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Preparation and Characterization of Ru/Al_2O_3 Catalysts by adsorption-precipitation-activation method and Selective Hydrogenation of Dimethyl Maleate to Dimethyl Succinate

Nuermaimaiti Abudukelimu[1,3], Hongjuan Xi[2], Zhixian Gao[1,2,4*], Yagang Zhang[1,4*], Yubo Ma[1], Xamxikamar Mamat[1] and Wumanjiang Eli[1]

[1]Xinjiang Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Urumqi 830011, China
[2]Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, China
[3]Graduate University of the Chinese Academy of Sciences, Beijing 100039, China
[4]Department of Chemical and Environmental Engineering, Xinjiang Institute of Engineering, Urumqi 830091, China

***Corresponding Author:** 1. Yagang Zhang PhD, Professor of Chemistry and Chemical Engineering, The Xinjiang Technical Institute of Physics & Chemistry, The Chinese Academy of Sciences, Urumqi, Xinjiang, China 830011, Tel: 86-18129307169, Fax: 86-991-3838957; Email: ygzhang@ms.xjb.ac.cn; zhangyg2005@hotmail.com

2. Zhixian Gao, The Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences, Urumqi, Xinjiang, China 830011, Fax: +86-991-3838957; Email: gaozx@sxicc.ac.cn

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Abstract

Supported Ru catalysts were prepared by adsorption-precipitation-activation method using $RuCl_3$ as Ru resource, NaOH as precipitant and Al_2O_3 as support. $Ru(OH)_3/Al_2O_3$ was first produced in the adsorption-precipitation process, and then activated with either calcination-reduction or direct reduction by H_2 to obtain Ru/Al_2O_3. The synthesized Ru catalysts were characterized with XRD, XPS, H_2-TPR techniques, and used for the catalytic hydrogenation of dimethyl maleate (DMM). It was found that the activation process strongly affected the catalytic performance. The highest hydrogenation activity was observed with catalysts activated by direct H_2 reduction, which produced the finest Ru particle on alumina. Unexpectedly, Ru metal formation was observed based on XRD and XPS data and was explained by the disproportionation reaction of Ruthenium hydroxide: $4Ru(OH)_3 = Ru + 3RuO_2 + 6H_2O$. This explanation was also supported by the H_2-TPR results of $Ru(OH)_3/Al_2O_3$ samples pretreated under different conditions, and by characterization data of unsupported Ru samples. XRD data demonstrated that large particles of Ru and RuO_2 were formed upon calcination of $Ru(OH)_3/Al_2O_3$ at above 200°C, and subsequent reduction of the calcined sample would give rise to Ru/Al_2O_3 with larger metal crystals as compared to that of directly reduced ones.

Keywords: Ru/Al_2O_3, $Ru(OH)_3/Al_2O_3$, Disproportionation, Hydrogenation, Dimethyl maleate.

Introduction

Ruthenium supported catalysts have found wide applications in many catalytic reactions. Ruthenium hydroxide $Ru(OH)_x$ or $RuO_2{\cdot}xH_2O$ has been reported to be the active species for catalytic reactions such as oxidation [1,2], N-alkylation of amines [3], Hydration of nitriles [4], and hydrogen-transfer [5]. However Ru metal is required to catalyzed the hydrogen involved reactions efficiently, such as hydrogenolysis of paraffins and olefins [6,7], isomerization of linoleic acid [8], selective hydrogenation of benzene [9,10], Fischer-Tropsch [11-13], ammonia synthesis [14-24] and oxidation of CO [25-27]. It was found and proposed that both the catalytic activity and selectivity of Ru catalysts are affected by the nature metal Ru such as dispersion, crystal size and structure [28]. It is also well-known that the nature of metal is strongly dependent on the method of catalyst preparation employed [29].

The general procedure for preparing supported metal catalysts comprises a process of distributing metal precursor onto a support, followed by reductive activation with various reducing reagents. In some cases, a calcination step may be applied prior to the reduction treatment. Common methods for the first step include impregnation or ion-exchange [30-32], coprecipatation [24], and deposition–precipitation [33, 34]. As for the reduction activation process, H_2 is highly preferred over other reagents due to its advantages of no contamination of other elements, water as product and environmental friendliness.

In the case of supported Ru catalysts, several papers using $RuCl_3$ as ruthenium precursor have been reported [10]. Lin et al [35] used the impregnation method to obtain $RuCl_3/Al_2O_3$, and then it was reduced with hydrazine or H_2. They found that there was almost no residual chlorine in the samples with hydrazine treatment, in contrast to the samples with conventional hydrogen reduction. Zonetti et al [36] found that the calcination treatment of $RuCl_3/CeO_2$ only lead to poor catalytic performance, while direct reduction at temperatures between 500°C and 750°C generated an active Ru/CeO_2 catalyst for the partial hydrogenation of benzene.

Nagai M et al [37] studied the effects of pretreatment procedures and found that direct reduction rather than calcination-reduction produced Ru/Al_2O_3 catalysts demonstrated good catalytic performances during the hydrodesulfurization (HDS) of thiophene.

