



Gas phase hydrogenolysis of methyl difluoroacetate to 1,1-difluoroethanol over Ru/C catalysts

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ABSTRACT

Ru/C catalysts were prepared by an impregnation method and their catalytic properties were tested for hydrogenolysis methyl difluoroacetate to difluoroethanol. The catalysts were characterized by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), CO chemisorption and H₂ temperature-programmed reduction (H₂-TPR). The effects of reaction temperature, Ru content and reduction temperature of the Ru/C catalysts on the reaction were investigated. It was found that with increasing Ru contents in the Ru/C catalysts, the methyl difluoroacetate conversion, the selectivity to difluoroethanol and the TOF value first increased and then decreased. A 3Ru/C catalyst reduced at 400 °C exhibited the highest selectivity to difluoroethanol (93.5%) and the highest activity (39.5%). It was also found that the Ru/C catalyst showed a good stability of catalytic hydrogenolysis of methyl difluoroacetate within 100 h.

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1. Introduction

Difluoroethanol is different from other fluorinated alcohols because of the presence of the difluoromethyl group. Difluoroethanol is mainly applied in synthesis of pharmaceutical and pesticides. Furthermore, the derivatives of difluoroethanol are used for weedicide and poisoning plant pest.

The synthesis routes of fluorinated alcohol include reduction of carbonyl compounds [1–3], oxidation of vinylidene fluoride [4], hydrolysis of fluoroethane [5–7], telomerization of fluoroalkenes [8–12], and so on. Reduction of carbonyl compounds has the advantages of simple reaction process, mild reaction conditions, high yield and less energy consumption, which is currently the major route for the production of fluorinated alcohols. Among the various carbonyl substrates, selective hydrogenation of fluorinated ester to synthesize fluorinated alcohol is one of the most promising processes, because of its easy operation, low production cost and it can avoid pollution problem which is brought by metal borohydride reduction. Willenberg et al. [13] reported a process for producing 2,2,2-trifluoroethanol by catalytic hydrogenolysis of 2,2,2-trifluoroethyl trifluoroacetate with hydrogen in the liquid phase at 100–210 °C in the presence of an oxide catalyst comprising oxides of copper, zinc, aluminum and chromium. In addition, Wujciak [14] used copper

chromite catalyst (10–80 bar, 30–300 °C) and palladium catalyst (20–60 bar, 70–175 °C) for hydrogenolysis trifluoroacetic acid and trifluoroacetic acid esters to form trifluoroethanol. Olivier et al. [15] took methyl difluoroacetate as the raw material to obtain difluoroethanol on Rh/C catalyst by liquid phase hydrogenolysis. The pressure was set to 40 bars and the reactor temperature was increased to 90 °C. However, the synthesis routes mentioned above were all conducted at high pressure. Because of the severe reaction conditions are prerequisites in liquid phase, difficulty in separating products from catalyst and continuous production, the liquid phase hydrogenolysis is not an ideal synthetic route. On the other hand, gas phase hydrogenolysis can realize continuous operation and has a low equipment corrosion and the operation can also be controlled easily. Up to now, the gas phase hydrogenation of fluorinated carboxylic esters for manufacturing of fluorinated alcohols has not been reported.

In the present work, Ru/C catalysts were prepared and were tested for gas hydrogenolysis of methyl difluoroacetate to synthesize difluoroethanol. And the influencing factors on catalytic performance were also discussed.

2. Results and discussion

2.1. Compositions and metal particle size of Ru/C catalysts

Fig. 1 shows the XRD patterns of the Ru/C catalysts with different Ru contents which were reduced in ultra-pure H₂ flow at

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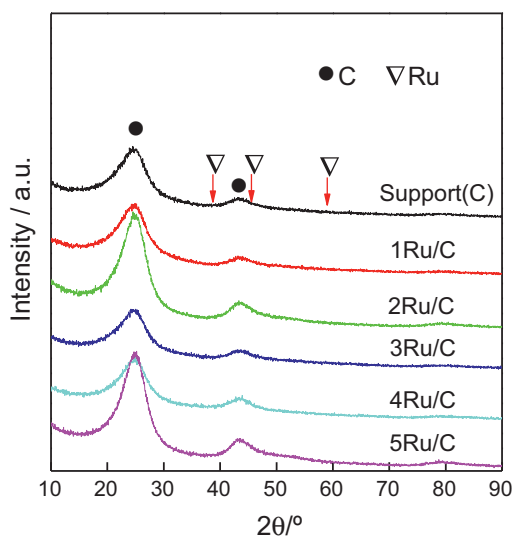


Fig. 1. XRD patterns of the Ru/C catalysts.

