Characterization of bimetallic Ru-Sn supported catalysts and hydrogenation of 1,4-cyclohexanedicarboxylic acid

Zhu Zhiqing\textsuperscript{a,}\textsuperscript{*}, Lu Zihong\textsuperscript{a}, Li Bin\textsuperscript{a}, Guo Shizhuo\textsuperscript{b}

\textsuperscript{a} Department of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, PR China
\textsuperscript{b} Chemical Research Institute, Shanghai Petrochemical Co. Ltd., Shanghai 200540, PR China

Received 26 August 2005; received in revised form 24 December 2005; accepted 4 January 2006
Available online 17 February 2006

Abstract

The supported catalysts were prepared by coimpregnation with aqueous solutions of ruthenium and tin salt and characterized by temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), carbon monoxide (CO) and oxygen (O\textsubscript{2}) chemisorption measurements. The surface of the reduced Al\textsubscript{2}O\textsubscript{3}-based bimetallic catalysts would be composed of metallic ruthenium and Sn(II) species. No evidence for substantial amounts of Sn(0) is found on reduced catalysts by XPS measurement. Based on the available evidence from the various techniques, the authors suggested that the high selectivity of the bimetallic Ru-Sn/Al\textsubscript{2}O\textsubscript{3} catalyst for production of 1,4-cyclohexanediol would be due to the action not only of the promoter (Sn) but also of the support (alumina).

Catalytic hydrogenation of 1,4-cyclohexanedicarboxylic acid to 1,4-cyclohexanediol over Ru-Sn supported catalysts was studied as functions of catalyst composition as well as various catalyst preparation parameters. Hydrogenation activity was affected by the kind of tin compounds and supports used for the preparation of the Ru-Sn catalyst. Stannous chloride and alumina were found to be the appropriate materials for the hydrogenation of –C=O group over the Ru-Sn catalysts. The yield for the 1,4-cyclohexanediol on Ru-Sn/Al\textsubscript{2}O\textsubscript{3} catalyst increased with Sn/Ru atomic ratio, reaching a maximum at a value of Sn/Ru = 1:1, which suggested a promotion of the –C=O bond hydrogenation by particular bimetallic Ru-Sn ensembles. The Ru-Sn/Al\textsubscript{2}O\textsubscript{3} catalysts without any calcination activated in a hydrogen stream at 550 °C were effective for the hydrogenation of 1,4-cyclohexanediylcic acid. Finally, we verified the durability of our catalyst by carrying out a catalyst-recycling test over five cycles.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Ru-Sn catalysts; 1,4-Cyclohexanedicarboxylic acid; 1,4-Cyclohexanediol

1. Introduction

1,4-Cyclohexanediol (CHDM) is useful in polyester paints and in synthetic fibers and synthetic resins of a polyester type and is used particularly as a material for resins and fibers having excellent thermal resistance, weather resistance and physical strength. On an industrial scale, CHDM has been made by a process in which dimethyl terephthalate is subjected to hydrogenation using a catalyst of Ru or Pd that is carried on a support to yield dimethyl cyclohexanedicarboxylate, and then a side chain of the resulting ester is subjected to a hydrogenation reaction in the presence of Cu–Cr oxide catalyst to manufacture CHDM. It is particularly preferred from an economic view to use terephthalic acid (TPA) as a starting compound instead of a dimethyl terephthalate, because esterification is not necessary. In recent years, a new process of the hydrogenation from TPA to CHDM by two-stages has been extensively explored by researchers. Ruthenium and palladium are well known as suitable catalysts for selective hydrogenation of an aromatic ring to cyclohexane and its derivatives [1–4]; a process for producing 1,4-cyclohexanedicarboxylic acid (CHDA) by treating TPA with hydrogen using water as the solvent in the presence of a catalyst containing Pd or Ru was described [5–7]. Therefore, the key technology for effective production of dioils and utilization of fatty acids as chemical resources is the hydrogenation of carboxylic acid. With regard to a process for hydrogenation of the –C=O group in carboxylic acid or carboxylate, a catalyst containing ruthenium and/or platinum and tin has been proposed [8–10]. Toba and Tanaka [11] made
Ru-Sn catalyst by different methods, and hydrogenated different dicarboxylic acids to respective dialcohols. Tahara et al. [12] prepared a series of Ru-Sn supported catalysts with different starting materials and supports, to be used for the hydrogenation of dicarboxylates.

