Platinum nanoparticles encapsulated in HZSM-5 crystals as an
efficient catalyst for green production of *p*-aminophenol

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Abstract

An intimately bifunctional catalyst composed of Pt nanoparticles encapsulated in crystals of HZSM-5 zeolite has been studied for one-pot hydrogenation of nitrobenzene (NB) to *p*-aminophenol (PAP) without the use of inorganic acid. The cooperation between the Pt-encapsulated nanoparticles and surrounding acid sites of HZSM-5 endowed the catalyst excellent performance, high selectivity and good recyclability, for the environmentally benign production of PAP. Interesting and importantly, the cooperation effect between metallic Pt sites and acid sites intimately surrounded affected the PAP selectivity and those acid sites that a little longer apart from the platinum particles were basically invalid.

Keywords: Pt nanoparticles, encapsulated, zeolite, hydrogenation, nitrobenzene, *p*-aminophenol

1. Introduction

The selective catalytic hydrogenation of nitrobenzene (NB) to p-aminophenol (PAP) is an important industrial reaction because PAP is widely used as an important intermediate for the production of medicines [1], pesticides and dyestuff [2]. The reaction contains the hydrogenation of NB to N-phenylhydroxylamine (PHA), followed by the Bamberger rearrangement of PHA to PAP in acidic medium, and the further hydrogenation of PHA resulted the main by-product of aniline (AN) [3]. Conventionally, sulfuric acid is used for the rearrangement of PHA to PAP [4]. However, the use of strong organic acid solution not only can corrode the facilities and destroy the catalysts, but also generate a large volume of effluents due to the neutralization step of the acidic reaction mixture for the separation of PAP [5,6]. In order to eliminate these problems, great efforts have been devoted on developing environment benign catalysts, including treating the supports with acid [7-9] or using solid acid substitute sulphuric acid [10-12]. Among which, solid acid catalysts have been attracted great attention due to their high acid density, mechanical stability, structural diversity and higher recycling rate. Various solid catalysts, such as HZSM-5 zeolites¹, MgAPO-5 crystals [2,11], and zirconium sulphate [12] et al. were employed as the support for the hydrogenation of nitrobenzene to PAP. However, these catalysts either require additives or difficult to recycle, which lead to complicated downstream processing and high cost. Therefore, it is necessary to develop a green composite solid catalyst for effective one-pot hydrogenation of nitrobenzene to PAP without the use of sulfuric acid.

It is well known that the metal nanoparticles and acid sites in catalysts are the two critical points on improving the product selectivity for the hydrogenation of nitrobenzene to PAP, and thus many works have been pay attention to improving the acidity of the solid acids [1,13,14] or changing the metal active sites [11]. Actually, the distance between metal sites and acid sites is more vital to the selectivity [15,16]. Weisz [17] put forward the intimacy criterion that the catalytic activity will decrease

as the distance between metal sites and acid sites become too large to lose cooperation efforts in hydrocracking reactions. Recently, Zecevic et al. [18] also proposed that the distance between metal sites and acid sites is very important due to the specific requirements of the target process. As to the rate kinetics controlled hydrogenation of NB to PAP (Scheme 1), the rearrangement rate of PHA to PAP is the critical factors to achieve a high PAP selectivity, which should be higher than the rate of complete hydrogenation of PHA to by-products aniline [12]. Therefore, the intimacy cooperation between metal sites and acid sites may accelerate the diffusion of hydrogenation intermediate product PHA to acid sites, where the rearrangement of PHA is proceeding. However, the reported catalysts scarcely take into account of the intimately cooperation effect between metal sites and acid sites for the hydrogenation of NB to PAP.

Aluminosilicate zeolites are widely applied in adsorption, catalysis and separation processes due to their uniform channel sizes, unique shape selectivity, high thermal and hydrothermal stability, and tunable strong acid sites [19]. Pt support on some zeolites, such as ZSM-5 [1], Beta [10] and SAPO-5 [13,20], were used as the catalyst for the hydrogenation of nitrobenzene, however, the yield of aim product PAP is low. In recent years, encapsulated metal nanoparticles within zeolites have attracted great attention due to its specific structure, which can keep metal nanoparticles against sintering and lead the metal sites intimacy contact and cooperate with the surrounding acid sites to create novel properties for catalysis [21,22]. Recently, we have designed a facile and effective two-step DGC synthesis route to encapsulate Pt nanoparticles in the interior of MFI zeolite crystals [23]. Herein, we extended the Pt@HZSM-5 zeolites to the hydrogenation of nitrobenzene to PAP and investigated the cooperation effect between Pt nanoparticles and acid sites of HZSM-5. Furthermore, we anticipate that the synthesis and application of Pt@HZSM-5 zeolites may expand the kinds of solid acid catalysts for the hydrogenation of PAP and benefit the design of multifunctional catalysts.

