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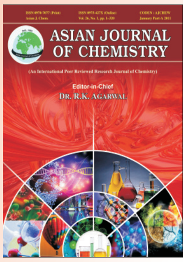

Characterization of Ru/Al_2O_3 System Prepared by Adsorption-Precipitation Method

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Alumina-supported Ru catalysts with different metal content were prepared *via* the adsorption-precipitation method using $RuCl_3$ as the precursor and characterized by temperature-programmed reduction and XRD techniques. These catalysts were evaluated using selective hydrogenation of dimethyl maleate as a probe reaction and results revealed that superior catalytic performances were obtained at mild hydrogenation conditions (1.0 MPa and 70 °C). From the temperature-programmed reduction results, several states of ruthenium on the support can be discerned and the proportion of ruthenium species reducible at the low temperature (95 ± 5 °C) decreased with increasing ruthenium loading and was largely influenced by pretreatment conditions. It has been confirmed that ruthenium species that can be reduced at low temperature may mainly contributed to the catalytic activity. On the basis of the above findings, effective turnover number was introduced to better evaluate the catalytic performance.

Keywords: Adsorption-precipitation, Ru/Al_2O_3, Temperature-programmed reduction, Dimethyl maleate.

INTRODUCTION

Ruthenium catalysts have been the subject of a variety of studies due to their relevance in hydrogenolysis of paraffins and olefins[1], selective hydrogenation of benzene and chloronitrobenzene[2-4], Fischer-Tropsch synthesis[5], ammonia synthesis[6] and methanation of CO and CO_2[7,8].

Many papers have been published on the supported-ruthenium catalysts and usually prepared by incipient wetness impregnation method using ruthenium chloride as the precursor due to its relative low cost and availability[9]. However, it was found that chlorine greatly affected the catalytic activity and the residual chlorine could not be completely removed even reduced at 900 K[10]. Also, pre-calcination treatment of the fresh catalyst caused a negative effect on the catalytic performance, while the catalyst sample activated by direct reduction was more effective[11,12].

In order to overcome these problems, an adsorption-precipitation method was developed to prepare the supported-Ru catalysts. It has been shown direct reduction of $Ru(OH)_3/Al_2O_3$ gave rise to an efficient Ru/Al_2O_3 catalyst for hydrogenation of dimethyl maleate and the active species has been confirmed to be Ru^0 metal[13]. Recent results indicated this catalyst system has some special features. First, pre-calcination in air or Ar prior to reduction of $Ru(OH)_3/Al_2O_3$ resulted in pretty low catalytic activity. Second, variation of direct reduction temperature strongly affects the catalytic behaviour. Hence, the object of this paper is to study the effects of pretreatment conditions on the catalytic performance, aiming at a deep understanding the catalytic nature of this catalyst system.

EXPERIMENTAL

A commercial Al_2O_3 (Yantai, Henhui Chemical Company) with specific surface area of 308 m^2/g was used as the support. The received material was calcined at 500 °C for 4 h prior to use. $RuCl_3{\cdot}xH_2O$, purchased from a commercial company, was used as received.

A series of supported Ru catalysts were prepared using the adsorption-precipitation method as follows:

(1) Adsorption: The support was added into a water solution of $RuCl_3{\cdot}xH_2O$ and variation of concentration of $RuCl_3$ was used to regulate the Ru content. The mixture was stirred at room temperature for 4 h.

(2) Precipitation: 1M NaOH solution was added to the mixture till the pH reaches about 9. After further stirring for another 4 h, the slurry was filtered and the solid phase, washed thoroughly with de-ionized water until pH = 7, was dried in air at room temperature.

