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Liquid Phase Hydrogenation of Nitrobenzene to Para-Aminophenol over Pt/ZrO_2 Catalyst and $SO_4^{2-}/ZrO_2–Al_2O_3$ Solid Acid

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Abstract $ZrO_2–Al_2O_3$ binary oxide was prepared by homogeneous coprecipitation method. SO_4^{2-}/ZrO_2 and $SO_4^{2-}/ZrO_2–Al_2O_3$ were prepared by impregnation method and were characterized by BET, XRD and TPD. Pt/ZrO_2 was prepared by incipient wetness impregnation of ZrO_2 with an aqueous solution of H_2PtCl_6. Subsequently, hydrogenation of nitrobenzene to para-aminophenol over Pt/ZrO_2 catalyst and $SO_4^{2-}/ZrO_2–Al_2O_3$ solid acid using water as solvent was performed. The results indicate that para-aminophenol as well as a small quantity of aniline and ortho-aminophenol are obtained without using any environmentally undesirable liquid acid. The para-aminophenol selectivity reaches to 74.9% with 44.8% of nitrobenzene conversion under the optimal reaction conditions. And the amount of Al_2O_3 in $SO_4^{2-}/ZrO_2–Al_2O_3$ has great influence on the selectivity to para-aminophenol.

Keywords Nitrobenzene hydrogenation · Para-aminophenol · Bamberger rearrangement · $SO_4^{2-}/ZrO_2–Al_2O_3$ solid acid

1 Introduction

Para-aminophenol (PAP) is a commercially important intermediate for the production of analgesic and antipyretic drugs, such as paracetamol and acetaminophen [1]. The commercial manufacture of PAP is typically carried out in stirred tank reactors in which a four-phase system is used to accomplish the Pt-catalyzed hydrogenation of nitrobenzene and the acid-catalyzed Bamberger rearrangement of the hydrogenation intermediate product, *N*-phenylhydroxylamine (PHA) (see Scheme 1). The first hydrogenation reaction is catalyzed by metal catalysts and the rearrangement process is catalyzed by acid catalysts. By-products are aniline through the successive hydrogenation of PHA intermediate and ortho-aminophenol (OAP) through the Bamberger rearrangement into ortho position [2]. The shortcomings of this route mainly involve the corrosion problems due to the necessary use of mineral acid and the loss of expensive active component of the catalyst. Hydrogenation of nitrobenzene to PHA has been studied with various metal catalysts [3–7], and the Bamberger rearrangement of PHA to PAP using a solid acid catalyst instead of sulfuric acid has seldom been studied. Wang et al. [8] used metal–solid acid bifunctional catalyst to synthesize PAP directly from nitrobenzene hydrogenation and the PAP yield was 23.9% with a selectivity of 46.6%. Chaudhari et al. [9] reported that ion-exchange resin and Pt–S/C were simultaneously used to synthesize PAP from nitrobenzene and the PAP yield was 13.9%. A series of Pt-solid acid bifunctional catalysts using HF-SiO_2, H-ZSM5 and supported heteropoly acid as support were prepared by Chu et al. [10]. Unfortunately, these catalysts showed very low activity in a non-acid medium. In this work, a single-step synthesis of PAP from nitrobenzene over Pt/ZrO_2 and $SO_4^{2-}/ZrO_2–Al_2O_3$ using water as solvent was carried out.

2 Experimental

2.1 Catalyst Preparation

$Zr(OH)_4$ was prepared by precipitation of aqueous solution of $ZrOCl_2$ with 28 wt% ammonia. ZrO_2 support was

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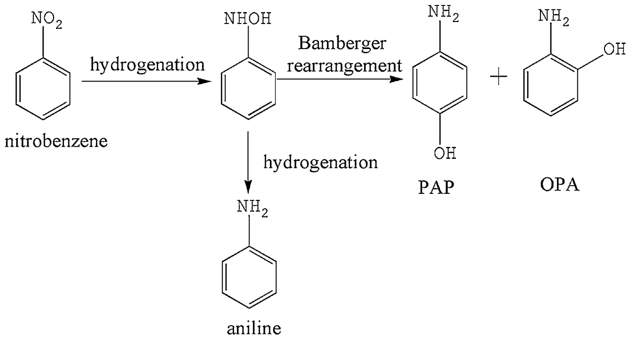

Scheme 1 Schematic of hydrogenation of nitrobenzene

prepared by calcination of $Zr(OH)_4$ at 873 K for 3 h under air flow. Pt/ZrO_2 was prepared by incipient wetness impregnation of the obtained ZrO_2 with an aqueous solution of H_2PtCl_6. Then the sample Pt/ZrO_2 was dried at 393 K for 2 h, calcinated under air flow at 633 K for 2 h and reduced at 723 K for 3 h.

