{out}) / (F(\text{CO}_{2,\text{in}}) - F(\text{CO}_{2,\text{out}})) \times 100\%$$

$$S(\text{CH}_4) = (1 - S(\text{CO})) \times 100\%$$

where F is the flow rate of each component in the feed or effluent.

3. Results and discussion

3.1. Catalyst morphologies and textural properties

Phase identification of the catalysts was analyzed by XRD, as shown in Fig. 1. It can be observed that the Fe₂O₃ structure is

Fig. 1. X-ray diffraction patterns of the Ru/FeO_x catalysts.

the major phase for the 0.01%Ru/FeO_x and 2.50%Ru/FeO_x samples.

The freshly prepared Ru/FeO_x samples do not show any diffraction peaks corresponding to crystalline Ru phases in the 0.01% or 0.25%Ru/FeO_x samples, indicating the presence of highly dispersed Ru species or very low Ru content beyond the detection limit of the diffractometer. However, there is also no observable diffraction peaks related to Ru in the 2.50%Ru/FeO_x sample, which suggests finely dispersed Ru species in this sample. Conversely, XRD analysis of the FeO_x sample shows a phase transition into Fe₃O₄ by thermal treatment under a N₂ atmosphere at 100 °C, which is consistent with the research of Lin et al. [12], based on Ir/FeO_x catalysts.

The textural properties of the catalysts are summarized in Table 1. The pore structure parameters are generally maintained after Ru addition, although the surface area, surface pore volume and the average diameter slightly decrease as a function of incremental Ru loading. It is suggested that the integrity of the mesoporous structures across the different samples are maintained after Ru loading.

TEM and EDX elemental mapping of the 0.25%Ru/FeO_x and 2.50%Ru/FeO_x catalysts after reduction (at 200 °C by H₂) are illustrated in Fig. 2. Even at the higher loading of 2.50% Ru, TEM observations show no visible sign of Ru nanoparticles in the 2.50%Ru/FeO_x sample. This also suggests that Ru exists as highly dispersed species across all of the FeO_x supported samples, which is consistent with the XRD results. EDX elemental mappings of the Ru-supported samples also suggest highly dispersed Ru species supported on the surface of the iron oxide regardless of the Ru loading. However, STEM-EDX analysis

Table 1

Textural properties of the Ru-supported FeO_x catalysts.

Catalyst	D_p^c (nm)	A_{BET}^a (m ² g ⁻¹)	V_p^b (cm ³ g ⁻¹)
FeO _x	3.58	249.37	0.195
0.01%Ru/FeO _x	3.44	246.79	0.183
0.10%Ru/FeO _x	3.36	232.68	0.187
0.25%Ru/FeO _x	3.32	237.46	0.159
2.50%Ru/FeO _x	3.14	226.53	0.127

^a Brunauer-Emmett-Teller specific areas. ^b Total pore volume was obtained at a saturation pressure of $P/P_0 = 0.99$. ^c Average pore diameter calculated using the Barrett-Joyner-Halenda method.

Fig. 2. TEM images and EDX analysis elemental mapping of 2.50%Ru/FeO_x (a), 0.25%Ru/FeO_x (b), and 0.01%Ru/FeO_x (c). Samples were preliminarily treated at 200 °C in H₂.

shows no discernible Ru peaks for the 0.01%Ru/FeO_x sample as a result of the low Ru concentration.

3.2. Catalyst surface chemical properties

For CO₂ hydrogenation reactions that are catalyzed by oxide-supported metals, it is generally accepted that H₂ molecules

are dissociated on the metallic component (i.e. Ru), while CO₂ can be activated on the oxygen vacancies of the oxides (i.e. FeO_x) [26,27]. Herein, only catalysts possessing dual functionality are able to enhance the CO and CH₄ selectivity. As the dissociation of the CO₂ step proceeds with a higher activation barrier [28], and more oxygen vacancies become available, the more favorable the overall CO₂ hydrogenation reaction rate [29]. In this regard, the capacity of the catalyst to generate oxygen vacancies are further elucidated by H₂-temperature-programmed experiments.