Previously, we found that Ru/Al_2O_3 catalysts prepared using an adsorption-precipitation-activation method presented higher catalytic activity than that of the conventional impregnation-activation. It was found that activation process strongly affected the catalytic performance while the adsorption-precipitation step did not. The direct H_2 reduction activation was far more superior to the calcination-reduction. However the negative effects of the calcination treatment have not been fully investigated. In the work reported here, this issue has been explored in detail through XPS, XRD and H_2-TPR analysis. Results showed that large particles of Ru metal and RuO_2 were formed upon calcination treatment of $Ru(OH)_3$/Al_2O_3 especially at higher temperatures, and subsequent reduction gave rise to Ru metal with larger crystal size. It was proposed that disproportionation reaction of ruthenium hydroxide occurred upon calcination treatment.

Experimental

Materials

Al_2O_3 was used as a support, was obtained from Yantai Henghui Chemical Co., Ltd, China (surface area was measured as 409m^2/g). Ruthenium trichloride was used as a catalyst precursor, was obtained from Sino-Platinum Metals Co., Ltd, China. Sodium hydroxide was used as a precipitant in catalyst preparation, was of analytical reagent grade. Dimethyl maleate (DMM) was prepared by esterification of analytical reagent grade maleic anhydride. Methanol, used as solvent and esterification reagent, was also of analytical reagent grade. Hydrogen was from a cylinder with a minimum stated purity of 99.999%. Nitrogen was from a cylinder with stated purity of 99.999%.

Catalyst Preparation

Ru/Al_2O_3 catalysts with nominal Ru loading of 5.0% were prepared by the adsorption-precipitation-activation method. The procedure for the preparation was described as follows: Al_2O_3 (as the support), was added into an aqueous solution of $RuCl_3$ under stirring at room temperature, and the suspension was stirred at this condition for 1h, and then a NaOH solution with NaOH/$RuCl_3$ molar ratio of 3:1 was added drop-wise. After further stirring for 1h, the suspension was filtered. Subsequently, the obtained solid was washed with distilled water until free of Cl^- ions as detected by $AgNO_3$ test and dried at 100˚C overnight. The obtained sample, denoted as $Ru(OH)_3$/Al, was further activated by direct reduction either with H_2 or by calcination-reduction. The alumina-supported ruthenium samples by different procedures are summarized in Table 1.

To gain more information about the state of ruthenium in catalysts, unsupported ruthenium samples were also prepared using the precipitation method. An aqueous solution of $RuCl_3$ in deionized water was contacted with an aqueous NaOH solution and adjusted to a pH of about 10~11, and stirred for 1h. Then the precipitate was separated from the mother liquor by centrifugation, followed by washing several times with deionized water until free of Cl^- ions. The washed precipitate was air dried at room temperature naturally, and then the resulting sample, denoted as $Ru(OH)_3$, was subjected to different treatments. The prepared unsupported samples by different procedures are also listed in Table 1.

Table 1: List of synthesized catalyst samples

Catalyst denotation	Preparation procedures
$Ru(OH)_3$-25	Precipitation at 25˚C
$Ru(OH)_3$-90	Precipitation at 90˚C
Ru-90	Reduction of the $Ru(OH)_3$-90 in H_2 at 400˚C for 2h
RuO_x-90-C200	Calcination of the $Ru(OH)_3$-90 in air at 200˚C for 4h
RuO_x-90-C200N_2	Calcination of the $Ru(OH)_3$-90 in N_2 at 200˚C for 4h
RuO_x-90-C450	Calcination of the $Ru(OH)_3$-90 in air at 450˚C for 4h
Ru-90-C450	Reduction of the RuO_x-90-C450 in H_2 at 400˚C for 2h
$Ru(OH)_3$/Al	Adsorption-precipitation
RuO_x/Al-C450	Calcination of the $Ru(OH)_3$/Al at 450˚C for 4h
Ru/Al	Reduction of the $Ru(OH)_3$/Al in H_2 at 400˚C for 2h
RuO_x/Al-C200	Calcination of the $Ru(OH)_3$/Al in air at 200˚C for 4h
Ru/Al-C200	Reduction of the RuO_x/Al-C200 in H_2 at 400˚C for 2h
RuO_x/Al-C300	Calcination of the $Ru(OH)_3$/Al in air at 300˚C for 4h
Ru/Al-C300	Reduction of the RuO_x/Al-C300 in H_2 at 400˚C for 2h
RuO_x/Al-C300N_2	Calcination of the $Ru(OH)_3$/Al in N_2 at 300˚C for 4h
Ru/Al-C300N_2	Reduction of the RuO_x/Al-C300N_2 in H_2 at 400˚C for 2h
RuO_x/Al-C450N_2	Calcination of the $Ru(OH)_3$/Al in N_2 at 450˚C for 4h
RuO_x/Al-C450	Calcination of the $Ru(OH)_3$/Al in air at 450˚C for 4h
Ru/Al-C450	Reduction of the RuO_x/Al-C450 in H_2 at 400˚C for 2h

Catalyst Characterization

The prepared catalysts were analyzed with D8 ADVANCE X-ray powder diffractometer (XRD). Diffraction patterns were obtained with Cu Kα radiation (40kv, 40mA) over a 2θ range of 10º-80º.

X-ray photoelectron spectroscopy (XPS) was recorded using a VG ESCALAB210 instrument with Mg Kα radiation (1253.6eV), and all the binding energies were referenced to the C1s at 285 eV.

