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Mesoporous silica gel as an effective and eco-friendly catalyst for highly selective preparation of cyclohexanone oxime by vapor phase oxidation of cyclohexylamine with air



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ABSTRACT

A simple and environmentally benign approach to highly selective preparation of cyclohexanone oxime by vapor phase catalytic oxidation of cyclohexylamine with air over mesoporous silica gel under atmospheric pressure has been successfully developed in this work. The results demonstrate that the nonmetallic mesoporous silica gel is an effective and eco-friendly catalyst for the vapor phase selective oxidation of cyclohexylamine to cyclohexanone oxime and the surface silicon hydroxyl groups as active sites are responsible for the excellent catalytic performance of silica gel. The present silica gel catalyst has advantages of low cost, long-time stable reactivity, easy regeneration, and reusability. This method employing inexpensive mesoporous silica gel as catalyst and air as green terminal oxidant under facile conditions is a promising process and has the potential to enable sustainable production of cyclohexanone oxime from the selective oxidation of cyclohexylamine with air in industrial applications.

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1. Introduction

Cyclohexanone oxime (CHO) is an important intermediate in the production of nylon-6 fibers and resins, which is widely used in polymer synthesis. At present, the preparation methods for CHO mainly include the "cyclohexanone-hydroxylamine" method [1,2], ammoximation of cyclohexanone, ammonia, and hydrogen peroxide over TS-1 zeolite [3,4], light-nitrosation of cyclohexane with nitrosyl chloride [5], aerobic oxidation of cyclohexylamine originated from nitrobenzene, aniline, cyclohexene, or cyclohexanol [6], and one-step synthesis from nitrobenzene, hydrogen, and hydroxylamine hydrochloride over Au/C and Pd/C catalysts [7] (Scheme 1). Nowadays, the modern chemical industry demands the intensification of chemical processes in order to save chemicals and energy, reduce environmental pollution, and enhance economic benefits. Therefore, developing an environmentally benign process for CHO production has been highly desired for a long time in the chemical industry.

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Considering the source and cost of reactants (starting materials and oxidants) and the energy efficiency of processes, as well as recent advances in the selective nitration of cyclohexane to nitrocyclohexane (NCH) [8,9], one-step hydrogenation of NCH into CHO is a promising and more economical route [10,11]. However, this process inevitably generates the main byproduct cyclohexylamine. Therefore, highly selective oxidation of cyclohexylamine to CHO under mild conditions is still one of the current challenges that must be met to make this process more economical and environmentally friendly. In recent years, some research on the selective oxidation of cyclohexylamine to CHO has been reported. The oxidizing agents mainly include molecular oxygen, hydrogen peroxide, and alkyl hydroperoxides [12]. Rakottyay et al. [13,14] report the oxidation of cyclohexylamine with molecular oxygen over modified alumina. Suzuki and co-workers report 1,1diphenyl-2-picrylhydrazyl and WO₃/Al₂O₃ as excellent composite catalysts for the selective oxidation of cyclohexylamine [15,16] with a satisfactory yield of CHO. Christensen [17] and Kaszonyi et al. [18] report bifunctional Au–TiO₂ and WO₃/ γ -Al₂O₃ as effective catalysts for the selective oxidation of cyclohexylamine with molecular oxygen, having around 70% of selectivity to CHO with ca. 20% conversion of cyclohexylamine. Recently, Zhong et al. reported that CHO could be obtained from the oxidation of

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Scheme 1. Currently employed routes for the synthesis of CHO.

cyclohexylamine with air over nonmetallic mesoporous SBA-15 catalyst [19]. In addition, several reagents, such as PCWP-H₂O₂ [20], VS-1-H₂O₂ [21], and TS-1-H₂O₂ [22,23], have been reported to catalyze the oxidation of amines into oximes. However, these methods show poor selectivity in terms of product distribution. Although the reduction product of hydrogen peroxide as oxidizer is ecological H₂O, its price and utilization efficiency should be considered cautiously. Likewise, if alkyl hydroperoxides are used as oxidizers, the separation of their reduction products from the reaction mixture is also necessary. Therefore, molecular oxygen, especially in air, as a green terminal oxidant for the selective oxidation of cyclohexylamine over heterogeneous catalysts is of increasing interest in view of environmental, economical, and synthetic aspects.

Silica gel is generally considered a catalytically inactive solid. Up to now, the silica gel directly used as a catalyst in oxidation reactions is little reported. However, some catalysts with silica as carrier have been proven to be effective for several oxidation reactions, for example, oxidation of methane [24,25], oxidation of carbon oxide [26], and selective oxidation of sulfides [27,28]. Importantly, the excellent catalytic performance of nonmetallic SiO₂ materials is linked to their manifold structures and surface chemistry [29,30]. Silica gel offers an opportunity to develop new catalysts for economical and environmentally friendly processes.

investigated, and the durability and reusability of the catalyst was evaluated. The detailed results obtained from the catalytic oxidation process will be reported in this paper.

