

Research Article

Partial Hydrogenation of Benzene to Cyclohexene over Ru-Zn/MCM-41

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Ru-Zn/MCM-41 catalysts for the partial hydrogenation of benzene with differing Zn contents were prepared by the incipient-wetness impregnation method. The evaluation results indicate that Zn simultaneously depresses the catalysts activity and cyclohexene selectivity. This can be attributed to the change in the amount of the different hydrogenation sites affected by Zn. The weak hydrogenation sites can promote benzene conversion, and the strong hydrogenation sites, a novel kind of hydrogenation site found on the surface of the catalysts under the influence of Zn, are beneficial for cyclohexene hydrogenation.

1. Introduction

Cyclohexene is of great industrial importance as it can be used as intermediate material for producing adipic acid, nylon-6, nylon-66, and other fine chemicals. Owing to its atom economy over the dehydration of cyclohexanol, the partial hydrogenation of benzene to cyclohexene has recently been the focus of much attention [1–35]. Ru has been found to be the most efficient catalyst for this process. To improve cyclohexene selectivity, the addition of a second element to the Ru-based catalyst, such as Zn [1, 3, 6, 9, 13, 21, 25, 29, 30], Co [4, 16], Ce [20], Ba [19], Fe [17], La [2, 5, 9, 33], B [7, 8, 28, 35], and Cu [24], is needed. Among these additives, Zn is the most popular, and to date the only industrialized production process for cyclohexene via the partial hydrogenation of benzene, developed by Asahi Chemical Industry Co., employs the Ru-Zn catalyst.

Though the use of Zn in the Ru catalyzed partial hydrogenation of benzene is extensive, its effect has not been fully understood up to now. Hu and Chen [6] have studied the partial hydrogenation of benzene over Ru-Zn/SiO₂ catalysts. The results of this study showed that the catalysts activity decreased with the increasing Zn content, whilst cyclohexene selectivity increased. Hydrogen temperature programmed desorption (H₂-TPD) tests revealed that two kinds of hydrogen, both strongly and weakly bonded on the surface of

the Ru-Zn/SiO₂ catalyst, were formed under the influence of Zn. The catalytic activity could be correlated to the total amount of hydrogen desorption on its surface, and as the amount of the weakly bonded hydrogen increases with Zn content this might be responsible for the increased cyclohexene selectivity. From the adsorption point of view, Yuan et al. [21] investigated the effect of Zn on a Ru-based catalyst for the partial hydrogenation of benzene. Density functional theory (DFT) calculations suggested that the chemisorption of benzene and cyclohexene on the catalyst was depressed by Zn, especially for the latter. Undesired deep hydrogenation from cyclohexene to cyclohexane in the middle and late reaction stages was effectively retarded, leading to an improved cyclohexene yield.

It has been shown that the addition of Zn can increase cyclohexene selectivity and give better results for the partial hydrogenation of benzene. In this study we have demonstrated a different phenomenon for the influence of Zn on the partial hydrogenation of benzene over Ru/MCM-41 catalysts.

MCM-41, one of the first developed mesoporous materials [36], has been widely used in catalysis [37, 38], adsorption [39], microreactor [40], and other fields because of its remarkable features, such as well-defined pore shape, narrow distribution of pore size, high surface area (~700–1500 m² g⁻¹), and large amount of internal hydroxyl (silanol) groups (~40–60%). As for the hydrogenation of benzene,

MCM-41 is more often used as catalyst support in the reaction to obtain cyclohexane [41, 42] and hardly used for the partial hydrogenation of benzene to cyclohexene. This difference could be attributed to its relatively smaller pore size with large specific surface area, which increases the diffusion resistance for the obtained cyclohexene from catalyst surface to bulk phase. Therefore, deep hydrogenation to cyclohexane can easily occur.

In our previous study [30], Ru-Zn/MCM-41 catalysts were prepared for partial hydrogenation of benzene and effect of different Zn precursors was evaluated. Herein, Ru-Zn/MCM-41 catalysts with different Zn contents were prepared by an incipient-wetness impregnation method. The role of Zn in the catalysts was discussed by studying the catalytic performance for partial hydrogenation of benzene and catalysts characterization. Interestingly, benzene conversion and cyclohexene selectivity decreased simultaneously with increasing Zn content, with the characterization results showing the appearance of a novel, strong hydrogenation site with the addition of Zn.