The ZrO_2–Al_2O_3 binary oxide was prepared by homogeneous coprecipitation method. For this purpose, aqueous solutions of $ZrOCl_2{\cdot}xH_2O$ and $Al(NO_3)_3{\cdot}xH_2O$ were mixed together. Then the mixture was hydrolyzed with dilute ammonium hydroxide under vigorous stirring until the pH reached to 9–10. A white precipitate was formed and the precipitate was allowed to age at 353 K for 12 h. After filtration, the samples were washed with deionized water for several times and dried at 393 K for 12 h. The prepared hydrous alumina–zirconia was immersed in 1 M H_2SO_4 for 30 min to incorporate sulfate ions. The excess water was evaporated and the obtained samples were dried at 393 K for 12 h, calcinated at 923 K for 4 h. The SO_4^{2-}/ZrO_2 solid acid catalyst was labeled as SZ. The SO_4^{2-}/ZrO_2–Al_2O_3 samples were labeled as SZA-1, SZA-2, SZA-3, SZA-4 and SZA-5 according to the Zr:Al molar ratio of 9:1, 7:3, 1:1, 3:7, and 1:9, respectively. The particle size of the catalyst used for the catalytic tests was between 100 to 120 mesh.

2.2 Catalyst Characterization

BET surface areas and pore volume distributions of the catalysts were measured on a Quantachrome NOVA 2200e by N_2 adsorption at 77 K. Prior to the analysis, each sample was degassed at 573 K for 3 h in vacuum under 10^{-3} Torr. BET nitrogen porosimetry analysis was done with multipoint calibration curves. The pore volume was calculated from the adsorption isotherms using Barrett–Joyner–Halenda (BJH) method.

X-ray diffraction (XRD) patterns of the solid catalysts were recorded on a DX-1000 diffractometer, operating at 40 kV and 25 mA and using nickel-filtered Cu Kα radiation. Scanning speed was 3.6° min^{-1} and scanning range was over 10°–70°.

Temperature programmed desorption (TPD) of NH_3 was performed on chem BET 3000. The catalysts were swept by N_2 flow at 573 K for 1 h and then cooled to 353 K. Pure NH_3 was introduced for about 20 min, followed by purging with N_2 for 30 min at 353 K, then the samples were purged further with He flow (50 ml/min) for 2 h at 373 K. And the samples were heated at a ramp of 10 K/min up to 973 K.

2.3 Typical Experimental Procedure

The reaction of hydrogenation of nitrobenzene to PAP was carried out in a 50 ml stainless steel autoclave with a magnetic stirrer. 0.02 g Pt/ZrO_2, 0.6 g SO_4^{2-}/ZrO_2–Al_2O_3, 2.4 g nitrobenzene and 0.01 g hexadecyl trimethyl ammonium bromide (CTAB) along with 30 ml H_2O as solvent were added into the autoclave. The autoclave was then purged with nitrogen. The reaction was carried out at 353 K and 0.3 Mpa H_2 pressure for 3 h. The reaction products were analyzed using a high performance liquid chromatograph equipped with a 4.6 mm × 250 mm C18 column, with 30:70 of $CH_3OH:H_2O$ as eluent.

3 Results and Discussion

3.1 The Characterizations of Catalysts

BET surface areas and pore volume of various samples are shown in Table 1. BET surface areas of all the catalysts are little lower than those reported in the literatures [11]. This may be attributed to the influence of preparation parameters such as the calcination temperature, sulfating agents and the concentration [12, 13]. As can be seen from Table 1, BET surface area increases when Zr:Al molar ratio decrease from 9:1 to7:3. And BET surface area increases greatly when Zr:Al molar ratio varies from 1:1 to 1:9. BET surface area reaches to the maximum of 177.59 m^2/g when Zr:Al molar ratio is 1:9, which indicates that the introduction of Al_2O_3 contributes to the increase of BET surface area.