400 °C for 2 h. As shown in the figure, diffraction peaks of all the catalysts are similar to that of the active carbon support and diffraction peaks due to Ru, RuO_x, RuCl₃ are not observed, indicating that the Ru species are highly dispersed on the catalysts.

Fig. 2 shows representative TEM images and Ru particle size distribution histograms of Ru/C catalysts. All the catalysts were reduced at 400 °C for 2 h in ultra-pure H₂ flow. It was found that the Ru particles on active carbon are uniform in sizes and distribution. The average particle size of Ru on the 1Ru/C catalyst is around 2.5 nm, while average sizes of Ru particles on the 3Ru/C and 5Ru/C catalysts are around 2.0 and 1.5 nm, respectively. Thus, it can be concluded that Ru particles size decreases with increasing Ru contents from 1 to 5%.

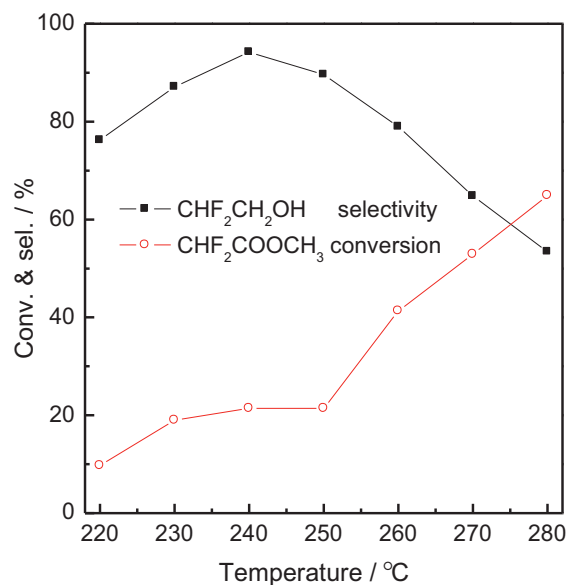


Fig. 3. Effect of reaction temperature on hydrogenolysis properties of methyl difluoroacetate over 3Ru/C catalyst.

2.2. Hydrogenolysis properties of methyl difluoroacetate over Ru/C catalysts

Fig. 3 shows the methyl difluoroacetate conversion and the selectivity to difluoroethanol as a function of reaction temperature over the 3Ru/C catalyst. As shown in the figure, the methyl difluoroacetate conversion was raised with the increase of reaction temperature from 220 to 280 °C, and the selectivity to difluoroethanol reached the highest value at 240 °C. Thus, 240 °C was chosen as the optimum reaction temperature for further experiments.