2. Experimental

2.1. Reagents and instrument

Cyclohexylamine (AR) was purchased from the Tianjin Kermel Reagent Development Center, China. Mesoporous silica gel (60 mesh) was purchased from the Qingdao Micro-Nano Silicon Technology Co., Ltd., China. The other reagents were purchased from the Sinopharm Chemical Reagent Co., Ltd., China. Except where specified, all chemicals were of analytical grade and used as received. Gas chromatography (GC) was performed on a Shimadzu GC-2010 plus equipped with a DB-5 (30 m × 0.25 mm × 0.25 μ m) column for quantitative analysis. Gas chromatographymass spectrometry (GC–MS) was run on a Shimadzu GCMS-QP2010 PLUS for qualitative analysis of products.

2.2. Experimental procedure

The vapor phase oxidation of cyclohexylamine with air was carried out in a fixed-bed vertical downward-flow quartz glass reactor of 60 cm length with 10 mm inner diameter (see Fig. 1). A certain amount of silica gel was placed at the center of the reactor, supported on either side by a thin layer of guartz wool and ceramic beads. The oxidation reaction was performed at atmospheric pressure and a preselected temperature. Cyclohexylamine was injected into the quartz glass reactor using a pulsation-free reciprocating pump with a calibrated constant flow rate, and the flow of air was measured by a mass flow controller. The resulting gas flowing from the outlet of the reactor was condensed with a lowtemperature cooling liquid at 6-8 °C to collect the products. The liquid phase products was collected at different time intervals and analyzed by a gas chromatograph with FID detector (quantitative analysis by internal standard methods with toluene as internal standard sample). The components of the gas phase were analyzed by gas chromatography with a TCD detector. The conversion of cyclohexylamine and selectivity of CHO were calculated using the following formulas:



Here, we report a simple and effective catalytic approach for highly selective preparation of CHO from cyclohexylamine employing mesoporous silica gel as a metal-free catalyst and air as a terminal oxidant, as is shown in Scheme 2. Several techniques, including N₂ adsorption–desorption, ²⁹Si MAS NMR, XRD, TG/DTG, FT-IR, and UV–vis DRS, were employed to characterize the structure of fresh and spent catalysts. Various parameters such as catalyst type, reaction temperature, residence time, and the molar ratio of cyclohexylamine to oxygen have been systematically

All raw materials and products were established carbon mass balances.

2.3. Activation and characterization of catalyst

Silica gel was calcined at 773 K in air for 6 h (with a heating rate of 5 °C min⁻¹) before used. X-ray diffraction (XRD) analysis of silica gel samples was performed in a Japan Rigaku D/Max-2550VB⁺ 18 kW X-ray diffractometer with a monochromatic CuK α radiation



Scheme 2. Catalytic synthesis of CHO from vapor phase selective oxidation of cyclohexylamine with air.



Fig. 1. Experimental equipment for vapor phase catalytic oxidation.

source (λ = 1.5418 Å) at a voltage and current of 40 kV and 300 mA. Fourier transform infrared (FT-IR) spectra of the samples were collected using a Nicolet-380 instrument in a KBr matrix in the range 400–4000 cm⁻¹. The ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of the samples were recorded in a UV-2550 spectrophotometer from 200 to 800 nm in the BaSO₄ phase. Thermogravimetric/derivative thermogravimetric (TG/DTG) analysis was conducted using a Mettler TGA/DSC1/1600HT thermogravimetric analyzer under nitrogen at a gas flow rate of 40 ml/min and a heating rate of 10 °C/min from 30 to 800 °C. The textural properties of the samples were characterized by N₂ physisorption on a NOVA-2200e (Quantachrome, USA) at 77 K after outgassing at 150 °C and 1 mmHg for 6 h. Elemental analyses (C, H, N) were performed using a Carlo Erba CE Instruments EA 1110. The solid state ²⁹Si NMR spectra were recorded on a Varian Infinity-plus400 NMR spectrometer with a commercial double-resonance MAS probe at a Larmor frequency of 79.47 MHz for ²⁹Si. The MAS speed was 3 kHz in all ²⁹Si DP/MAS (direct-polarization magic angle spinning) NMR measurements. The ²⁹Si chemical shifts were determined using solid kaolin as an external reference resonating at -91.5 ppm relative to tetramethylsilane (TMS).

