Aerobic oxidation of cyclohexene catalyzed by NiO/MCM-41 nanocomposites in the gas phase

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Abstract. The nanoparticles of NiO supported on mesoporous MCM-41 were synthesized and characterized with X-ray diffraction (XRD) and transmission electron microscopy (TEM). In this study, catalytic activities of the supported NiO nanoparticles for oxidation of cyclohexene to 2-cyclohexene-1-ol and 2-cyclohexene-1-one with air in the gas phase were considered. These nanoparticles of NiO supported on mesoporous MCM-41 were effective catalysts in a temperature range of 220–310°C at 1 atm of air. Under these reaction conditions, the activity of the catalysts decreases in the following order: 5 wt.% NiO/MCM-41 > 7.5 wt.% NiO/MCM-41 > 2.5 wt.% NiO/MCM-41. With 5 wt.% NiO supported on mesoporous MCM-41 and under our experimental conditions, the conversion percent of cyclohexene is 62.3% with 65.9% selectivity of 2-cyclohexene-1-ol + 2-cyclohexene-1-one and 12.2% cyclohexadiene at 280°C. To achieve higher conversion of cyclohexene and better selectivity towards 2-cyclohexene-1-ol + 2-cyclohexene-1-one, factors such as reaction temperature, loading amount of nickel oxide and space velocity were studied, and optimized conditions were investigated.

Keywords. Oxidation; cyclohexene; NiO/MCM-41; 2-cyclohexene-1-ol; 2-cyclohexene-1-one

1. Introduction

Catalytic partial oxidation of hydrocarbons with air has important economic and industrial significances. Most hydrocarbon oxidations in the gas phase have shown low selectivity and conversion. In this regard, the main goal is to increase conversion and selectivity of these gas phase reactions.^{1–3} The allylic oxidation of olefin into α,β -unsaturated ketones is an important transformation in natural product synthesis.⁴ In particular, the oxidation products of cyclohexene and their derivatives, viz. 2-cyclohexen-1-one, 1-methylcyclohex-1-en-3-one, etc., are important in organic synthesis due to the presence of a highly reactive carbonyl group, which is utilized in cycloaddition reactions.^{5–7} Great efforts have been devoted to the oxidation of cyclohexene in the past years.^{8–10}

At the beginning of the 1990s, a new class of mesoporous materials composed of ordered silica was synthesized. These materials were first reported by Kato and co-workers,¹¹ but rapid development began after introducing micelle templated silica by the group from Mobil Oil.^{12,13} Investigations into the synthesis, structural characterization and catalytic properties of the M41S family of periodic mesoporous silicas led to

the development of a major area of research into mesoporous molecular sieves, primarily due to the numerous applications in which these materials can be employed.^{14–16} The development of Ni-based catalysts (with NiO as the main active component) and their commercial application is promising, due to their high effectiveness in oxide hydrogenation and oxidation of hydrocarbons.^{17,18} In recent years, nanomaterials have attracted extensive interest for their unique properties in various fields in comparison to their bulk counterparts.^{19,20} In particular, nickel oxide (NiO) has received a considerable amount of attention for its catalytic properties.

Oxide powders such as NiO and CoO are important catalysts in the chemical industry, and silica is usually preferred as a catalyst carrier since nickel or cobalt oxide layers deposited onto silica, exhibit good catalytic activity.^{21–23}

NiO, supported on a matrix, has been used in a wide variety of catalytic processes such as hydrodesulfurization (HDS) and hydrodechlorination (HDC), since Ni is inexpensive and functions as an active catalyst in such reactions. Relatively few studies, however, have been reported on applications of NiO inside mesoporous materials. In this work, the nano-sized MCM-41 was synthesized and used as a support to disperse NiO catalyst and the resulting nanocomposite

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showed enhanced activity. The correlation of the structural activity of NiO and NiO/MCM-41 catalysts is well discussed in the present investigation. The nanocomposites of NiO/MCM-41 could effectively catalyze the oxidation of cyclohexene to 2-cyclohexene-1-ol and 2-cyclohexene-1-one in the gas phase under atmospheric pressure.

2. Experimental

2.1 Preparation of the catalysts

Sodium silicate solution (25.5–28.5 wt.% SiO₂ and 7.5–8.5 wt.% Na₂O, MERK), cetyltrimethylammonium bromide (CTAB, 99%, BDH), acetic acid glacial (100%, analytical reagent grade), nickel nitrate-hexahydrate, polyvinylpyrrolidone (PVP) and sodium hydroxide used in this work, all were of analytical grade.