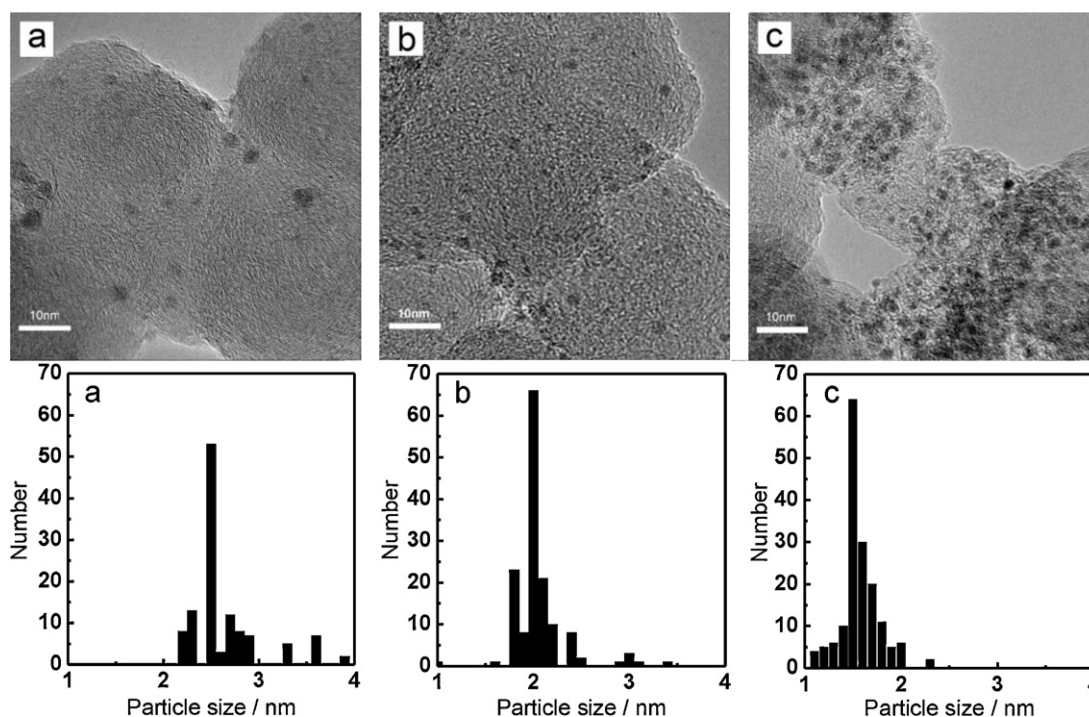


Fig. 2. TEM micrographs and Ru particle size distribution histograms of (a) 1Ru/C, (b) 3Ru/C, and (c) 5Ru/C catalysts.

Table 1

Methyl difluoroacetate conversions, selectivities to difluoroethanol, Ru dispersion and TOFs on Ru/C catalysts.^a

Catalyst (%)	Conversion (%)	Selectivity (%)	Ru dispersion ^b (%)	TOF ^c (10 ⁻³ /s)
1Ru/C	8.0	71.9	28.8	2.70
2Ru/C	17.8	91.0	30.9	2.79
3Ru/C	39.5	93.5	42.7	3.01
4Ru/C	20.9	88.0	48.4	1.05
5Ru/C	13.7	87.1	58.1	0.46

^a Reaction temperature: 240 °C.

^b Ru dispersion determined based on chemisorption value.

^c TOF calculated according to the Ru dispersion and difluoroacetate conversion.

Table 1 lists methyl difluoroacetate conversions, selectivities to difluoroethanol, Ru dispersion and TOF values over the Ru/C catalysts. As can be seen in Table 1, with increasing Ru content, Ru dispersion increases, and the methyl difluoroacetate conversion, the selectivity to difluoroethanol and TOF first increase and then decrease. Both the highest activity (39.5%) and the highest selectivity to difluoroethanol (93.5%) are obtained on 3Ru/C catalyst. The by-products were methane and ethane based on gas chromatography analysis, which were formed by the further hydrogenation of alcohols.

Table 2 shows the methyl difluoroacetate conversions, selectivities to difluoroethanol, Ru dispersion and TOF values over the 3Ru/C catalysts reduced at different temperatures. As can be seen in Table 2, with increasing reduction temperature from 200 to 500 °C, the Ru dispersion decreases, and the conversion of methyl difluoroacetate and TOF value first increase and then decrease. The optimum reduction temperature is 400 °C at which the highest activity of 39.5% and TOF of $3.01 \times 10^{-3} \text{ s}^{-1}$ were obtained. It was also found that the selectivity to difluoroethanol remained at about 94% when the catalyst was reduced at 200–400 °C. However, it decreased significantly as the catalyst was reduced at 500 °C. Thus, 400 °C was chosen as the optimum reduction temperature.

Fig. 4 shows the stability of catalytic hydrogenolysis of methyl difluoroacetate over the 3Ru/C catalyst. It is found that during 100 h catalytic test, the conversion of methyl difluoroacetate on 3Ru/C catalyst first increases and reaches a steady state (40%) after 5 h. The selectivity to difluoroethanol remains about 93%. This suggests that the catalyst has a good stability of catalytic

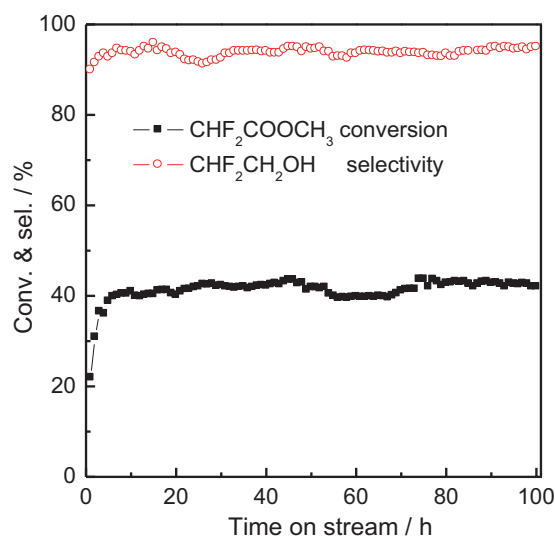


Fig. 4. Reaction stability of 3Ru/C catalysts (reaction temperature 240 °C).