It is our purpose to hydrogenate CHDA to CHDM in high yield on the supported Ru-Sn as a catalyst prepared by a more practical coimpregnation method. In this paper, we report the behavior of Ru-Sn supported catalyst prepared with different raw materials and through changing composition of Ru-Sn. Our objective was to develop an effective catalyst for hydrogenating the title compound to the corresponding dialcohol and to examine the relationship between catalyst properties and hydrogenation profiles. We also tested the application durability of the Ru-Sn/Al2O3 catalyst.

2. Experimental

2.1. Preparation of the Ru-Sn supported catalysts

The preparation of the supported Ru-Sn catalyst with different Ru/Sn ratios by coimpregnation method is described as follows. Appropriate quantities of aqueous solutions of RuCl3·3H2O and SnCl2·2H2O (except for SnCl4·5H2O as mentioned) are mixed in a beaker. A weighed amount of support was impregnated with the aqueous solution by the conventional incipient wetness technique. This paste was aged for 15 h at room temperature and dried at 70 °C in vacuum for 5 h. The catalysts were activated by heating at high temperature in H2 flow of 200 ml min⁻¹ for 2 h and cooled under hydrogen atmosphere, then moved into reaction solvent in an autoclave. All catalysts were prepared so as to obtain a ruthenium content of 5 wt.%, while the tin content was varied in order to obtain different Sn/Ru atomic ratios.

2.2. Hydrogenation reaction

The hydrogenation reactions were carried out in a stainless-steel autoclave (volume: 300 ml) that is equipped with a mechanical stirrer. The autoclave was charged with 15 g of CHDA as starting material, 4 g of catalyst and 150 ml deionized water as a solvent. After purging with hydrogen at 0.2 MPa for three times, hydrogen was introduced to a pressure of 2.0 MPa and then the autoclave was heated. When the temperature was gradually raised to 230 °C, hydrogen was introduced again to a pressure of 10.0 MPa, and the reaction was allowed to proceed for 4 h. At the end of the reaction, the autoclave was cooled to room temperature.

2.3. Analysis of hydrogenation products

The products of the hydrogenation of CHDA were analyzed on a gas chromatograph (GC-9800) equipped with a 0.32 mm × 30 m capillary column (OV-1701). An internal standard method was used to precisely calculate the content of CHDM in the hydrogenation product. The acid value of the reaction solution was also analyzed for estimating the conversion of CHDA.

2.4. Temperature-programmed reduction (TPR)

TPR experiments were performed in a laboratory-made apparatus consisting of a gas supply system, a quartz tubular reactor with a sample of the catalyst bed, a water vapor trap and a Thermal Conductivity Detector. The catalytic sample was swept by pure nitrogen at 150 °C for 2 h. After cooling, it was treated with 20 °C min⁻¹ linear rise in temperature from 50 °C to 600 °C under a 10 vol.% H2/N2 flow. The hydrogen consumption peak is the consequence of the reduction process of the metal precursor on the support that was obtained after drying.

2.5. X-ray photoelectron spectroscopy (XPS)

XPS tests were made on samples prereduced at 550 °C for 2 h in a separate reactor under a flow of hydrogen and passivated in nitrogen. XPS analyses were performed on a MicroLab 310-F electron spectrometer fitted with an Al Kα radiation (1486.6 eV) operated at 10 kV and 10 mA. The ion pumper analysis chamber was maintained below 10⁻¹¹ Torr during the data acquisition. The calibration of the spectra was performed with the Al 2p line (74.4 eV) from the Al2O3 support.