2. Experimental

2.1. Catalyst Preparation. First of all, the pure siliceous mesoporous MCM-41, with a BET specific surface area of $743.3 \text{ m}^2/\text{g}$ and a total pore volume of $0.77 \text{ cm}^3/\text{g}$, was synthesized according to the procedure described in [43]. The Ru-Zn/MCM-41 catalysts were then prepared by an incipient-wetness impregnation method. RuCl_3 and ZnSO_4 were used as precursors for Ru and Zn, respectively. They were dissolved into appropriate amount of deionized water and impregnated on MCM-41 support. Within all the catalysts, nominal contents of Ru were kept constant at 1 wt%. After the impregnation, the catalysts were dried at 353 K overnight and reduced with H_2 at 573 K for 6 h.

2.2. Catalyst Characterization. X-ray diffraction (XRD) was carried out using a Rigaku D/Max-2500 X-ray diffractometer and Cu K_α radiation, at 40 kV and 100 mA.

Temperature programmed reduction (TPR) was carried out with a Micromeritics 2920 AutoChem II chemisorption analyzer. 100 mg of catalyst and a 10% (v/v) H_2 -Ar mixture ($50 \text{ cm}^3 \text{ (STP) min}^{-1}$) were used. The sample was preheated to 573 K under Ar ($50 \text{ cm}^3 \text{ (STP) min}^{-1}$) for 1 h and subsequently cooled to room temperature. The temperature was then increased under the H_2 -Ar mixture at 10 K min^{-1} and TPR profiles recorded at temperatures up to 773 K.

The dispersion of Ru metal was measured by CO pulse chemisorption method using a Micromeritics 2920 AutoChem II chemisorption analyzer. The stoichiometry of CO to Ru was assumed to be 1. Before CO chemisorption was performed, catalyst samples of approximately 500 mg were rereduced in a quartz reactor with pure H_2 ($50 \text{ cm}^3 \text{ (STP) min}^{-1}$) for 3 h at 573 K and then purged in He flow. The temperature of samples was decreased to 323 K in He flow. The CO chemisorption was performed by pulse injection of pure CO gas at 323 K.

Hydrogen temperature programmed desorption (H_2 -TPD) was carried out also with a Micromeritics 2920

TABLE 1: Catalytic performance of Ru-Zn/MCM-41 catalysts with different contents of Zn^a.

Zn content (wt%)	t^b (min)	Conv. ^b (%)	S_{CHE}^b (%)	Y_{CHE}^b (%)
null	35.0	63.3	27.6	17.5
0.25	35.0	23.3	15.0	3.5
0.64	15.0	1.8	45.6	0.82
1.0	10.0	1.0	60.0	0.60

^aReaction conditions are the same as those of Figure 1. ^bThe results are provided at the maximum yield of cyclohexene. Conv.:conversion of benzene; S_{CHE} : selectivity to cyclohexene; Y_{CHE} : yield of cyclohexene.

AutoChem II chemisorption analyzer. About 100 mg of sample was preheated to 573 K under He ($50 \text{ cm}^3 \text{ (STP) min}^{-1}$) for 1 h and subsequently cooled to 323 K. The sample was then saturated with H_2 under a 10% (v/v) H_2 -Ar mixture ($25 \text{ cm}^3 \text{ (STP) min}^{-1}$) for 30 min and then purged with He to remove the physisorbed H_2 . Finally, the temperature was increased under He atmosphere ($50 \text{ cm}^3 \text{ (STP) min}^{-1}$) at 10 K min^{-1} and TPD profiles were recorded at temperatures up to 1073 K.

Transmission electron microscopy (TEM) images were obtained with a FEI TECNGI G² microscope.

2.3. Catalytic Activity Test. The partial hydrogenation of benzene was carried out in a 200 mL stainless steel autoclave fitted with a magnetic stirrer. In a typical experiment, 30 mL benzene and 0.48 g Ru-Zn/MCM-41 catalyst with 3.4 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, the cocatalyst, were introduced into the autoclave, together with 60 mL H_2O to act as solvent. The autoclave was sealed and pressurized with N_2 for leak testing and then purged by low pressure H_2 four times to remove N_2 and the temperature adjusted to 403 K. Pressurized H_2 (5.5 MPa) was then introduced into the autoclave and reacted with benzene. At the end of the reaction the autoclave was cooled in an ice bath and vented. The catalyst was separated by centrifugation, and the liquid was separated into water and an oil phase.

