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Short Communication

New non-metallic mesoporous SBA-15 catalyst with high selectivity for the gas-phase oxidation of cyclohexylamine to cyclohexanone oxime

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ABSTRACT

Non-metallic mesoporous SBA-15 is firstly used for the gas-phase selective oxidation of cyclohexylamine to cyclohexanone oxime with air and exhibits the best performance among the investigated silica catalysts. The experimental results show that the catalytic activity is strongly dependent on the pore diameter of SBA-15. By combining catalytic performance experiments with the monitoring of catalyst transformations using themogravimetric analyses, N_2-physisorption, and solid-state ^{29}Si MAS NMR spectra, we show that the surface silanols play important roles to form a catalytically active carbon species, which is believed to be favorable to the activation of molecular oxygen. The carbon species formed are also studied by IR-spectroscopy, coke analysis by a catalyst dissolution/extraction protocol and elemental analyses.

1. Introduction

The selective oxidation of amine is an important chemical transformation in the synthesis of fine chemicals, medicines, and biologically active compounds [1]. Selective oxidation of cyclohexylamine is one such reaction, one of the products of which viz. cyclohexanone oxime is a valuable intermediate in the manufacture of nylon-6 [2]. Several oxidation procedures using oxidants such as some salts of Cr^{VI} or Mn^{VII} [3], alkylhydroperoxide [4] and hydrogen peroxide [5] have been reported in the presence of transition metal compounds as catalysts for this reaction. Currently, a catalytic system using air/molecular oxygen as a sole oxidant has been desired in view of green chemistry. For example, diphenyl-2-picrylhydrazyl and tungstated alumina are found to be good catalysts for cyclohexylamine selective oxidation [6]. Gold nanoparticles supported on titania are also known to be effective for oxidation of cyclohexylamine [7]. The environmental limitation for the usage of solvent and the catalyst separation is, however, still one of the important remaining problems in the liquid systems. To overcome these problems and make the processes "greener", heterogeneously catalyzed reactions for gas-phase oxidation are under investigation. Most of these solid catalysts are Al_2O_3-based catalysts such as WO_3/Al_2O_3 [8] and $H_4[Si(W_3O_{10})_4/Al_2O_3$ [9], which exhibit moderate deactivation. In particular, the sensitivity of cyclohexylamine to metal catalysts leads to relatively low selectivity for oxime.

Silica is generally considered as catalytically inactive solid. Some silica-based materials have been already proven; however, to be attractive alternatives to conventional metal-based catalysts for several oxidation reactions, for example, ammoximation of cyclohexanone [10], oxidation of methane [11], butane [12], carbon oxide [13] or photo-oxidation processes [14]. They have attracted much interest for their extraordinary catalytic performance, exhibiting an opportunity to develop new catalysts for more economic and environmentally friendly processes. Importantly, the excellent catalytic performances of non-metallic SiO_2 materials are linked to their manifold structures and surface chemistry [15,16]. Mesoporous SBA-15 has attracted a great deal of attention for applications in the fields of adsorption and heterogeneous catalysis, due to its well-defined hexagonal structure and high hydrothermal stability [17]. In catalysis, many efforts have been focused on metal-supported SBA-15 for heterogeneous catalytic oxidation reactions. However, in the literature there are also some announcements concerning the activity of SBA-15 silica in the oxidation processes [18]. Herein, we report a highly selective and efficient catalytic method for the oxidation of cyclohexylamine to oxime by employing mesoporous SBA-15 itself acting as a metal-free catalyst with air as the terminal.

2. Experimental

2.1. Catalyst preparation

The mesoporous SBA-15 materials were synthesized by a template method as described in the previous paper [19]. For a typical synthesis, 4.0 g of P_{123} [$EO_{20}PO_{70}EO_{20}$, poly(ethyleneglycol)-

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block-poly(propyleneglycol)-block-poly(ethyleneglycol), average molecular weight = 5800, Aldrich] was dissolved in 90 ml deionized water at ambient temperature under violent stirring. Subsequently, 60 ml of 4 mol l^{-1} HCl (CR, Sinophar) was introduced with continuous stirring. 9.8 ml of tetraethyl orthosilicate (CR, Damao) was added dropwise into the former solution at 40 °C. After being stirred continuously for 24 h, the mixture was transferred to a Teflon-lined stainless steel autoclave and placed in an oven at 100 °C (aging temperature) for 24 h. The precipitate was in turn filtered, washed with deionized water, and dried at 80 °C overnight. The obtained powders were finally heated up to 550 °C at a ramp rate of 1 °C/min and calcined at this temperature in air for 8 h. To investigate the effect of the structural properties on the catalytic performance, the preparation was conducted with different aging temperatures (60, 80, 100, 110, 120 and 140 °C) and the addition of a swelling agent (trimethylbenzene) according to [20], which allow one to change the pore diameter and pore volume. For comparison, the other mesoporous silicas MCM-41, SBA-3 and HMS were also prepared according to [21–23], respectively. Grance gel was supplied by Aldrich.

2.2. Catalyst characterization

The nitrogen adsorption–desorption measurements were carried out at −196 °C on a Tristar 3000 sorptometer. Themogravimetric analyses (TGA) were performed with TA Instruments equipment from 50 to 800 °C operating at 10 °C/min under airflow. Solid-state ^{29}Si MAS NMR spectra were recorded on a Varian Infinitypuls at a Larmor frequency of 121.35 MHz. The chemical shifts for the ^{29}Si resonance were referred to tetramethylsilane. All solid-state NMR experiments were carried out with a spinning rate of 8 kHz and silanol concentrations were calculated by dividing the molar fraction of the respective silicon species by the molar weight of the sample (determined as sum of molar weights and fractions of the different silicon species). Fourier transformation infrared (FT-IR) spectra were obtained on an AVATAR 370 Thermo Nicolet spectrophotometer with a resolution of 4 cm^{-1}. Samples were dehydrated at 200 °C for 6 h under nitrogen and ground with KBr in the ratio 1:150 and pressed into thin wafers. Elemental analyses (C, H, N) were performed using a Carlo Erba CE Instruments EA 1110.

