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Research Note

Superior performance in deep saturation of bulky aromatic pyrene over acidic mesoporous Beta zeolite-supported palladium catalyst

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Abstract

Palladium species were loaded into mesoporous Beta zeolite (Beta-H), and transmission electron microscopy images showed that the Pd particles are located in both mesopores and micropores. As a model reaction, the deep hydrogenation of bulky aromatic pyrene showed that the Pd/Beta-H catalyst exhibits higher activity than Pd/Beta, Pd/Al-MCM-41, and Pd/γ-Al_2O_3 catalysts. The superior performance of the Pd/Beta-H catalyst is attributed to its unique porous structure and acidity. The mesoporous volume in Beta-H (0.17 cm^3/g) is greater than that of Beta (0.06 cm^3/g), which is advantageous for adsorption and mass transport of pyrene over Pd/Beta-H catalyst. The amount of acidic sites is greater on Beta-H (480 μmol/g) than on Al-MCM-41 (280 μmol/g) and γ-Al_2O_3 (220 μmol/g), which also favors improved catalytic activity in hydrogenation of pyrene over Pd/Beta-H catalyst.

Keywords: Mesoporous Beta zeolite; Noble metal catalyst; Deep hydrogenation of pyrene

1. Introduction

The high aromatic content in diesel fuel both decreases fuel quality and contributes significantly to the formation of undesirable emissions in exhaust gases [1–7]. One solution to this problem is deep saturation of aromatic hydrocarbons over a supported noble metal (e.g., Pd, Pt, or Pd–Pt) catalyst [1,2]. Generally, acidic sites in the supports of noble metal catalysts are advantageous for the deep saturation of aromatic hydrocarbons [1,3]. Among these catalyst supports, microporous crystals of zeolites with strongly acidic sites have increasingly been receiving more attention [3,8,9], but one disadvantage of these zeolite supports is that their pore sizes are too small to allow access to bulky aromatic hydrocarbons, which severely hinders hydrogenation of these bulky molecules [10]. Recently, Meng et al. [11] tailored the pores of zeolite Y to introduce mesopores by silicon tetrachloride treatment and steam dealumination. A Pd–Pt catalyst was prepared with this support, but although this approach enhanced the catalyst's ability in pyrene hydrogenation, unfortunately, introduction of mesoporosity by this method is limited [11]. Significant progress was realized using ordered mesoporous materials as catalyst supports [12,13]. But although this approach overcame the pore size limitation, higher activities were not achieved for aromatic hydrogenation over materials with supported metal catalysts; this was attributed to the lower acidity of ordered mesoporous materials due to the amorphous nature of mesoporous walls [13–15]. γ-Al_2O_3 and amorphous silica-alumina have a mesoporosity that favors the mass transfer of bulky molecules; however, compared with zeolites, their relatively weak acidity is a challenge for preparing supported metal catalysts with very high activity [16,17].

Recently, we synthesized hierarchical mesoporous zeolites templated from a mixture of small organic ammonium salts and mesoscale cationic polymers [18]. After ion exchange of NH_4^+ and calcination, these mesoporous zeolites showed strong acidity and very high activity for the chemical conversion of bulky molecules [18]. In the present work, we demonstrate that the assembly of Beta-H with Pd particles is a highly active catalyst for the deep saturation of bulky aromatic pyrene. We believe that this finding will open a door for the preparation of a series of novel catalysts with very high activity in the deep saturation

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of bulky aromatic hydrocarbons, which is very important to increasing fuel quality and controlling the undesirable emissions in exhaust gases.

2. Experimental

Mesoporous Beta zeolite (Beta-H), conventional Beta zeolite, and mesoporous aluminosilicate (Al-MCM-41) were synthesized as described previously [15,18]. The H-forms of samples were ion-exchanged twice with a NH_4NO_3 solution (1 M) at 70 °C for 3 h, followed by calcination at 500 °C for 4 h. γ-Al_2O_3 was purchased from Fushun Petrochemical Company.

Zeolite and Al-MCM-41-supported palladium catalysts were prepared by ion exchange with a $[Pd(NH_3)_4]^{2+}$ solution. A γ-Al_2O_3-supported palladium catalyst was prepared by incipient wetness impregnation. The palladium content was determined by the inductively coupled plasma (ICP) method, using a Perkin–Elmer 3300 DV spectroscope, after calcination of the samples at 450 °C for 100 min in flowing oxygen.

