Catal Lett (2010) 136:150–154
DOI 10.1007/s10562-010-0306-3

Preparation of SiO_2–Al_2O_3 and Its Supported Co_3O_4 Catalysts for Nitrosation of Cyclohexane

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Received: 29 June 2009 / Accepted: 8 February 2010 / Published online: 25 February 2010
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Abstract Amorphous SiO_2–Al_2O_3 was prepared by sol–gel method and cobalt oxide supported on SiO_2–Al_2O_3 was prepared by impregnation method. These materials were characterized by BET, XRD, TPD and FT-IR. The activity of SiO_2–Al_2O_3 and Co_3O_4/SiO_2–Al_2O_3 catalysts for nitrosation of cyclohexane with nitrosyl sulfuric acid in the presence of fuming sulphuric acid was evaluated. The results indicate that SiO_2–Al_2O_3 and Co_3O_4/SiO_2–Al_2O_3 can catalyze efficiently this nitrosation reaction. And Co_3O_4/SiO_2–Al_2O_3 gave better results with 11.93% of conversion and 54.68% of selectivity to ε-caprolactam. This discovery establishes a potential method for one-pot synthesis of ε-caprolactam from cyclohexane. It may be of potential application prospect and of prominent theoretical significance.

Keywords Cyclohexane · ε-Caprolactam · Nitrosation · Co_3O_4/SiO_2–Al_2O_3 catalyst

1 Introduction

ε-Caprolactam is an important intermediate primarily used in the production of nylon 6 fibers and resins. The conventional method of manufacturing caprolactam is the reaction of cyclohexanone with hydroxylamine hydrochloric and rearrangement of the resulting cyclohexanone oxime via a Beckmann rearrangement with fuming sulfuric acid [1, 2]. However, this process has some disadvantages, such as production of large amounts of ammonium sulfate as byproduct, the corrosive reaction medium due to the necessary use of fuming sulphuric acid, and complex technology route.

To overcome the problem of environmental pollution, many research groups have attempted to use ionic liquids as environmentally friendly medium for catalytic liquid-phase Beckmann rearrangement [3–5]. However, it is difficult to separate products from ionic liquids in this rearrangement route.

Some researchers have conducted studies on the vapor-phase Beckmann rearrangement of cyclohexanone oxime on solid acid catalyst instead of fuming sulfuric acid [6–8]. However, the catalyst deactivates rapidly due to the coke formation [9].

Ammoximation of cyclohexanone were reported over titanium silicate (TS-1) catalyst using hydrogen peroxide and ammonia as oximation reagents in the liquid phase [10–12]. In addition, there was a report on oximation of cyclohexanone using nitric oxide and ammonia as the oximation reagents over amorphous SiO_2–Al_2O_3 catalyst. In this process the production of oxime and its rearrangement to caprolactam occured simultaneously [13].

The research group of university of Cambridge reported that bifunctional molecular sieve catalysts promoted the reaction of cyclohexanone with ammonia and hydrogen peroxide or molecular oxygen to directly give cyclohexanone oxime along with a small amount of ε-caprolactam [14].

The photonitrosation of cyclohexane for the production of ε-caprolactam is much more effective with regards to the material costs compared to important thermochemical processes, and the overall selectivity to caprolactam is higher than the selectivity of the classical routes. However,

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the chlorinated compounds are environmentally unfriendly and photonitrosation of cyclohexane is a process of high energy consumption. Moreover, all of the above methods still underwent the multi-step conversion from elementary material.

Although from both synthetic and industrial points of view, considerable attentions have been focused on the development of a new system for the production of ε-caprolactam to overcome above-mentioned drawbacks. Searching for a catalyst which has high conversion to cyclohexane and high selectivity to ε-caprolactam is the key to the liquid phase nitrosation reaction. In this paper, we found that these SiO_2–Al_2O_3 and Co_3O_4/SiO_2–Al_2O_3 catalysts could efficiently catalyze the reaction of cyclohexane with nitrosyl sulfuric acid to afford ε-caprolactam directly in the presence of fuming sulphuric acid.

