Chinese Journal of Catalysis 37 (2016) 234–239

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Article

Selective hydrogenation of phenol to cyclohexanone in water over Pd catalysts supported on Amberlyst-45

Mengsi Zhao, Juanjuan Shi, Zhaoyin Hou *

Institute of Catalysis, Department of Chemistry, Zhejiang University, Hangzhou 310028, Zhejiang, China

ARTICLE INFO

Article history:
Received 3 September 2015
Accepted 29 September 2015
Published 5 February 2016

Keywords:
Phenol
Hydrogenation
Cyclohexanone
Palladium
Amberlyst-45 resin
Supported catalyst

ABSTRACT

A series of Pd catalysts were prepared on different supports (Fe_2O_3, SiO_2, ZnO, MgO, Al_2O_3, carbon, and Amberlyst-45) and used in the selective hydrogenation of phenol to cyclohexanone in water. The Amberlyst-45 supported Pd catalyst (Pd/A-45) was highly active and selective under mild conditions (40–100 °C, 0.2–1 MPa), giving a selectivity of cyclohexanone higher than 89% even at complete conversion of phenol. Experiments with different Pd loadings (or different particle sizes) confirmed that the formation of cyclohexanone was a structure sensitive reaction, and Pd particles of 12–14 nm on Amberlyst-45 gave better selectivity and stability.

1. Introduction

Cyclohexanone is an important organic compound in the manufacture of nylon. Cyclohexanone is produced by the selective oxidation of cyclohexane in air over cobalt catalysts [1–4]. Alternatively, cyclohexanone can also be synthesized by the selective hydrogenation of phenol, but this requires high temperature and gives several byproducts such as cyclohexanol and cyclohexane [2,3]. Ways to increase the selectivity to cyclohexanone have been much studied in recent years [5–7]. Several catalysts including Pd [8–12], Pt [13,14], Rh [15], and Ni [16,17] catalysts were reported frequently, and Pd-based catalysts are favored for this reaction for its high activity and selectivity. At the same time, many supports, including NaY zeolite [1], carbon [18], hydrophilic carbon [19], MgO [20], Fe_2O_3 [20], mesoporous CeO_2 [21], HZSM-5 [22], metal organic frameworks (MOFs) [23,24], SiO_2, γ-Al_2O_3 [25,26], and mpg-C_3N_4 [5,27], have been used as the support of Pd. The product distribution depends on both the active metal and support, and a co-added acid or acidity of the catalyst can improve the conversion of phenol [1,28]. However, achieving a high selectivity of cyclohexanone (> 90%) at high phenol conversion (> 80%) with a single catalyst remains challenging.

An ion exchange resin is a porous, insoluble matrix with a high surface area. It is widely used in catalysis for its strong acidity. The Amberlyst-45 resin (A–45) is a new macroporous polymer designed for use at high temperature. It is made of polystyrene sulfonate and its concentration of acid sites can reach 2.95 eq/kg. In this work, Pd nanoparticles (NPs) were loaded on A-45 by a facile routine, and this Pd/A-45 catalyst was used in the selective hydrogenation of phenol to cyclohexanone in water.

* Corresponding author. Tel/Fax: +86-571-88273283; E-mail: zyhou@zju.edu.cn
This work was supported by the National Natural Science Foundation of China (21473155, 21273198, 21073159) and the Natural Science Foundation of Zhejiang Province (LZ12B03001).
DOI: 10.1016/S1872-2067(15)60997-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 2, February 2016

2. Experimental

2.1. Catalyst preparation

Commercial resin Amberlyst-45 (A-45, Dow Chemical Company) was purchased from Sigma Co. (China Branch). It was washed with distilled water 3 times and dried in vacuum at 50 °C for 12 h before use. First, 1.0 g of A-45 was immersed in an aqueous solution of $PdCl_2$ (30 mL, containing a controlled amount of Pd) under stirring at 50 °C for 24 h. Then, the solid particles were separated by filtration, washed with a mixed solution of ethanol/water (1:1 by volume) until free of Cl^-, and further dried under vacuum at 50 °C for 12 h. Finally, the dried solid was pretreated in a flow of H_2 at 120 °C for 1.0 h before the catalytic reaction. These catalysts were denoted as Pd(*x*)/A-45, where *x* wt% is the loading of Pd.

As references, Fe_2O_3, SiO_2, ZnO, MgO, Al_2O_3, and active carbon (AC) supported Pd catalysts were also prepared by an impregnation method described elsewhere [29]. Before impregnation, the support was first calcined at 500 °C in N_2 flow for 4 h and then impregnated with an aqueous solution of $PdCl_2$ with equal weight ratio of Pd and support. The precursor was dried in N_2 at 110 °C overnight followed by calcination in N_2 at 500 °C for 4 h. Before the catalytic reaction, the catalyst was reduced in H_2 at 120 °C for 1 h.