XRD patterns were obtained with a RIGAKU D/MAX-2550 diffractometer using Cu$K\alpha$ radiation. Nitrogen physisorption was carried out using a Micromeritics ASAP 2010M system. The sample was degassed for 10 h at 300 °C before the measurement. The acidity of the materials was determined using the stepwise temperature-programmed desorption of ammonia. About 100 mg of sample was placed in a quartz tubular reactor and pretreated in a nitrogen stream, heated to 450 °C at 10 °C/min, and remained at 450 °C for 2 h. After cooling to 150 °C, gaseous NH_3 was passed over the sample for 30 min. After removal of physical adsorbed NH_3 by flowing nitrogen for 2 h at 150 °C, the sample was heated as follows: increasing from 150 to 250 °C at a rate of 10 °C/min and holding at 250 °C for 30 min, increasing from 250 to 350 °C at a rate of 10 °C/min and holding at 350 °C for 30 min, and increasing from 350 to 700 °C at a rate of 10 °C/min. The desorbed NH_3 was collected in dilute hydrochloric acid and then titrated with a dilute sodium hydroxide solution to determine the total acidic site density of the materials. The Pd/Beta-H sample for TEM experiment was reduced by mixed gases of H_2–N_2 with 6% H_2, which is the same as the reduction procedure in pyrene hydrogenation. The TEM images were obtained on a Philips CM 200 LaB_6 instrument operating at 200 kV.

Pyrene (0.92 × 1.17 nm) [11] hydrogenation was carried out in an autoclave (Parr 5500, 300 ml). Before reaction, the catalyst powders (<53 μm) were calcined in flowing oxygen (150 ml/min, STP) from room temperature to 450 °C at a rate of 1 °C/min and holding at 450 °C for 100 min, followed by cooling to room temperature. The calcined catalysts (300 mg) were reduced in a mixed gas of H_2–N_2 with 6% H_2 (80 ml/min, STP) from room temperature to 300 °C at a heating rate of 2 °C/min and holding at 300 °C for 100 min. After cooling to room temperature, the reduced catalyst was put into the autoclave under nitrogen stream. In a typical run, the reaction conditions were as follows: 3.5 g of pyrene in 120 ml of tridecane, reaction temperature 250 °C, hydrogen pressure 40 bar, total pressure 65 bar, and stirring rate 800 rpm. The reaction products were analyzed with an Agilent 6890N gas chromatograph equipped with a flame ionization detector and mass spectrometer.

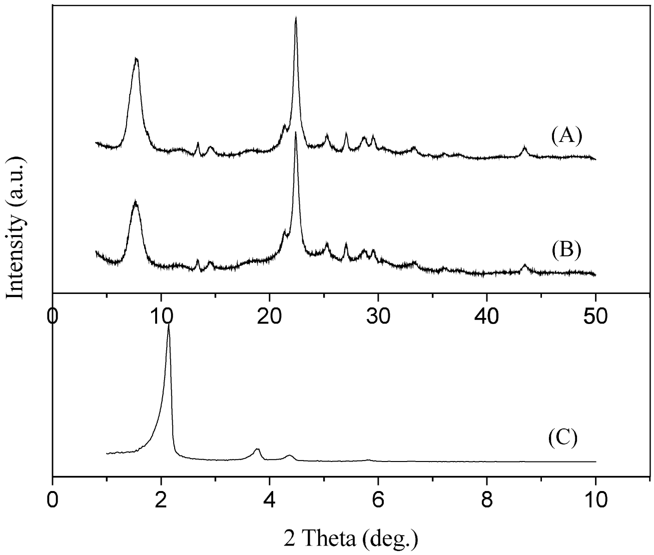

Fig. 1. XRD patterns of various catalysts. (A) Pd/Beta; (B) Pd/Beta-H; (C) Pd/Al-MCM-41.

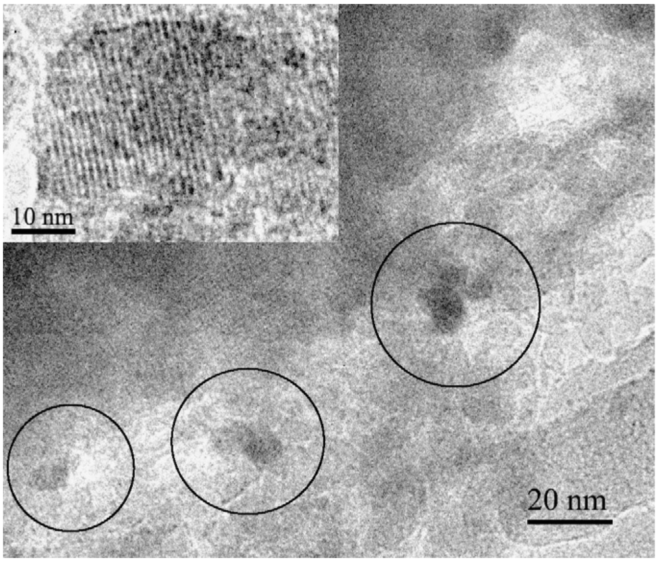

Fig. 2. TEM image of the reduced Pd/Beta-H. Insert: HR-TEM of Pd/Beta-H.