Mesoporous MCM-41 silica was synthesized using a gel mixture with a composition of 4SiO₂: 1CTAB: 250 H₂O, which was described in the literature.²⁴ A required amount of the CTAB was dissolved slowly in an appropriate amount of water and sodium silicate solution and stirred for 30 min. By adding acetic acid drop by drop, pH of the mixture reached 10 and the obtained gel was placed in a polypropylene bottle and refluxed at 100 °C for 24 h. After cooling and adjusting the pH at 10 with acetic acid the mixture was refluxed again for 24 h at 100 °C. The pH adjustment and subsequent heating operations were repeated several times for 5 days and the obtained gel was filtered and washed with distilled water and dried in an oven to obtain a white MCM-41 nanopowders. NiO nanoparticles were prepared with some modifications in the described procedure in the literature.²⁵ Chemical preparation of NiO nanoparticles composed of two stages: the formation of nickel hydroxide precursor precipitate and subsequent transformation to NiO by thermal treatment. Nickel hydroxide precursor was prepared by slow dropwise addition of 0.1 M sodium hydroxide (NaOH) to the mixed solution of 0.1 M nickel nitrate-hexahydrate and 0.5 g polyvinylpyrrolidone (PVP) as surfactant. The solution was vigorously stirred until the pH reached 7. The resulting precipitate was filtered and washed thrice with distilled water and final washing was carried out using alcohol. The wet cake obtained after filtration was oven dried for 100°C overnight. The oven-dried cake was heated at 450°C for 3h to form NiO nanoparticle.

NiO/MCM-41 catalysts were finally prepared via simple solid-state dispersion (SSD) method by mixing different amounts of NiO nanoparticles with required

nano-sized mesoporous MCM-41 in a minimum quantity of ethanol. The mixture was dried in an oven at 100°C overnight followed by calcination at 450°C for 3h.

2.2 Experimental procedure

A vertical fixed-bed glass reactor of 9 cm length and internal diameter of 1.5 cm operating at atmospheric pressure was utilized for the catalytic oxidation of cyclohexene. About 1 g of the catalyst sample with 60–80 mesh was placed on a sinter glass and fed with a 50 mL cyclohexene syringe by the automatic injector (Fresenius injectomats) at the desired temperature. The reactor was placed inside a temperature-controlled heating jacket with a thermocouple at the centre of the catalyst bed. The liquid product was collected by passing the hot gases through a water-cool condenser. The range of reaction temperature was 220–310°C, space velocity of 2878–3176 h⁻¹ (air was injected at 30 mL/min velocity and cyclohexene at 1.5–2.5 mL/h velocity) under 1 atm pressure. The reaction time was 3 h and a dual-channel (Shimadzu Model 8A) gas chromatograph (GC) was used online for analyzing the product.

2.3 Structural characterization

The powder x-ray diffraction (XRD) patterns were recorded on a Bruker Advance D8 Diffractometer with Cu K α radiation (λ = 0.154 nm). The TEM measurements were performed on a Philips CM 200 FEG/HRTEM (high-resolution transmission electron microscope) instrument operating at 200 Kv. Products were analyzed by a GC, Shimadzu 8A, using authentic samples equipped with a TCD detector using OV-17, Propak-N, packed (2 m) columns and Helium as the carrier gas. GC-MS analysis of the products was performed with the GC-MS model of Thermoquest-Finnigan Trace, equipped with a DB-1 fused silica column (with a length of 60 m and internal diameter of 0.25 mm and film thickness of 0.25 μ m) with helium as the carrier gas.

3. Results and Discussion

3.1 Characterization of the catalysts

XRD patterns of the samples are shown in figure 1. The very intense peak appeared at low angle (2θ = 2.55) on the figure 1a is assigned to reflections at (100) and two other additional picks with low intensities at

Figure 1. XRD patterns of samples (a) MCM-41 and NiO/MCM-41 (b) NiO nanoparticles.

(110) and (200) reflections indicate the regular pore structure of MCM-41 and can be attributed to quasi-two-dimensional hexagonal lattice of MCM-41.¹² On dispersing NiO over MCM-41, a decrease in the peak intensity of the characteristic (100) plan is predominant, while at higher NiO loading samples, the peaks of (110) and (200) planes tend to merge with the base line. Decrease in the intensity can be attributed to the pores covering effects that reduce the scattering contrast between the pores and the framework of MCM-41 sample. It may also indicate a distortion of the long-range ordering of the mesoporous structure and/or badly built hexagonal array.

All these diffraction peaks in figure 1b, including not only the peak positions appearing at 37.28°, 43.28°, 62.88°, 75.28° and 79.48°, but also their lattice parameters, are well consistent with that of the standard JCPDS Card No. 04-0835 for the standard spectrum of pure and cubic NiO.^{26,27} The results indicate that the products are nano-NiO crystal of cubic structure with high purity. It is seen in figure 1 that these characteristic diffraction

peaks in the pattern have a markedly broadening effect. According to the Debye-Scherrer's equation:

$$D = k\lambda/\beta \cos \theta$$

where D is the average crystallite size, k is a constant equal to 0.9, λ is the x-ray wavelength equal to 0.15406 nm and β is the half-peak width, the mean crystallite size of the as-synthesized products calculated according to this equation is about 21 nm.