3. Results and discussion

3.1. Comparison of catalytic performance of various catalysts in the oxidation reaction

To seek an effective catalyst for the vapor phase oxidation of cyclohexylamine with air, we screened several typical oxidation catalysts. For example, vanadium phosphorus oxide (VPO) composite catalyst is well known in the vapor phase oxidation of *n*-butane to maleic anhydride (MA) [31,32]. *N*-Hydroxyphthalimide (NHPI) is

famous as a radical catalyst for the oxidation of alkane to the corresponding oxygen-containing compounds [33–35]. In addition, WO₃, γ -Al₂O₃, and sepiolite were also used as typical catalysts in this oxidation reaction. Unfortunately, all these attempts failed to obtain acceptable conversion and selectivity to the desired product; especially, VPO and WO₃ catalysts exhibited no catalytic activity in the oxidation reaction of cyclohexylamine with air. Then we tried some catalysts containing hydroxyl groups on the surface, such as H β , MCM-41, and silica gel, to catalyze this oxidation reaction. The catalytic activity of various catalysts for the oxidation of cyclohexylamine with air is summarized in Table 1. Obviously, CHO was not obtained in the absence of any catalysts, which indicates that the catalyst plays an extraordinarily important role in the formation of the desired product. In this catalytic system, the catalytic performance of the catalysts was different. CHO could

Table 1	
Comparison of catalytic performance of various catalysts in the oxidation in	eaction.

Catalyst	Conversion (%)	Selectivity (%)		
		СНО	NCH	CCA
None	-	-	-	-
VPO	-	-	-	-
WO ₃	-	-	-	-
NHPI	0.9	63.9	-	36.1
γ -Al ₂ O ₃	1.1	81.3	5.85	12.85
Sepiolite	1.2	14.9	-	85.1
Ηβ	4.7	63.6	2.6	33.8
MCM-41	8.3	80.3	7.2	12.5
Silica gel	10.2	88.6	4.7	6.7

^a Reaction conditions: the molar ratio of cyclohexylamine to O₂ is 1:5, the flow rate of air is 100 ml/min, time on stream is 6 h, reaction temperature is 140 °C, the residence time is 4.6 s, and GHSV is 784.8 h^{-1} .

be formed from the aerobic oxidation of cyclohexylamine catalyzed by NHPI, γ -Al₂O₃, and sepiolite catalyst; however, the conversion was below 2% and the selectivity to oxime was also not considerable. The cyclohexylamine conversion was slightly improved as H β was introduced into this oxidation reaction, and 4.7% conversion with 63.6% selectivity to oxime was obtained. The cyclohexylamine conversion and selectivity to CHO were evidently enhanced as the catalysts MCM-41 and silica gel containing hydroxyl groups on the surface were introduced into the oxidation reaction. Silica gel catalyst exhibited excellent catalytic performance. Under our present conditions, 10.2% cyclohexylamine conversion with 88.6% selectivity to CHO was obtained. This result showed that catalysts containing hydroxyl groups on the surface were very suitable for the oxidation of cyclohexylamine with air to CHO.

3.2. Effects of reaction temperature on the oxidation reaction

Fig. 2 shows the effects of reaction temperature on the oxidation reaction of cyclohexylamine in air. It is clearly found that there is significant influence of reaction temperature on the conversion and selectivity. The conversion of cyclohexylamine increased from 10.2% to 22.8% and the selectivity to CHO decreased gradually from 88.6% to 66.1% as the reaction temperature was elevated from 140 to 180 °C. Obviously, the selectivity of byproducts were found to increase with elevated temperatures; especially the selectivity to cyclohexyl-cyclohexylidene-amine (CCA) increased rapidly with reaction temperature from 6.5% at 140 °C to 17.2% at 180 °C. In this oxidation process, the main reaction to generate CHO and the side reaction to product NCH and CCA may be competitive. Cyclohexylamine can be partly oxidized into CHO. However, it can be completely oxidized into NCH and cyclohexanone, while cyclohexanone can easily react with cyclohexylamine to generate CCA [10,11,36]. The reaction network is drawn in Scheme 3. The side reaction may be very sensitive to reaction temperature. To explore the activation energy level of the main reaction and side reactions, we investigated the variation of selectivity to CHO and CCA with altering reaction conditions (e.g., temperature, residence time, and GHSV) for the same conversion of cyclohexylamine, and the results are depicted in Fig. 3. It can be seen that selectivity of CHO gradually decreases with elevated temperatures, while selectivity to CCA gradually increases with temperature. This indicates



Fig. 2. Effects of reaction temperature on oxidation reaction. Reaction conditions: the molar ratio of cyclohexylamine to O_2 is 1:5, the flow rate of air is 100 ml/min, residence time is 4.6 s, time on stream is 6 h, and GHSV is 784.8 h^{-1} .



Scheme 3. The schematic reaction network for the oxidation of cyclohexylamine with air.



Fig. 3. Comparison of catalytic performance of silica gel at different reaction conditions in the oxidation reaction. Reaction conditions: (a) reaction temperature is 140 °C, residence time is 4.6 s, and GHSV is 784.8 h^{-1} ; (b) reaction temperature is 160 °C, residence time is 2.9 s, and GHSV is 1259.3 h^{-1} ; (c) reaction temperature is 180 °C, residence time is 2.1 s, and GHSV is 1750.2 h^{-1} .

that the activation energy of side reactions is higher than that of the main reaction.

