The effect of support on RhFe/Al₂O₃ for ethanol synthesis via CO hydrogenation

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Received: 27 January 2021 / Accepted: 12 July 2021 / Published online: 21 July 2021
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Abstract

Different alumina samples prepared with sol–gel, chemical precipitation and hydrothermal synthesis were used as supports of Fe-promoted Rh-based catalysts for ethanol synthesis via CO hydrogenation. The samples were characterized by means of N₂-adsorption, XRD, H₂-TPR, XPS, STEM, H₂-TPD, DRIFTS, H₂ and CO chemisorption. The results indicated that the Al₂O₃ prepared by hydrothermal synthesis exhibited nano-fiber morphology and constituted of mixed crystal phases, while Al₂O₃ prepared by sol–gel and chemical precipitation shows no changes of morphology and crystal phases compared with the commercial Al₂O₃. In addition, nano-fiber Al₂O₃-supported Rh-based catalyst shows higher ethanol selectivity, which is ascribed to the lower metal–support interaction, higher dispersion and stronger CO insertion ability.

Keywords Ethanol synthesis · Al₂O₃ · Interaction · DRIFTS

Introduction

Ethanol synthesis via syngas directly has attracted a great deal of attentions in recent years [1–3]. However, there is still a challenge for improving the selectivity of catalysts. Fe-promoted Rh-based catalysts have been reported to work well for ethanol synthesis [4–7]. For instance, Fukushima et al. [8] found the addition of Fe to Rh/SiO₂ can enhance the formation of intermediate species for ethanol synthesis by high-pressure FT-IR study. A good choice of support would be helpful to explore the potentiality of Fe-promoted Rh-based catalysts. Al₂O₃ had been investigated as the support of Rh-based catalysts since it is extensively used as commercial carrier [9]. Burch et al. [10] found that the Al₂O₃-supported Rh-based catalysts exhibited excellent ethanol selectivity. However, Chen et al. [9] proposed that the Al₂O₃ support was not the best choice for Rh-based catalysts since it had strong interaction with the metals. The above

two opposite findings suggest that the interaction between metal and Al₂O₃ should be adjusted carefully to meet the requirement of ethanol synthesis from syngas.

The interaction between Al₂O₃ support and metal depends on the nature of the Al₂O₃, such as the texture, crystal and chemical properties. In the reaction of CH₄ reforming, the good performance was presented on the nano-fiber Al₂O₃-supported Pt catalysts, Garcí'a-Die'guez et al. [11] ascribed it to the mixed crystal of the Al₂O₃ support prepared by hydrothermal synthesis. Zhang et al. [12] concluded that different crystal structures of Al₂O₃ could decrease the metal–support interaction due to its modified hydroxyl group. For supported Rh-based catalyst, it is reported that the weakly H-bonded surface hydroxyls of SiO₂ have an important effect on the interaction between Rh and promoter [13]. Therefore, a comprehensive understanding of the interaction between support and active metals is very important for design of the supports for Rh-based catalysts. Moreover, this understanding would be strengthened if we know the effect of support at some curial steps, such as CO adsorption, dissociation and hydrogenation, during ethanol formation.

In this study, three Al₂O₃ supports were prepared by sol–gel, chemical precipitation and hydrothermal synthesis. The commercial γ -Al₂O₃ was also used as reference. The typical physical–chemical properties of samples were characterized by different techniques, such as X-ray

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diffraction (XRD), nitrogen physisorption, H_2 temperature-programmed reduction (H_2 -TPR), H_2 and CO chemisorption, H_2 temperature-programmed desorption (H_2 -TPD), X-ray photoelectron spectroscopy (XPS) and high resolution scanning transmission electron microscopy (STEM). Furthermore, diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) was used to determine CO adsorption, hydrogenation behavior, and surface hydroxyl group of samples.