2.6. CO or O2 chemisorption

Chemisorption of CO or O2 has been performed using a conventional pulse system operating at 260 K temperature. After reduction with H2 at 550 °C for 2 h, the catalyst was cooled down under hydrogen flow. A fixed amount of gas was then periodically injected into the H2 stream over the sample and carbon monoxide or oxygen not adsorbed on the catalyst was analyzed with a TC detector.

2.7. BET surface and pore diameter

The characterization of the porous structure of supports was carried out by physical adsorption of N2 at 77 K by using a Micromeritics ASAP 2010 apparatus.

3. Results and discussion

3.1. Temperature-programmed reduction of supported Ru-Sn catalysts

In Fig. 1, the effect of the supports on the TPR profiles of supported Ru-Sn catalysts with Sn/Ru atomic ratio of 1.0 is presented. The differences in the H2 consumption patterns of different samples after impregnation and drying reflect the changes in reduction behaviors. For the alumina and titania supports, the two consumption peaks around 300 °C result from the free Ru and the Ru-Sn(II) interaction. These features can also be rationalized by assuming that tin deposits preferentially
in sites with strong interaction with alumina. Moreover, the H₂ consumption of sample reveals that the tin–titania interaction is stronger than the tin–alumina one. However, the TPR profiles of Ru-Sn/kieselguhr and Ru-Sn/zirconia catalysts showed only one H₂ consumption peak each. These results indicate that practically no free Ru was detected in bimetallic catalysts by TPR measurement, because of the Ru-Sn(II)–support surface complex that was formed.

The effect of the tin content on TPR profiles of Ru-Sn/Al₂O₃ catalyst precursors is presented in Fig. 2. It must be noted that no hydrogen consumption peak was observed up to 600 °C on the TPR profile of monometallic Sn/Al₂O₃, which indicated that tin would not be reduced to a low valence state in the presence of Cl. This is completely different from the previous TPR results reported by Sexton et al. [13]. They reported that the decomposition and probable reduction of bulk SnO₂ supported on alumina was observed between 200 °C and 600 °C. On the other hand, one hydrogen consumption peak was observed on the TPR profile of monometallic Ru/Al₂O₃, thus being attributed to free Ru formed on support. However, we can see that the addition of tin increases the hydrogen consumption and that the maximum temperature of the reduction step increases with Sn/Ru ratio. In our system with a lower ratio (0 ≤ Sn/Ru ≤ 0.7) which is easily reducible, only one reduction peak is observed with a maximum at 240–310 °C. For such low tin contents all the Sn-chlorinated would be in direct contact with ruthenium and would experience catalytic hydrodechlorination by ruthenium. Consequently, a possible trace of free Ru can exist together with a large portion of Ru species that interact with Sn(II). The TPR profiles for Su/Ru ≥ 1.0 present two distinct reduction peaks. The maximum temperature for the reduction step is known to increase with the incorporation of Sn; the H₂ consumption peak around 250 °C is due to the free Ru and that around 350 °C can be ascribed to Ru that interacted with Sn(II). There would be no free Sn species for the bimetallic Ru-Sn Al₂O₃ system because we did not observe a distinct peak at the higher temperature above 600 °C at which the Sn-chlorinated supported on carbon has been known to uptake H₂ [14].