2. Experimental

2.1 Catalyst preparation

Pt@HZSM-5 zeolites were synthesized by the two-step dry gel conversion (DGC) method which reported in our previous publications [23]. Firstly, alkali treatment was employed to introduce intracrystalline mesopores within commercial ZSM-5 zeolites, followed with the deposition of platinum in the pores of hierarchical ZSM-5 by impregnation method. Then, the Pt-containing alkali-treated hierarchical ZSM-5 was highly dispersed in ZSM-5 synthesis gel to form an aluminosilicate coating and crystallized at 453K using the dry gel conversion method. The obtained as-calcined Pt@ZSM-5 zeolites were transformed into H-form by ion-exchanging with an aqueous solution of ammonium nitrate twice, and the final obtained products were as-calcined Pt@HZSM-5(*n*) zeolites. The *n* in the sample name is the platinum content in the synthesis gels. **The poisoned Pt@HZSM-5 samples were prepared by impregnating the Pt@HZSM-5 with an ethanol solution of dibenzothiophene.** The compared sample of Pt/HZSM-5 was prepared by impregnation method. The detailed procedure of the above samples has been thoroughly described in supporting information.

2.2 Catalytic testing

The hydrogenation of nitrobenzene was tested by adding catalyst (100 mg), nitrobenzene (80 mg) and deionized water (600 μ l) were added to a batch-type autoclave reactor and performed at 1.0 MPa H₂ and 130 °C for 3 hours under stirring at 180 rpm. The detailed procedure of the above tests has been thoroughly described in supporting information.

3. Results and discussion

3.1 Catalyst characterization

The XRD patterns of Pt@HZSM-5(*n*) with various Pt contents synthesized by the two-step DGC synthesis route are illustrated in Fig. S1. All of the Pt@MFI samples displayed a set of Bragg reflections assigned to MFI structure with higher intensities, similar to commercial ZSM-5. The degree of crystallization for the final samples declines slightly with the increasing of Pt

loading in the initial synthetic gels, which is caused by the increased Pt content in the synthesis gel hampers the formation of the zeolite.

The HRTEM images of Pt@HZSM-5 zeolites calcined at 550 °C with various Pt contents are shown in Fig. S2. It can be seen that a uniform size of ca. 3 nm Pt nanoparticles are distributed throughout the zeolite crystallites, which shown a coffin morphologies. As can be seen from HAADF-STEM images in Fig. 1 and Fig.S3, the bright spots, which represent Pt nanoparticles, are uniformly distributed in the interior of ZSM-5 crystals. These results were in accordance with our previous work [23], suggesting the successful encapsulation of Pt nanoparticles in the HZSM-5 crystals.

3.2 Catalytic performance of Pt@HZSM-5 zeolites with different Pt loading

The catalytic performance of the Pt@HZSM-5 zeolites with various Pt contents for the hydrogenation of nitrobenzene to PAP was investigated. As shown in Fig. 2, Pt/HZSM-5(0.5) sample exhibits a 100% NB conversion and 11% PAP selectivity, indicated that the Pt nanoparticles on the surface of zeolites have poor selectivity for the target product. In contrast, all of the Pt@HZSM-5(n) zeolites obtained by two-step DGC synthesis route exhibit superior catalytic performance with 100% conversion and high selectivity of ca. 60%. As the increasing of Pt loading in Pt@HZSM-5 (Table S1), the selectivity of the target product PAP increased from 50% to 60%, indicated that the selectivity of PAP increased with the increasing of Pt-encapsulated contents in HZSM-5 zeolites.