2 Experimental

2.1 Catalyst Preparation

Amorphous SiO_2–Al_2O_3 was prepared by sol–gel method. Cogelling aluminum sec-butoxide dissolved in ethanol was added to a solution of tetraethyl orthosilicate at 85 °C with vigorous stirring. The molar ratio of Si/Al was kept at 2.5. Hydrolysis was performed by addition of a small amount of water to the mixture. The solution became a rigid and transparent gel immediately after addition of water. The gel was recovered by filtration and dried in an oven at 120 °C overnight.

Co_3O_4/SiO_2–Al_2O_3 was prepared by impregnating the prepared SiO_2–Al_2O_3 in cobalt acetate solution for 1 h at 25 °C (the loading amount of cobalt acetate were about 30 wt%), and then the resulted mixture was dried at 100 °C for 10 h. Finally, it was heated from 20 °C to corresponding calcination temperature at a rate of 2 °C min^{-1} in dry air and kept at this temperature for 5 h.

2.2 Catalyst Characterization

X-ray diffraction (XRD) data were collected using a Japan Rigaku D/Max 2550 VB^+ 18 kW X-ray diffractometer under the following conditions: 40 kV, 30 mA, Cu Kα radiation, with a scanning rate of 1° min^{-1} in the range of $2\theta = 5$–85°.

Specific surface area, pore volume and pore size distribution of the catalysts were measured using a NOVA-2200e automated gas sorption system.

Temperature-programmed desorption (TPD) of NH_3 was carried out on a CHEMBET-3000 instrument. The sample (100 mg) was pretreated at a heating rate of 10 °C min^{-1} to 400 °C and was held for 1 h under a flow of helium. After cooling to 120 °C, a mixture of 10% NH_3-90% He was introduced until the acid sites of the catalyst were saturated with NH_3. Finally, desorption was carried out from 10 °C to 1000 °C at a heating rate of 10 °C min^{-1}.

Fourier transform infrared (FT-IR) spectra of pyridine temperature-programmed desorption was carried out on a FT-IR adsorption system.

2.3 Typical Experimental Procedure

The catalytic reaction was carried out in a glass reactor under atmospheric pressure. A mixture of cyclohexane, nitrosyl sulfuric acid and catalyst was stirred at 81 °C for 24 h in the presence of fuming sulfuric acid. After cooling to 20 °C, the inorganic phase was dissolved by deionized water in ice-water bath and successively treated with $Ba(OH)_2$ to neutralize H_2SO_4. The pH value of solution was adjusted to 7–8 [15–17]. The final product was analyzed using a LC-20AT and SPD-20A liquid chromatograph with 40:60 of CH_3OH:H_2O as eluant and detected at wavelength of 210 nm.

3 Results and Discussion

3.1 Physicochemical Properties of the Catalysts

Figure 1a shows the nitrogen adsorption–desorption curves for SiO_2–Al_2O_3 and Co_3O_4/SiO_2–Al_2O_3. Co_3O_4/SiO_2–Al_2O_3 exhibits a much higher nitrogen adsorption capacity than SiO_2–Al_2O_3. By contrast, SiO_2–Al_2O_3 shows an adsorption isotherm of type IV according to the IUPAC classification and has a H4 hysteresis loop that is representative of mesopores. The volume adsorbed for bare SiO_2–Al_2O_3 steeply increases at a relative pressure (p/p_0) of approximately 0.45, representing capillary condensation of nitrogen within the uniform mesoporous structure. Co_3O_4/SiO_2–Al_2O_3 shows an adsorption isotherm of type IV and has a H3 hysteresis loop that is representative capillary condensation of nitrogen within the non-uniform mesoporous structure.

Figure 1b shows the pore size distribution calculated from desorption isotherms of SiO_2–Al_2O_3 and Co_3O_4/SiO_2–Al_2O_3. A very broad pore size distribution is observed in Co_3O_4/SiO_2–Al_2O_3, and its mean pore size calculated from the desorption branch by the BJH model is 3.85 nm. A large volume of irregular and non-uniform macropores are formed when Co_3O_4/SiO_2–Al_2O_3 is calcinated at 400 °C. However, the mesoporous SiO_2–Al_2O_3 has a pore size distribution centered at 3.82 nm, and possesses relatively more uniform mesopores.