The reaction products in the oil phase were identified and quantified by capillary gas chromatography using a BAIF SP-3420 instrument with a $30 \text{ m} \times 0.25 \text{ mm}$ PEG 20 M column and FID.

3. Results and Discussion

The Ru-Zn/MCM-41 catalysts with differing contents of Zn were evaluated for their activity to partial hydrogenation of benzene and the results are shown in Figure 1 and Table 1. When Ru/MCM-41 was used as catalyst, benzene content decreased gradually and the completely hydrogenated product cyclohexane increased monotonically with reaction time. Regarding cyclohexene content, a maximum was obtained at a certain reaction time, exhibiting the well-known behavior of consecutive reactions. The maximum cyclohexene yield was 17.5% with 62.3% benzene conversion at 35 min over Ru/MCM-41 catalyst. When 0.25 wt% Zn was introduced into the catalyst, hydrogenation rate decreased obviously. This

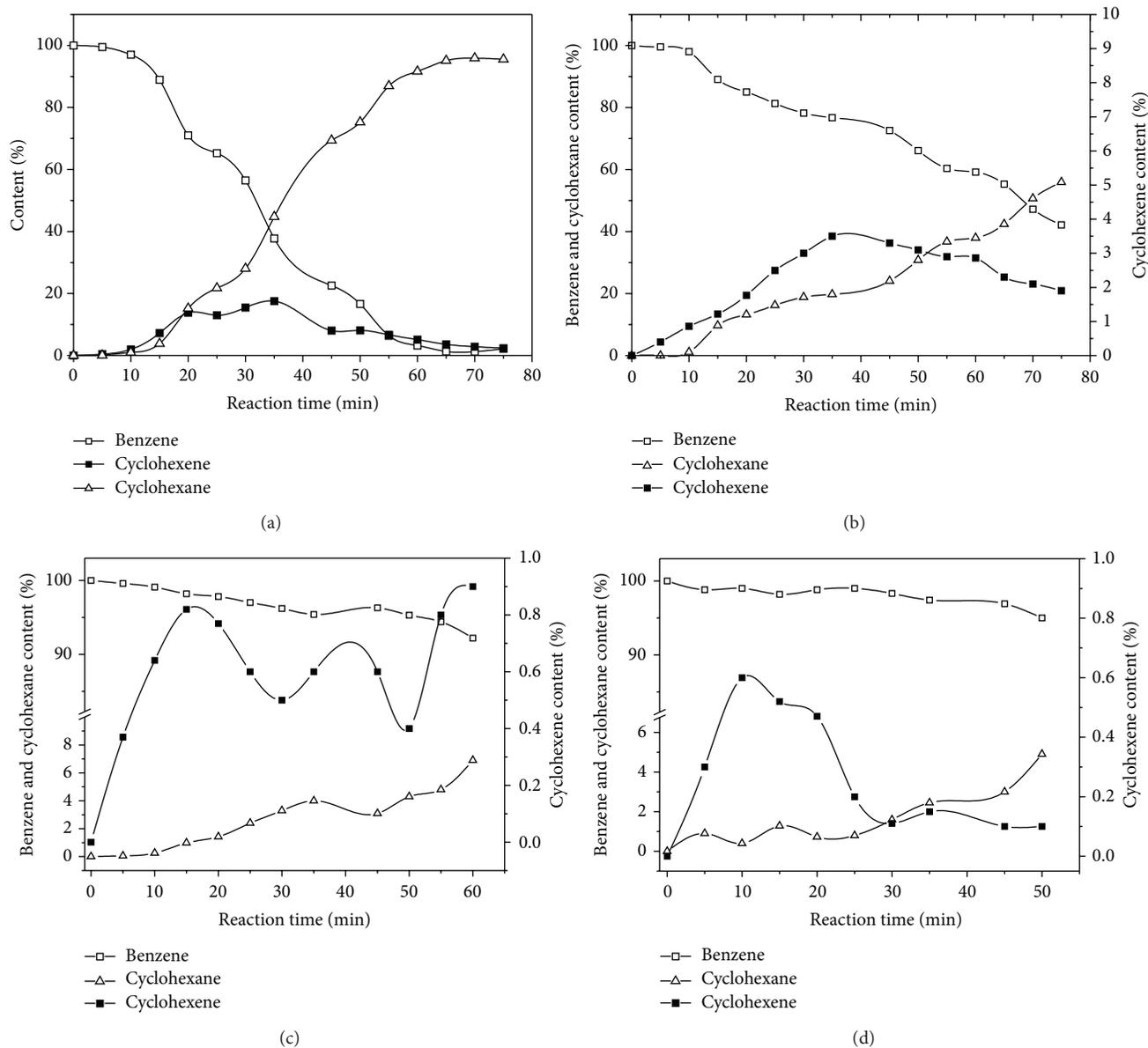


FIGURE 1: Partial hydrogenation of benzene over Ru-Zn/MCM-41 with different contents of Zn. Zn content: (a) null; (b) 0.25 wt%; (c) 0.64 wt%; (d) 1 wt%. Reaction conditions: benzene 30 mL (0.338 mol), Ru-based catalyst 0.48 g (Ru 4.7×10^{-5} mol), 3.4 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ in 60 mL H_2O , H_2 5.5 MPa, and 403 K.