To investigate the catalytic performance of Pt nanoparticles encapsulated in HZSM-5 crystals, dibenzothiophene poisoned catalysts was employed to eliminate the influence of Pt nanoparticles on the surface of zeolites. Because dibenzothiophene has a molecular diameter (ca. 0.8 nm) larger than the widths of the tunnels in ZSM-5 zeolite (ca. 0.46-0.56 nm), the dibenzothiophene molecules could only contact the surface Pt while the Pt particles inside the HZSM-5 crystals remained untouched [25,26]. Comparing with Pt@HZSM-5(0.5), the selectivity of poisoned Pt@HZSM-5(0.5) improved to 74%, demonstrated that the Pt-encapsulated nanoparticles is the vital active sites for the target products of PAP. However, a longer

reaction time was needed by the poisoned Pt@HZSM-5(0.5) zeolites to get the 100% conversion. Because the dibenzothiophene with a large molecular not only poisoned the Pt nanoparticles but also block off some pores of HZSM-5 zeolites, the diffusion of reactants become more difficult. Therefore, the Pt-encapsulated nanoparticles in HZSM-5 zeolites are the active sites for the hydrogenation of nitrobenzene to PAP. It is concluded that the Pt-encapsulated nanoparticles in Pt@HZSM-5 zeolites intimacy cooperate with the surrounding acid sites, which leading a high diffusivity of hydrogenation intermediate product PAP to acid sites and thus proceeding the rearrangement of PHA to PAP.

As listed in Table S3, publications mainly focused on support Pt on different solid acids for the hydrogenation of NB to PAP. Deshpande et al. [12] studied a catalyst composed of Pt/ZrO₂ and zirconium sulphate shown 87% conversion and 88% of PAP selectivity, however, there were no recycle tests to investigate the stability of the catalyst. Recently, Wang et al. [11] using Pb-Pt/MgAPO-5 catalyst with the addition of surfactant processed 100% conversion and 75.5% selectivity. Comparing with the reported catalysts used in the mentioned reaction (Table S3), the Pt@HZSM-5 zeolites with a novel encapsulated structure not only exhibited 100% conversion and excellent PAP selectivity as high as 74% , but also shown good stability in recycle tests.

3.3 The recycle tests of Pt@MFI(0.5) zeolites

The recycle test in Fig. 3A shows a good reusable characterization of Pt@HZSM-5 zeolites. In the first and second cycle test, the conversion of nitrobenzene largely decreased but the PAP selectivity increased. In order to investigate the increasing of PAP selectivity, the reaction solutions were collected and analyze the Pt contents (Table S1). It was found that litter Pt existed in the first and second recycled solution and the Pt content is decreasing with the cycle index, indicating some Pt nanoparticles may drop out from the zeolites. As the HRTEM of the recycled Pt@HZSM-5(0.5) zeolites shown (Fig. S3), there were small cracks or defective sites existing in the crystal, which may be formed by the acuity reaction

condition or the fierce H-exchange preparation processing. Moreover, these small cracks or defective sites may increased as the increasing of Pt content in zeolites due to the thinner aluminosilicate hydrogel coating of the Pt-contained precursor. However, there was no Pt in the third recycled solution, indicating that the remaining effective Pt nanoparticles are well encapsulated in crystals and stable in reactions. Thus, the catalyst still maintained high yield with slightly decreasing compared to the original yield data in the following recycles tests.

The recycle tests of the poisoned Pt@HZSM-5(0.5) zeolites were also investigated in Fig. 3B. As can be seen, the conversion is near 100% even recycled five times due to the prolonging of the reaction time. However, the selectivity slowly decreased with the increasing of cycle times, which may be caused by the falling of the poisoned agent of dibenzothiophene. When fresh poisoned Pt@HZSM-5(0.5) zeolites were supplemented in reaction 6* as half of the catalysts, the conversion and the PAP selectivity were all recovery to the primary level of the first cycle test.

3.3 The investigation of cooperation effort between Pt nanoparticles and acid sites

The acid strength of solid acid catalysts is important in the selectivity hydrogenation of nitrobenzene to PAP [17], and it has been found by Komatsu et al. [1] that the selectivity of Pt/HZSM-5 was affected by different $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in the HZSM-5. In order to investigate the cooperation between Pt nanoparticles and acid sites, a series of Pt@HZSM-5(0.5) catalysts with different Al concentration were synthesized by changing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios in the synthesis gel.

A set of MFI characteristic diffractions in XRD patterns (Fig. S4) and high BET surface area (Table S1) indicated that Pt@HZSM-5(0.5) zeolites with various $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were formed. As can be seen from Fig. S4, the Pt@HZSM-5(0.5) samples with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 100 and 40 and Al-absent sample all show high crystallinity. However, the sample with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 20 shown relatively low crystallinity, because heavy amounts of Al in the synthesis gel hamper the crystallization of the zeolites. As the NH_3 -TPD measurements shown in Fig. 4,

Pt@HZSM-5(0.5) with Al-absent exhibits two desorption signals at ca. 150 °C and 200°C corresponded to NH₃ adsorbed on acid sites with weak and medium strength respectively, and the third desorption signal at 430 °C ascribed to strong acid site. When increasing the Al content in the synthesis gel, the desorption signals shifted to the high temperature, indicating that the acid strength of the Pt@HZSM-5(0.5) increased with the increasing of Al contents in the synthesis gel.