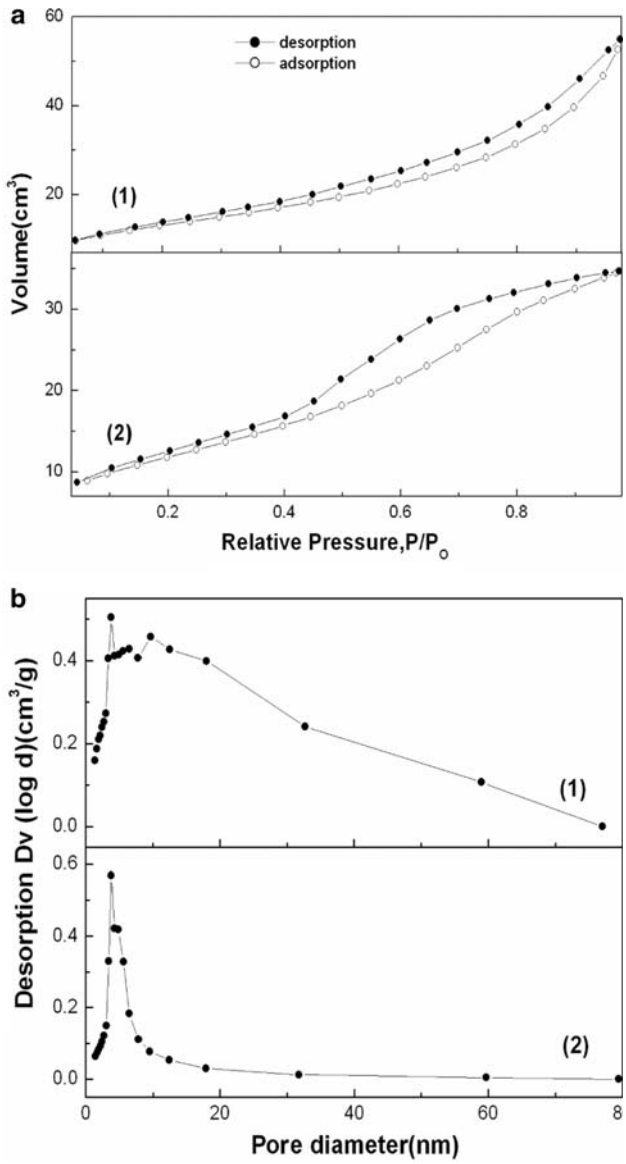


Fig. 1 **a** N_2 adsorption–desorption isotherms for different catalysts. (1) $Co_3O_4/SiO_2–Al_2O_3$; (2) $SiO_2–Al_2O_3$. **b** BJH pore size distribution for different catalyts. (1) $Co_3O_4/SiO_2–Al_2O_3$; (2) $SiO_2–Al_2O_3$

The BET surface area data of $SiO_2–Al_2O_3$ and $Co_3O_4/SiO_2–Al_2O_3$ are summarized in Table 1. The BET results of $Co_3O_4/SiO_2–Al_2O_3$ depict that the surface area increases after Co_3O_4 is introduced to $SiO_2–Al_2O_3$, and the surface area of Co_3O_4 free containing samples is only half that of Co_3O_4 samples, which indicates a great influence of cobalt acetate on BET surface area during the impregnation process. As displayed in Table 1, the surface area of $Co_3O_4/SiO_2–Al_2O_3$ calcinated at 300–600 °C is similar. These results show that the textural properties of $Co_3O_4/SiO_2–Al_2O_3$ depend weakly on the calcination temperature.

Figure 2 shows the XRD patterns of $Co_3O_4/SiO_2–Al_2O_3$ with different calcination temperature. The pattern for the supports is that of crystallized materials with the well defined broad diffraction lines bands of amorphous $SiO_2–Al_2O_3$ mixed oxide around $2\theta = 23°$ [18]. The spectra show characteristic diffraction lines of the Co_3O_4 phase and support, and no CoO and Co_2O_3 phases are identified. However, an observation of the spectra indicate that Co_3O_4 diffraction peaks are very weak when Si/Al = 2.5. This may be due to the poor crystallinity of the catalysts and the formation of amorphous phase.