Temperature-programmed reduction of hydrogen (H_2-TPR) was carried out on TPR flow system equipped with a TCD detector. TPR analysis was conducted with 10% H_2/Ar (10ml min^{-1}) using 20 mg sample, and the profile was recorded at a heating rate of 10˚C min^{-1} from room temperature to 500˚C.

Catalytic Hydrogenation Test

The hydrogenation of dimethyl maleate in methanol was conducted at 70˚C, 675 r/min and hydrogen pressure of 1.0 MPa. The hydrogen consumption rates and cumulative volumes were recorded by a mass flow meter during the hydrogenation process, and were applied in the calculation of DMM conversion.

Results

Activity Studies

Selective hydrogenation of DMM in the liquid phase was carried out to evaluate the catalytic properties of the Ru catalyst. For all catalysts tested, only dimethyl succinate product was detected, indicating high hydrogenation selectivity. However, substantial differences in catalytic activity were observed, as shown in Tables 2a and 2b.

For unsupported Ru samples, the highest activity was obtained with the as-synthesized sample at room temperature. Both the

$Ru(OH)_3$-25 and $Ru(OH)_3$-90 catalysts showed an activation period, implied that the hydrogenation rate increasing over time until reaching a maxima. Upon additional treatments of the fresh $Ru(OH)_3$-90 at higher temperatures, the catalytic activity decreased dramatically.

As for the supported Ru catalysts, the as-synthesized $Ru(OH)_3$/Al that was obtained by adsorption-precipitation method, also showed an activation period as indicated by the variation of average rates listed in Table 2b.

The highest activity of supported catalyst was obtained with the Ru/Al which was activated by direct reduction of $Ru(OH)_3$/Al. Calcination treatment prior to reduction was found to have a negative effect on the catalytic performance, and a substantial decrease in catalytic activity was observed when the calcination temperature was above 300˚C.

X-ray Diffraction (XRD) Analysis

Figures 1a, 1b and 1c depicts the XRD patterns of support and samples with different treatment processes.

Table 2a: Catalytic behaviors of unsupported catalysts for hydrogenation of DMM

Time(min) / catalyst		0	5	10	15	17	20	25	30
$Ru(OH)_3$-25	Conversion (%)	0	17.6	58.4	96.9	99.3	100		
	Average rate(×10^{-4} mol/min)	0	26.5	44.0	48.7	44.0	37.7		
$Ru(OH)_3$-90	Conversion (%)	0	7.5	32.4	66.8	93.7	96.2	100	
	Average rate(×10^{-4} mol/min)	0	11.3	24.4	33.6	41.5	36.2	30.1	
Ru-90	Conversion (%)	0	2.2	4.1	6.9	8.3	10.3	12.4	stopped
	Average rate(×10^{-4}mol/min)	0	3.3	3.1	3.5	3.7	3.9	3.7	
RuO_x-200Air	Conversion (%)	0	33.6	77.1	98.9	100			
	Average rate(×10^{-4}mol/min)	0	50.6	58.1	49.7	44.3			
RuO_x-200N_2	Conversion (%)	0	29.9	68.3	95.4	98.9	100		
	Average rate(×10^{-4}mol/min)	0	45.1	51.5	47.9	43.8	37.7		
RuO_x-90-C450	Conversion (%)	0	1.1	1.5	1.7	1.7	1.8	1.9	stopped
	Average rate(×10^{-4} mol/min)	0	1.7	0.8	0.9	0.8	0.7	0.6	
Ru-90-C450	Conversion (%)	0	1.2	1.9	2.2	2.3	2.4	2.6	stopped
	Average rate(×10^{-4} mol/min)	0	1.8	1.4	1.1	1.0	0.9	0.8	

Reaction conditions: Catalyst loading 25 mg DMM initial amount 0.695 mol, total volume of reactant and solvent 100 ml, pressure 1.0 MPa, temperature 70˚C.

Table 2b: Catalytic behaviors of supported catalysts for hydrogenation of DMM

Time(min) / catalyst		0	4	8	12	14	17	30	60	90
Al_2O_3(Al)	Conversion (%)	0	0	0	0	0	0	0	0	0
	Average rate(×10^{-4} mol/min)	0	0	0	0	0	0	0	0	0
$Ru(OH)_3$/Al	Conversion (%)	0	2.0	2.7	3.8	4.2	5.3	12	75	100
	Average rate(×10^{-4} mol/min)	0	3.8	2.5	2.4	2.3	2.3	3.0	9.4	8.4
RuO_x/Al-C450N_2	Conversion (%)	0	1.9	2.8	3.5	4.1	4.7	5.2	6.0	6.6
	Average rate(×10^{-4} mol/min)	0	3.6	2.6	2.2	2.2	2.1	1.3	0.8	0.6
RuO_x/Al-C450	Conversion (%)	0	2.1	3.3	4.3	4.7	5.9	6.8	7.4	8.5
	Average rate(×10^{-4} mol/min)	0	3.9	3.1	2.7	2.5	2.6	1.7	0.9	0.7
Ru/Al	Conversion (%)	0	45.5	91.7	99.5	100				
	Average rate(×10^{-4} mol/min)	0	85.7	86.4	62.5	53.8				
Ru/Al-C200	Conversion (%)	0	29.4	65.1	92.1	98.1	100			
	Average rate(×10^{-4} mol/min)	0	55.4	61.3	57.8	52.8	44.3			
Ru/Al-C300N_2	Conversion (%)	0	6.4	11.1	15.6	17.8	20.9	32.0	49.4	67.3
	Average rate(×10^{-4} mol/min)	0	12.1	10.5	9.8	9.6	9.3	8.0	6.2	5.6
Ru/Al-C300	Conversion (%)	0	4.8	10.1	14.9	16.9	23.9	35.4	60	75
	Average rate(×10^{-4} mol/min)	0	9.0	9.5	9.4	9.1	10.6	8.9	7.5	6.3
Ru/Al-C450	Conversion (%)	0	4.9	8.6	11.5	14.2	15.4	21.7	35	46
	Average rate(×10^{-4} mol/min)	0	9.2	8.1	7.2	7.6	6.8	5.5	4.4	1.3