is in accordance with the other results previously obtained using other Ru-based catalysts [6, 21]. However, in contrast to the usual assumption the cyclohexene content significantly decreased likewise. Most of benzene was hydrogenated completely to cyclohexane. The maximum cyclohexene yield was only 3.5% with 23.3% benzene conversion over Ru-Zn/MCM-41 catalyst with 0.25 wt% Zn. With increasing Zn content the catalyst activity reduces further. A 1 wt% of Zn content gave a maximum cyclohexene yield of 0.6% with 1.0% benzene conversion. That is to say, the catalyst lost almost all of its hydrogenation activity under these conditions. And the high cyclohexene selectivity over Ru-Zn/MCM-41 catalysts with high Zn content may be the results of ultralow hydrogenation activity.

Characterizations were carried out to understand the influence of Zn on the Ru/MCM-41 catalysts. Figure 2(a) shows the small-angle XRD pattern of Ru-Zn/MCM-41 catalyst in 1:1 ratio. The sample gave a well-defined hexagonal XRD pattern with a main peak at 2° and up to three signals in the region $3\text{--}8^\circ$. Figure 2(b) shows the wide-angle XRD patterns of Ru-Zn/MCM-41 catalysts with differing contents of Zn. There is no diffraction peak corresponding to the crystalline compound in the patterns of all samples, which suggested that Ru and Zn compounds were highly dispersed in the catalysts.

To investigate the effect of Zn on the reducibility of Ru species over MCM-41, H_2 -TPR measurements of the Ru-Zn/MCM-41 catalysts with differing Zn contents, before