Figure 3 shows the acidity and the number of acidic sites of $Co_3O_4/SiO_2–Al_2O_3$ calcinated at 400–600 °C estimated by NH_3-TPD. There are two clear desorption peaks, indicating the existence of two acid sites. The first one is described as the low temperature peak and it is found between 138 °C and 280 °C. It is attributed to desorption of weakly bound ammonia. The second peak typically found in a temperature range between 550 °C and 700 °C is called the high temperature peak. Ammonia desorption at the higher temperature region is usually attributed to the strong acid sites. The strength of acidity decreases in the following order of A > C > B.

Figure 4 shows the FT-IR spectra of pyridine temperature-programmed desorption on $Co_3O_4/SiO_2–Al_2O_3$ at different temperature. The spectra show the ring vibration of pyridine detected in the frequency range of 1400–1650 cm^{-1} commonly used to characterize the concentrations of Brønsted and Lewis acid sites. From Fig. 4, it can clearly be seen that the Brønsted acid sites correspond to the 1545 cm^{-1} band, which is characteristic peak of pyridinium ion and the Lewis acid sites correspond to the 1450 cm^{-1} band attributed to pyridine coordinative bound to accessible Cobalt ion. Therefore, the results illustrate that the two different acid sites exist in $Co_3O_4/SiO_2–Al_2O_3$.

3.2 Catalytic Performance

Table 2 summarizes representative results for the nitrosation of cyclohexane over different catalysts. ε-Caprolactam can be formed from cyclohexane and nitrosyl sulfuric acid catalyzed by $SiO_2–Al_2O_3$, however, the selectivity to ε-caprolactam was only 13.78%. It can further be noticed that the surface areas of catalyst affect the catalytic performance. The selectivity to ε-caprolactam is clearly improved when the cobalt is introduced to $SiO_2–Al_2O_3$, which is related to the BET result (the surface area of $Co_3O_4/SiO_2–Al_2O_3$ is much higher than that of $SiO_2–Al_2O_3$). The selectivity to ε-caprolactam increases with the elevated surface area of catalyst. It is obvious that $Co_3O_4/SiO_2–Al_2O_3$ shows better activity in the liquid phase nitrosation of cyclohexane. This illustrates that the introduction of Co_3O_4 to $SiO_2–Al_2O_3$ plays an important role in improving the selectivity of ε-caprolactam. However, $Co_3O_4/SiO_2–Al_2O_3$ can not be recycled to use repeatedly in

Table 1 Textural properties of different catalysts

Catalyst	Surface area (m^2 g^{-1})	Average pore size (nm)	Pore volume (cm^3 g^{-1})
SiO_2–Al_2O_3	148.304	3.82	0.195
Co_3O_4/SiO_2–Al_2O_3 calcinated at 300 °C	270.650	3.82	0.439
Co_3O_4/SiO_2–Al_2O_3 calcinated at 400 °C	289.003	3.85	0.534
Co_3O_4/SiO_2–Al_2O_3 calcinated at 500 °C	244.968	3.82	0.420
Co_3O_4/SiO_2–Al_2O_3 calcinated at 600 °C	240.371	3.85	0.411

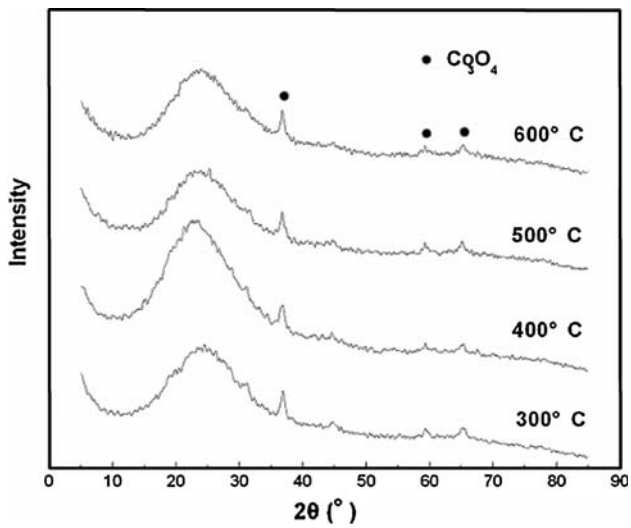


Fig. 2 XRD patterns of Co_3O_4/SiO_2–Al_2O_3 catalysts calcinated at different temperatures