The catalytic performance of Pt@HZSM-5(0.5) with different SiO₂/Al₂O₃ ratios was investigated in Fig. 5. As can be seen, the Pt@HZSM-5(0.5) zeolites with SiO₂/Al₂O₃ ratios of 40, 100 and Al-absent sample, which have the different acid strength (Fig. 4), all shown similar PAP selectivity around 60% together with 100% conversion, indicated that the changing of acid strength in Pt@HZSM-5 samples does not affect the PAP selectivity. This is because the Pt@HZSM-5 zeolites were prepared by coating Pt-contained precursor with synthesis gel followed by crystallization, the Pt-contained precursor with a constant Al content was acted as the core of the ZSM-5 crystal and the synthesis gel with different SiO₂/Al₂O₃ ratios were acted as the shell of the crystal [23]. Therefore, the changing of the SiO₂/Al₂O₃ ratios in the synthesis gel can not affect the interior environment of the crystal where Pt located in. As a result, it is confirmed that the hydrogenation of nitrobenzene to PAP mainly took place on the interior of the HZSM-5 crystals, where Pt nanoparticles cooperate with the around acid sites. Moreover, it may be concluded that the intimacy cooperation between metal sites and acid sites accelerate the diffusion of hydrogenation intermediate product PHA to acid sites, where the rearrangement of PHA is proceeding, and thus obtained the high yield of aim-products of PAP. When changing the SiO₂/Al₂O₃ ration to 20, the selectivity was slightly decreased attributed to the lower crystallinity of the crystal (Fig. S4).

4 Conclusions

In conclusion, Pt-encapsulated HZSM-5 zeolite crystals with different Pt loading were studied as catalysts for one-pot hydrogenation of nitrobenzene to p-aminophenol without the use of inorganic strong acid. Comparing with the documented results,

the Pt@HZSM-5 zeolites showed high selectivity and stability for the production of p-aminophenol. The p-aminophenol selectivity is just related to the zeolitic acid sites contacted with the platinum nanoparticles and those acid sites far away from the Pt nanoparticles, even at the same zeolite crystals, are invalid, reflecting the importance of intimate cooperation of the two kinds of active sites.

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References

- [1] T. Komatsu and T. Hirose, *Appl. Catal. A: Gen.* 276 (2004) 95.
- [2] S. Wang, Y. Ma, Y. Wang, W. Xue and X. Zhao, *J. Chem. Technol. Biotechnol.* 83 (2008) 1466.
- [3] T. Zhang, J. Jiang and Y. Wang, *Org. Process Res. Dev.* 19 (2015) 2050.
- [4] T. Wang, Z. Dong, T. Fu, Y. Zhao, T. Wang, Y. Wang, Y. Chen, B. Han and W. Ding, *Chem. Commun.* 51 (2015) 17712.
- [5] C. V. Rode, M. J. Vaidya, R. Jaganathan and R. V. Chaudhari, *Chem. Eng. Sci.* 56 (2001) 1299.
- [6] S. K. Tanielyan, J. J. Nair, N. Martin, D. J. Wang and R. L. Augustine, *Org. Process Res. Dev.* 11 (2007) 681.
- [7] R. V. Chaudhari, S. S. Divekar, M. J. Vaidya and C. V. Rode, *US Pat.* 6028227, 2000.
- [8] Y. Liu, Y. Y. Fang, X. L. Lu, Z. J. Wei and X. N. Li, *Chem. Eng. J.* 229 (2013) 105.
- [9] P. Liu, Y. Hu, M. Ni, K. You and H. Luo, *Catal Lett.* 140 (2010) 65.
- [10] K. J. Ratnam, R. S. Reddy, N. S. Sekhar, M. L. Kantam, A. Deshpande and F. Figueras, *Appl. Catal. A: Gen.* 348 (2008) 26.
- [11] S. F. Wang, B. B. He, Y. J. Wang and X. Q. Zhao, *Catal. Commun.* 24 (2012) 109.
- [12] A. Deshpande, F. Figueras, M. L. Kantam, K. J. Ratnam, R. S. Reddy and N. S. Sekhar *J.Catal.* 275 (2010) 250.
- [13] S. F. Wang, Y. J. Wang, Y. Gao and X. Q. Zhao, *Chin. J. Catal.* 31 (2010) 637.
- [14] S. F. Wang, Y. D. Jin, B. B. He and Y. J. Wang, *Sci. China* 53 (2010) 1514.

