

PREPARATION OF A NOVEL CATALYST FOR SELECTIVE HYDROGENATION OF PYROLYSIS GASOLINE

Zhi-Ming Zhou*, Tian-Ying Zeng, Zhen-Min Cheng and Wei-Kang Yuan
State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

Summary

Novel palladium catalysts supported on alumina supports with the hierarchically macro-mesoporous structure were prepared and applied to selective hydrogenation of pyrolysis gasoline. Characterization of the supports by scanning electron microscopy and N₂ adsorption-desorption analysis revealed their high thermal stability. By comparison with a commercial catalyst, these novel catalysts exhibited much better catalytic performance, i.e., higher activity and selectivity, which was mainly ascribed to their unique structures of hierarchical mesopores and macropores.

Keywords

Rational design of catalysts; Nanotechnology applications

Introduction

Selective hydrogenation of pyrolysis gasoline (pygas) is an important chemical process in olefin plants, which aims at converting styrene and diolefins into ethylbenzene and monoolefins, respectively.¹ The commercial catalysts for pygas hydrogenation are usually Pd/Al₂O₃ with the pore size distribution between 4 nm and 20 nm,² which exhibits notable internal diffusion limitations of species,³ resulting in blockage of many mesopores with gums formed by polymerization of styrene and diolefins after a period of application. The strategy to overcome this problem is to reduce the internal diffusion to a great extent as well as release the intermediate products monoolefins from the internal pores of catalysts as soon as possible. Recently, we found that some metal oxides with hierarchically macro-mesoporous structures, such as TiO₂ and Al₂O₃, exhibited high catalytic performance for pygas selective hydrogenation.^{4,5} As a part of a series of studies, the objective of this work is to further evidence and highlight the predominant effect of the hierarchical pore structure on the reaction.

Experimental

Alumina samples with hierarchically macro-mesoporous structures were prepared at various conditions (Table 1). In a typical synthesis, 0.4 g cetyltrimethylammonium bromide (CTAB) was added into a mixture of 35 mL two-distilled water and 15 mL ethanol with slow stirring at room temperature. Then, the pH value of the solution was adjusted to 10.0 by NH₃·H₂O. Finally, 2 g aluminum tri-*sec*-butoxide was added. After 1 h, the precipitates formed were separated by centrifugation, washed by Soxhlet extraction for 30 h, and dried in air for 24 h. The as-prepared samples were finally calcined at 800 °C for 5 h.

The palladium-supported catalysts with 0.3 wt.% metal loading were prepared by incipient-wetness impregnation of the aforementioned 800 °C calcined samples. The impregnated powders were then dried at 120 °C for 6 h, and finally calcined at 400 °C for 5 h. Before activity tests, the catalysts were reduced by hydrogen at 150 °C for 8 h. Hydrogenation of a model pygas composed of styrene, cyclopentadiene, 1-hexene and *n*-heptane (solvent) was carried out in a stirred autoclave at 40 °C and 2.0 MPa. Detailed information was reported elsewhere.¹

Results and Discussion

As shown in Figure 1, the as-prepared samples displayed macroporous channels, and these channels were parallel to each other and perpendicular to the tangent of the outer surface. The textural properties of these samples are listed in Table 1.

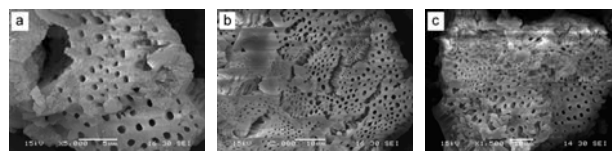


Figure 1. SEM images of the synthesized aluminum oxide samples. Scale bar: (a) 5 μm; (b) 10 μm; (c) 10 μm.

Table 1. Preparation conditions and textural properties of samples^a

No	Water (mL)	Ethanol (mL)	CTAB (g)	pH	S _{BET} (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)	Macropore size ^b (μm)	Mesopore size ^c (nm)
a	35	15	0.4	10	514.1	0.81	0.45	5.1
b	35	15	0	10	403.5	0.39	0.60	3.2
c	50	0	0	10	320.8	0.31	1.75	3.3

^a Preparation conditions: room temperature, 200 rpm, 1 h. ^b The average macropore diameter obtained from analysis of the image. ^c BJH pore diameter determined from the desorption branch.

* To whom all correspondence should be addressed. Tel.: +86 21 6425 2230; fax: +86 21 6425 3528; Email: zmzhou@ecust.edu.cn.

Corresponding to samples a, b and c, the SEM images of these samples after calcination at 800 °C are presented in Figures 2a₁, 2b₁ and 2c₁, respectively. It is obvious that the macroporous structures of the calcined alumina were well preserved, indicating their high thermal stability. Table 2 summarizes their textural properties. Compared with the samples without calcination, the 800 °C calcined alumina showed a little bit smaller macropores due to expansion of the walls after thermal treatment, which was consistent with the increase in the mesopore size (as illustrated in Figure 3). Sample cc listed in Table 2 is a commercial Pd/ δ -Al₂O₃ catalyst for pygas selective hydrogenation, and it has no macroporous channels.²

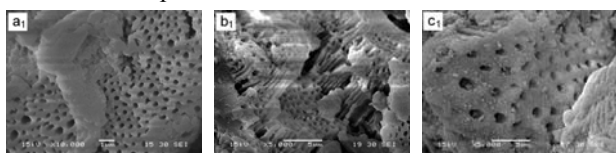


Figure 2. SEM images of the 800 °C calcined alumina (corresponding to Figure 1). Scale bar: (a₁) 1 μm; (b₁) 5 μm; (c₁) 5 μm.