In order to determine the nature of the carbon species, ca. 15 mg of the spent SBA-15 was dissolved in 1 cm^3 of a concentrated HF aqueous solution (40%, Sinophar) at room temperature. Subsequently, 4 cm^3 of CH_2Cl_2 was added to extract the soluble carbon material which, after its separation from the aqueous phase, was analyzed by HPLC–MS (Agilent 1260/6120).

2.3. Catalyst testing

The vapor phase oxidation of cyclohexylamine was carried out in a fixed bed vertical downward flow glass reactor of internal diameter 2 cm. About 1.2 g of a catalyst was placed at the center of the reactor supported on either side with a thin layer of quartz wool and ceramic beads. The weight hourly space velocity (WHSV) of cyclohexylamine was 43.2 h^{-1}. The oxidation was performed by air at atmospheric pressure and at a temperature of 190 °C. The flow rate of gases was 70 $cm^3\ min^{-1}$. The reactant was fed into the reactor using a syringe infusion pump. The products, collected in the receiver flask, were analyzed in a gas chromatograph (Agilent 6890N) equipped with a DB-5 capillary column (30 m) and a flame ionization detector using naphthalene as an internal standard. The components of the gas phase were analyzed by gas chromatography with a TCD detector. The products were identified by GC–MS (SHIMADZU, QP2010 PLUS) and by comparison with commercially pure products. The conversion of cyclohexylamine and selectivity of cyclohexanone oxime were calculated using the following formulas (Eqs. (1) and (2)). All raw materials and products were established carbon mass balances.

$$\text{Conversion of cyclohexylamine } (\%) = \frac{[\text{the amount (mol) of starting cyclohexylamine}] - [\text{the amount (mol) of cyclohexylamine recovered}]}{[\text{the amount (mol) of starting cyclohexylamine}]} \times 100\% \quad (1)$$

$$\text{Selectivity of cyclohexanone oxime}(\%) = \frac{[\text{the amount (mol) of cyclohexanone oxime}]}{[\text{the amount (mol) of starting cyclohexylamine}] - [\text{the amount (mol of cyclohexylamine recovered)}]} \times 100\% \quad (2)$$

3. Result and discussion

3.1. Catalytic performance of various silica catalysts

Catalytic performances of various silica materials are summarized in Table 1. As expected, the blank experiment without any catalyst gives no cyclohexylamine conversion as a result of the catalytic oxidation reaction. High activity is obtained over SBA-15 to yield a conversion of 11.2% (with 96.6% cyclohexanone oxime selectivity), which is remarkably higher than those on the other silica catalysts. When silica gel is applied to the reaction, the selectivity for the oxidation is as low as 61.3%, which is the lower compared with the other mesoporous silica catalysts (>93%). This great difference between the catalytic activities of SBA-15 and the other silica catalysts is very interesting considering that the various walls of mesoporous silica and silica gel are all made of amorphous silica. What is the cause of this great difference? First, we compare the specific surface area, pore volume size and pore size distribution of various silica catalysts obtained by using N_2-physisorption. As shown in Table 1, the commercial silica gel with the lower specific surface area has higher catalytic activity than those of mesoporous silica (MCM-41, HMS, SBA-3). This indicates that the specific surface area is not the most important factor which determines the oxidation activity of silica. On the other hand, both SBA-15 and silica gel have relatively high pore volume with a wide pore size distribution centered above 6 nm and the higher conversions are achieved, indicating that pore volume size is more responsible for the formation of oxime. Next, we studied the dependence of catalytic activity on the pore size of the SBA-15 samples, as shown in Fig. 1. Surprisingly, catalytic activity is strongly dependent on the pore diameter of the catalyst and is maximized at around 6.1 nm. Smaller or larger pores are not suitable for the catalytic oxidation of cyclohexylamine, which can not be only associated that the shape selective catalysis may be involved in this process. In the present reaction, the diameter of cyclohexylamine is 0.79 nm (the distance between hydrogen and the most distant hydrogen is 0.59 nm; the van der Waals radius of hydrogen is 0.10 nm) and that of the product should be 0.86 nm, while the most appropriate pore diameter for the catalyst is approximately 6.1 nm. The phenomenon may be accounted for by structural characteristics of SBA-15. First, some synergistic effect may be involved at larger pores, but for pores less than 4 nm in size, diffusion

Table 1
Physicochemical properties and catalytic performances of various silicas.[a]

Sample	D[b] (nm)	S_{BET}[b] (m^2/g)	V_p[b] (cm^3/g)	Conversion (%)	Selectivity (%)
Silica gel	9.25	314	0.86	3.7	61.3
SBA-15	6.13	783	1.33	11.2	96.6
MCM-41	3.32	736	0.69	1.6	93.4
SBA-3	2.86	594	0.33	0.15	98.1
HMS	3.01	785	0.45	0.24	96.4
Null	–	–	–	–	–

[a] Reaction conditions: space velocity 43.2 h^{-1}; air, 70 cm^{-3}/min; temperature, 190 °C; time, 11 h.

[b] D: pore size; S_{BET}: surface area calculated by BET method; V_p: pore volume.