### 3.2. X-ray photoelectron spectroscopy

XPS test was made on the reduced catalyst for a Sn/Ru atomic ratio of 1.0 in order to see the changes in electronic states of the metals. Reference binding energies were Al 2p 74.4 eV, which gave values for Sn⁰, Sn(II, IV) and Ru⁰ of 484.8 eV, 486.7 eV and 280.1 eV, respectively, but one is unable to separate Sn(II) and Sn(IV) in XPS analyses [15]. From the results shown in Fig. 3, the XPS spectra of Ru 3d on surface of catalyst are not very clear because the peaks of Ru 3d and C 1s overlapped each other, but the catalyst shows a small shoulder at 280.0–280.3 eV, which may be assigned to Ru⁰ in accordance with the literature [16]. The Sn 3d XPS spectra of the reduced sample show a peak at 486.5–486.8 eV corresponding to Sn(II) and/or Sn(IV) species in Fig. 4. Due to the fact that the catalysts were prepared by coimpregnation techniques from SnCl₂ compound without calcinations, it is reasonable to suppose that tin exists in oxidation states of Sn(II) in major concentration on the surfaces of reduced samples. No evidence for metallic tin can be seen from XPS studies. According to these results and TPR data, we can say that the surface of the reduced bimetallic Ru-Sn/Al₂O₃ catalysts is composed of metallic ruthenium and...
Sn(II) species. The tin is tightly bonded (via oxygen) to the alumina support and may act as an electronic promoter [13].

3.3. Chemisorption of the Ru-Sn/Al2O3 catalysts

Figs. 5 and 6 show the results of carbon monoxide (CO) and oxygen (O2) chemisorption studies of the bimetallic Ru-Sn/Al2O3 catalysts. These results show that the catalysts had poor capacity for CO adsorption and high capacity for O2 adsorption. It is generally known that CO is chemisorbed on neither Sn nor alumina surfaces irreversibly. It is considered that CO was chemisorbed only on the Ru surface in the Ru-Sn bimetallic system. On the other hand, O2 was chemisorbed both on the Ru and Sn because of the high affinity of Sn for oxygen atoms [17].

We can see in Fig. 5 that increasing the reduction temperature decreased slowly the amount of adsorbed CO, whereas O2 adsorption capacity remarkably increased. The low adsorption capacity of CO at higher reduction temperature seems to indicate the sintering of Ru particles, while a great increase of adsorption capacity of O2 suggests that the tin-rich surfaces in the Ru-Sn/Al2O3 catalysts were formed. Consequently, the reduction temperature affected the adsorbed characteristics of Ru-Sn/Al2O3 bimetallic catalyst surface.

The results in Fig. 6 show the effect of tin content on carbon monoxide and oxygen adsorption of the catalysts. A low adsorption capacity of O2 in Sn/Ru ratio of 0 and no increase of adsorption capacity of CO on increasing Sn/Ru ratio is agreement with the suggestion of a chemisorption mechanism mentioned above. We can see that amounts of absorbed gas decreased with an increase in Sn/Ru ratio from 0.4 to 1.3 from Fig. 6. These results reveal that the surface Ru concentration would be decreased with an increase of Sn content. Therefore, the high Sn surface concentration brought about the decrease of selective adsorption capacity of CO. However, smaller decrease of adsorption capacity of O2 was the effect of varying surface Ru and Sn concentrations. From these results, it can be inferred that the incorporation of tin into the Ru/Al2O3 catalyst has a large influence on the adsorbed characteristics of the catalyst surface.

3.4. Hydrogenation of 1,4-cyclohexanedicarboxylic acid over Ru-Sn/Al2O3 catalysts

In order to discuss the hydrogenation yield, we show a simplified reaction schema for CHDA hydrogenation to CHDM in Fig. 7. The 1,4-cyclohexane-hydroxymethyl carboxylic acid (CHMA) formed by hydrogenating one carboxylic group of CHDA can be regarded as an intermediate in the consecutive
pathway towards CHDM. The yield for CHDM was defined as the amount of this product referred to the total amount of the products including the intermediate CHMA.

3.4.1. Effect of supports on the Ru-Sn catalysts

The results of the hydrogenation of CHDA over supported Ru-Sn catalyst prepared by the coimpregnation method with differential supports are shown in Table 1. The activity of the catalysts depends on their support and decreases in the order of alumina > titania > kieselguhr ~ zirconia. By comparison, BET surface area of supports decreases also in the same order, but the average pore diameter increases in the opposite order. It is clear that a direct relation would be established between the surface structure of the supports and the catalytic activity of the Ru-Sn catalysts supported on them. From Fig. 1 and Table 1, the changes in activity with support may be not only a result of changes in dispersion of Ru-Sn species, but also of the interaction of Ru-Sn with support. The bimetallic Ru-Sn catalyst supported on alumina gave the desired product CHDM in 97.9% yield with a conversion of 99.2%. Alumina is the best support for the hydrogenation of CHDA to CHDM.