Table 2

Effect of reduction temperature on methyl difluoroacetate conversions, selectivities to difluoroethanol, Ru dispersion and TOFs on 3Ru/C catalyst.^a

Reduction temperature (°C)	Conversion (%)	Selectivity (%)	Ru dispersion ^b (%)	TOF ^c (10 ⁻³ /s)
200	9.9	93.7	52.5	0.61
300	10.0	94.2	48.7	0.66
400	39.5	93.5	42.8	3.01
500	21.8	77.1	37.7	1.87

^a Reaction temperature: 240 °C.

^b Ru dispersion determined based on chemisorption value.

^c TOF calculated according to the Ru dispersion and difluoroacetate conversion.

hydrogenolysis on methyl difluoroacetate during the reaction period.

2.3. Reduction properties of Ru/C catalysts

To analyze the reduction behaviors of Ru/C catalysts, H₂-TPR experiments were carried out and the results are shown in Fig. 5. It is found that for all the catalysts, no peaks are observed after 350 °C. This suggests that the Ru species could be completely reduced to Ru⁰ at 350 °C. Moreover, two peaks at ca. 130 °C (α peak) and 230 °C (β peak) are observed, with the former being less intense compared to the latter. The α peak is assigned to the reduction of the Ru species not interacting with active carbon [16]. This type of Ru species can be easily reduced, so the corresponding peak started at lower temperature. The β peak is assigned to the reduction of the Ru species strongly interacting with the active carbon [16]. Moreover, the peak areas of β were calculated to be 322, 430, 670, 674 and 663, respectively, with increasing Ru contents in the catalysts. Therefore, it is found the β peak reaches a maximum when the Ru content is 3% and kept unchanged with further increasing Ru content. Thus, it can be concluded that Ru species that strongly interact with support are saturated when the Ru content reaches 3%. Higher Ru content in the catalyst (>3%) may result in the formation of free Ru species, and may even cover those strongly interacting with the support. The TPR profiles clearly indicate that during the reaction, Ru species in the catalysts are metallic (Ru⁰) since they are pre-reduced at 400 °C prior to the reaction. However, a close investigation of the Ru

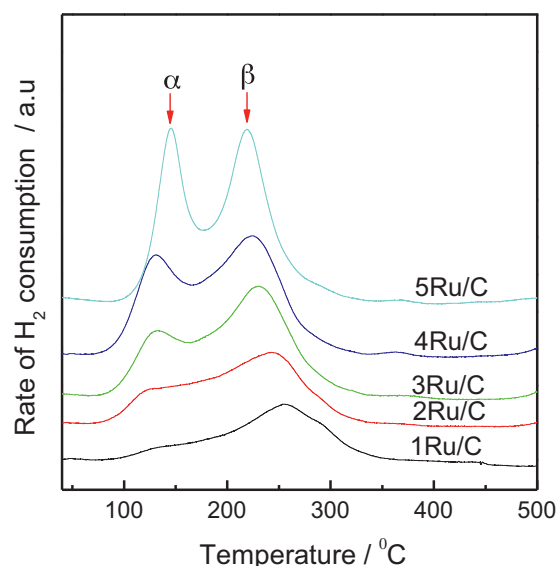


Fig. 5. H₂-TPR patterns of Ru/C catalysts.

particles on the support is necessary in order to establish a correlation between the morphologies of the Ru particles and their catalytic behaviors. Concerning the active sites/phase, the results shown in Table 1 indicate that the TOF value decreases on the Ru/C catalysts at high Ru content. Note that the ratio of Ru species interacting with support/total exposed Ru atoms decreases with increasing Ru loading in the catalyst (71.2% for 1Ru/C, 73.1% for 2Ru/C, 74.4% for 3Ru/C, 66.6% for 4Ru/C, 62.6% for 5Ru/C, based on the TPR profiles in Fig. 5), which is consistent with the changes in TOFs. Therefore, it seems that the Ru species that strongly interact with the support might be the catalytically active components for the reaction.