Reaction conditions: Catalyst loading 200 mg, DMM initial amount 0.695 mol, total volume of reactant and solvent 100 ml, pressure 1.0 MPa, temperature 70˚C.

For the $Ru(OH)_3$/Al sample, only peaks assigned to alumina support was identified, suggesting ruthenium species being well dispersed in an amorphous state on the support [35].

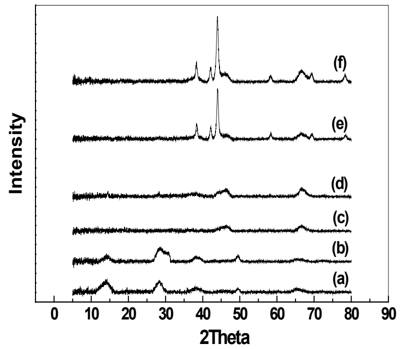

Figure 1a: XRD patterns of (a) Al, (b) $Ru(OH)_3$/Al, (c) Ru/Al, (d) Ru/Al-C200, (e) Ru/Al-C300, (f) Ru/Al-C450

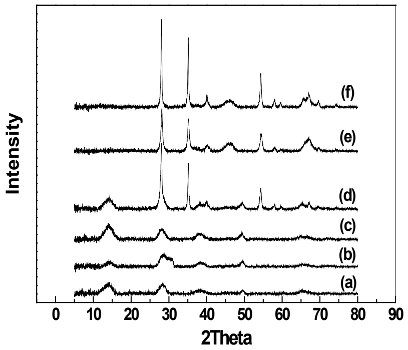

Figure 1b: XRD patterns of (a) Al, (b) $Ru(OH)_3$/Al, (c) RuO_x/Al-C200, (d) RuO_x/Al-C300, (e) RuO_x/Al-C450N_2, (f) RuO_x/Al-C450

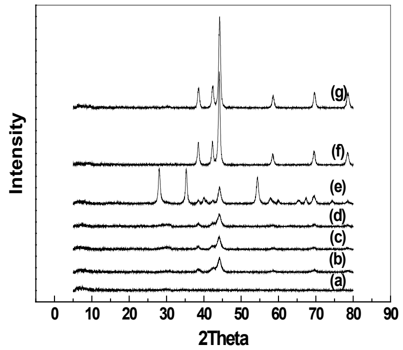

Figure 1c: XRD patterns of (a) $Ru(OH)_3$-25, (b) $Ru(OH)_3$-90, (c) RuO_x-90-C200, (d) RuO_x-90-C200N2, (e) RuO_x-90-C450, (f) Ru-90, and (g) Ru-90-C450

Upon calcination of $Ru(OH)_3$/Al up to 200°C, nearly the same patterns were obtained as compared with that of fresh $Ru(OH)_3$/Al. However, additional peaks were observed when the calcination temperature was increased up to 300°C, and the peak intensities and sharpness increased with elevated temperature. The peaks at 28.1°, 35.1° and 54.3° were attributed to RuO_2 [38], while peaks at 58.5° and 69.5° denoted the presence of Ru metal. Upon calcination in N_2, the same pattern was obtained as compared with that of calcination in air. Thus the disproportionation reaction of Ruthenium hydroxide was proposed to produce Ru metal and RuO_2. This result will be addressed in the discussion section.

As shown in Figure 1a, the XRD patterns of Ru/Al, which was obtained by direct reduction of $Ru(OH)_3$/Al, demonstrated two broad peaks. The peak at 46.1° can be attributed to Ru metal being well dispersed, while the peak at 66.5° can be assigned to alumina precursor.

From Figure 1b, one can see that the calcination treatments prior to reduction have substantial impacts on states of Ru metal. When calcination was carried out below 200°C prior to reduction, the obtained diffraction patterns were almost identical as those of the directly reduced sample. However, upon calcination pretreatment up to 300°C and 450°C, different XRD patterns with enhanced intensity of diffraction peaks were registered, suggesting Ru/Al with larger metal crystals as compared to that of directly reduced ones.

Figure 1c shows the XRD patterns of various unsupported Ru samples that were pretreated under various conditions. For the $Ru(OH)_3$-25sample, no peaks can be seen, indicating that ruthenium species exited in the amorphous state. However with the increase of precipitation temperature, the reflections at 37.9°, 43.5°,58.5°, 69.5° and 78.5° appeared, indicating the presence of Ru metal in $Ru(OH)_3$-90 sample.