Experimental

Support and catalyst preparation

Alumina samples were prepared by chemical precipitation, sol–gel and hydrothermal synthesis methods, denoted as Al-CP, Al-SG and Al-HS, respectively. Commercial γ - Al_2O_3 was abbreviated as Al-CM. Al-CP was prepared in the following procedure: 45.0 g of $Al(NO_3)_3 \cdot 9H_2O$ was dissolved in 250 mL of de-ionized water with strong agitation to form transparent solution. Simultaneously, the above solution and aqueous ammonia (2.5 wt %) solution were added dropwise into a beaker at constant pH with magnetic stirring. After that, the suspension was aged for 12 h at room temperature, and then filtered, washed with de-ionized water many times until no change of pH. At last, the obtained precipitate was dried at 110 °C for 12 h, and then calcined at 500 °C for 4 h. For the preparation of Al-SG, alumina sol was first prepared. Aluminum isopropoxide was added slowly to the water and kept at 90 °C for 2 h. Then, nitric acid was added to the solution very slowly and kept stirring at 95 °C for 6 h. The obtained alumina sol was heated in a water bath at 80 °C for 2 h and cooled to room temperature. The resulting solid was dried in a vacuum oven at 80 °C for 24 h and then calcined in a muffle furnace at 500 °C for 4 h. Al-HS was prepared by the following procedure. Typically, 45 g of $Al(NO_3)_3 \cdot 9H_2O$ was dissolved in 250 mL of deionized water and then was mixed with 20 wt% TEAOH solution (tetraethyl ammonium hydroxide) under rigorous stirring till pH reached 5.0. The mixture was continuously stirred for 30 min before transferring into an autoclave equipped with a Teflon-liner. The hydrothermal treatment was conducted at 170 °C for 72 h. The as-prepared sample was calcined at 500 °C for 5 h with a heating rate of 5 °C/min.

Fe-promoted Rh-based catalysts supported on the different Al_2O_3 samples were prepared by incipient wetness method. Before impregnation, Al_2O_3 samples were ground and sieved to 40–60 mesh. Aqueous solution of $Rh(NO_3)_3 \cdot 2H_2O$ (9.35 wt % Rh, Helishi) and $Fe(NO_3)_2 \cdot 6H_2O$ were added dropwise to the given weight of support. The samples were kept stirring for 2 h and then dried at 110 °C for 12 h. Finally, the samples were

calcined at 500 °C for 4 h. The nominal loading of Rh is 2 wt% and Fe 4 wt% for all the catalysts. The catalysts supported on Al-CM, Al-SG, Al-CP and Al-HS were named as RhFe/Al-CM, RhFe/Al-SG, RhFe/Al-CP and RhFe/Al-HS, respectively.

Characterization

The N_2 adsorption–desorption isotherms for alumina samples and the corresponding catalysts were measured in a Micromeritics ASAP 2000 equipment. XRD patterns were recorded on a diffractometer operating with Cu K α radiation at 40 kV. The power diffractograms of the samples were collected from 10 to 80° at a rate of 6°/min. H_2 /CO chemisorption and TPR/TPD experiments were carried out on a Micromeritics Autochem 2920 apparatus. The H_2 -TPR profile was recorded with a TCD detector according to H_2 consumption during sample was reduced from room temperature to 800 °C ramped at a rate of 10 °C/min under a 10% H_2 /Ar (v/v) flow. For H_2 -TPD experiments, typically, 200 mg of sample was placed in a U-shaped quartz tube and pre-reduced in 50 mL/min of 10% H_2 /Ar (v/v) flow at 350 °C for 2 h, and then switched to He flow for 30 min. After that, H_2 was introduced into catalyst bed until saturation, and purged again by He for 30 min. Finally, the sample was heated up to 800 °C under He atmosphere at a rate of 10 °C/min, while the desorbed products were detected with a TCD detector. XPS experiments were performed using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. STEM measurements were performed on a Tecnai G2 F30 S-TWIN electron microscope with 300 kV accelerating voltage via high-angle annular dark-field (HAADF). Point energy-dispersive X-ray spectroscopy (EDS) was taken in an area within 5 nm diameter. DRIFTS was carried out with a Nicolet 6700 spectrometer equipped with infrared cell (PIKE). The DRIFTS experiments contain CO adsorption, CO temperature-programmed surface reduction (CO-TPSR) and determination of surface hydroxyl group. For CO adsorption, first, the sample was reduced under pure H_2 flow at 350 °C for 2 h. After flushed by N_2 for 30 min, the sample was degassed under vacuum until that 10^{-4} mbar was achieved, and then background spectra were collected at designated temperature. Second, a flow of 5% CO/He (v/v) was introduced to reduced catalysts for 30 min. Finally, the IR spectra were recorded after flushed by N_2 for 30 min. For CO-TPSR, the IR spectra were recorded under 10% H_2 /Ar (v/v) flow with the temperature linearly increased from 30 to 260 °C after CO adsorption. For the determination of surface hydroxyl group, the sample was flushed by N_2 at 300 °C and then degassed under 10^{-4} mbar vacuum for 2 h. The