(3) Activation: The thus obtained samples, denoted as $xRu(OH)_3/Al$ (x is the Ru loading in wt. percentage) were subjected to different pretreatments as listed in Table-1. For

TABLE-1
CATALYST CODES AND PRETREATMENT PROCEDURES

Catalyst code	Ru content (%)	Pretreatment procedure
0.5Ru(OH)$_3$/Al	0.5	No pretreatment
0.5Ru/Al-H400	0.5	Reduced in pure H$_2$ flow at 400 °C for 120 min
0.5Ru/Al-H100	0.5	Reduced in pure H$_2$ flow at 100 °C for 120 min
0.5Ru/Al-LR	0.5	Reduced in methanol solution under hydrogen pressure of 1 MPa and 70 °C
1.0Ru(OH)$_3$/Al	1.0	No pretreatment
1.0Ru/Al-H400	1.0	Reduced in pure H$_2$ flow at 400 °C for 120 min
1.0Ru/Al-H100	1.0	Reduced in pure H$_2$ flow at 100 °C for 120 min
1.0Ru/Al-LR	1.0	Reduced in methanol solution under hydrogen pressure of 1 MPa and 70 °C
2.0Ru(OH)$_3$/Al	2.0	No pretreatment
2.0Ru/Al-H400	2.0	Reduced in pure H$_2$ flow at 400 °C for 120 min
2.0Ru/Al-H100	2.0	Reduced in pure H$_2$ flow at 100 °C for 120 min
2.0Ru/Al-LR	2.0	Reduced in methanol solution under hydrogen pressure of 1 MPa and 70 °C
5.0Ru(OH)$_3$/Al	5.0	No pretreatment
5.0Ru/Al-H400	5.0	Reduced in pure H$_2$ flow at 400 °C for 120 min
5.0Ru/Al-H100	5.0	Reduced in pure H$_2$ flow at 100 °C for 120 min
5.0Ru/Al-LR	5.0	Reduced in methanol solution under hydrogen pressure of 1 MPa and 70 °C
Ru-H400	100	Unsupported Ru sample reduced in pure H$_2$ flow at 400 °C for 120 min

comparison reasons, unsupported Ru(OH)$_3$ was also prepared in the same way without addition of support.

Catalytic reaction: The hydrogenation reaction was conducted in a 200 mL batch reactor at 1 MPa and 70 °C. After placing 10 g dimethyl maleate dissolved in 90 mL anhydrous methanol, the reactor was purged three times with nitrogen gas to remove air in order to ensure an inert atmosphere. Hydrogen was then used to purge out the nitrogen. The reactor was heated to 70 °C without stirring and then the pressure was adjusted to 1 MPa with a pressure regulator. To start the reaction, the speed of agitation was adjusted to 675 rpm. During the reaction, consumption rate and cumulative amount of consumed hydrogen were recorded *via* a mass flow meter. The products were analyzed by GC equipped with FID and a HP-5 column and verified by GC-MS.

Temperature-programmed reduction: H$_2$-TPR was carried out on a Finsorb instrument as follows: After loading the catalyst sample (30-150 mg), the system was purged in Ar for 0.5 h prior to the temperature-programmed reduction test. Typically, the temperature was ramped from room temperature to 400 °C at a rate of 10 °C/min in a continuous flow of a H$_2$/Ar gas mixture (10 % H$_2$). H$_2$ consumption was measured both by a thermal conductivity detector (TCD) and an on-line mass spectrometer.

X-ray diffraction: Powder X-ray diffraction was recorded on a Bruker D8 Advance instrument with CuK$_\alpha$ radiation (λ = 0.15406 nm). 2θ angles ranged from 5 to 80 °C.

RESULTS AND DISCUSSION

The catalytic activities were investigated at a moderate condition of 70 °C and 1 MPa in a batch reactor using methanol as a solvent and the results are presented in Fig. 1. For all the hydrogenations, the reaction selectivity was nearly 100 % as identified from GC-MS analysis. The results of catalytic performances show that the conversion on each sample is nearly 100 %, which was supported by LC analysis of the reaction mixture.