Table 2. Textural properties of the calcined Al₂O₃

No	S _{BET} (m ² ·g ⁻¹)	Pore volume (cm ³ ·g ⁻¹)	Macropore size (μm)	Mesopore size (nm)
a ₁	126.4	0.51	0.45	12.1
b ₁	108.0	0.38	0.50	10.9
c ₁	87.6	0.24	1.25	11.1
cc ^a	98.1	0.37	–	13.6

^a The commercial Pd/ δ -Al₂O₃ catalyst.

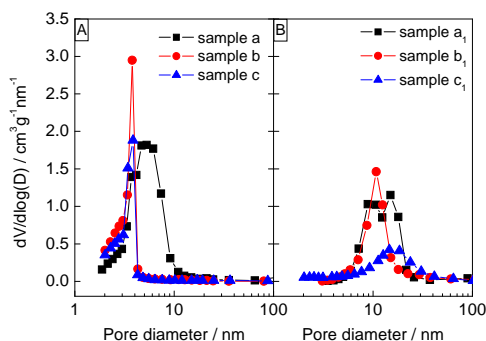


Figure 3. Pore size distribution curves of the as-prepared (A) and the 800 °C calcined alumina (B).

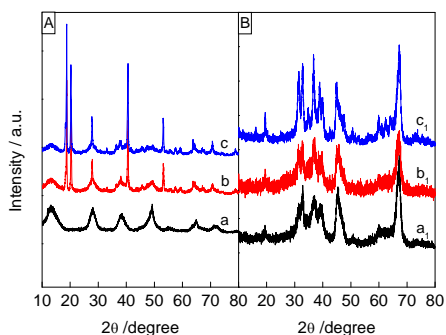


Figure 4. X-ray diffraction patterns of the as-prepared (A) and the 800 °C calcined alumina (B).

Figure 4 presents the X-ray diffraction patterns of the as-prepared and the corresponding calcined alumina. Sample a exhibited diffraction peaks assigned to the boehmite phase (JCPDS 21-1307), while samples b and c showed the bayerite phase (JCPDS 20-0011). The difference may

be caused by the effect of the surfactant during preparation. After calcination at 800 °C, sample a₁ exhibited δ -Al₂O₃ (JCPDS 16-0394), and samples b₁ and c₁ showed θ -Al₂O₃ (JCPDS 11-0517).

Values of palladium dispersion obtained from CO chemisorption were similar for the four catalysts: Pd/a₁, Pd/b₁, Pd/c₁ and Pd/cc, being 32.5%, 26.0%, 37.2% and 29.6%, respectively.

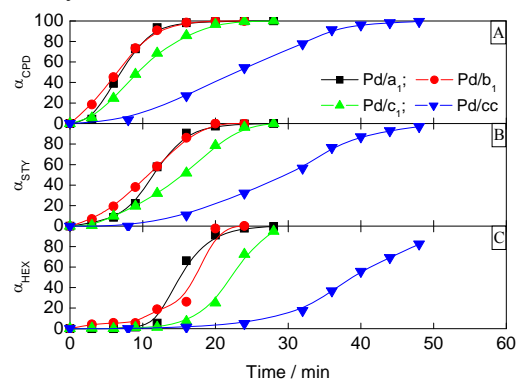


Figure 5. Comparison of catalytic activities of four catalysts: (A) cyclopentadiene; (B) styrene; (C) 1-hexene.

Figure 5 shows conversion variations of different species with time for the four catalysts. Compared with the commercial catalyst Pd/cc, the three novel catalysts (Pd/a₁, Pd/b₁ and Pd/c₁) with the hierarchically porous structure obviously exhibited much higher reaction activities. As listed in Table 2, although Pd/c₁ had smaller pore volume and specific surface area than Pd/cc, the former showed much higher activities than the latter. Apparently, the uniquely hierarchically macro-mesoporous structure of the novel catalysts plays a significant role in improving the activity. As far as the novel catalysts are concerned, Pd/a₁ and Pd/b₁ had similar activities, and both of them displayed higher activities than Pd/c₁. This is reasonable considering that Pd/a₁ and Pd/b₁ possessed similar textural properties and had larger pore volume and specific surface area than Pd/c₁.

In addition, comparison of the hydrogenation selectivity of diolefins to monoolefins among the four catalysts revealed that the three novel catalysts had the higher selectivity than the commercial Pd/cc catalyst.

Conclusions

The hierarchically macro-mesoporous structure of the novel palladium catalysts is greatly favorable for the selective hydrogenation of pyrolysis gasoline.

References

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