IR spectra were collected at room temperature in the range of 3200–4000 cm^{-1} .

Catalytic reaction

Reaction was carried out in a stainless fixed bed reactor with an inner diameter of 10 mm. 1.0 g catalyst (1.3 mL) was diluted with quartz sand (4.2 mL) and then placed in the middle of the reactor. The catalyst was heated to 350 °C and reduced in H_2 at a flow rate of 60 mL/min for 10 h, then cooled down to the reaction temperature (260 °C) in H_2 flow. Subsequently, 60 mL/min syngas ($\text{H}_2/\text{CO}=2$) was introduced to reactor and kept at a pressure of 2 MPa. The flow rates of gas were controlled by a Brooks 5050 mass flowmeter. The effluent gas from the reactor was passed through a hot trap and a cold trap successively to separate gaseous and liquid products. A 24 h liquid sample was collected after steady state was achieved. Outlet gases and liquid sample were detected with two chromatographs (Agilent GC7890A), one is equipped with two TCD to analyze CO , CO_2 , N_2 and H_2 using a 5-A molecular sieve column online and the other fitted with one FID and TCD to separate C_1 – C_6 hydrocarbons, oxygenates and water using Plot Q column offline.

Results and discussion

Characterization of support

Figure 1 shows the N_2 adsorption isotherms of the four Al_2O_3 samples. The type IV of isotherms and the existence

Fig. 1 Nitrogen adsorption isotherms and pore distribution for different alumina samples. **a** Nitrogen adsorption isotherms; **b** pore distribution

of hysteresis loop indicate all the samples are mesopore structure. The type of hysteresis loop for Al-CM, Al-CP, Al-SG, Al-HS is attributed to H4, H4, H2 and H3, respectively. It is well known that the type of hysteresis loop is related with the special pore structure [14]. For instance, the presence of H3 hysteresis loop for Al-HS sample indicates the slit pore formed by the fibrous or sheet particle. Table 1 showed the textural properties of the different samples. Obviously, the surface areas of the samples are as follows: Al-CP (398) > Al-SG (336) > Al-CM (256) > Al-HS (90). Among the four alumina samples, Al-HS presents the lowest specific surface area. The enlarging pore effect, as a result of hydrothermal treatment, may be responsible for its low specific surface area.

Figure 2a presents the XRD profiles of the four Al_2O_3 samples. Typical characteristic peaks of $\gamma\text{-Al}_2\text{O}_3$ were observed for all the samples. However, besides $\gamma\text{-Al}_2\text{O}_3$, characteristic peaks of $\alpha\text{-Al}_2\text{O}_3$, Al_2O_3 for Al-HS were observed in Fig. 2b. The results indicate that Al-HS is constituted of mixed crystal phases, while Al-CM, Al-CP and Al-SG are mainly consistent with the $\gamma\text{-Al}_2\text{O}_3$ crystal phase. In general, alumina with different forms presents different specific surface areas with the order of $\alpha\text{-Al}_2\text{O}_3 < \gamma\text{-Al}_2\text{O}_3$ [15], which can be responsible for the lowest specific area of Al-HS material.