- [15] J. Francis, E. Guillon, N. Bats, C. Pichon, A. Corma and L. J. Simon, *Appl. Catal. A* 409-410 (2011) 140.
- [16] J. Kim, W. Kim, Y. Seo, J. C. Kim and R. Ryoo, *J. Catal.* 301(2013)187.
- [17] P. B. Weisz, *Adv. Catal.* 13 (1962) 137.
- [18] J. Zecevic, G. Vanbutsele, K. P. D. Jong and J. A. Martens, *Nature*, 528 (2015) 245.
- [19] C. S. Cundy and P. A. Cox, *Chem. Rev.* 103 (2003) 663.
- [20] B. Liu, Y. C. Qin, L. Wang, Z. S. Mo, X. T. Zhang, L. J. Song, *Petrochem. Technol. Appl.* 32 (2014) 298-301.
- [21] S. Goel, S. I. Zones and E. Iglesia, *J. Am. Chem. Soc.* 136 (2014) 15280.
- [22] T. L. Cui, W. Y. Ke, W. B. Zhang, H. H. Wang, X. H. Li and J. S. Chen, *Angew. Chem. Int. Ed.* 55 (2016) 1.
- [23] J. Gu, Z. Zhang, P. Hu, L. Ding, N. Xue, L. Peng, X. Guo, M. Lin and W. Ding, *ACS Catal.* 5 (2015) 6893.
- [24] Y. T. Bai, X. C. Zhu, L. X. Zhang, N. P. Xu, *Chin. J. Catal.* 34(2013)263-271.
- [25] H. Zhou, J. Gong, B. Xu, S. Deng, Y. Ding, L. Yu, Y. Fan, *Chinese J. Catal.* 2017, Doi:10.1016/S1872-2067(17)62750-5.
- [26] R. Contreras, R. Cuevas-Garcia, J. Ramirez, L. Ruiz-Azuara, A. Gutierrez-Alejandre, I. Puente-Lee, P. Castillo-Villalon, C. Salcedo-Luna, *Catal. Today*, 130 (2008) 320-326.

Figure captions

Scheme 1 Hydrogenation of nitrobenzene to p-aminophenol by Pt@HZSM-5 zeolites.

Fig. 1 HAADF-STEM images of as-calcined Pt@HZSM-5(0.8) zeolites obtained by the two-step dry gel conversion synthesis route.

Fig. 2 Catalytic activities of different samples: Pt@HZSM-5 (*n*) with various Pt contents prepared by two-step synthesis route; Poisoned Pt@HZSM-5(0.5) crystals (metal sites on the surface of HZSM-5 crystals was selective poisoned by dibenzothiophene); impregnated Pt/HZSM-5(0.5) zeolites. The reaction time of all samples were 3 h except the poisoned Pt@HZSM-5(0.5) zeolites with a longer time of 5 h.

Fig. 3 The recycle tests: (A) Pt@HZSM-5(0.5) zeolites, reaction time 3 h. (B) Poisoned Pt@HZSM-5(0.5) samples, reaction time 5 h. Some fresh poisoned Pt@HZSM-5(0.5) zeolites were supplemented in reaction 6*. Reaction conditions of all experiments: 100 mg catalyst, 80 mg nitrobenzene, 600 μ l deionized water, 1.0 MPa H₂, 130 °C. Catalyst was filtrated, washed, and dried at 353 K before next use.

Fig. 4 NH₃-TPD of Pt@HZSM-5(0.5) with different SiO₂/Al₂O₃ ratios obtained by the two-step DGC route: (a) no Al; (b) 100; (c) 40; (d) 20.

Fig. 5 Effect of the SiO₂/Al₂O₃ ratios on the conversion of nitrobenzene and the selectivity of PAP by Pt@HZSM-5(0.5) zeolites. When Al was absent in the synthesis gel, the SiO₂/Al₂O₃ ratio was noted as *. Reaction conditions: 100 mg catalyst, 80 mg nitrobenzene, 600 μ l deionized water, 1.0 MPa H₂, 130 °C, 3 h.

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Graphical abstract