In order to further understand the dynamic properties of this oxidation reaction, the reaction rates of the main reaction and side reaction are measured in the temperature range 413–453 K, and the obtained reaction data are summarized in Table 2. The Arrhenius fittings of the main reaction to form the desired product

Table 2

The reaction data for the main reaction (R_{main}) to form CHO and the side reaction (R_{side}) to form CCA at different temperatures.

Temperature (F	K) 413	423	433	443	453
$1/T (K^{-1})$	0.00242	0.00236	0.00231	0.00226	0.00221
Yield ^a (%) R _n	_{nain} 9.04	10.89	12.9	15.0	17.2
Rs	_{de} 0.68	1.24	1.97	3.27	4.89
Y ^b (mol/ R _n	_{nain} 0.00181	0.00218	0.00258	0.00030	0.00344
min) R _s	de 0.00014	0.00025	0.00039	0.00065	0.00098

^a Reaction conditions: the molar ratio of cyclohexylamine to O_2 is 1:5, the flow rate of air is 100 ml/min, the flow rate of cyclohexylamine is 0.02 ml/min, residence time is 4.6 s, time on stream is 6 h, and GHSV is 784.8 h^{-1} .

^b Y (mol/min) = Yield × flow rate of cyclohexylamine (mol/min).



Fig. 4. Arrhenius fitting of ln Y versus 1/T for the main reaction to form CHO (A) and the side reaction to form CCA (B).

CHO and the side reaction to form the byproduct CCA are depicted in Fig. 4. Using the Arrhenius formula, $\ln k = \ln A - E_a/RT$, we can find the apparent activation energy for the main reaction and side reaction. The calculated results show the apparent activation energy to form the desired product, CHO, and to form the byproduct, CCA, are 25.65 and 77.53 kJ/mol, respectively. Obviously, the apparent activation energy of the side reaction is much higher than that of the main reaction. Therefore, elevating the temperature was not beneficial for the formation of CHO. These results indicate that the reaction temperature was a significant factor in cyclohexylamine conversion and CHO selectivity. From the point of view of CHO selectivity, the favorable reaction temperature was 140 °C.

3.3. Effects of residence time on the oxidation reaction

As we know, the residence time is an important factor in material conversion and products selectivity in the vapor phase oxidation reaction. To investigate the effects of residence time on cyclohexylamine conversion and selectivity to products, the vapor phase oxidation reaction was performed at different bed heights of the catalyst, and the results are shown in Fig. 5. It can be seen that the conversion of cyclohexylamine gradually increased with elevated residence time, and 10.2% conversion with 88.6% selectivity to CHO was achieved at 4.6 s of residence time. However, the



Fig. 5. Effects of the residence time on the oxidation reaction. Reaction conditions: the molar ratio of cyclohexylamine to O_2 is 1:5, the flow rate of air is 100 ml/min, reaction temperature is 140 °C, time on stream is 6 h, and the catalyst is silica gel.

selectivity to CHO showed a declining trend, and the selectivity to NCH and CCA slowly increased with prolonged residence time. This reason may be that it is difficult for the formed products to desorb quickly from the catalyst surface, which results in a consecutive side reaction to form by-products, so that the selectivity to CHO decreases with residence time. Therefore, selecting a suitable residence time is very important for the selective oxidation of cyclohexylamine in air to CHO. From the point of view of conversion and selectivity, a suitable residence time would be 4.6 s under the present reaction conditions.

3.4. Effects of the molar ratio of cyclohexylamine to oxygen on the oxidation reaction

As the molar ratio of reactants has a strong influence on the conversion and selectivity of products, the reactivity of the silica gel at different molar ratios of cyclohexylamine to oxygen was evaluated at a reaction temperature of 140 °C and a residence time of 4.6 s, and the results are listed in Table 3. It can be seen that the conversion of cyclohexylamine increases with decreasing molar ratio or rising concentration of oxygen. However, the increased conversion is accompanied by a rapid decline in CHO selectivity, and 88.6% selectivity to CHO with 10.2% of cyclohexylamine conversion was achieved at molar ratio 1:5. When the molar ratio reached 1:9, cyclohexylamine conversion increased significantly to 17.6% and CHO selectivity slowly decreased to 74.9%. However, the selectivity to NCH and CCA increased gradually with reduced molar ratio. This phenomenon indicates that a high concentration of oxygen facilitates the formation of NCH and CCA instead of

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Effects of the molar ratio of cyclohexylamine to oxygen on the oxidation reaction.^a

Molar ratio ^b	Conversion (%)	Selectivity (%)			
		СНО	NCH	CCA	Others ^c
1:1	4.3	90.3	3.8	5.9	-
1:2	6.8	89.5	3.9	6.6	-
1:5	10.2	88.6	4.1	7.3	-
1:7	12.6	85.3	5.8	7.8	1.1
1:9	17.6	74.9	6.4	13.8	4.9

^a Reaction conditions: the flow rate of cyclohexylamine is 0.02 ml/min, the flow rate of feed gas is 100 ml/min, temperature is 140 °C, the residence time is 4.6 s, time on stream is 6 and GHSV is 784.8 $h^{-1}.$

and N-cvclohexvlaniline

^b This denotes the molar ratio of cyclohexylamine to O₂.