As shown in Fig. 3(a), it can be observed that the pure FeO_x support displays one small peak at ~330 °C with a corresponding shoulder attributed to the reduction of various surface iron oxide species. The overlapped reduction peaks at higher temperatures (500–900 °C) are ascribed to the sequential reduction of Fe₂O₃ to metallic Fe *via* FeO in the bulk phase of the catalyst. Compared with the pure FeO_x support, the addition of Ru leads to a considerable and progressive reduction of the temperature at which chemical reduction occurs, as a function of increased Ru loading. The addition of Ru species results in the ascribed reduction peaks to shift to lower temperatures of 100–200 °C, except for 0.01%Ru/FeO_x. Additionally, the reduction peaks attributed to the surface iron oxide also shift to lower temperatures. Two overlapped reduction peaks (190 and 227 °C) with a corresponding shoulder are observed in 0.10%Ru/FeO_x. While the 0.25% and 2.50%Ru/FeO_x catalysts display two separate reduction peaks in the range of 100–300 °C. It is suggested that the first reduction peak in the range of 100–200 °C is related to the reduction of positively charged Ru species to Ru⁰, in addition to surface iron oxide in the vicinity of the Ru species, which can be easily reduced because of the Ru-FeO_x synergistic interaction. Such reduction peaks shift to lower temperatures with increased Ru loading. Conversely, the reduction peaks at higher temperatures also shift from 870 °C on bare FeO_x to 755 °C on the 2.50%Ru/FeO_x catalyst. Furthermore, the shifting of both the Ru and FeO_x reduction peaks to lower temperatures across all Ru/FeO_x samples suggest the existence of a synergistic interaction between Ru and iron oxide, which benefits the co-reduction of the different species in addition to enhancing the redox properties. The uncorrelated H₂ consumption ratio between 0.10% of RuO_x and 99.9% of

Fig. 3. H₂-TPR (a) and H₂-TPD (b) profiles of Ru/FeO_x catalysts as a function of Ru loading. Freshly dried samples were used for H₂-TPR directly, and samples for H₂-TPD were preliminary treated at 200 °C in H₂.

FeO_x is suggested to be attributed to the fact that the FeO_x support was unable to be fully reduced during the reduction process, since bulk FeO_x existed as the main phase. Similarly, only the reduction of the positively charged Ru species can yield the corresponding H_2 consumption peaks. The relatively high Ru loading amount does not equate to the observed higher levels of effective reducible components that are actually involved in the hydrogen consumption, that in turn would proportionally increase the numbers of active reaction sites. The low temperature peaks present in 2.50%Ru/ FeO_x and 0.25%Ru/ FeO_x are quite similar, signifying no significant increase in either the effective reactive sites or the reductive components in the 2.50%Ru/ FeO_x catalyst.

H_2 -TPD experiments of selected catalysts were also performed to elucidate the activation and adsorption behaviors of H_2 as shown in Fig. 3(b). The FeO_x support displays very broad H_2 desorption peaks having a maxima at 280 °C, reflecting the certain ability of the support to adsorb and activate H_2 . The addition of only 0.01% Ru species displays apparent H_2 desorption peaks at 112 and 408 °C, fully demonstrating the significant contribution of even only a small Ru loading to activate H_2 . Such phenomenon may relate to the H_2 spillover effect [30,31] on noble metals (such as Ru), where H_2 is activated on Ru and dissociated into atomic hydrogen having a stronger reductive ability, which can further diffuse through the metal-support interface to the FeO_x support. Since the reduction ability of atomic hydrogen is much stronger than that of molecular hydrogen, the reduction of iron oxide will be greatly facilitated at significantly lower temperatures in the presence of any hydrogen spillover [25,32]. With increasing Ru loading, the lower temperature desorption peak associated with the 2.50%Ru/ FeO_x catalyst does not shift significantly (106 °C). However, the peak area (at 106 °C) is significantly less than that of the 0.01%Ru/ FeO_x catalyst, despite the significantly increased Ru loading. It can be observed that both the 0.01%Ru/ FeO_x and 2.50% Ru/ FeO_x catalysts are highly efficient in H_2 activation at low temperature. It is also remarkable that the 0.01%Ru/ FeO_x sample has more hydrogen spillover

sites on the FeO_x surface than the 2.50%Ru/ FeO_x catalyst based on its easier desorption at 106 °C [33].

Conversely, the H_2 desorption peak associated with the FeO_x support shifts from 408 °C in 0.01%Ru/ FeO_x to a much lower temperature range of 298 °C in the 2.50%Ru/ FeO_x sample, which is thought to be attributed to the strong interaction between Ru and H_{ads} [34,35]. Such strong interactions will prevent the activated H_{ads} from facile removal. Hence, the reaction energy barrier is greatly enhanced [36] and the reaction between H_{ads} and CO_{ads} will be inhibited, which is further evidenced by both the TPSR data and the catalytic test data. Conversely, the 2.50%Ru/ FeO_x catalyst with moderate hydrogen desorption behavior is relatively more conducive in promoting further hydrogenation of CO_{ads} to CH_4 .