Characterization of catalysts

The H_2 -TPR profiles of the four catalysts were presented in Fig. 3. It can be observed two peaks of H_2 consumptions in Fig. 3, namely, one low temperature reduction peak (peak I) located at 50–300 °C and one high temperature board peak (peak II) in the range of 350–550 °C. According to the literature [18], the peak II was ascribed to the reduction of Fe_2O_3 to Fe_3O_4 and Fe_3O_4 to Fe species.

The theoretical and calculated H_2 consumptions of Fe-promoted Rh-based catalysts are listed in Table 2. Therefore, the peak I should be ascribed to the co-reduction of Rh_2O_3 and Fe_2O_3 species. The area of peak I is in order of $\text{RhFe}/\text{Al-HS} > \text{RhFe}/\text{Al-CM} > \text{RhFe}/\text{Al-SG} > \text{RhFe}/\text{Al-CP}$. Distinctly, the $\text{RhFe}/\text{Al-HS}$ catalyst exhibits the highest reduction degree and $\text{RhFe}/\text{Al-CM}$ less. In addition, for $\text{RhFe}/$

Table 1 Textural properties of different type of Al_2O_3

Samples	BET surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Pore diameter (nm)
Al-CM	256	0.46	9.0
Al-CP	398	0.48	4.9
Al-SG	336	0.43	5.0
Al-HS	90	0.33	14.6

Fig. 2 XRD profiles of different alumina samples

Fig. 3 H₂-TPR profiles of Fe-promoted Rh-based catalysts

Al-HS and RhFe/Al-CM catalysts, the reduction temperature of peak I shifts to lower temperature, in comparison with the corresponding un-promoted ones. It can be concluded that

the interaction between metal and support got weaker and the contact between Rh and Fe was enhanced for the above two catalysts. Considering with the activity data, the catalysts owning stronger Rh–Fe interaction correspond to the higher ethanol selectivity, which indicates that the weaker interaction between Rh and Al may be conducive to the formation of ethanol.

The H₂-TPD profiles of catalysts are presented in Fig. 4. As can be seen, two peaks were presented on all the samples. The peaks at lower temperature (50–200 °C) and higher temperature (300–500 °C) are denoted as H_α and H_β, respectively. H_α is ascribed to the weak adsorption of hydrogen and H_β the strong adsorption of it. It is accepted that H_β is responsible for the hydrogenation ability of Rh-based catalysts [16]. Obviously, RhFe/Al-HS exhibits higher peak area and higher temperature of H_β compared with the other catalysts. This indicates that the RhFe/Al-HS has stronger ability to activate hydrogen, which is helpful for promoting the catalytic activity.

Since metal particles cannot be easily distinguished from alumina, dark-field imaging technique (HAADF) was used to observe surface metal particle morphology of catalysts

Table 2 H₂ consumption of catalysts

Catalysts	Reduction peak (°C)	Calculated ^a and theoretical ^b H ₂ consumption (mmol)	Catalysts	Reduction peak (°C)	Calculated ^a and theoretical ^b H ₂ consumption (mmol)
RhFe/Al-CM	111	40 ^a (249 ^b)	Rh/Al-CM	120	36 ^a (58 ^b)
RhFe/Al-CP	167	37 ^a (249 ^b)	Rh/Al-CP	131	22 ^a (58 ^b)
RhFe/Al-SG	210	35 ^a (249 ^b)	Rh/Al-SG	160	30 ^a (58 ^b)
RhFe/Al-HS	114	53 ^a (249 ^b)	Rh/Al-HS	132	48 ^a (58 ^b)