^c Other byproducts are N,N'-dicyclohexyl-hydrazine (
$$\langle - \rangle_{N-N-N-}^{H-H} \rangle$$
), N-cyclo-

hexyl-N'-cyclohexylidene-hydrazine (\searrow_{N-N}^{H}

CHO. Therefore, from the point of view of CHO selectivity and cyclohexylamine conversion, the favorable molar ratio of cyclohexylamine to oxygen is about 1:5. In order to gain simpler and more convenient operation in industrial production, we use air directly as oxidizer (the molar ratio of cyclohexylamine to oxygen is ca. 1:5) to obtain CHO in the present reaction system.

In summary, from the single-factor-experiment results, the optimal reaction conditions obtained were that the molar ratio of cyclohexylamine to oxygen was 1:5, the reaction temperature was 140 °C, the residence time was 4.6 s, and the GHSV was 784.8 h⁻¹ in the oxidation reaction of cyclohexylamine with air; 88.6% selectivity to CHO with 10.2% cyclohexylamine conversion was achieved.

3.5. Durability test of silica gel in the oxidation of cyclohexylamine with air

Catalyst durability is one of the key issues in the development of efficient catalysts for the oxidation of cyclohexylamine to CHO. To investigate the stability of the silica gel catalyst, long-term performance tests were performed at 413 K. The effect of time on stream on cyclohexylamine conversion and CHO selectivity over silica gel was studied, and the results are depicted in Fig. 6. It is clearly seen that cyclohexylamine conversion as well as CHO selectivity increased mildly in the first 6 h, and 10.2% cyclohexylamine conversion with 88.6% selectivity to CHO was achieved. After that, the conversion and selectivity to oxime slightly decreased with time on stream. A possible reason was that more and more organic species were formed and deposited on the catalyst's surface with time on stream, covering some active sites, which resulted in blocking part of the pores, keeping the reactants from accessing the active sites. Furthermore, along with time on stream, the formed CHO can be hydrolyzed to cyclohexanone, which is easily converted to CCA in the presence of cyclohexylamine. In addition, N-cyclohexyl-N'-cyclohexylidene-hydrazine traces of $\rightarrow H_{N-N} =$), N-cyclohexylaniline ($/ H_{N-N} =$), and N,N'dicyclohexyl-hydrazine ($\langle \begin{tabular}{c} \overset{H}{\longrightarrow} \overset{H}{\longrightarrow} & & \\ \hline & & \\ &$ sent reaction conditions, while some deep oxidation byproducts such as CO₂ and CO are not detected. It is worth noting that CHO selectivity can be stabilized at around 81% with 8.5% cyclohexylamine conversion till 58 h. These results indicate that the silica gel catalyst exhibits better stability and catalytic activity in the oxidation of cyclohexylamine to CHO.



Fig. 6. Durability test of silica gel in the oxidation reaction. Reaction conditions: the flow rate of air is 100 ml/min, the molar ratio of cyclohexylamine to O_2 is 1:5, temperature is 140 °C, the residence time is 4.6 s, and GHSV is 784.8 h^{-1} .

3.6. Effects of solvent methanol addition on the oxidation reaction

To verify the promotion effect of solvent methanol in the cyclohexylamine oxidation reaction, the selectivity to CHO in the absence and presence of MeOH solvent was compared at the same cyclohexylamine conversion, and the results are depicted in Fig. 7. In the range of the examined time on stream (4–34 h), the curve of selectivity in a pure cyclohexylamine medium increased gradually from 85.2% to 88.6% and then decreased with time on stream. The selectivity to CHO was ultimately maintained at around 81.2% with 8.1% cyclohexylamine conversion at 34 h (curve a). When an added 10 wt.% of methanol solvent was introduced into the oxidation reaction system, an increase in CHO selectivity was observed (curve b, finally achieving ca. 8.2% conversion with 82.5% oxime selectivity at 34 h). When 30 wt.% of methanol solvent was added to the oxidation reaction system, the selectivity to CHO was further improved, and could reach 92.0% with 9.9% of cvclohexvlamine conversion at 6 h time on stream. Finally, 89.2% selectivity to oxime with 7.8% conversion was achieved (curve c). It is noted that when 50 wt.% of methanol solvent was introduced into this oxidation reaction system, the selectivity to oxime was further improved; 93.4% selectivity to CHO with 9.0% cyclohexylamine conversion was achieved at 6 h time on stream, and could be stabilized at around 91% with ca. 8.0% conversion (curve d), finally. These results show that the addition of methanol solvent can effectively improve the selectivity of oxime. This likely implies that methyl alcohol can effectively remove the organic products deposited on the surface of silica gel, which prevents side reactions and improves the selectivity to oxime.