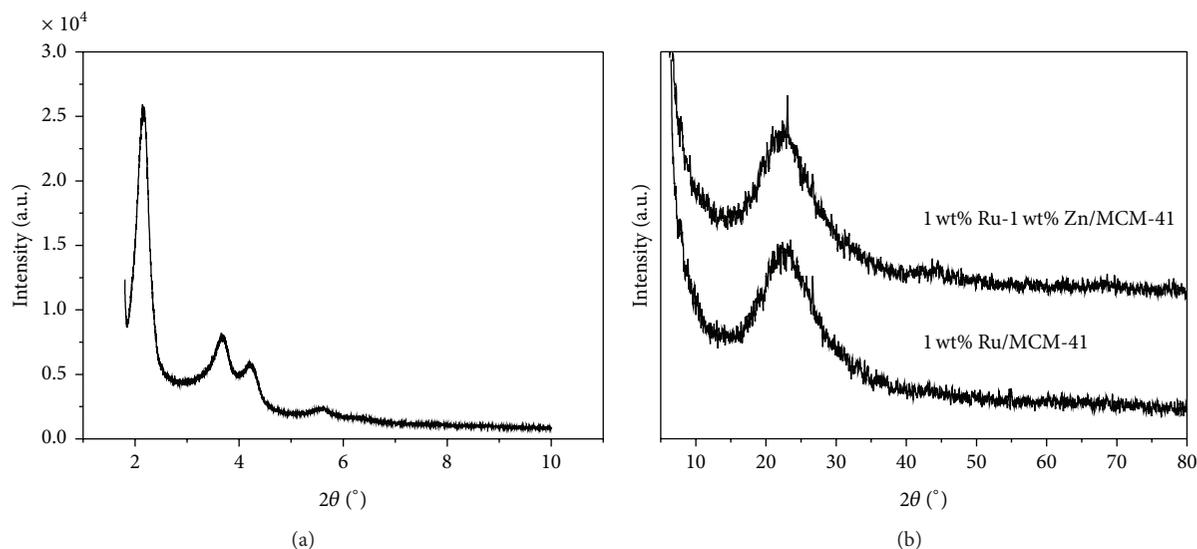


FIGURE 2: XRD patterns of Ru-Zn/MCM-41 catalysts: (a) small angle XRD; (b) wide angle XRD.

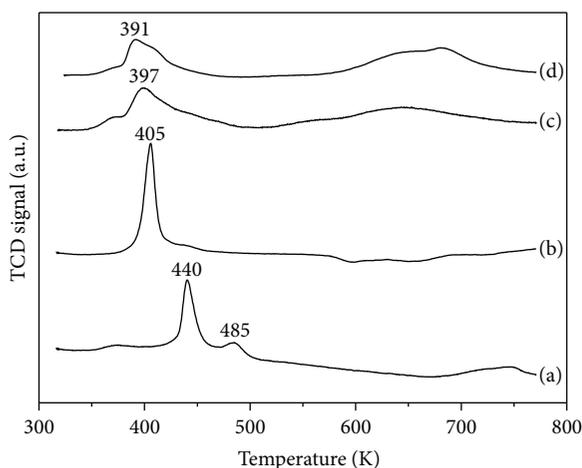


FIGURE 3: TPR profiles of Ru-Zn/MCM-41 catalysts. Zn contents: (a) null; (b) 0.25 wt%; (c) 0.64 wt%; (d) 1 wt%.

reduction by hydrogen, were carried out. The profiles are shown in Figure 3.

The TPR profile of Ru/MCM-41 catalyst (Figure 3(a)) shows a peak with maximum (T_m) at about 440 K, which is related to RuCl_3 reduction in the preparation method. However, this peak is a little beyond the range reported for the complete reduction of unsupported RuCl_3 (433 K, [44]). This difference could be due to the interaction between RuCl_3 and MCM-41 support. Zonetti et al. [14] found two peaks in the TPR profile of Ru/ CeO_2 , a principal peak at 453 K with a shoulder around 423 K. They considered the peak at lower temperature corresponding to the reduction of RuCl_3 weakly interacting with CeO_2 and the peak at higher temperature relating to RuCl_3 reduction strongly interacting with the support. There is still a weak peak at 485 K in the TPR profile of Ru/MCM-41, which can be assigned to the reduction of

RuO_x . It has been found that RuCl_3 can be oxidized at the surface by exposure to air at room temperature [45].

With the addition of Zn, the reduction peaks changed significantly as observed in Figure 3. Starting with 0.25 wt% Zn content the two reduction peaks resolved into one at about 405 K. With each further addition of Zn, T_m decreased slightly down to 391 K for 1 wt% Zn. These results showed that Zn promoted the reduction of Ru, which differs from that previously reported by Hu and Chen [6]. da-Silva and Cobo [17] showed that the addition of Fe to Ru/ TiO_2 and Ru/ SiO_2 catalysts favored the reduction of RuO_2 . This might be the result of higher dispersion of the RuO_2 particles, induced by Fe. Fan et al. [4] also reported a better dispersion of Ru caused by a high content of cobalt in the Ru-Co-B/ Al_2O_3 catalyst. From the literature mentioned above, it is reasonable to presume that the lowering of reduction temperature of Ru resulted from the better dispersion caused by Zn.

To determine Ru dispersion in Ru-Zn/MCM-41 catalysts, CO chemisorption was carried out. The molar ratio of CO/Ru of the catalysts was 0.475, 0.398, 0.354, and 0.386, respectively, with Zn content of 0, 0.25 wt%, 0.64 wt%, and 1 wt%. Contrary to our assumption Ru dispersion decreases with the addition of Zn, and this indicates that there must be other factors that favor the reduction of Ru species.