The H_2 -TPD results clearly demonstrate that the addition of Ru to the catalysts significantly promotes H_2 activation spillover. The 0.01%Ru/ FeO_x catalyst having an extremely low Ru loading moderately activates H_2 . However, the distinctive Ru-support interactions arise as a function of Ru loading, which results in the observed variation to effectively activate H_{ads} , and its subsequent reaction with CO_{ads} , thus promoting alternative reaction paths that yield different products (CO or CH_4).

The XPS spectra in the Ru $3d_{5/2}$ region and Fe $2p_{1/2}$ region of the catalysts are presented in Fig. 4 [37]. The XPS data clearly shows differences between the spectra as a function of Ru loading. There is no observable peak related to any Ru-based species when the Ru loading is only 0.01%. Further increasing the Ru loading to 0.25%, a weak signal attributed to Ru $3d_{5/2}$, begins to appear, whereas, a clearly observable peak is present when increasing the Ru loading to 2.50%.

Two overlapping peaks with an associated satellite peak can be observed in the XPS spectra of the Fe $2p_{1/2}$ region [38]. The $\text{Fe}2p_{1/2}$ region can be fitted by several deconvoluted peaks. The symmetry peaks at 710.2 and 713.0 eV are related to Fe^{2+} and Fe^{3+} , respectively [39]. The Fe^{2+} and Fe^{3+} species exist as the major compositions across all the Ru/ FeO_x samples. The surface atomic ratio between Fe^{2+} and Fe^{3+} is ~ 1.4 for all samples, and the same degree of variation is largely dependent on the

Fig. 4. Ru $3d_{5/2}$ (a) and Fe $2p_{1/2}$ (b) region XPS spectra of different Ru/ FeO_x catalysts.

specific Ru loading in each sample. The surface atomic ratios are: 1.39, 1.45, 1.51, and 1.54 with increased Ru loading, respectively. It can be observed that degree of Ru loading leads to a slight variation of the iron oxide surface state. As previously reported, the electron transfer originates from the precious metal to the oxide support [15,20], and the variation of the surface iron species may result from the electron transfer from Ru to FeO_x .

3.3. Catalytic performance

A one-step TPRS experiment of CO_2 hydrogenation (Fig. 5) was designed to elucidate the reaction mechanism in detail. A $\text{CO}_2/\text{H}_2/\text{Ar}$ (46 mL min^{-1} , 3/3/40 v/v/v) flow was introduced into the reactor at 100 °C prior to heating to 500 °C at a rate of 10 °C min^{-1} before maintaining for 30 min. There are no significant CO_2 consumption peaks evident across all samples (Fig. 5(a)). The consumption peaks attributed to the H_2 reactant are given at ~360 and 110 °C for FeO_x and the 2.50%Ru/ FeO_x catalyst, respectively, which show a gradual shift to lower temperatures with increased Ru loading (Fig. 5(b)). It is worth noting that the generation of the CO signal across all samples lags behind the H_2 consumption peak. The H_2 -TPR and H_2 -TPD results infer that H_2 is activated on the Ru species and dissociated into atomic H, which effectively promotes the reduction of the FeO_x support, resulting in rich oxygen vacancies. Thereafter, CO_2 is activated on the oxygen vacancy of the FeO_x support to form the CO_{ads} species [40]. Varying the Ru loading modifies the surface coverage of Ru on the support, leading to differ-

ences in the adsorption strength between H_{ads} and the Ru species. This directly impacts H_{ads} adsorption, and thus the reaction with CO_{ads} , causing the production of CO or CH_4 via excessive reduction. As a result, a clear CH_4 peak at ~350 °C (Fig. 5(c)) over the 2.50%Ru/ FeO_x sample is observed, which is absent in the samples with lower Ru content.

Prior to catalyst testing, the samples were reduced with pure H_2 at 200 °C for 2 h. The catalytic activities of the Ru/ FeO_x catalysts for CO_2 reduction are shown in Fig. 6(a). All catalysts show increased CO_2 conversion as a function of increased reaction temperature (260–360 °C). The pure FeO_x support also displays initial catalytic activity. The CO_2 conversion of 0.10%Ru/ FeO_x is 14.5% at 360 °C, which is similar to that of the 0.25% and 2.50%Ru/ FeO_x catalysts (12.9% and 15.6%). However, when comparing the normalized specific rate of 0.01%Ru/ FeO_x (7.71 $\text{mol}_{\text{CO}_2} \text{mol}_{\text{Ru}}^{-1} \text{min}^{-1}$) with the other catalysts (Table 2), the specific rate is ~154 times that of 2.50%Ru/ FeO_x (0.05 $\text{mol}_{\text{CO}_2} \text{mol}_{\text{Ru}}^{-1} \text{min}^{-1}$).