Comparing the data of samples with different pretreatments, it can be found that samples reduced in liquid phase demonstrate the best performance, followed by the sample

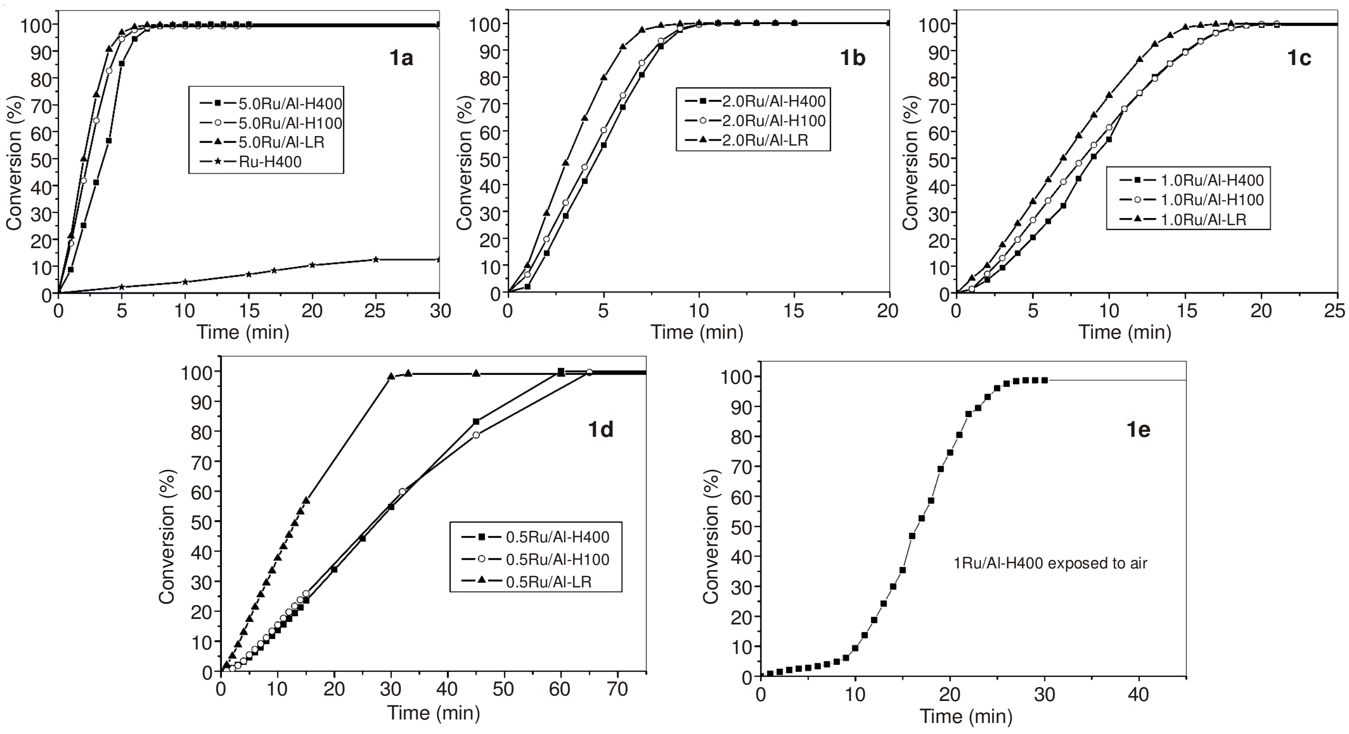

Fig. 1. Catalytic performances of catalyst samples

reduced at 100 °C and then the one reduced at 400 °C. In addition, supported Ru samples had a far better catalytic performance than the unsupported Ru catalysts.

For the samples with different Ru content, it is obvious that the reaction rate increases with the Ru loading. Here, the samples reduced in H_2 flow at 400 °C are taken as examples. The conversion is 100 % in 8 min for 5 Ru/Al-H400, 12 min for 2 Ru/Al-H400, 18 min for 1 Ru/Al-H400 and 33 min for 0.5 Ru/Al-H400. When turnover frequency (TOF) was introduced to evaluate the catalytic performance, the TOF of 5 Ru/Al-H400 was 125 min^{-1}, 208 min^{-1} for 2 Ru/Al-H400, 263.2 min^{-1} for 1 Ru/Al-H400 and 166.7 min^{-1} for 0.5Ru/Al-H400, assuming all Ru on the support take part in the catalytic reaction.