The loading of Pd on the above catalysts was checked by inductively coupled plasma atomic emission spectroscopy (ICP, Plasma-Spec-II spectrometer). The results are summarized in Table 1.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were performed on a Rigaku D/MAX 2550/PC diffractometer (18 kW) at 40 kV and 100 mA with Cu K_α radiation (λ = 1.5406 Å) in the range of 5°–80°. The surface area of the catalysts was measured by N_2 adsorption using an ASAP 2010 analyzer (Micromeritics) after pretreatment at 100 °C for 4 h under vacuum. X-ray photoelectron spectra (XPS) were recorded on a Perkin-Elmer PHI ESCA System. The X-ray source was an Mg standard anode (1253.6 eV) at 12 kV and 300 W. Transmission electron microscopy (TEM) images were obtained using an accelerating voltage of 200 kV (TEM, JEOL-2010F).

Table 1
Physical properties of the catalysts.

Catalyst	Pd loading [a] (wt%)	Particle size of Pd [b] (nm)	Surface area [c] (m^2/g)
Pd/Fe_3O_4	2.5	5.5	9.2
Pd/SiO_2	2.7	7.4	289.3
Pd/ZnO	2.8	10.1	14.7
Pd/MgO	2.8	8.0	39.4
Pd/Al_2O_3	2.6	4.5	156.2
Pd/AC	2.9	6.6	1396.0
Pd(0.9)/A-45	0.9	9.0	40.3
Pd(2.7)/A-45	2.7	12.0	39.8
Pd(4.5)/A-45	4.5	14.5	38.0

[a] Measured by ICP.
[b] Calculated using Scherrer's equation.
[c] Measured by N_2 adsorption.

2.3. Hydrogenation of phenol

The hydrogenation of phenol was carried out in a 50 mL custom designed stainless steel autoclave with a Teflon inner layer. In a typical reaction, a controlled amount of catalyst was dispersed in 20 mL aqueous solution of phenol. Then, the reactor was sealed, purged with purified hydrogen 5 times, and pressurized to the desired pressure. The reactor was heated in an oil bath and stirred with a magnetic stirrer (MAG-NEO, RV-06M, Japan). After reaction, the solid catalyst was separated by centrifugation. The liquid reaction mixture was analyzed by a gas chromatograph (HP 5890, USA) with a 30 m capillary column (HP-5) using a flame ionization detector. All products were confirmed by GC-MS (Agilent 6890-5973N). For each successive use, the catalyst was washed with water three times and dried under vacuum at 40 °C for 6 h. The conversion of phenol and selectivity for cyclohexanone (and cyclohexanol) were calculated as:

$$\text{Conversion} = (\text{phenol}_{\text{added-mol}} - \text{phenol}_{\text{remain-mol}})/\text{phenol}_{\text{added-mol}} \times 100\%$$

$$\text{Selectivity} = \text{cyclohexanone}_{\text{formed-mol}}/(\text{phenol}_{\text{added-mol}} - \text{phenol}_{\text{remain-mol}}) \times 100\%$$

3. Results and discussion

3.1. Characterization of the catalysts

Figure 1 shows the XRD patterns of the pristine A-45 resin and Pd/A-45 catalysts with different loadings of Pd. Only a broad peak of amorphous carbon appeared with A-45. Beside the peak of amorphous carbon, four characteristic diffraction peaks of Pd were detected at 40.0°, 46.5°, 68.1°, and 82.1° with all the Pd/A-45 catalysts, which corresponded to the (111), (200), (220), and (311) crystalline planes of face centered cubic of Pd (JCPDS 46-1043). The crystalline size of Pd was calculated from the half-width of the Pd(111) peak using the Scherrer equation. The results are summarized in Table 1. The particle size of Pd on A-45 increased from 9.0 nm (in Pd(0.9)/A-45) to

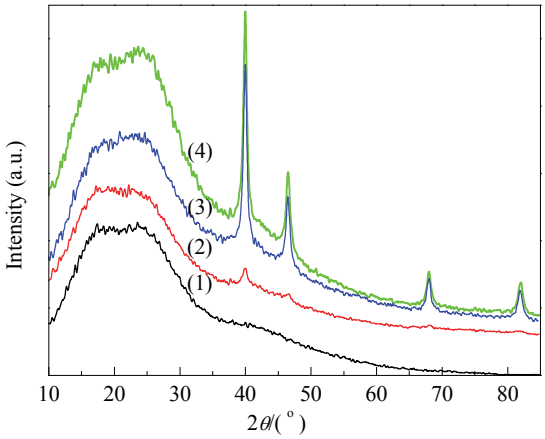

Fig. 1. XRD patterns of A-45 (1), Pd(0.9)/A-45 (2), Pd(2.7)/A-45 (3), and Pd(4.5)/A-45 (4).