Conversely, the 2.50%Ru/ FeO_x catalyst displays significantly higher selectivity toward CH_4 (82%). For the 0.10%Ru/ FeO_x and 0.25%Ru/ FeO_x samples, the capacity to selectively produce CO is enhanced, while the selectivity toward CH_4 is reduced to 20%. It is demonstrated that the hydrogenation ability of the catalysts is influenced by reducing the Ru loading, which results in the facile formation of CO—the primary hydrogenation product. Further reducing the Ru loading to 0.01% results in 100% selectivity toward CO. The results indicate that CO_2 hydrogenation selectivity can be tuned by varying the Ru loading. There is no obvious variation or decrease in CO selectivity over

Fig. 5. TPRS studies of *in situ* CO_2 activation and conversion over Ru/ FeO_x catalysts as a function of Ru loading. Mass signals of CO_2 ($m/z = 44$) (a), H_2 ($m/z = 2$) (b), CH_4 ($m/z = 16$) (c), and CO ($m/z = 28$) (d) were detected.

Fig. 6. CO₂ conversion (a), CO selectivity (b) and CH₄ selectivity (c) on Ru-supported catalysts as a function of operating temperature and schematic illustrations (d1), (d2) of the representative catalysts. Reaction conditions: CO₂:H₂ = 1:1, GHSV = 1800 mL h⁻¹ g⁻¹_{cat}, *P* = 0.1 MPa.

the 0.01%Ru/FeO_x catalyst as a function of reaction temperature. The other catalysts display a gradual increase in CO selectivity up to 320 °C before finally plateauing. The CO selectivity of the 2.50%Ru/FeO_x sample increases from 21.4% at 260 °C to 41.0% at 360 °C, while the CO selectivity of the other samples is >92% (Fig. 6 and Table 2).

Summarizing the results shows that the main factors influencing CO₂ conversion and CO production result from the Ru loading, which is related to the Ru coverage over the FeO_x surface, as shown in Fig. 6(d1) and (d2). The catalyst samples display varying degrees of electron transfer from active Ru species

to the FeO_x support and the chemical properties, including the Ru-FeO_x synergistic interaction, the Ru-H_{ads} interaction and the redox properties, depend specifically on the Ru surface coverage. For 2.50%Ru/FeO_x with a higher Ru loading, the interaction between Ru and H_{ads} is proved to be weak, which results in facile hydrogen desorption and excessive reduction by further reacting with CO or CO₂ to yield CH₄ as the major product. While 0.01%Ru/FeO_x with a lower Ru content displays a stronger Ru-H_{ads} interaction and hinders H_{ads} from being easily desorbed. Here, CO selectivity is 100% and the only product formed as the formation of CH₄ is inhibited.

Table 2
CO₂ hydrogenation performance of the Ru/FeO_x catalysts ^a.

Catalyst	<i>X</i> (CO ₂) (%)		<i>S</i> (CO) (%)		Specific rate ^b (10 ⁻⁶ mol _{CO2} g _{catalyst} ⁻¹ min ⁻¹)	Comparative specific rate ^c (mol _{CO2} mol _{Ru} ⁻¹ min ⁻¹)
	260 °C	360 °C	260 °C	360 °C		
FeO _x	3.1	12.9	83.6	92.2	1.03	—
0.01%Ru/FeO _x	2.3	14.5	100.0	100.0	1.15	7.71
0.10%Ru/FeO _x	12.8	18.2	79.7	93.6	1.45	2.56
2.50%Ru/FeO _x	6.7	15.6	21.4	41.0	1.24	0.05

^a Reaction conditions: catalyst (300 mg), H₂/CO₂ = 3 mL min⁻¹/3 mL min⁻¹, 0.1 MPa.

^b Based on per gram of catalyst at 360 °C.

^c Based on pure Ru species by subtracting out the specific rate of the pure support at 360 °C.

4. Conclusions

Finely dispersed Ru species were synthesized on FeO_x supports as a function of Ru loading and evaluated for the selective hydrogenation of CO_2 . The results suggested that both CO_2 conversion and CO selectively were largely promoted by small Ru loading amounts compared with the pure FeO_x support. While the CO selectivity can be further controlled by adjusting the Ru loading. Regardless of the ability for the catalysts to facilitate H_2 activation, it is the variation in Ru loading that results in differences in the Ru- H_{ads} interactions, which in turn accounted for the distinctive H_{ads} desorption behavior. Although CO_2 conversion displays a volcanic trend as a function of Ru loading, with a maxima at 0.1% Ru loading, the 0.01%Ru/ FeO_x catalyst displayed 100% selectivity toward CO because of the hard desorption of H_{ads} with excessive reduction of CO_2 to CH_4 being hindered. The normalized specific rate of 0.01%Ru/ FeO_x ($7.71 \text{ mol}_{\text{CO}_2} \text{ mol}_{\text{Ru}}^{-1} \text{ min}^{-1}$) is ~ 154 times that of the 2.50%Ru/ FeO_x catalyst.