The catalytic performance of the 1 Ru/Al-H400 exposed to air for 3 days is showed in Fig. 1e. An induction period is observed at the beginning of the first 10 min. After that, catalytic rate increase rapidly. This issue will be documented later.

XRD studies: XRD patterns of the samples reduced in H_2 flow at 400 °C are displayed in Fig. 2. There is no obvious diffraction peak of ruthenium for the supported catalysts, indicating a well dispersion of ruthenium on the support. However, it displays that characteristic diffraction peaks of metal ruthenium appear for the unsupported ruthenium catalyst. Hence, it has been inferred that alumina plays a crucial role in dispersing Ru species.

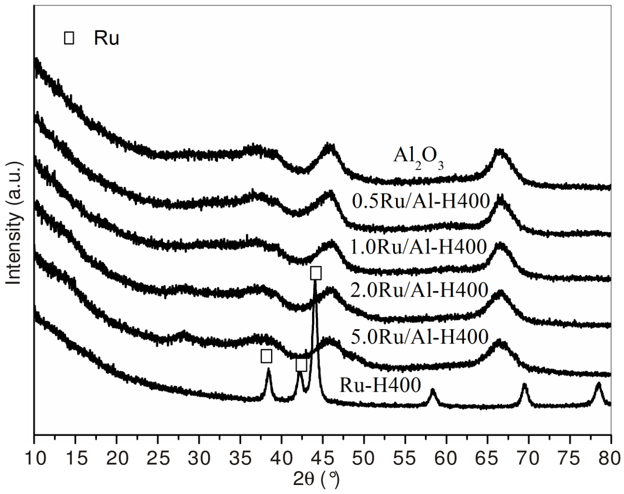

Fig. 2. XRD patterns of the samples pretreatment in H_2 flow at 400 °C

Temperature-programmed reduction studies: The temperature-programmed reduction profiles of fresh samples with different Ru contents were presented in Fig. 3. It was observed that states of Ru species on the support were distinct with different Ru contents. Profile of 0.5 Ru/Al showed that there was only one peak at a low temperature. With increasing Ru content, a weak peak 245 ± 5 °C appeared, as shown in the Figure for the 1 Ru/Al and 2 Ru/Al. Moreover, a peak at high temperature was observed for 2 Ru/Al. When the Ru content increased to 5 %, a totally different result was obtained. There was a sharp peak at low temperature and a broad peak from 180 to 300 °C.

In all, though the states of Ru have been not definitely distinguished, Ru species that could be reduced at low temperature existed on all these catalysts. To better evaluate these catalysts, the ratio of the areas of peak at low temperature (AL) to the total areas [the areas of low temperature (AL), middle temperature (AM) and high temperature (AH)] were calculated and the results are presented in Table-2. It is clear that the proportion of Ru species reducible at low temperature decreased with the increase of Ru content.

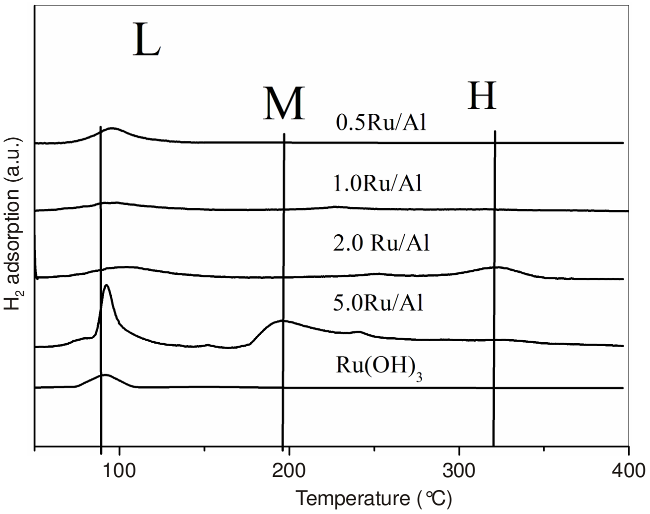

Fig. 3. Temperature-programmed reduction profiles of fresh samples with different Ru content