3. Conclusion

For the Ru/C catalyst, with increasing Ru content, Ru dispersion increased and the methyl difluoroacetate conversion, selectivity to difluoroethanol and TOF first increased and then decreased. Both the highest conversion (39.5%) and the highest selectivity to difluoroethanol (93.5%) were obtained on 3Ru/C catalyst. It was also found that the reduction temperature had great effect on catalytic activity, and the catalyst reduced at 400 °C exhibited the best catalytic performance. Furthermore, the 3Ru/C catalyst was quite stable during the reaction period within 100 h.

4. Experiment

4.1. Catalyst preparation

Supported Ru/C catalysts were prepared by impregnating the active carbon support (XC-72, $S_{\text{BET}} = 223 \text{ m}^2 \text{ g}^{-1}$) with an aqueous solution of RuCl_3 for 8 h. Excess solution was removed by mild evaporation, and then the samples were dried at 110 °C for 12 h. Before the catalytic test, the catalysts were pre-reduced in ultra-pure H_2 flow (99.999%, 30 ml min^{-1}) at different temperatures for 2 h. The catalysts were denoted as xRu/C, where x refers to the weight percent of Ru (wt.%) in the catalyst.

4.2. Catalytic performance test

Gas phase hydrogenolysis of methyl difluoroacetate was performed in a stainless steel tubular reactor (i.d. = 10 mm, length = 300 mm) at atmospheric pressure. About 500 mg of the catalyst was loaded in the reactor with a thermal couple placed in the middle of the catalyst bed to monitor the reaction temperature. Methyl difluoroacetate was introduced in a trap set maintained at 0 °C before the reactor to achieve a constant methyl difluoroacetate partial pressure, then methyl difluoroacetate at constant partial pressure was carried over the catalyst by hydrogen flow (20 ml min^{-1}). The gas line was kept at about 110 °C to avoid any condensation. The reaction products and reactants were analyzed on line using a gas chromatography (Shimadzu GC-2014) equipped with a flame ionization detector (FID) and a DB-Wax column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$) capillary column.

4.3. Catalyst characterizations

X-ray diffraction (XRD) patterns were recorded using a PANalytic X'Pert PW3040 diffractometer with $\text{Cu K}\alpha$ radiation operating at 40 kV and 40 mA. The patterns were collected in a 2θ range from 10 to 90°, with a scanning step of $0.15^\circ \text{ s}^{-1}$.

Transmission electron microscopy (TEM) analysis was performed on a JEM-2100F electron microscopy with a field emissive gun, operated at 200 kV and with a point resolution of 0.24 nm. The samples were prepared by dispersing a few milligrams of powder in ethanol. The dispersion was then immersed for 10 min in an ultrasonic bath in order to disagglomerate the powder particles. Finally, one drop was deposited on a Formvar/carbon copper grid. Various regions of the grid were observed and the particle sizes were measured from the observation of 150–250 particles.

CO chemisorption experiments were carried out on a Quantachrome CHEMBET-3000 instrument in order to determine the dispersion of Ru. The sample was placed in a U-shaped quartz reactor and a high-purity He (99.999%) gas flow of 70 ml min^{-1} was used as the carrier gas. Before CO chemisorption, the samples were reduced in a $\text{H}_2\text{-N}_2$ mixture (5 vol% H_2) stream for 2 h, cooled down to 30 °C, and then purged with a pure He gas flow for 1 h at the same temperature. Then pulses of CO were fed into the stream of carrier gas with a precision analytical syringe.

The reducibility of the catalysts was measured by hydrogen temperature-programmed reduction ($\text{H}_2\text{-TPR}$) experiments. 100 mg of sample was placed in a quartz tubular reactor (i.d. = 6 mm). After that the sample was heated from 40 to 600 °C at a rate of $10^\circ \text{ C min}^{-1}$ in a $\text{H}_2\text{-N}_2$ gas mixture (5 vol% H_2 , 30 ml min^{-1}). The hydrogen consumption during the reduction was determined by a gas chromatograph with a thermal conductivity detector.

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