3.4.2. Effect of the atomic ratio Sn/Ru in the catalyst

In order to examine the effect of the tin content on bimetallic Ru-Sn/Al₂O₃ catalysts, we have prepared a series by varying the tin content; the effect of the tin content on the activity of catalyst is shown in Fig. 8. The conversion of CHDA was not significantly changed, but yields for CHDM depended on the composition of the catalysts. The monometallic Ru/Al₂O₃ (Sn/Ru = 0) catalyst showed a poor yield (2.9%) for CHDM but a high conversion (97.2%) of CHDA. In this case, a considerable amount of CHMA was obtained, which was the intermediate in the consecutive hydrogenation pathway. This result means that the catalytic activity is not enough for the reaction to go towards completion under the prescribed conditions. With increasing tin contents up to a Sn/Ru atomic ratio of 1.0, the intermediate of this kind gradually decreases and the CHDM yield simultaneously increases. However, the further addition of Sn led to a decrease in the CHDM yield. By comparison with the results of Figs. 2, 6 and 8, we can see that the activity of catalyst is proportional to the amount of hydrogen consumed in TPR and inversely proportional to the amount of CO adsorbed. When tin contents increase, the activation of hydrogen by Ru goes weaker and the adsorption of carboxylic group by Sn(II)-rich surface goes stronger. This will decrease the catalytic activity of the catalyst system because the carboxylic group will be strongly adsorbed on the active site of the catalyst, which will prevent hydrogen from reaching the catalyst surface [17].

As a result, an optimal value of Sn exists from the viewpoint of catalytic activity and it is important to understand the amount of Sn needed for maximizing the performance in our catalyst system.

3.4.3. Effect of reduction temperature

We have studied the effect of reduction temperature on the activity of Ru-Sn/Al₂O₃ catalyst. The results of CHDA hydrogenation catalyzed by catalyst that was reduced at different temperature are shown in Fig. 9. It should be noted that the reduction temperature had more effect on the yield for CHDM than on CHDA conversion as shown in the same figure. The yield for CHDM was increased by increasing the reduction temperature from 400 °C to 550 °C. From the results of Figs. 5 and 9, it is evident that the yield for CHDM is proportional to the amount of O₂ absorbed and inversely proportional to the amount of CO adsorbed. It is well known that the Sn(II) species attracts and activates the carboxylic group of substrate and then the hydrogen activated on Ru(0) metal by dissociation.
migrates to the carboxylic group to result in the product desired [18]. As is generally known, chlorides can be a poison to the noble metal catalysts on alumina and may drastically change the activity and selectivity of final catalyst [8,19,20]. The presence of Cl inhibited the hydrogenation of \(-\text{C}==\text{O}\) group with the Ru-Sn catalyst which was prepared from SnCl\(_2\) [12,14]. Therefore, most Cl could be removed at higher reduction temperature, because a catalytic hydrodechlorination of SnCl\(_2\) by free Ru to form Sn(II)-rich surface on Ru-Sn/Al\(_2\)O\(_3\) catalyst would be accelerated. The removed Cl and Ru-Sn(II) interaction may be important for the hydrogenation activity of CHDA by promotion to enhance the affinity to oxygen molecules. However, the hydrogenation over the Ru-Sn/Al\(_2\)O\(_3\) catalysts reduced at 600 °C gave a decreased yield. It is reasonable to suppose that an amount of hydrogen molecule attached to the surface would be decreased because of the Ru particles on catalyst growing up by sintering. Consequently, the Ru-Sn/Al\(_2\)O\(_3\) catalyst reduced around 550 °C without calcinations seems to be the optimum.