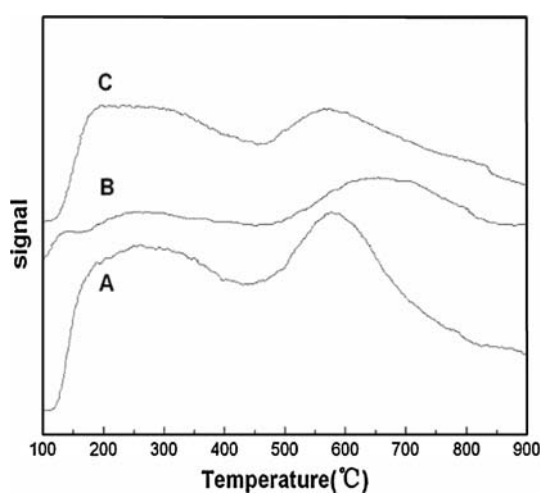


Fig. 3 TPD spectra of Co_3O_4/SiO_2–Al_2O_3 calcinated at 400 °C (*A*), 500 °C (*B*), 600 °C (*C*)

the presence of fuming sulfuric acid. The further studies for the stability and recycling of the catalyst are now in progress.

Furthermore, Co_3O_4/SiO_2–Al_2O_3 catalysts calcinated at different temperature are evaluated in Table 3. Among these catalysts, Co_3O_4/SiO_2–Al_2O_3 calcinated at 400 °C

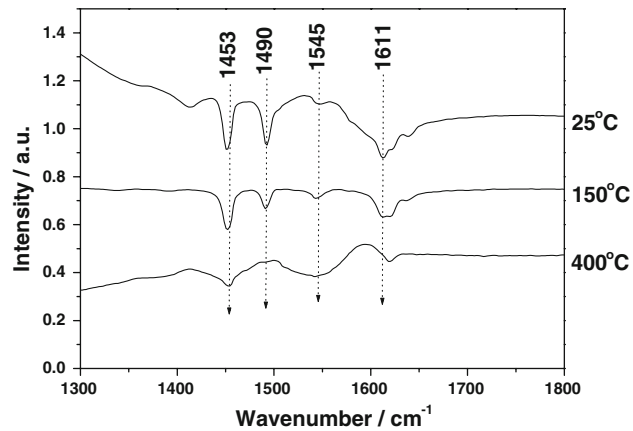


Fig. 4 The FT-IR spectra of pyridine adsorption/desorption on Co_3O_4/SiO_2–Al_2O_3 at different temperature

Table 2 Effect of different catalysts on the nitrosation of cyclohexane[a]

Catalysts	Conversion of cyclohexane (%)	Selectivity of ε-caprolactam (%)
SiO_2–Al_2O_3	34.08	13.87
Co_3O_4/SiO_2–Al_2O_3	11.93	54.68

Temperature: 81 °C; Reaction time: 24 h

[a] Reaction condition: nitrosyl sulfuric acid:oleum = 1:3 (weight ratio) (cyclohexane = 20 g); Catalyst mass: 0.5 g

Table 3 Effect of Co_3O_4/SiO_2–Al_2O_3 catalysts calcinated at different temperature on the nitrosation[a]