^aH₂ consumption was calculated with 50 mg CuO as external reference

^bSample weight, 200 mg

Fig. 4 H_2 -TPD profiles of Rh-based catalysts supported on different type of Al_2O_3

after reduction. Figure 5 shows STEM images of catalysts. From STEM images (Fig. 5A, D) of the RhFe/Al-CM and RhFe/Al-HS, it can be observed that the metal particle sizes of them are both in the range of 1–4 nm with the average diameter of 2.7 and 3.8 nm, respectively. However, it can be seen from the images of RhFe/Al-SG (Fig. 5C) and RhFe/Al-CP (Fig. 5B) that the metal particle size is approximately about or less than 1 nm. The favorable metal particle size for ethanol formation was reported to be 2–4 nm [17]. In our case, the metal particles less than 2 nm may form stronger interaction with alumina support leading to decreased reducible species according to the TPR results. Figure 6 shows the corresponding EDS spectra of catalysts, in which one point within the metal particle region (P1) and the other metal particle-free region (P2) was selected at random. There exists Rh and Fe signal in the EDS spectra of P1 for all the samples, indicating Rh and Fe are in close contact. However, only Fe signal was observed in the EDS spectra of P2 for RhFe/Al-CP, RhFe/Al-SG and RhFe/Al-CM samples, which means some single Fe species distribute on the surface of these catalysts. Exceptionally, on RhFe/Al-HS catalyst, there is a weak signal of Rh and Fe within metal particle-free region on the EDS spectrum, indicating that more Fe and Rh species are in intimate contact on the surface of support.

To get the information of Rh dispersion of catalysts more accurately, CO and H_2 chemisorption experiments in a pulse mode were both carried out. Tables 3 and 4 show the results of the chemisorption of CO and H_2 , respectively. The results summarized in Tables 3 and 4 show that Rh dispersion calculated by the H_2 chemisorption is higher than the CO chemisorption. Despite this, the same trend about Rh dispersion can be gotten. Namely, RhFe/Al-HS

has a higher Rh dispersion while RhFe/Al-CP and RhFe/Al-SG shows a lower dispersion compared with RhFe/Al-CM. However, RhFe/Al-CP and RhFe/Al-SG should have higher Rh dispersion according to STEM results. The possible reason for the inconsistent results given by chemisorption and STEM may be due to that the smaller Rh particles enhanced the interaction with alumina support, resulting in a part of Rh particles incorporation into the alumina skeleton.

XPS spectra of fresh catalysts were shown in Fig. 7. The XPS intensity ratios and binding energies (BEs) of Rh 3d and Fe 2p was presented in Table 5. The surface atom concentrations of Rh/Al are in the order of RhFe/Al-HS > RhFe/Al-CM > RhFe/Al-CP > RhFe/Al-SG. The ratio of Rh/Fe for RhFe/Al-HS is 0.28, which is even higher than the expected value (0.27). The above indicated that more rhodium species enrichment on the surface of RhFe/Al-HS. In addition, the binding energy of Rh 3d_{5/2} and Fe 2p_{3/2} of RhFe/Al-HS exhibits obvious shift compared to the other catalysts. This further proved stronger interaction exists between Rh and Fe for this catalyst.