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Graphical Abstract

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Ru/ FeO_x catalyst performance design: Highly dispersed Ru species for selective carbon dioxide hydrogenation

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Ru/ FeO_x catalysts were prepared for the selective hydrogenation of CO_2 to CO. The 0.01% Ru-loaded FeO_x catalyst exhibited 100% selectivity toward CO. Lower Ru surface coverage resulted in strong Ru- H_{ads} interactions to directly form CO.

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高分散Ru/FeO_x催化剂在二氧化碳选择加氢反应中的应用及其催化活性的调控

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摘要: 由于化石能源的大量开采和利用造成CO₂过度排放, 从而导致严重的温室效应和气候环境问题, 给人类生存带来极大威胁. CO₂选择加氢反应可以将CO₂催化加氢生成高附加值的CO产物. 与其他的CO₂转化反应策略相比, 该过程中H₂的消耗更少, 成为可有效处理及转化CO₂的手段之一. 同时, 应尽可能抑制CO₂深度加氢以及甲烷的产生, 研制及设计具有高CO选择性的新型高效催化剂及其构效关系的分析仍十分重要.

据报道, 负载型贵金属基催化剂的使用有利于H₂分子的活化, 具有优异的催化活性, 因而广泛应用于多种催化反应中. 然而, 贵金属催化剂实现工业应用的最大挑战是资源的限制及其高额的成本. 近年来, 由贵金属制备的负载型亚纳米团簇受到广泛关注, 主要包括如Au, Pt, Pd, Ru等贵金属, 可有效应用于多相催化反应. 人们还致力于提高负载型亚纳米团簇的分散度, 促进催化剂活性位点的有效暴露, 有利于大幅度提高催化剂的有效利用率.

本文采用共沉淀法成功制备了超高分散的负载型Ru基催化剂, 通过CO₂选择加氢-程序升温表面反应(TPSR)和质谱联用技术测试了催化剂性能, 发现CO₂加氢反应生成CO选择性达100%. 采用XRD, BET和TEM等方法对催化剂结构进行表征, 并结合H₂-TPR, H₂-TPD和XPS等表征结果深入探讨了催化剂构效关系, 并提出了针对该催化剂体系较为合理的反应模型.

在CO₂选择加氢反应的催化性能测试中, 2.50%Ru/FeO_x催化剂对目标产物CO选择性仅为41%; 随着Ru负载量降低至0.25%和0.1%时, CO选择性明显提高至80%; 当进一步降低Ru含量至0.01%时, CO选择性接近100%, 且表现出优异的反应速率. 在360 °C时, 0.01%Ru/FeO_x催化剂的相对反应速率为7.71 mol_{CO2} mol_{Ru}⁻¹ min⁻¹, 是2.50%Ru/FeO_x催化剂相对反应速率的154倍. H₂-TPR结果表明, 贵金属Ru可以明显促进载体FeO_x的还原, 并产生丰富的氧空位, 进而促进CO₂的吸附、活化. 而且CO₂选择加氢TPSR结果显示, 目标产物CO的起始生成温度总是滞后于原料H₂的初始活化温度, 与H₂-TPR结果及文献报道的CO₂选择加氢反应机理一致. 通过H₂-TPD深入理解H₂在催化剂表面的活化和氢溢流现象, 以及H_{ads}与不同催化剂之间的相互作用力, 0.01%Ru/FeO_x催化剂相对较高的H₂脱附峰温度表明, 该样品中Ru与H_{ads}具有极强的相互作用力, 相对抑制了H_{ads}与CO_{ads}深入加氢生成CH₄, 从而提高了CO选择性, 而2.50%Ru/FeO_x催化剂的情况则与此相反.

本文提出了从 H_{ads} 吸附作用力强弱来考虑 CO_2 选择加氢反应选择性的新思路, 同时为设计 CO_2 选择加氢制高附加值CO的高催化反应速率、高CO选择性的高分散Ru基催化剂提供了一种经济简易的催化剂设计思路.

关键词: 高分散Ru基催化剂; 程序升温表面反应; 二氧化碳选择加氢; 选择性调控; 氢原子表面吸附

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