When the $Ru(OH)_3$-90 sample was subjected to direct H_2 reduction, the obtained Ru-90 sample showed sharp peaks at 37.9°, 43.5°, 58.5°, 69.5° and 78.5°, indicating the presence of larger Ru metals. Similar results were obtained with the Ru-90-C450 sample that encountered a calcination step prior to reduction.

When the $Ru(OH)_3$-90 sample was calcined in air, the formed RuO_x-90-C450 sample demonstrated both strong sharp peaks at 28.1°, 35.1° and 54.4°, and small ones at 37.9°, 43.5°,58.5°, 69.5° and 78.5°, suggesting the coexistence of RuO_2 and Ru metals. This data also indicated that Ru metal cannot be fully oxidized at the calcination process.

X-ray Photoelectron Spectroscopy (XPS) Investigation

X-ray photoelectron spectroscopy (XPS) is a powerful tool to investigate the chemical environment of elements on the surface of a catalyst. To determine the state of Ru species of samples pretreated under different conditions, both supported and unsupported samples were characterized with XPS.

Figure 2 depicts the XPS spectra of various unsupported samples. A typical Ru $3d_{5/2}$ XPS spectrum of the sample $Ru(OH)_3$-25 shows peak at 281.7eV.

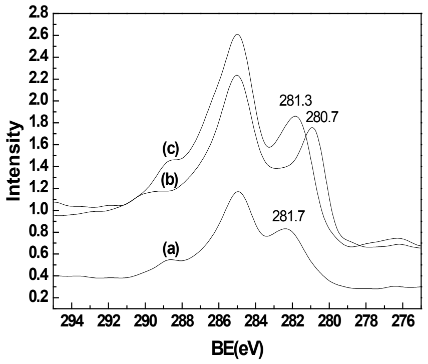

Figure 2: XPS spectra of (a), $Ru(OH)_3$-25, (b) RuO_x-90-C450, and (c) $Ru(OH)_3$-90

With the sample of $Ru(OH)_3$-90, Ru $3d_{5/2}$, XPS spectrum shows a peak at 281.3eV, and a shift of binding energy to a lower value

(BE=280 eV), suggesting that the sample contained lower valence ruthenium species, probably Ru^0, which is consistent with XRD results of $Ru(OH)_3$-90 (Figure 1c). With the sample of RuO_x-90-C450, XPS spectrum shows a peak at 280.7eV, indicating the coexistence of Ru^0 with $Ru^{4+}$of RuO_2 as also supported by XRD results (Figure 1c).

Table 3 shows the maxima Ru $3d_{5/2}$ binding energy for supported samples pretreated under different conditions. For the sample RuO_x/Al-C450, the binding energy is 280.6 eV, suggesting ruthenium exists mainly as RuO_2, and possibly coexistence of Ru^0, this is in good agreement with XRD results (Figure 1b). With the sample of Ru/Al-C450 the binding energy is 279.6 eV, implied that these components are mainly attributed to Ru^0.

Table 3: Binding energy of various samples

sample	Ru3$d_{5/2}$ Binding energy(eV)
Ru/Al	280.6
Ru/Al-C450	279.6
RuO_x/Al-C450	280.6

With the sample of Ru/Al, the maxima Ru $3d_{5/2}$ binding energy is 280.6eV, which is the same as that of RuO_x/Al-C450, hence it was speculated that the Ru might be exists as $Ru^{4+}$of RuO_2 and Ru^0. However the XRD results showed Ru mainly exists as Ru^0, so a possible explanation could be that a shift of Binding energy to a higher value could be attributed to the interaction of highly dispersed Ru with alumina support.

Temperature-Programmed Reduction (TPR) Investigation

In order to accurately determine the Ru oxidation state upon thermal treatment, H_2-TPR technique were used to characterize $Ru(OH)_3$/Al samples pretreated by one of three procedures (a) heated from ambient temperature to 600˚C at 10˚C/min in Air, and then maintain for 30 minutes; (b) had the same procedure as (a) except Air was replaced by Argon; and (c) heated from ambient temperature to 100˚C at 10˚C/min in Argon, and then maintained for 60 minutes.

As shown in Figure 3, with the three different pretreated procedures, no reduction peaks above 400˚C were registered.

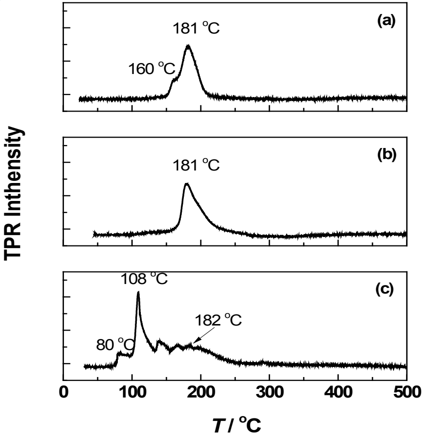

Figure 3: H_2-TPR profiles of $Ru(OH)_3$/Al catalyst with different pretreatment procedures:(a) pretreated in air at 600˚C for 30 min, (b) pretreated in argon at 600˚C for 30 min, (c) pretreated in argon at 100˚C for 60 min

Sample (a) has a maximum peak at 181˚C with a shoulder at about 160˚C; sample (b) has a single peak at 181˚C; and sample (c) has several peaks ranging from 66˚C to 307˚C with a maximum peaks at 108˚C.