3. Results and discussion

Fig. 1 shows XRD patterns of various supported palladium catalysts, exhibiting typical peaks associated with Beta (Figs. 1A and 1B) and hexagonal mesostructure (Fig. 1C). Fig. 2 shows TEM images of the reduced Pd/Beta-H catalyst. The Pd particles are located mainly in disordered mesopores (marked circles, Fig. 2) and in ordered micropores (insert, Fig. 2), which is attributed to the fact that Beta-H sample contains both hierarchical mesopores (5–40 nm) and ordered micropores (0.74 nm) [18].

Table 1 presents textural parameters and acidic properties of the various supports as well as the Pd loading on these sup-

Table 1
Textural and acidic parameters of the samples and their palladium loadings

Samples	BET surface area (m^2/g)	External surface area[a] (m^2/g)	Mesoporous volume (cm^3/g)	Microporous volume (cm^3/g)	Acidic amounts of the support (μmol/g)				Pd loading (wt%)
					150–250 °C	250–350 °C	>350 °C	Total	
Beta-H	493	151	0.17	0.16	150	205	125	480	3.7
Beta	561	134	0.06	0.21	142	210	138	490	3.7
Al-MCM-41	684	677	0.56	–	130	100	50	280	3.8
γ-Al_2O_3	195	183	0.53	–	115	80	25	220	3.5

[a] Mesoporous surface area is included.

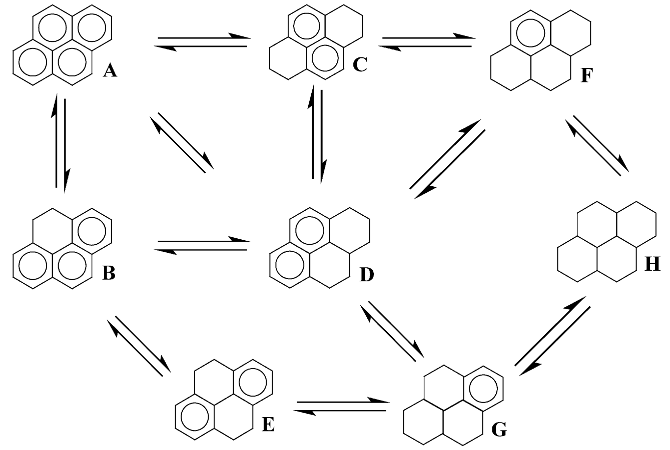

Fig. 3. The schematic representation of pyrene hydrogenation products. (A) Pyrene; (B) 4,5-dihydropyrene; (C) 1,2,3,6,7,8-hexahydropyrene; (D) 1,2,3,3a,4,5-hexahydropyrene; (E) 4,5,9,10-tetrahydropyrene; (F) 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene; (G) 1,2,3,3a,4,5,9,10,10a,10b-decahydropyrene; (H) perhydropyrene.

ports. The mesopore volume of Beta-H is higher than that of Beta, but much lower than that of Al-MCM-41 and γ-Al_2O_3. The total numbers of acidic sites of Beta-H and Beta are very similar, but greater than those of Al-MCM-41 and γ-Al_2O_3. In addition, the strength distribution is quite different for the various samples. The percentages of middle strong (250–350 °C) and strong (>350 °C) acidic sites of Beta-H and Beta are higher than those of Al-MCM-41 and γ-Al_2O_3.

Fig. 3 shows the proposed network of pyrene hydrogenation [19]. Pyrene hydrogenation first creates dihydropyrene, followed by the formation of tetrahydropyrene, hexahydropyrene, decahydropyrene, and perhydropyrene. Usually, hydrogenation of polycyclic aromatics is a consecutive reaction; the rate of hydrogenation of the first ring is fast, that of the succeeding rings gradually decreases, and that of the last ring is very difficult [1,19,20]. For example, the rate for hydrogenation of the first ring of naphthalene is 10–40 times higher than that of the second ring [16,20–22].