3.4.4. Effect of starting material of Sn on catalytic activity and selectivity

We have prepared the supported Ru-Sn catalysts by coimpregnation method without calcinations using various tin compounds. The Ru-Sn/Al\(_2\)O\(_3\) catalyst prepared from SnCl\(_2\) gave CHDM in a high yield in comparison with that prepared from SnCl\(_4\) as shown in Table 2. The effect of starting material of Sn on catalytic activity and selectivity is quite significant. Toba and Tanaka [11] reported that the optimum oxidation states of ruthenium and tin existing in Ru-Sn catalyst are zero and two, respectively. Kikuchi et al. [18] illustrated that when the actual oxidation state of tin in the Ru-Sn catalyst was zero or four, the conversion and selectivity were quite low. But when it was two, the catalyst proved to be active. Apparently, the catalyst prepared from SnCl\(_4\) had not enough Sn(III) formed on the surface of catalyst after reduction, and thus activity is too low for the reaction to go towards completion. Therefore, Sn(II) is the active oxidation state, and then the tin compound of SnCl\(_4\) is not oxidation state, and then the tin compound of SnCl\(_4\) is not responsible for the tendency to decrease activity. The eventual durability of the catalyst shows a service life of the catalyst for five times.

4. Conclusions

1. TPR profiles reveal that the ruthenium component of the catalysts transforms easily to zero oxidation state. However, there are practically no free Sn species on the support.
2. The XPS studies have clearly shown that tin exists in oxidation states of Sn(II) in major concentration on the surfaces of reduced Ru-Sn/Al\(_2\)O\(_3\) catalyst.
3. The Ru-Sn catalyst prepared from SnCl\(_2\) without calcinations shows a high activity, and therefore the Sn(II) is found to be the optimum oxidation state for the formation of CHDM.
4. When Sn is added to Ru/Al\(_2\)O\(_3\) catalyst, an important additional effect was found on the activity. This fact reveals that the Sn addition to Ru/Al\(_2\)O\(_3\) enhances the polarization of the \(-\text{C}==\text{O}\) bond of the CHDA molecule, thus leading to CHDM formation. The optimistic atomic ratio of Ru/Sn was 1:1.
5. The use of alumina as a support produces an important modification on the activity in the hydrogenation of 1,4-cyclohexanedicarboxylic acid. Alumina is the best support among those studied here.
6. Reduction temperature is also an important aspect affecting the activity of the catalyst. The catalyst that is reduced around 550 °C showed the highest yield for CHDM.

Table 3

<table>
<thead>
<tr>
<th>Run no.</th>
<th>CHDA conversion (%)</th>
<th>CHDM yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99.2</td>
<td>97.9</td>
</tr>
<tr>
<td>2</td>
<td>98.5</td>
<td>94.2</td>
</tr>
<tr>
<td>3</td>
<td>98.5</td>
<td>87.1</td>
</tr>
<tr>
<td>4</td>
<td>98.5</td>
<td>86.5</td>
</tr>
<tr>
<td>5</td>
<td>97.7</td>
<td>84.2</td>
</tr>
</tbody>
</table>

3.4.5. Durability of Ru-Sn/Al\(_2\)O\(_3\) catalyst

Table 3 illustrates the durability of our catalyst. The catalyst recycling procedure was described as follows. After the reaction, the sedimentary catalyst was carefully recovered from the reaction solution by filtration, which then together with a new reactant and solvent was charged in the autoclave, followed by the sequent reaction. In all batch reactions, a high reaction conversion and a little decrease of yield were observed with catalyst recycle. Yoshinori and Endou [16] reported that an amount of Sn dissolved into the reaction solution during the hydrogenation for the bimetallic Ru-Sn catalysts might be responsible for the tendency to decrease activity. The eventual durability of the catalyst shows a service life of the catalyst for five times.

References