Koopman et al [39] assigned a peak between 177 and 205˚C to the reduction of RuO_2 on silica, while Mazzieri V et al [10] found calcined $RuCl_3$/Alumina sample presented a peak with maximum at 197˚C and a shoulder at about 156˚C, which could be attributed to the reduction of ruthenium oxide and of ruthenium oxychloride, respectively. In the work presented here, the peak at 181˚C was proposed due to the reduction of RuO_2 as supported by the XRD data, and a shoulder at about 160˚C might be assigned to a RuO_2 of a different phase.

Compared with samples (a) and (b), sample (c) had broad reduction peaks with the maximum at lower temperature of 108˚C, which implied that it can be reduced more easily. Thus it was clear that $Ru(OH)_3$/Al consisted of several Ru species with different oxidation states, the main peak can be attributed to $Ru(OH)_3$ species, and the higher reduction peaks to RuO_2. These assignments were also in good agreement with the fact that $Ru(OH)_3$ could disproportional decompose to Ru and RuO_2 at 100˚C during the pretreatment process.

Discussions

A detailed literature survey indicated that residual chlorine in the supported Ru catalysts had negative effects on their catalytic performances [11,13,14,16,22,23]. With conventional hydrogen reduction of $RuCl_3/Al_2O_3$, temperatures above 500˚C, could result in the agglomeration of Ru metals, should be applied to remove residual chlorine [20,40,41]. Alternatively, the use of a hydrazine treatment led to the formation of a chlorine-free catalyst, as reported by Lin et al [35,42], but the method was not environmental-benign and cost effective.

In order to eliminate residual chlorine in the final catalyst, we proposed and applied the so called adsorption-precipitation-activation method to prepare Ru catalyst supported on alumina. After adsorption of $RuCl_3$ on to alumina, chlorine was released by precipitating Ru as $Ru(OH)_3$, and then the precipitate was washed with water until free of chlorine. The obtained $Ru(OH)_3$/Al was further treated with different activation processes.

Upon calcination treatment of $Ru(OH)_3$/Al at temperatures above 300˚C in air or N_2, Ru metal other than RuO_2 was identified in the sample as shown by the characterization data of RuO_x/Al-C300, RuO_x/Al-C300N_2, RuO_x/Al-C450 and RuO_x/Al-C450N_2. To understand better for the preparation chemistry, unsupported $Ru(OH)_3$ samples were also synthesized and characterized as a control. As listed in Figure 1c, and Figure 2, the reduced samples Ru-90 and Ru-90-C450, showed only Ru metal, while the thermal treated ones such as RuO_x-90-C200, RuO_x-90-C200N_2 and RuO_x-90-C450, showed both the signals of RuO_2 and Ru^0. We proposed that it was due to the following disproportional decomposition reaction of Ruthenium hydroxide upon thermal treatment:

$$4Ru(OH)_3 = Ru + 3RuO_2 + 6H_2O$$

Comparing the XRD patterns of $Ru(OH)_3$-25 with that of $Ru(OH)_3$-90, one can clearly see that the disproportionation reaction can occur even at a temperature as low as 90˚C during the preparation process.

The catalytic hydrogenation results indicate that Ru metal is the active species for both the supported and unsupported catalysts. The Ru/Al in its reduced form showed pretty decent catalytic activity, and the non-reduced $Ru(OH)_3$/Al demonstrated an activation induction period during the hydrogenation process. However, when a calcination step was applied at temperatures above 300˚C prior to H_2 reduction, the catalytic activity decreased remarkably due to the formation of larger Ru particles. The calcined form of RuO_2/Al also contained Ru metals, but existed as large particles, thus resulting in poor hydrogenation activity.

With unsupported catalyst, both $Ru(OH)_3$-25, and $Ru(OH)_3$-90 showed an activation period, and the hydrogenation rate increased in a short period of time than that of a supported $Ru(OH)_3$/Al, indicating unsupported $Ru(OH)_3$ can be more easily reduced than the supported $Ru(OH)_3$. When $Ru(OH)_3$-90 was treated by either direct reduction with H_2 or calcination-reduction at temperatures up to 400˚C, the obtained catalysts showed substantial activity loss, which could be attributed to the formation of very large Ru metals.

By comparing supported Ru with unsupported catalysts, it was clearly found that alumina support played a crucial role in stabilizing Ru metals, and keeping Ru in high dispersion state.

Conclusions

The catalytic activity of Ru/Al depended greatly on the activation treatment. Thermal treatment in air or in N_2 at temperatures above 300˚C is not ideal catalyst activation procedure, while direct reduction with a hydrogen resulted in catalysts with high activity in the selective hydrogenation of DMM. The characterization data revealed that disproportionation reaction of Ruthenium hydroxide took place during thermal treatment, even at the precipitation temperature as low as 90˚C. The active species for the selective hydrogenation of DMM was highly dispersed Ru metal onto the support. Direct reduction of $Ru(OH)_3$/Al resulted in well dispersed, smaller Ru metal than the indirect reduction involving a calcination pretreatment, thus demonstrating superior catalytic activity. For unsupported $Ru(OH)_3$, direct reduction with H_2 up to 400˚C yielded catalyst with larger Ru metals with poor catalytic activity. When supported on alumina, the agglomeration of Ru could be effectively hindered and reduced Ru species could be preserved in highly dispersed states due to the interaction with alumina.