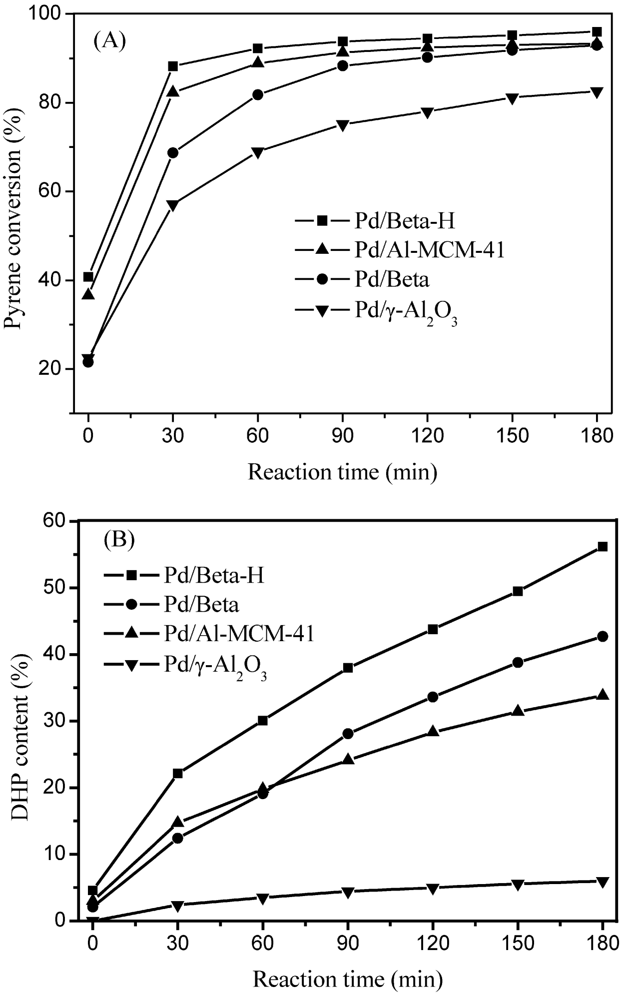

Fig. 4. Dependences of (A) pyrene conversion and (B) DHP content on reaction time over (■) Pd/Beta-H; (●) Pd/Beta; (▲) Pd/Al-MCM-41; (▼) Pd/γ-Al_2O_3.

Fig. 4A shows the dependence of the conversion on reaction time over various catalysts in pyrene hydrogenation. To compare the capability of deep hydrogenation of pyrene over various catalysts, the dependence of the sum of hexahydropyrene, decahydropyrene, and perhydropyrene (products of deep hydrogenation of pyrene, DHP) with reaction time is shown in Fig. 4B. Fig. 5 shows the change in all products versus reaction time over various catalysts. Generally, the catalytic performance of supported metal catalysts is influenced by many support parameters, such as surface area and acidity. Beta-H with a crystal size of about 600 nm shows a mainly mesopore surface area of about 151 m^2/g, whereas Beta with a crystal size of about 300 nm has an external surface area of 134 m^2/g (Table 1) [18]. Because pyrene hydrogenation occurs mainly on the external surface and in mesopores, it is reasonable that both Pd/Beta-H and Pd/Beta catalysts show high conversion in pyrene hydrogenation. However, as observed in the initial stage of pyrene hydrogenation, the conversion on Pd/Beta-H is clearly higher than that on Pd/Beta (Fig. 4A). Interestingly, the DHP content over Pd/Beta-H is much higher than that over Pd/Beta (Fig. 4B), which is attributed to the difference in meso-