Table 1 BET surface areas and pore volume of SZ and SZA

Materials	Specific area (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
SZ	74.11	0.07	1.42
SZA-1	71.08	0.15	6.57
SZA-2	90.29	0.26	6.60
SZA-3	71.35	0.24	7.89
SZA-4	87.53	0.16	3.82
SZA-5	177.59	0.19	3.84

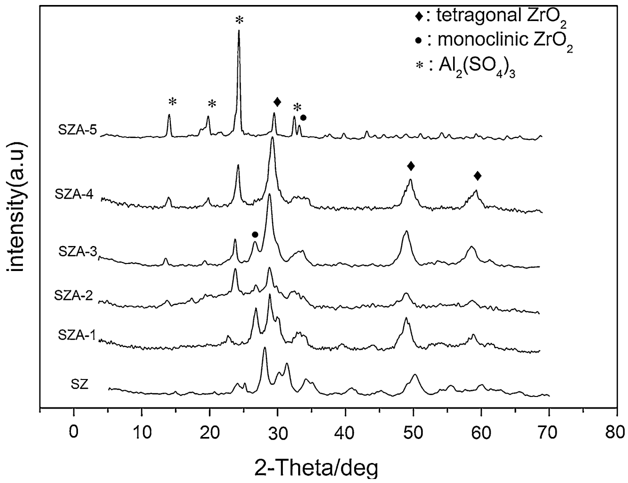

Fig. 1 X-ray powder diffraction patterns of SZ and SZA

XRD patterns of the samples are shown in Fig. 1. The tetragonal ZrO_2 and monoclinic ZrO_2 phase are observed in SO_4^{2-}/ZrO_2. The $Al_2(SO_4)_3$ crystalline phase emerges in $SO_4^{2-}/ZrO_2–Al_2O_3$ in addition to zirconium species. It can be seen from Fig. 1 that the tetragonal phase increases slightly and the monoclinic phase reduces with the increase of the content of Al. It might be due to the interaction of Al, Zr and sulfating agents resulting in the formation of Al–O–Zr bands [14]. It is shown that the Al_2O_3 plays an important role in stabilizing tetragonal ZrO_2, and the introduction of Al prevents the tetragonal ZrO_2 from transforming to the monoclinic ZrO_2. Among all these catalysts, no diffraction pattern for Al_2O_3 is observed, which indicates that the Al_2O_3 is uniformly distributed in ZrO_2 [15].

TPD of NH_3 spectra of SZA are shown in Fig. 2. It can be seen that all the catalysts afford a broad desorption profiles over the range from 373 to 973 K, suggesting a broad distribution of heterogeneous acid sites. The acidic sites are artificially divided into weak, middle and strong acidic centers [16, 17]. SZA-1 with small amount of Al_2O_3 has the largest amount of acid sites. It has been reported that the increase of acid strength was caused by the formation of Al–O–Zr [14]. And the acid strength of the SZA samples decrease gradually with the increased content of Al. There is a strong acid site on SZA-3 and SZA-5, respectively, which give NH_3-TPD peaks about at 870 K. Combined with the results of XRD, the enhanced acid strength on the SZA-3 sample might be related to the formation of the tetragonal ZrO_2 phase [12].

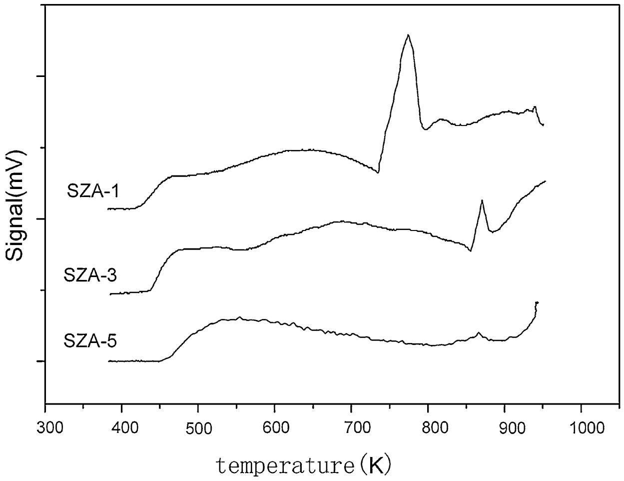

Fig. 2 NH_3-TPD profiles of the catalysts

3.2 Catalytic Performance

The influence of different solid acid on the reaction is shown in Table 2. As can be seen from Table 2, the selectivity to PAP is only 0.33% in the absence of solid acid catalyst. The selectivity to PAP is enhanced significantly with the action of SZ or SZA solid acid catalysts. And the SZA catalysts give better results, especially, the SZA-5 with the Zr:Al molar ratio of 1:9 gives the best result with the selectivity of 74.9%.

From the results of the catalytic test, it shows that acidic sites on the catalyst are necessary for Bamberger rearrangement process. However, SZA-1 catalyst with the strongest and the largest amount of acidic site does not give the best result. On the contrary, SZA-4 and SZA-5 with less acidic site give better performance. It might be an integrated effect of suitable amounts of acidic sites and BET surface area on the performance of nitrobenzene hydrogenation to PAP.