Figure 4 shows the H_2 -TPD profiles of Ru-Zn/MCM-41 catalysts with differing Zn contents, with all the profiles demonstrating two main peaks. One is in the range of 350 K–500 K and the other is higher than 600 K. This indicates two forms of hydrogenation active sites. With the addition of Zn, the integrated area of the low-temperature peak decreased, while that of the high-temperature peak increased. This change represents changes in the number of the two forms of hydrogenation active sites. With increasing Zn content, the number of relative weak hydrogenation sites (WHS) decreases and that of the strong hydrogenation sites (SHS) increases on the surface of Ru-Zn/MCM-41 catalysts. Hu and Chen [6] have reported the desorption peak with T_m

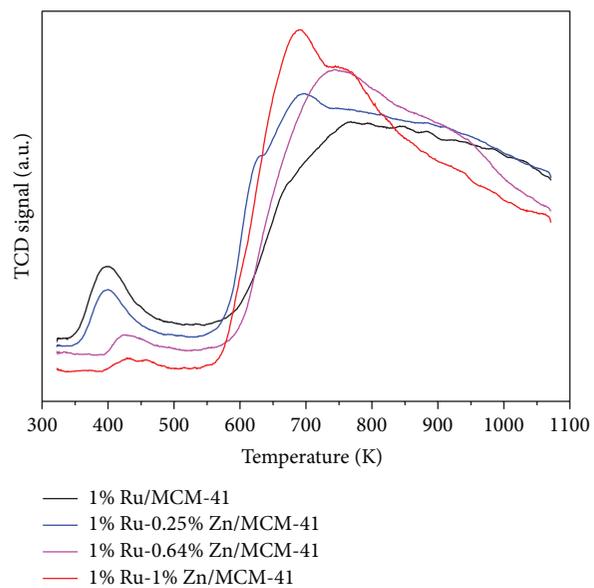
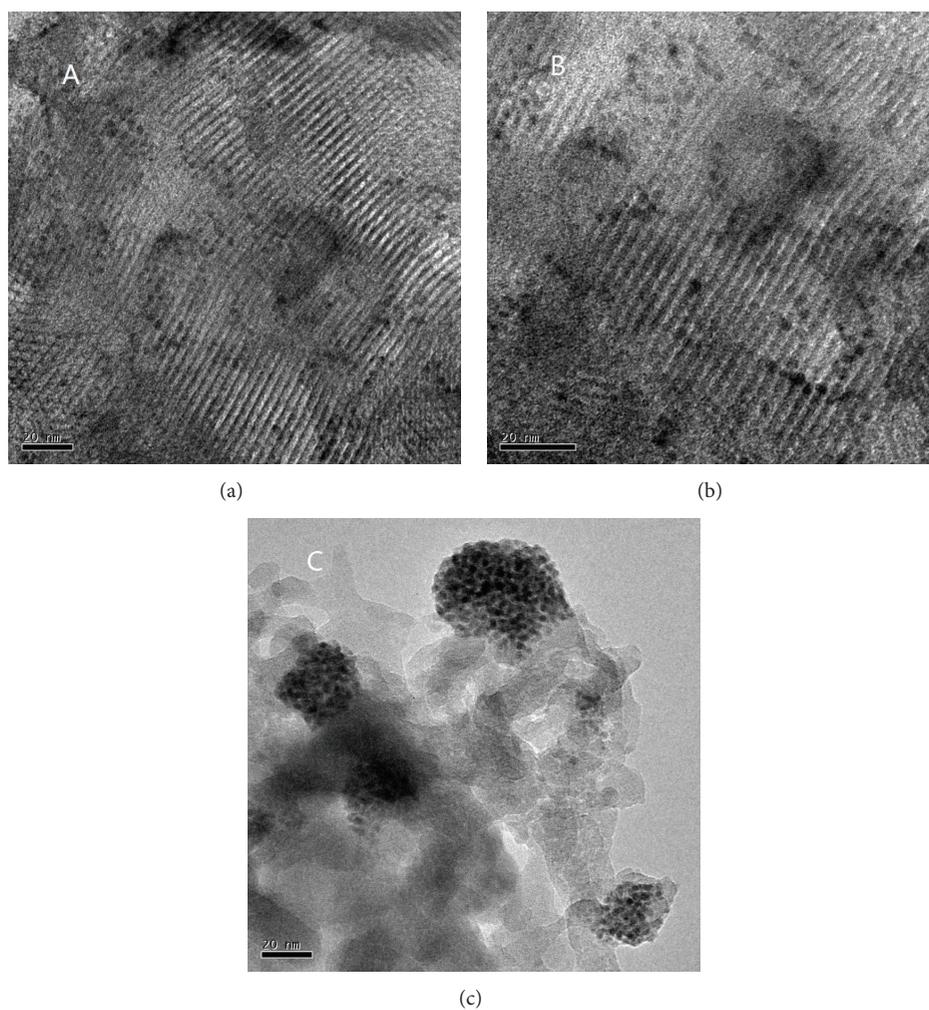
FIGURE 4: H_2 -TPD profiles of Ru-Zn/MCM-41 catalysts.