Figure 2 shows UHTM images of as-prepared pure MCM-41 and 5%NiO/MCM-41. The ordered hexagonal pore arrangements of these two samples were clearly visible and the pores size and the thickness of the wall were estimated in the range of about 2–3 nm and 1 nm, respectively. The images indicate that the hexagonal mesostructures of MCM-41 have not been affected by loading NiO nanoparticles.

Specific surface area measured with BET method was 1081 m²/g for MCM-41, 1022 m²/g for 5 wt.% NiO/MCM-41 and 915 m²/g for 7.5 wt.% NiO/MCM-41.

Figure 2. TEM images of samples (a) MCM-41 (b) 5% NiO/MCM-41.

3.2 Air oxidation of cyclohexene

Cyclohexene was oxidized with air to 2-cyclohexene-1-ol and 2-cyclohexene-1-one at 62.3% conversion and 65.9% selectivity in the presence of 5 wt.% NiO supported on mesoporous MCM-41 when this reaction proceeds under atmospheric pressure at 280°C. This is a relatively mild system for industry. Another major product was obtained by dehydrogenation of cyclohexene. In this regard, 12.2% of cyclohexadiene was formed. The by-products of the reaction were 2-cyclohexene-1-hydroperoxide, cyclohexadiene, CO and CO₂. The product distribution for 5% NiO/MCM-41 nanocomposite is summarized in table 1. Selvam *et al.*²⁸ reported that with Cr/MCM-41 molecular sieve catalyst and in the liquid phase a conversion of around 51.1% with 76.3% selectivity towards 2-cyclohexene-1-one was obtained. They also concluded that 2-cyclohexene-1-one was obtained as the major product. In another report, Dias and co-workers²⁹ used metalloporphyrin catalysts (FeTPPCI, MnTPPCI and CoTPP) supported

on MCM-41 in the cyclohexene oxidation reaction. They concluded that FeTPPCI/MCM-41 presented the highest conversion (25.8%).

Experimental tests proved that in absence of the catalysts, oxidation of cyclohexene is negligible and unsupported mesoporous MCM-41 has shown lower catalytic activity than the supported catalyst.

When the reaction was catalyzed with mesoporous MCM-41 without any NiO, the reaction yield and conversion reduced considerably compared with NiO supported on mesoporous MCM-41. This showed that the active species responsible for oxidation of cyclohexene were loaded NiO on the support, since, with the use of only mesoporous MCM-41 as a catalyst, no reactivity and activity towards cyclohexene oxidation were observed.

3.3 The influences of the loading amount of nickel oxide on cyclohexene oxidation reaction

For investigating the effect of the loading amount of nickel oxide on mesoporous MCM-41 upon yield of products, three catalysts were tested. In table 2, details of the conversion and selectivity of the products for each catalyst are shown. It was observed that maximum conversion and selectivity for 2-cyclohexene-1-ol and 2-cyclohexene-1-one occurred with the catalyst of 5 wt.% NiO. It is known that NiO nanoparticles can be highly dispersed on mesoporous MCM-41 at 5 wt.% loading. A drop in conversion of cyclohexene and selectivity for 2-cyclohexene-1-ol and 2-cyclohexene-1-one for the catalyst with higher loadings than 5 wt.% is possibly due to a distortion of the long-range ordering of the mesoporous structure and/or badly built hexagonal array and more reduction of the specific surface area of the catalyst. Under these reaction conditions, the order of

Table 1. Product distribution for cyclohexene partial oxidation by air at T = 280°C, P = 1 atm, space velocity = 3027 h⁻¹ and catalyst 5 wt.% NiO/MCM-41.

Product ^a	Selectivity (%)
2-Cyclohexene-1-hydroperoxide	8.9
2-Cyclohexene-1-ol	29.8
2-Cyclohexene-1-one	36.1
CO ₂	3.6
Cyclohexadiene	12.2
CO	6.6
Methanol	0.8
Ethanol	0.7
Phenol	0.6
5-Hexen 1 al	0.5

^aOnly products with ≥0.5% selectivity are shown.

Table 2. Effect of temperature on partial oxidation^a of cyclohexene by air.