TABLE-2
RATIO OF THE AREA OF PEAKS

Catalysts code	A_L/A_M+A_H+AL	Effective Ru content*(%)
Cat-0.5 fresh	1.00	0.50
Cat-1 fresh	0.80	0.80
Cat-2 fresh	0.51	1.02
Cat-5 fresh	0.25	1.25

$$^{*}\text{Effective Ru content} = \text{Ru content} \times \frac{A_L}{A_L + A_M + A_H}$$

Fig. 4 shows the temperature-programmed reduction profiles of samples which have been pre-reduced in H_2 flow at 100 °C and Fig. 5 presents the temperature-programmed reduction profiles of samples pre-reduced in liquid phase. 5 Ru/Al-H100 and 5 Ru/Al-LR display reduction peaks at middle temperature and high temperature, indicating pre-reduction treatment can only reduce a proportion of Ru species. The same results were obtained for the samples with 2 % loading. For samples with a Ru loading less than 2 %, no obvious peaks were observed. Thus, it can be said that only Ru metal presented in both 1 Ru/Al-H100 and 1 Ru/Al-LR, suggesting $Ru(OH)_3$/Al with lower Ru loading could be reduced completely by reduction treatment either in liquid phase or in H_2 flow at 100 °C. When 1 Ru/Al-H400 was exposed to air at room temperature for three days, reduction peaks appear in the temperature-programmed reduction profile as shown in Fig. 6. This confirms that Ru metal on the support can be oxidized with air at ambient conditions. Thus, pre-reduced 1 Ru/Al-H400 catalyst exposed to air for three days showed an induction period.

Therefore, combining the temperature-programmed reduction results with those of the catalytic performances, it is concluded that Ru species reducible at low temperature mainly

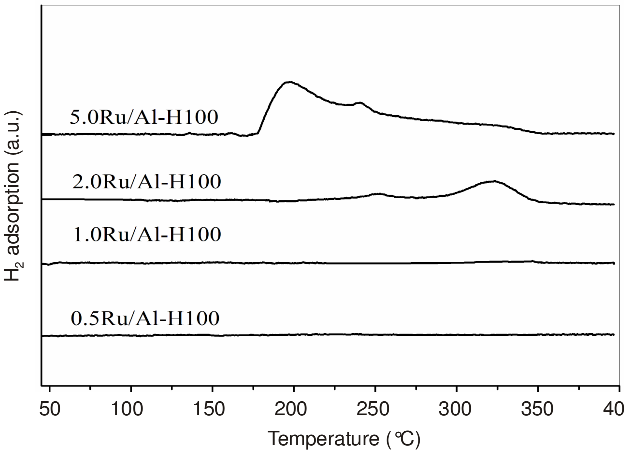

Fig. 4. Temperature-programmed reduction profiles of samples pre-reduced in H_2 flow at 100 °C for 120 min

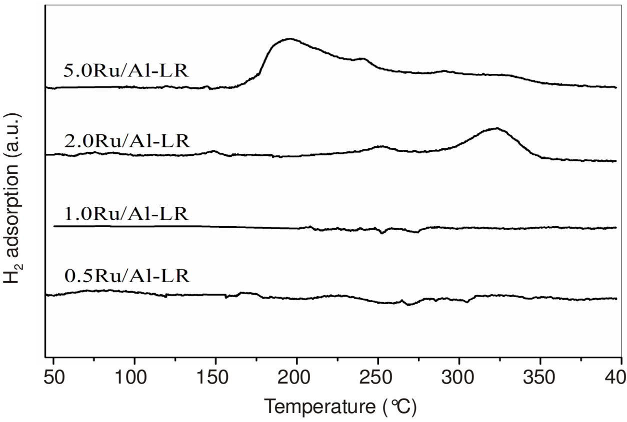

Fig. 5. Temperature-programmed reduction profiles of samples that pre-reduced in liquid phase