3.7. Characterization of silica gel samples

The structural characteristics of silica gel and spent samples are characterized using N₂-physisorption, ²⁹Si MAS NMR, XRD, TG/ DTG, FT-IR, and UV-vis DRS. Nitrogen adsorption-desorption iso-therms of samples are shown in Fig. 8 and the textural properties (surface area, pore volume, and pore diameter) are summarized in Table 4. Obviously, all samples are similar to a type IV isotherm with an H1 hysteresis loop, which is characteristic of mesoporous materials. From Table 4, it is clearly seen that the BET surface area



Fig. 7. Comparison of the selectivity to CHO in the oxidation reaction in the absence and presence of MeOH solvent. Reaction conditions: the flow rate of feed liquid is 0.02 ml/min and the flow rate of air is 100 ml/min; (a) reaction temperature is 140 °C, residence time is 4.6 s, and GHSV is 784.8 h⁻¹; (b) reaction temperature is 142 °C, residence time is 4.6 s, and GHSV is 784.8 h⁻¹; (c) reaction temperature is 145 °C, residence time is 4.6 s, and GHSV is 784.8 h⁻¹; (d) reaction temperature is 145 °C, residence time is 4.5 s, and GHSV is 784.8 h⁻¹; (d) reaction temperature is 145 °C, residence time is 5.2 s, and GHSV is 687 h⁻¹.



Fig. 8. N2 adsorption-desorption isotherms of silica gel samples.

Table 4

Textural properties of fresh and spent silica gel.

Samples	Surface area	Pore volume	Pore diameter
	(m²/g)	(cm ³ /g)	(nm)
Silica gel – fresh	395.3	1.02	7.93
Silica gel – 2 h	280.0	0.88	7.91
Silica gel – 4 h	218.7	0.76	7.89
Silica gel – 12 h	157.0	0.53	7.89
Silica gel – 12 h	391.2	1.0	7.92
Silica gel – 58 h ^b	278.6	0.85	7.91
Silica gel – regenerated ^c	393.6	1.01	7.92

^a Spent silica gel sample soaked in methanol at 60 °C for 10 h.

^b Spent silica gel sample soaked in methanol for 4 h.

^c Spent silica gel sample calcined at 600 °C in air for 4 h.

of silica gel samples sharply decreases from 395.3 to $62.7 \text{ m}^2/\text{g}$ at 58 h time on stream, and the pore volume of samples also gradually decreases from 1.02 to $0.25 \text{ cm}^3/\text{g}$ at 58 h. However, the pore size distribution obtained from the desorption branches of the N₂ isotherms using the BJH method reveals that the pore diameter of the samples remain substantially unchanged. When the silica gel sample run for 58 h was soaked in methanol for 4 h, the BET



Fig. 9. XRD patterns of silica gel samples.

surface area and pore volume could be recovered from $62.7 \text{ m}^2/\text{g}$ and $0.25 \text{ cm}^3/\text{g}$ to $278.6 \text{ m}^2/\text{g}$ and $0.85 \text{ cm}^3/\text{g}$, respectively. When the silica gel sample run for 12 h was soaked with methanol at 60 °C for 10 h, the BET surface area were recovered from 157.0 to $391.2 \text{ m}^2/\text{g}$ again, and the catalytic activity still reached the same conversion and CHO selectivity as with the fresh catalyst. In addition, the BET surface area and pore volume of the spent silica sample were basically recovered to those of fresh silica gel by calcining in air at 600 °C for 4 h. These results demonstrate that the polar organic species formed in the reaction process block the porous structure of the catalyst, which results in a decrease of BET surface area and pore volume. The textural properties and catalytic performance of spent silica gel catalyst can be restored by calcination or an organic solvent soaking method.

The XRD patterns of silica gel samples are shown in Fig. 9. It is clearly seen that the patterns of all samples exhibited a broad diffraction peak at 22°, indicating the typical amorphous structure of silica gel. Furthermore, the characteristic peaks of silica gel were not destroyed and silica gel still kept its unordered mesoporous structure in the reaction process.

The TG/DTG curves of the samples are shown in Fig. 10. Obviously, for the fresh and spent samples, a mass loss process occurred below 100 °C, which was assigned to the loss of adsorbed water, and there was only a mass loss stage (ca. 5%) in the fresh silica



Fig. 10. TG/DTG curves of fresh and spent silica gel samples.

gel. This demonstrates that silica gel is thermally stable at temperatures below 800 °C. However, the mass loss of the spent catalyst increased with time on stream. From the TGA curves in Fig. 10A, it can be seen that the total mass loss percentage for silica gel samples at time on stream of 2, 4, 12, and 58 h are about 10%, 13%, 20%, and 30%, respectively. This shows that the accumulated amount of organic species deposited on silica gel surface increases gradually with time on stream.