The interaction between highly dispersed active metal and support for different Al_2O_3 -supported catalysts varies greatly from the above analysis. Surface hydroxyls of catalysts may be one possible reason for this interaction. Figure 8 presents the surface hydroxyl group of catalyst and supports. The hydroxyl groups on the surface of alumina were classified into I, II, and III, in which type I > type II > type III in order of frequencies of them [15]. As shown in Fig. 8, the bands at 3723 (I), 3687 (II), 3572 cm^{-1} (II or III) are ascribed to the absorption of isolated —OH groups, weakly H-bonded and strongly H-bonded OH groups, respectively [18]. It can be seen from Fig. 8a that the intensity of hydroxyl groups for alumina samples is in order of Al-SG > Al-CP > Al-CM > Al-HS. The corresponding catalysts also show the same order as can be seen in Fig. 8b. Some researchers believed CO_2 comes from the reaction of strongly adsorbed CO species with hydroxyl groups of Al_2O_3 support [20]. This is in accordance with our experiments results that RhFe/Al-SG shows the highest CO_2 selectivity with the most amount of surface hydroxyl group. However it may be, there is no doubt that the metal–support interaction increases with the increasing amount of hydroxyl group. Moreover, it can be observed from Fig. 8b that the ratio of different type of hydroxyl groups for RhFe/Al-CP and RhFe/Al-SG catalyst is similar with that of RhFe/Al-CM. However, the proportion of type I (isolated hydroxyl) increases for RhFe/Al-HS.

The infrared spectra of the catalysts after CO adsorption at 30 °C are shown in Fig. 9. The 2055 cm^{-1} band can be ascribed to linear adsorbed CO (CO (I)) and double band at 2084 and 2017 cm^{-1} can be assigned to the symmetric and asymmetric carbonyl stretching of the dicarbonyl

Fig. 5 STEM images of Rh-based catalysts supported on different type of Al_2O_3 . **A** RhFe/Al-CM; **B** RhFe/Al-CP; **C** RhFe/Al-SG; **D** RhFe/Al-HS

$\text{Rh}^+(\text{CO})_2$ (CO(gem)) [19]. The broad band centered at 1860 cm^{-1} is assigned to bridge bonded CO (CO (b)), whose intensity was found to be related with the selectivity of CH_4 [10]. It is widely accepted that CO (gem) is formed on Rh^+ , which is favorable for CO insertion, while CO (l) and CO(b) formed on Rh^0 , which is helpful for CO dissociation [20]. It can be seen from Fig. 9 that the intensity of CO (gem) is in the order of $\text{RhFe/Al-HS} > \text{RhFe/Al-CM} > \text{RhFe/Al-CP} > \text{RhFe/Al-SG}$, which means that RhFe/Al-HS has more Rh^+ center. It was reported that

isolated hydroxyl groups is favorable to transfer Rh^0 into Rh^+ [21]. Therefore, we presume that more abundant isolated hydroxyl groups are responsible for more Rh^+ on RhFe/Al-HS. Moreover, the bridged adsorbed CO is strongest on the RhFe/Al-HS catalyst, which is consistent with the activity data for methane selectivity of this catalyst (see Table 6).

To know the dissociation ability and hydrogenation rate of the catalyst, CO-TPSR was carried out. As shown in Fig. 10, the band at 3015 cm^{-1} is ascribed to the stretching

Fig. 6 EDS profiles of Rh-based catalysts supported on different type of Al_2O_3 . **a** RhFe/Al-CM; **b** RhFe/Al-CP; **c** RhFe/Al-SG; **d** RhFe/Al-HS

Table 3 CO chemisorption results of catalysts

Catalysts	CO-chemisorbed/ $\mu\text{mol g}^{-1}$	Metal dispersion/%
RhFe/Al-CM	71.2	36.6
RhFe/Al-CP	64.6	32.7
RhFe/Al-SG	43.1	22.2
RhFe/Al-HS	116.6	58.6

Table 4 H_2 chemisorption results of catalysts

Catalysts	H_2 -chemisorbed/ $\mu\text{mol g}^{-1}$	Metal dispersion/%
RhFe/Al-CM	92.3	47.4
RhFe/Al-CP	89.6	40.1
RhFe/Al-SG	85.2	35.1
RhFe/Al-HS	160.8	82.7

vibration of gaseous methane, which intensity can be used as a tool to measure CO dissociation ability of catalyst [22]. The formation of methane for RhFe/Al-CM, RhFe/Al-CP, RhFe/Al-SG and RhFe/Al-HS appeared at 220 °C, 210 °C, 200 °C, 190 °C, respectively, which means that RhFe/Al-HS possessed strongest CO dissociation ability, whereas the RhFe/Al-CM showed the weakest dissociation. In addition, it was observed from the spectra in the range of 1800–2200 cm^{-1} that the hydrogenation rate of adsorbed CO is as follows: RhFe/Al-SG > RhFe/Al-CP > RhFe/Al-HS > RhFe/Al-CM.