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References

1. Li F, Chen J, Zhang QH, Wang Y. Hydrous ruthenium oxide supported on Co_3O_4 as efficient catalyst for aerobic oxidation of amines. Green Chem. 2008; 10(5):553-562. doi: 10.1039/B715627H.
2. Costa VV, Jacinto MJ, Rossi LM, Landers R, Gusevskaya EV. Aerobic oxidation of monoterpenic alcohols catalyzed by ruthenium hydroxide supported on silica-coated magnetic nanoparticles. J Catal. 2011; 282(1):209-214. doi:10.1016/j.jcat.2011.06.014.
3. Kim JW, Yamaguchi K, Mizuno N. Heterogeneously catalyzed selective N-alkylation of aromatic and heteroaromatic amines with alcohols by a supported ruthenium hydroxide. J Catal. 2009; 263(1):205-208. doi:10.1016/j.jcat.2009.01.020.
4. Yamaguchi K, Matsushita M, Mizuno N. Efficient Hydration of Nitriles to Amides in Water, Catalyzed by Ruthenium Hydroxide Supported on Alumina. Angew Chem Int Ed. 2004; 43(12):1576-1780. doi: 10.1002/anie.200353461.
5. Kim JW, Koike T, Kotani M, Yamaguchi K, Mizuno N. Synthetic scope of Ru(OH)x/Al_2O_3-catalyzed hydrogen-transfer reactions: an application to reduction of allylic alcohols by a sequential process of isomerization/ Meerwein-Ponndorf-Verley-type reduction. Chemistry. 2008; 14(13):4104-4109. doi: 10.1002/chem.200701917.
6. Madon RJ, Reyes SC, Iglesia E. Primary and secondary reaction pathways in ruthenium-catalyzed hydrocarbon synthesis. J Phys Chem. 1991; 95(20):7795-7804. doi: 10.1021/j100173a046.
7. Sinfelt JH. Catalytic Hydrorogenolysis over Supported Metals. Catal Rev. 1970; 3(1):175-205. doi:10.1080/01614947008076859.
8. Bernas A, Kumar N, Laukkanen P, Vayrynen J, Salmi T, Murzin DY. Influence of ruthenium precursor on catalytic activity of Ru/Al_2O_3 catalyst in selective isomerization of linoleic acid to cis-9, trance-11- and trance-10, cis-12-conjugated linoleic acid. Appl Catal A. 2004; 267:121-133.
9. Milone C, Neri G, Donato A, Musolino MG, Mercadante L. Selective Hydrogenation of Benzene to Cyclohexene on Ru/γ-Al_2O_3. J Catal. 1996; 159(2):253-258. doi:10.1006/jcat.1996.0086.
10. Mazzieri VC, Pascual F, Arcoya A, L'Argentiere PC, Figoli NS. XPS, FTIR and TPR characterization of Ru/Al_2O_3 catalysts.Appl Surf Sci. 2003; 210:222-230.
11. Iyagba ET, Eddy HT, Nwalor JU, Goodwin JG. The effect of chlorine modification of silica-supported Ru on its CO hydrogenation properties. J Catal. 1990; 123:1-11.
12. Reinikainen M, Niemela MK, Kakuta N, Suhonen S. Characterisation and activity evaluation of silica supported cobalt and ruthenium catalysts.Appl Catal A. 1998; 174:61-75.
13. Ragaini V, Carli R, Bianchi CL, Lorenzetti D, Vergani G. Fische-Tropsch synthesis on alumina-supported ruthenium catalysts I. Influence of K and Cl modifiers. Appl Catal A. 1996; 139:17-29.
14. Murata S, Aika K. Removal of chlorine ions from Ru/MgO catalysts for ammonia synthesis. Appl Catal A. 1992; 82:1-12.
15. Murata S, Aika K. Preparation and characterization of chlorine-free ruthenium catalysts and the promoter effect in ammonia synthesis: 2. A lanthanide oxide-promoted Ru/Al_2O_3 catalyst. J Catal. 1992; 136:118-125.
16. Moggi P, Albanesi G, Predieri G, Spoto G. Ruthenium cluster-derived catalysts for ammonia synthesis. Appl Catal A. 1995; 123:145-159.
17. Kadowaki Y, Aika K. Promoter Effect of Sm_2O_3 on Ru/Al_2O_3 in Ammonia Synthesis. J Catal. 1996; 161:178-185.
18. Miyazaki A, Balint L, Aika K, Nakano Y. Preparation of Ru Nanoparticles Supported on γ-Al_2O_3 and Its Novel Catalytic Activity for Ammonia Synthesis. J Catal. 2001; 204:364-371.
19. Bielawa H, Hinrichsen O, Birkner A, Muhler M. The Ammonia-Synthesis Catalyst of the Next Generation: Barium-Promoted Oxide-Supported Ruthenium. Angew Chem Int Ed. 2001; 40:1061-1063.
20. Murata S, Aika K. Preparation and characterization of chlorine-free ruthenium catalysts and the promoter effect in ammonia synthesis: 1. An alumina-supported ruthenium catalyst. J Catal. 1992; 136:110-117.
21. Aika K, Takano T, Murata S. Preparation and characterization of chlorine-free ruthenium catalysts and the promoter effect in ammonia synthesis: 3. A magnesia-supported ruthenium catalyst. J Catal. 1992; 136:126-140.