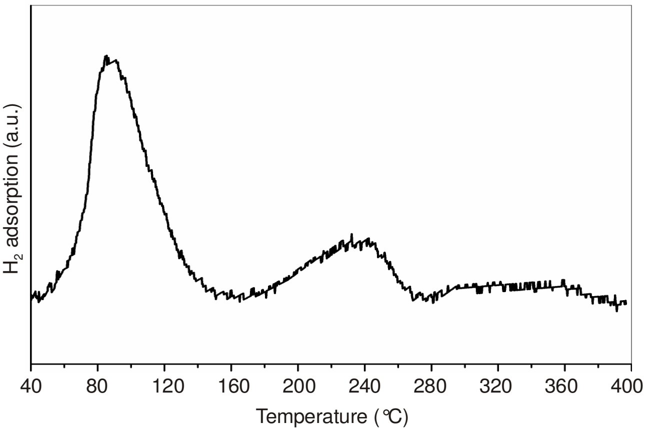

Fig. 6. Temperature-programmed reduction profile of 1 Ru/Al-H400 exposed to air for three days

contribute to the catalytic activity, which accounts well for the higher activity with catalyst samples activated at lower temperatures. As a result, the use of turnover frequency (TOF) mentioned above is incorrect in evaluating the catalytic performance of the catalyst system. The relationship between TOF and Ru content, presented in Fig. 7, indicates that there is no certain correlation between them. So, in order to assess the catalytic performance objectively, effective turnover number (ETOF) should be introduced and it is defined as below:

$$ETOF = \frac{m_{(DMM)}}{E * t_{(min)}}$$

where: m is the converted dimethyl maleate, t is the reaction time and E is effective Ru content which can be obtained by the temperature-programmed reduction characterization. Thus, for the samples reduced at 400 °C, the calculated ETOFs are plotted against the effective Ru contents (Table-2) and demonstrates a good linear correlation with a R value of 0.995 (Fig. 7). This result clearly indicates that the ratio of active centers to effective Ru content is constant for these catalyst samples, suggesting highly dispersed Ru metal is the active sites.

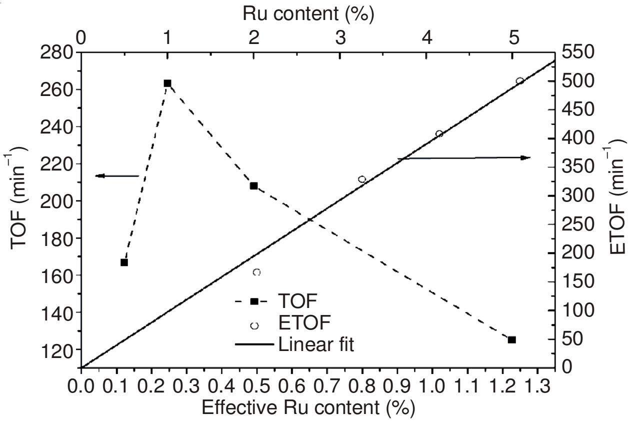

Fig. 7 Linear fit between ETOF and effective Ru content

Conclusion

Superior catalysts prepared by adsorption-precipitation method using $RuCl_3$ as precursor are obtained. The perfect catalytic result is ascribed to the well dispersed Ru metal on the support, which can be obtained via activating by direct reduction.

On the basis of characterization data, it is confirmed that Ru species reducible at low temperature, the ratio of which to total loading decrease with the increase of Ru content supported on alumina, mainly contribute to the catalytic activity. For that reason, ETOF is introduced to evaluate the catalytic performance objectively. A good linear correlation between ETOF and effective Ru contents suggests that the ratio of the active centers to effective Ru content is almost the same on the supported catalyst samples.

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