In addition, from the DTG curves in Fig. 10B, for silica gel samples at time on stream of 2 and 4 h, it is clearly seen that a distinct two-step mass loss process occurred. The first peak at lower temperatures (ca. 55 °C) is generally attributed to the loss of adsorbed water, while the second peak at higher temperatures (ca. 170 °C) can be attributed to the decomposition of low-boiling organic species adsorbed on the silica gel surface. However, silica gel samples at time on stream of 12 h and 58 h underwent a three-step mass loss, with two peaks at lower temperatures (ca. 70 and 210 °C) and a third peak at higher temperature (ca. 350 °C) attributed to the decomposition of high-boiling organic species formed in the reaction process are gradually accumulated on the catalyst surface with time on stream.

To obtain further insights into the organic species deposited on the silica gel framework, FT-IR spectroscopy was performed on the fresh and spent silica gel samples, and the results are depicted in Fig. 11. The weak band at 1630 cm^{-1} and the broad band at 3432 cm^{-1} can be attributed to a combination of the stretching vibration of silanol groups or silanol "nests" with cross hydrogen-bonding interactions and the H–O–H stretching mode of adsorbed water [37]. The bands at 809 and 468 cm⁻¹ are attributed to the Si–O–Si symmetric stretching and bending vibration, respectively, and the strong band at 1102 cm^{-1} is attributed to the asymmetric stretching vibration of framework Si–O–Si bridges for silica gel [38]. It is evident that the C–H stretching bands in the methylene group (CH₂) are found at 2938 and



Fig. 11. FT-IR spectra of fresh and spent silica gel samples.

The elemental	analysis	data	of organic	species in	the spent	samples

Table 5

C (%)	H (%)	N (%)	Atom ratio (C:N)
7.82	1.72	1.48	6.15:1
9.13	1.84	1.7	6.3:1
16.24	2.4	2.79	6.77:1
26.4	3.32	4.61	6.65:1
	C (%) 7.82 9.13 16.24 26.4	C (%) H (%) 7.82 1.72 9.13 1.84 16.24 2.4 26.4 3.32	C (%) H (%) N (%) 7.82 1.72 1.48 9.13 1.84 1.7 16.24 2.4 2.79 26.4 3.32 4.61



Fig. 12. UV-vis spectra of fresh and spent silica gel samples.



Fig. 13. Results of recycling test of silica gel catalyst. Reaction conditions: the flow rate of air is 100 ml/min, the molar ratio of cyclohexylamine to O_2 is 1:5, reaction temperature is 140 °C, residence time is 4.6 s, time on stream is 6 h, and GHSV is 784.8 h^{-1} .



Fig. 14. FT-IR spectra of samples: (a) fresh silica gel, (b) recycling one time, (c) recycling eight times.

2857 cm⁻¹, and these bands increase in intensity with time on stream. The 2363 and 2341 cm⁻¹ bands are assigned to the vibration of the N—N band in the N species adsorbed on active sites, in accordance with previous work [39,40]. In addition, the bands at 1450, 1520, and 1580 cm⁻¹ are assigned to the C=C stretching vibration in the aromatic ring. Furthermore, the band at 1650 cm⁻¹ can be associated with the band containing C=N species [41]. These results show that some organic species containing CH₂ and C=N or N–N groups were deposited on the catalyst surface in the results are summarized in Table 5. It is obviously seen that the organic species are mainly composed of C, H, N, and O elements, and the percentage of elements gradually increased with time on stream.

The UV-vis spectra of samples are shown in Fig. 12. It is clearly seen that the fresh silica gel has no evident absorption peak in the

200–800 nm regions. In the UV–vis spectra of spent silica gel samples, there are obvious UV–vis absorption peaks at 254 and 330 nm, which are assigned to the delocalized electrons π – π * transition of conjugated organic species in the aromatic ring [42], and the absorption intensity increases with time on stream. In addition, there is a certain absorption peak at ca. 500 nm that shows that the large conjugated organic species is deposited on the catalyst surface. These results indicate that some conjugated organic species were gradually formed with time on stream in the reaction process.

3.8. The recycling of the silica gel catalyst in the oxidation reaction of cyclohexylamine in air

In order to evaluate the recycling of the catalyst in this oxidation reaction, silica gel was reused for eight runs. After each reaction, the catalyst was calcined at 600 °C in air for 4 h. The



Fig. 15. Possible reaction path of cyclohexylamine with air over silica gel.

regenerated catalyst was used for a recycling study under the same reaction conditions. The results for the reusability of the catalyst are shown in Fig. 13. It can be seen that the present catalyst was easily to regenerate and the catalytic performance of the regenerated catalyst was stable in the eight runs, and the cyclohexylamine conversion and selectivity to CHO were basically maintained at 10.2% and 88.6%, respectively.