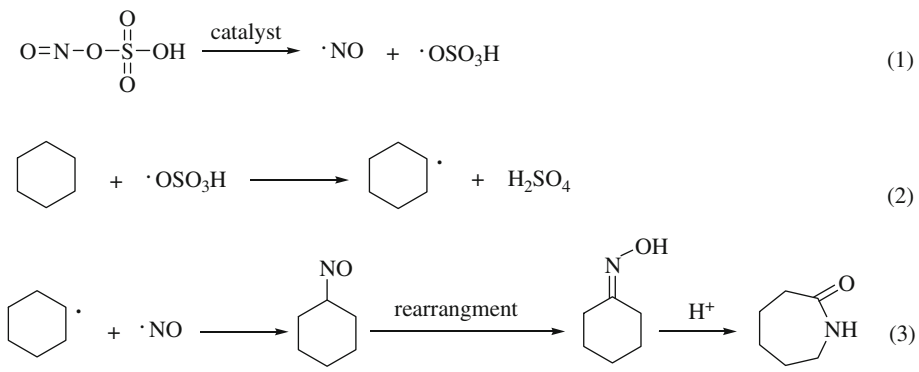
Calcination temperature (°C)	Conversion of cyclohexane (%)	Selectivity of ε-caprolactam (%)
300	11.49	53.02
400	11.93	54.68
500	13.71	51.25
600	14.04	41.03

Temperature: 81 °C; Reaction time: 24 h

[a] Reaction condition: nitrosyl sulfuric acid:oleum = 1:3(weight ratio) (cyclohexane = 20 g); Catalyst mass: 0.5 g

gives the best result of the conversion of 11.93% with the selectivity of 54.68% to ε-caprolactam. BET and TPD results show that Co_3O_4/SiO_2–Al_2O_3 calcinated at 400 °C

Scheme 1 The possible reaction mechanism of liquid phase nitrosation of cyclohexane



has the largest surface area, pore volume and greater acidic properties (greater number of acidic sites and their greater acidity). It indicates that the optimal calcination temperature for $Co_3O_4/SiO_2–Al_2O_3$ is about 400 °C.

3.3 The Possible Reaction Mechanism of Liquid-Phase Nitrosation of Cyclohexane

On the basis of these results in this work, the possible reaction mechanism of liquid-phase nitrosation of cyclohexane with nitrosyl sulfuric acid over $Co_3O_4/SiO_2–Al_2O_3$ catalyst is proposed in Scheme 1. Firstly, the nitrosyl sulfuric acid could be decomposed to $NO^{\bullet}$ and $HO_3SO^{\bullet}$ free radical *via* the N–O bond cleavage in the presence of catalyst (Eq. 1). The formed $HO_3SO^{\bullet}$ free radical reacts with cyclohexane giving sulphur acid and cyclohexyl free radical (Eq. 2). Then the resulting cyclohexyl free radical reacts with nitroso free radical ($^{\bullet}NO$) to form nitroso cyclohexane ($C_6H_{11}NO$) as an important intermediate, which is easy to isomerize to cyclohexanone oxime, followed by Beckmann rearrangement to afford ε-caprolactam (Eq. 3).

4 Conclusion

In conclusion, amorphous $SiO_2–Al_2O_3$ is successfully prepared by sol–gel method. $Co_3O_4/SiO_2–Al_2O_3$ catalysts are prepared by impregnation method. BET and TPD analysis show that $Co_3O_4/SiO_2–Al_2O_3$ calcinated at 400 °C has the largest surface area and greater acidic properties. The results for the nitrosation process show that $SiO_2–Al_2O_3$ and $Co_3O_4/SiO_2–Al_2O_3$ catalysts are proven to be active for catalytic synthesis of ε-caprolactam from cyclohexane and nitrosyl sulfuric acid in the presence of fuming sulfuric acid. The results indicate that $Co_3O_4/SiO_2–Al_2O_3$ shows better activity in the liquid phase nitrosation of cyclohexane. $Co_3O_4/SiO_2–Al_2O_3$ calcinated at 400 °C having higher activity indicates that the calcination temperature could influence the reaction selectivity to some extent. Assuming that better catalysts can be developed, this method would provide a novel strategy for the synthesis of ε-caprolactam from cyclohexane.

Acknowledgments This work was supported by the NSFC (20976148, 20736009), Scientific Research Fund of Hunan provincial Education Department (09A090), Hunan Provincial Natural Science Foundation (07JJ6017) and project of Ministry of Education of China (081053010, 09HJYH03).

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