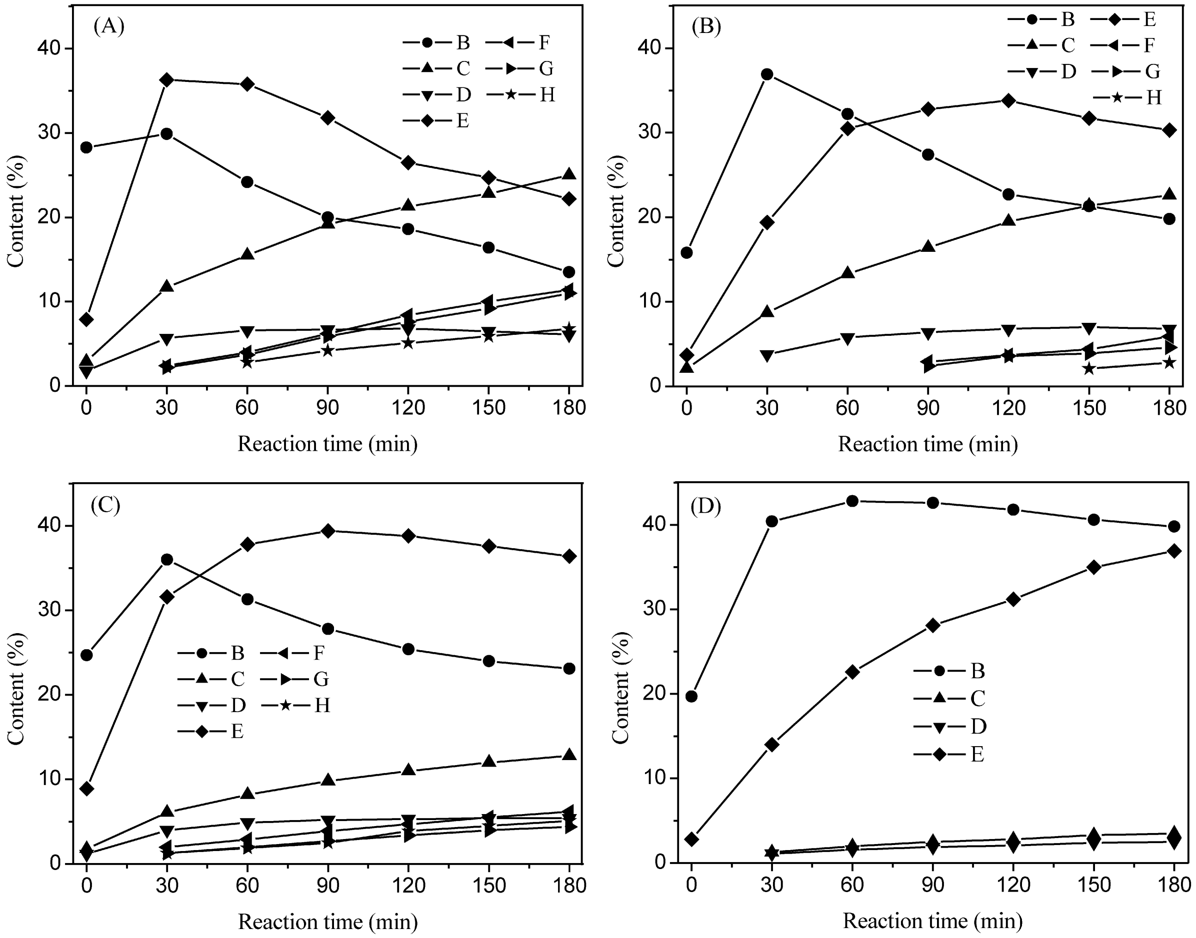

Fig. 5. Dependences of product contents in pyrene hydrogenation vs reaction time over (A) Pd/Beta-H, (B) Pd/Beta, (C) Pd/Al-MCM-41, and (D) Pd/γ-Al_2O_3 catalysts.

porosity between Pd/Beta-H and Pd/Beta, because acidic properties and Pd loading of the two catalysts are very similar. Pu et al. [23] reported that the pores of zeolite Y are too small to be accessible for bulky pyrene in catalytic isopropylation. Possibly, the presence of hierarchical mesopores in Pd/Beta-H (Table 1) is favorable for pyrene transport, forming DHP products in pyrene hydrogenation.

Compared with Beta-H, Al-MCM-41 and γ-Al_2O_3 have a relatively high mesopore volume, but their supported palladium catalysts still showed a low deep hydrogenation capability, which may be related to the change in acidity between Beta-H and Al-MCM-41 and γ-Al_2O_3. A number of reports have shown that acidic sites on supports facilitate aromatics hydrogenation [1,24–34], and in this work Pd/Beta-H zeolite with strong and abundant acidic sites gives higher pyrene conversion and DHP content compared with Pd/Al-MCM-41 and Pd/γ-Al_2O_3 with relatively weak acidity (Table 1). Reddy and Song [35] and Jongpatiwut et al. [36] reported that the deep hydrogenation of phenanthrene over F–Pd–Pt/γ-Al_2O_3 and Pd/Al-MCM-41 is also limited, although high conversion is present.

It is noteworthy that the unique porous structure of Beta-H may be favorable for the hydrogenation of bulky aromatic pyrene. Bulky pyrene could be easily adsorbed inside the mesopores of Beta-H, and the large numbers of acidic sites on the Pd/Beta-H could enhance pyrene hydrogenation activity.

4. Conclusion

Palladium particles were successfully supported inside the mesopores and micropores of Beta-H, and the Pd/Beta-H catalyst thus obtained showed higher activity and selectivity for products of deep hydrogenation than a conventional Beta zeolite-supported Pd catalyst (Pd/Beta) and Pd catalysts supported on mesoporous materials (Pd/Al-MCM-41) and alumina (Pd/γ-Al_2O_3).

Acknowledgments

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