Table 6 lists the activities data of the catalysts. These data were taken with 2:1 H_2 :CO mix at a total pressure 2 MPa and a temperature of 260 °C. The results show that product contains CO_2 , hydrocarbons, methanol, ethanol and other oxygenates. Among the by-products, CO_2 , CH_4 and higher hydrocarbons should be inhibited more seriously due to higher separation cost and lower economic value. Among the four catalysts, RhFe/Al-HS shows the highest

Fig. 7 XPS spectra of **a** Rh 3d and **b** Fe 2p for the catalysts

Table 5 Binding energy and surface composition of catalysts determined by XPS

Catalysts	Atomic ratio from XPS			Binding energy (eV)	
	Rh/Al	Rh/Fe ^a	Rh/Fe ^a	Rh 3d _{5/2}	Fe 2p _{3/2}
RhFe/AI-GM	0.79	0.24	0.27	309.3	710.4
RhFe/AI-CP	0.74	0.22	0.27	309.4	710.4
RhFe/AI-SG	0.64	0.19	0.27	309.4	710.4
RhFe/AI-HS	1.21	0.28	0.27	309.5	710.8

^aAtomic ratio of Rh/Fe expected in the whole sample

Fig. 8 Surface hydroxyl groups of different Al₂O₃ support and corresponding catalysts **a** support; **b** catalysts

Fig. 9 FTIR spectra of adsorbed CO on different type of Al_2O_3 -supported Rh-based catalysts. **a** RhFe/Al-CM; **b** RhFe/Al-CP; **c** RhFe/Al-SG; **d** RhFe/Al-HS

ethanol selectivity ($\sim 24.6\%$) and the lowest CO_2 selectivity ($\sim 8\%$), and also, RhFe/Al-CM exhibits higher ethanol selectivity with moderate CO conversion. It can be seen that Al-CP- and Al-SG-supported RhFe catalysts exhibit higher CO conversion but only with 7.3% and 5.8% ethanol selectivity, respectively. In general, for CO conversion, RhFe/Al-SG > RhFe/Al-CP > RhFe/Al-CM > RhFe/Al-HS. And for ethanol selectivity, RhFe/Al-HS > RhFe/Al-CM > RhFe/Al-SG > RhFe/Al-CP.

It has been reported that $(\text{Rh}_x^0\text{-Rh}_y^+)\text{-O-Fe}^{3+}(\text{Fe}^{2+})$ is the active site for the formation of ethanol [23]. Therefore, the synergy effect between Rh and Fe, the formation of Rh^+ would be beneficial to form the active site for ethanol synthesis.

The characterization and catalytic results show that the Rh–Fe interactions are greatly affected by the support. The surface areas of the samples are as follows:

Al-CP > Al-SG > Al-CM > Al-HS. Among them, Al-HS-supported catalysts have the highest ethanol selectivity although with the lowest specific area, indicating the specific area of the catalysts was not in direct proportion to their catalytic performances. XRD showed the presence of mixed Al_2O_3 crystalline phases in the Al-HS support prepared by hydrothermal synthesis. Compared to the Al-CM carrier, the greater specific area for Al-CP and Al-SG supported catalyst may lead to too stronger interaction between metal and support, which is not good for Rh–Fe interaction. Al-HS carrier with nano-fibrous morphology supported catalysts may weaken the interaction between metal and support, correspondingly, the contact between Rh and Fe is strengthened, which can also be proved by H_2 -TPR and EDS. The lower surface hydroxyl group intensity of Al-HS support may be responsible for the above interactions. The higher specific surface area Al-SG- and Al-CP-supported catalysts exhibited a higher CO conversion, but most of CO was converted into hydrocarbon and CO_2 . From the results of TPR, it can be inferred that there exists more single Fe species over the above two catalysts, which is favorable for hydrogenation and water gas shift reaction. On the other hand, some researchers believed CO_2 comes from the reaction of strongly adsorbed CO species with hydroxyl groups of Al_2O_3 support [20, 24]. This is in accordance with our experiments results that RhFe/Al-SG has strongest hydroxyl group and shows the highest CO_2 selectivity.