FIGURE 5: TEM photos of Ru-Zn/MCM-41 catalysts: (a) 1 wt% Ru/MCM-41; (b) and (c) 1 wt% Ru-1 wt% Zn/MCM-41.

about 423 K on Ru/SiO₂, which may be assigned to the H₂ desorption from the Ru surface. Therefore, it is reasonable to conclude that the lower-temperature desorption peak is related to the H₂ desorption from the free Ru surface, the WHS, and the latter is related to the H₂ desorption from Ru surface affected by Zn and/or MCM-41, which is the SHS. In view of the catalytic activity results shown in Figure 1, it might be concluded that the number of WHS is correlated to benzene conversion, while the SHS is beneficial for cyclohexene hydrogenation. Therefore, with increasing Zn content, benzene hydrogenation activity decreases whilst cyclohexene hydrogenation activity increased.

To show more direct and convincing evidence for the existence of the novel Ru species, TEM photos were recorded. Figure 5(a) shows the TEM photo of Ru/MCM-41 and Figures 5(b) and 5(c) show the photos of Ru-Zn/MCM-41 catalyst with Zn content equaling 1 wt%. In Figure 5(a), there are small Ru particles, with average size about 2.2 nm calculated from 25 particles, in the pores of MCM-41. When Zn is added to the catalyst, besides the small Ru particles shown in Figure 5(b), a novel kind of Ru conglomeration comes into being as shown in Figure 5(c). The conglomeration of Ru particles, with diameter about 30–50 nm, was composed of small Ru particles less than 3 nm. Its formation might be due to the effect of Zn, because Zn can spread on the Ru particle surface as an overlayer [6] and then may act as a kind of adhesive to bind the Ru particles with each other. In addition, the slight decrease of Ru dispersion, caused by Zn, indicates the loose combination of Ru particles in the conglomeration. In other words, there is space in the conglomeration to ensure the diffusion and adsorption of CO.

The decrease of Ru reduction temperature could be explained by the loose conglomeration structure with confined space effect. During the reduction process, part of the Ru(III) was firstly reduced to Ru(0). Then H₂ adsorbed dissociatively on the Ru(0) surface to form H atoms, which were more active. Furthermore, there was a high concentration of H atoms in the conglomeration. So, Ru(III) could be reduced at low temperature by the active H atoms.

4. Conclusions

With addition of Zn into Ru/MCM-41 catalysts, a kind of Ru particles conglomeration, with diameter about 30–50 nm, comes into being on the support. Its formation might be due to the fact that Zn can spread on the Ru particle surface as an overlayer and then may act as a kind of adhesive to bind the Ru particles with each other.

Ru-Zn/MCM-41 catalysts showed a decreased hydrogenation activity and cyclohexene selectivity with increasing Zn content. It can be attributed to the change of the amount of the hydrogenation sites affected by Zn. The amount of weak hydrogenation sites, which can promote benzene conversion, decreases with the addition of Zn. However, the amount of strong hydrogenation sites, which are beneficial for cyclohexene hydrogenation, changes in the reverse. And Ru species in the conglomeration were thought to be the strong hydrogenation sites.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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