The effect of reaction temperature on the nitrobenzene conversion and PAP selectivity is reported in Table 3. From the results reported in Table 3, it can be noted that both nitrobenzene conversion and PAP selectivity increase as the reaction temperature increases from 333 to 353 K. And nitrobenzene conversion is found to increase from 44.82 to 68.77% with further increase in temperature from 353 to 373 K. However, the selectivity to PAP decreases sharply from 74.91 to 43.5%.

Table 2 Conversion of nitrobenzene to PAP over different catalysts

Catalyst	Conversion (%)	Selectivity (%)
Pt (1%)/ZrO_2	48.66	0.33
Pt (1%)/ZrO_2 and SZ	49.86	12.38
Pt (1%)/ZrO_2 and SZA-1	50.13	15.65
Pt (1%)/ZrO_2 and SZA-2	46.83	21.33
Pt (1%)/ZrO_2 and SZA-3	47.71	37.93
Pt (1%)/ZrO_2 and SZA-4	46.64	60.19
Pt (1%)/ZrO_2 and SZA-5	44.82	74.91

Reaction conditions: temperature: 353 K, pressure: 0.3 Mpa, reaction time: 3 h

Table 3 Effect of reaction temperature

Temperature(K)	Conversion (%)	Selectivity (%)
333	32.21	50.63
343	37.88	66.03
353	44.82	74.91
363	54.13	62.42
373	68.77	43.50

Reaction conditions: catalyst: Pt (1%)/ZrO_2 and SZA-5, pressure: 0.3 Mpa, reaction time: 3 h

Table 4 Effect of platinum loading

Catalyst	Conversion (%)	Selectivity (%)
Pt (0.5%)/ZrO_2 and SZA-5	19.77	79.44
Pt (1%)/ZrO_2 and SZA-5	44.82	74.91
Pt (2%)/ZrO_2 and SZA-5	78.89	37.67

Reaction conditions: temperature: 353 K, pressure: 0.3 Mpa, reaction time: 3 h

Table 5 Stability and reusability of catalyst

Run	Conversion (%)	Selectivity (%)
1	44.82	74.91
2	41.77	65.12
3	43.25	63.69

Reaction conditions: catalyst: Pt (1%)/ZrO_2 and SZA-5, the catalyst used in the first run was used in the second and third run after simple treatment, temperature: 353 K, pressure: 0.3 Mpa, reaction time: 3 h

The influence of platinum loading was studied for the catalyst prepared with $H_2PtCl_6 \cdot 6\,(H_2O)$ within the range of 0.5–2% (w/w) platinum. As can be seen from Table 4, increasing platinum loading increases nitrobenzene conversion and decreases the selectivity towards PAP. It may because the increasing platinum loading helps to promote over hydrogenation of PHA intermediate to byproduct aniline.

The Pt (1%)/ZrO_2 and SZA-5 were selected to test the stability and reusability (Table 5). After reaction, the catalysts were separated by filtration, washed with ethanol and calcined at 923 K. The results of reusability of the catalysts are shown in Table 5. It can be seen from Table 5 that the selectivity to PAP decreases from 74.9 to 65.1% in the second run and almost keeps the value of about 60–64%. We find that the deactivation of the catalysts is mainly caused by the adsorbed species on the surface of the catalysts and removal of these species is helpful to restore the activity of the catalyst.

On the basis of the results in this work and the reported findings [2, 8], the possible reaction mechanism of liquid hydrogenation of nitrobenzene with solid acid over Pt/ZrO_2 is proposed. Firstly, nitrobenzene is adsorbed on the active center of Pt/ZrO_2 catalyst and reacts with the adsorbed activated hydrogen molecule to form PHA intermediate. The formed PHA desorbs from Pt/ZrO_2 and adsorbs on the acid sites of SO_4^{2-}/ZrO_2–Al_2O_3 and then rearranges to PAP with the aid of water molecules as a nucleophilic reagent. And the undesorbed PHA will further react with hydrogen to obtain aniline.

4 Conclusions

In conclusion, the hydrogenation of nitrobenzene to para-aminophenol over Pt/ZrO_2 and SO_4^{2-}/ZrO_2–Al_2O_3 was developed in this work. The prepared catalysts were characterized by BET, XRD and TPD. The results indicate that the amount of Al_2O_3 in SO_4^{2-}/ZrO_2–Al_2O_3 solid acid catalyst has remarkable influence on the selectivity to para-aminophenol. And an optimized para-aminophenol selectivity of 74.9% was obtained over Pt/ZrO_2 and SO_4^{2-}/ZrO_2–Al_2O_3 with Zr:Al molar ratio of 1:9.

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