22. Rosowski F, Hornung A, Hinrichsen O, Herein D, Muhler M, Ertl G. Ruthenium catalysts for ammonia synthesis at high pressures: Preparation, characterization, and power-law kinetics. Appl Catal A. 1997; 151:443-460.
23. Shiflett WK, Dumesic JA. Ammonia synthesis as a catalytic probe of supported ruthenium catalysts: the role of the support and the effect of chlorine.Ind Eng Chem Fund. 1981; 20:246-250.
24. Wang X, Ni J, Lin B, Wang R, Lin J, Wei K. Highly efficient Ru/MgO-CeO_2 catalyst for ammonia synthesis.Catal Commun. 2010; 12:251-254.
25. Park JE, Park ED. Optimal Ru particle size for selective CO oxidation in H_2 over Ru/κ-Al_2O_3. Korean J Chem Eng. 2014; 31:1985-1993.
26. Joo SH, Park JY, Renzas JR, Butcher DR, Huang W, Somorjai GA. Size Effect of Ruthenium Nanoparticles in Catalytic Carbon Monoxide Oxidation.Nano Lett. 2010; 10:2709-2713.
27. Qadir K, Joo SH, Mun BS, Butcher DR, Renzas JR, Aksoy F, et al. Intrinsic Relation between Catalytic Activity of CO Oxidation on Ru Nanoparticles and Ru Oxides Uncovered with Ambient Pressure XPS. Nano Lett. 2012; 12:5761-5768.
28. Gonzalez RD, Miura H. Methanation and Fischer-Tropsch studies on potassium-promoted silica-supported Ru catalysts. J Catal. 1982; 77:338-347.
29. Delmon B, Jacobs PA. Preparation of Catalysts I. Amsterdam: Elsevier; 1975. 761 p.
30. Gong BB, Wang R, Lin BY, Xie F, Yu XJ, Wei KM. Preparation of Carbon Nanotubes (CNTs)-Cordierite Monoliths by Catalytic Chemical Vapor Deposition as Catalyst Supports for Ammonia Synthesis. Catal Lett. 2008; 122:287-294.
31. Wang PY, Zheng XP. Pd/SBA-15 nanocomposite: Synthesis, structure and catalytic properties in Heck reactions. Powder Tech. 2011; 210:115-121.
32. Yu XJ, Lin BY, Gong BB, Lin JX, Wang R, Wei KM. Effect of Nitric Acid Treatment on Carbon Nanotubes (CNTs)-Cordierite Monoliths Supported Ruthenium Catalysts for Ammonia Synthesis.Catal Lett. 2008; 124:168-173.
33. Van der Lee MK, Van Dillen AJ, Bitter JH, de Jong KP. Deposition precipitation for the preparation of carbon nanofiber supported nickel catalysts. J Am Chem Soc. 2005; 127:13573-13582.
34. Li J, Zhan Y, Zhang F, Lin X, Zheng Q. Au/Fe_2O_3 water-gas shift catalyst prepared by modified deposition-precipitation method. Chin J Catal. 2008; 29: 346-351.
35. Lin BY, Wang R, Yu XJ, Lin JX, Xie F, Wei KM. Physicochemical Characterization and H_2-TPD Study of Alumina Supported Ruthenium Catalysts. Catal Lett. 2008; 124:178-184.
36. Zonetti PC, Landers R, Cobo AJG. Thermal treatment effects on the Ru/CeO_2 catalysts performance for partial hydrogenation of benzene.Appl Surf Sci. 2008; 254:6849-6853.
37. Nagai M, Koizumi K, Omi S. NH_3-TPD and XPS studies of Ru/Al_2O_3 catalyst and HDS activity. Catal Today. 1997; 35:393-405.
38. Zhang J, Xu HY, Ge QJ, Li WZ. Highly efficient Ru/MgO catalysts for NH_3 decomposition: Synthesis, characterization and promoter effect. Catal Commun. 2006; 7:148-152.
39. Koopman PGJ, Kieboom APG, van Bekkum H. Characterization of ruthenium catalysts as studied by temperature programmed reduction.J Catal. 1981; 69:172-179.
40. Koopman PGJ. Ruthenium Hydrogenation Catalysts Activation Characterization Application. Thesis, Delft University Press. 1980.
41. Narita T, Miura H, Ohira M, Hondou H, Sugiyama K, Matsuda T, et al. The effect of reduction temperature on the chemisorptive properties of Ru/Al_2O_3: Effect of chlorine.Appl Catal. 1987; 32:185-190.
42. Echeverri DA, Marín JM, Restrepo GM, Rios LA. Characterization and carbonylic hydrogenation of methyl oleate over Ru-Sn/Al_2O_3: Effects of metal precursor and chlorine removal. Appl Catal A. 2009; 366:342-347.