In addition, in order to gain further insight into the change in physical structure of the catalyst in reaction and regeneration processes, the regenerated catalysts after recycling one time and eight times were characterized by FT-IR, as shown in Fig. 14. Compared with the FT-IR characteristic peaks of the fresh catalyst, it is clearly seen that the characteristic peaks of the regenerated catalyst were unchanged, which shows that the physical structure of regenerated silica gel is still maintained.

3.9. Possible reaction pathway of cyclohexylamine with air catalyzed by silica gel

On the basis of these results in this work, the obtained products were mainly CHO, CCA, NCH, and a small amount of cyclohexanone in the present reaction. We suggested a possible formation pathway of products in the catalytic oxidation reaction of cyclohexylamine with air over silica gel, as shown in Fig. 15. First, cyclohexylamine should be adsorbed onto the surface of silica gel by hydrogen bonds before oxidation. Then, the adsorbed cyclohexylamine will be rapidly oxidized by dioxygen to hydroperoxide species (Fig. 15a). Finally, the formed hydroperoxide species leave the catalyst surface under the action of water. Meanwhile, such hydroperoxide species in our system are decomposed rapidly to form intermediate nitrosocyclohexane, which is easy to isomerize or rearrange to CHO. However, the resulting nitrosocyclohexane can be also overoxidized to NCH. The previous literature reported that the autooxidation of amines was initiated on the α -C–H group or N–H group [19,43]. Likewise, we assume that the oxidation of cyclohexylamine adsorbed with oxygen also can form two hydroperoxide species at the α -C–H and N–H sites (Fig. 15b). The formed hydroperoxide species at the α -C–H site may be decomposed to cyclohexanone and hydroxylamine [14]. The cyclohexanone can react with hydroxylamine to form CHO, and can also react with cyclohexylamine to generate CCA. In this process, the surface silicon hydroxyl groups in silica gel play important roles in initiating the oxidation reaction of cyclohexylamine with oxygen.

In order to further verify the surface silicon hydroxyl groups as catalytic active sites, we examined the catalytic performance of silylated silica gel (the silica gel was silylated using a trimethylchlorosilane agent), as shown in Fig. 16. This results indicate that the catalytic activity (cyclohexylamine conversion) of silylated silica gel was decreased remarkably compared with unsilylated silica gel. In order to explore the change of the silicon hydroxyl groups in the samples, ²⁹Si MAS NMR characterizations of fresh silica gel, silylated silica gel, spent silica gel, and regenerated silica gel were performed, as shown in Fig. 17. Obviously, the spectra of fresh silica gel, spent silica gel, and regenerated silica gel samples displayed three resonances centered at ca -98.0, -101.0, and -110.2 ppm, which can be assigned to $(HO)_2Si(OSi)_2$ (Q_2) , HOSi(OSi)₃ (Q_3) , and Si(OSi)₄ (Q_4) environments around silicon, respectively. Interestingly, the peaks of silvlated silica gel at -98.0 and -101.0 ppm significantly disappeared, indicating that the silicon hydroxyl groups in the samples took part in reacting with the silvlation agent. Furthermore, the spectrum of the regenerated silica gel was similar to that of fresh silica gel, which showed that the surface silicon hydroxyl groups could be recovered and the structure was not damaged in the oxidation process.



Fig. 16. Comparison of the catalytic performance of silylated silica gel and silica gel. Reaction conditions: the molar ratio of cyclohexylamine to O_2 is 1:5, the flow rate of air is 100 ml/min, reaction temperature is 140 °C, residence time is 4.6 s, and GHSV is 784.8 h⁻¹.



Fig. 17. ²⁹Si MAS NMR spectra of samples.

These results demonstrate that the surface silicon hydroxyl groups in silica gel play a crucial role in initiating this oxidation reaction.

4. Conclusions

In conclusion, a simple and environmentally friendly approach to highly selective preparation of CHO from vapor phase catalytic oxidation of cyclohexylamine using air as a green terminal oxidant under atmospheric pressure has been successfully developed in this work. We have demonstrated that nonmetallic mesoporous silica gel is an effective catalyst for the vapor phase selective oxidation of cyclohexylamine to CHO. The surface silicon hydroxyl group as active site is responsible for the excellent catalytic performance of silica gel, and 88.6% selectivity to CHO with 10.2% cyclohexylamine conversion was obtained under optimal reaction conditions. Moreover, the addition of methanol solvent in cyclohexylamine can effectively improve the selectivity of CHO. It is noted that silica gel catalyst has long-term stable activity, and the spent catalyst can be easy to regenerate and reuse in the present oxidation reaction. Finally, a possible reaction pathway for the oxidation reaction of cyclohexylamine in air over silica gel

was also suggested. This synthetic method employing inexpensive silica gel as catalyst and air as green oxidant under facile conditions is a promising process, and has the potential to enable sustainable production of CHO in industrial applications.

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