The formation of Rh^+ is also important for the formation of active sites. It is widely accepted that the dicarbonyl species can only be formed on highly dispersed rhodium [24]. H_2 and CO chemisorptions showed that Rh dispersion was in order of RhFe/Al-HS > RhFe/Al-CM > RhFe/Al-CP > RhFe/Al-SG. This indicated Al-HS-supported catalyst has a higher Rh dispersion than others, which also evidenced by XPS. On the other hand, DRIFTS of CO adsorption shows that RhFe/Al-HS has more dicarbonyl species, which comes from Rh^+ sites.

Table 6 CO hydrogenation over Rh-based catalysts supported on different type of Al_2O_3

Catalysts	$X_{\text{CO}}/\%$	Product selectivity/ $\text{C}\%$ ^a					
		CH_4	C_{2+}HC	MeOH	EtOH	CO_2	Others ^b
RhFe/Al-CM	25.8	28.6	13.3	15.2	20.5	14.2	8.2
RhFe/Al-SG	38.6	24.1	23.9	5.7	7.3	29.1	9.9
RhFe/Al-CP	35.4	24.8	27.2	5.2	5.8	28.8	8.2
RhFe/Al-HS	13.6	29.1	10.1	19.4	24.6	8.0	8.7

Catalyst: 1 g; reaction conditions: $T = 260^\circ\text{C}$ $P = 2\text{ MPa}$, $\text{H}_2/\text{CO} = 2$, space velocity = 3600 mL/(h. gcat)

^aProduct selectivity = $n_i M_i / \sum (n_i M_i)$, where n_i and M_i are the carbon atoms number and molar percent of product i , respectively

^bOxygenates with two or more carbons except ethanol (acetaldehyde, acetone, *n*-propanol, *i*-propanol, *n*-butanol, *i*-butanol and *n*-pentanol)

Fig. 10 DRIFTS spectra of CO-TPSR on different type of Al_2O_3 -supported Rh-based catalysts. **a** mRhFe/Al-CM; **b** RhFe/Al-CP; **c** RhFe/Al-SG; **d** RhFe/Al-HS

According to widely accepted mechanism for ethanol synthesis (see Fig. 11), a good Rh-based catalyst should balance the ability of CO dissociation, CO insertion and CO hydrogenation. DRIFTS study indicates that RhFe/Al-HS have stronger CO dissociation capacity, moderate CO hydrogenation rate and more Rh^+ sites for CO insertion. Therefore, stronger CO dissociation capacity, moderate CO hydrogenation rate and stronger CO insertion may be responsible for the good performance of RhFe/Al-HS.

Conclusion

Four kinds of alumina were used as supports of Fe-promoted Rh-based catalysts. The ethanol selectivity of RhFe/Al-HS catalysts supported on alumina prepared by hydrothermal synthesis was superior than the other catalysts, which were mainly due to the moderate metal particle size, the enhanced synergic between Rh and Fe, and the improved the Rh dispersion. Moreover, moderate CO hydrogenation rate, stronger CO dissociation and CO insertion ability was also favorable to increase the ethanol selectivity.

Fig. 11 Mechanism of ethanol formation [25]

Acknowledgements This work was supported by the National Natural Science Foundation of China (No. 31671797).

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