Catalyst	Temperature (°C)	Conversion (%)	Selectivity products ^b (%)				
			A	B	C	D	E
2.5% NiO/MCM-41	220	18.2	20.7	20.2	15.3	10.8	29.1
2.5% NiO/MCM-41	250	37.4	15.3	22.6	19.4	11.5	27.6
2.5% NiO/MCM-41	280	48.9	11.4	28.3	21.7	12.1	22.7
2.5% NiO/MCM-41	310	66.8	6.8	19.9	14.6	11.8	43.0
5% NiO/MCM-41	220	24.8	18.5	27.4	22.7	9.8	17.7
5% NiO/MCM-41	250	40.6	12.5	31.7	25.4	11.5	14.9
5% NiO/MCM-41	280	62.3	8.9	36.1	29.8	12.2	10.2
5% NiO/MCM-41	310	80.6	4.5	28.4	21.2	13.7	28.4
7.5% NiO/MCM-41	220	21.8	20.4	24.6	19.8	10.1	21.3
7.5% NiO/MCM-41	250	36.4	14.9	29.2	23.6	11.4	16.8
7.5% NiO/MCM-41	280	54.2	10.1	32.2	25.9	11.9	15.7
7.5% NiO/MCM-41	310	71.8	6.9	25.5	18.1	12.6	33.1
MCM-41	220	9.4	53.2	2.1	1.3	5.6	34.9
MCM-41	250	16.8	37.8	8.7	5.8	11.7	33.3
MCM-41	280	23.5	19.4	13.5	9.9	17.2	36.9
MCM-41	310	30.4	9.3	13.6	10.1	19.4	44.6

^a Catalyst = X% NiO/MCM-41 nanocomposites, catalyst weight = 1 g, reaction time = 3 h, P = 1 atm, rate of cyclohexene injection = 2 mL/h and rate of air flow = 30 mL/min.

^b A = 2-cyclohexene-1-hydroperoxide, B = 2-cyclohexene-1-one, C = 2-cyclohexene-1-ol, D = cyclohexadiene, E = CO_x.

catalytic activities is as follows: 5 wt.% NiO / MCM-41 > 7.5 wt.% NiO / MCM-41 > 2.5 wt.% NiO / MCM-41.

3.4 The influences of temperature on cyclohexene oxidation reaction

Table 2 shows the effects of reaction temperature on the conversion percent of cyclohexene and selectivity of 2-cyclohexene-1-ol and 2-cyclohexene-1-one. Considering the fact that selectivity is more important than the conversion percent, all three catalysts showed their best performance at 280°C. Figure 3 shows the conversion

percent of cyclohexene in the presence of various catalysts in different temperatures and figure 4 indicates the selectivity of product formation.

These studies showed that the rise in reaction temperature from 220°C to 310°C increased the conversion of cyclohexene and the highest value of the conversion was obtained when the reaction temperature was increased to 310°C. As for the distribution of the products, with increasing reaction temperature from 220°C to 280°C, the selectivity of 2-cyclohexene-1-one and 2-cyclohexene-1-ol increased and reached its maximum in 280°C, but the selectivities of 2-cyclohexene-1-hydroperoxide decreased and reached

Figure 3. The diagram of cyclohexene conversion versus temperature.

Figure 4. The changes of 2-cyclohexene-1-ol and 2-cyclohexene-1-one selectivity with respect to the reaction temperature in the presence of various catalysts.

its minimum in 310°C. It is indicative of a free radical reaction pathway.³⁰ When reaction temperature was increased from 280°C to 310°C, selectivity of the 2-cyclohexene-1-one and 2-cyclohexene-1-ol decreased considerably. In addition, at higher temperatures, more CO and CO₂ were formed that were the products of complete oxidation. The reduction of selectivity at higher temperatures may be due to oxidative degradation of the products.

3.5 The influences of space velocity on cyclohexene oxidation reaction

Table 3 shows how cyclohexene conversion and selectivity of 2-cyclohexene-1-ol and 2-cyclohexene-1-one change with space velocity. Space velocity is a criterion for contact time of substrate with the catalyst. In space velocities higher than 3176 h⁻¹ (rate of cyclohexene injection = 2.5 mL/h and rate of air flow = 30 mL/min), contact time of cyclohexene with catalyst

was short and conversion percent and selectivity for the major products were low. However, in space velocities lower than 2878 h⁻¹ (rate of cyclohexene injection = 1.5 mL/h and rate of air flow = 30 mL/min), the contact time seems too much; the main oxidation products are CO and CO₂ and selectivity of 2-cyclohexene-1-ol and 2-cyclohexene-1-one decreased. When the oxygen flow rate was lowered, the conversion percent of cyclohexene and selectivity for the major products is also decreased, i.e., for space velocity 2217 h⁻¹ (rate of cyclohexene injection = 2 mL/h and rate of air flow = 20 mL/min). The best combination for high conversion percent and good selectivity for 2-cyclohexene-1-ol and 2-cyclohexene-1-one was obtained at 3027 h⁻¹ space velocity (rate of cyclohexene injection = 2 mL/h and rate of air flow = 30 mL/min). Therefore, contact time of substrate with catalyst seems an important factor for high conversion and specificity of the products.

3.6 Discussion

To explain how the oxidation occurred, based on the literatures^{30–32}, it seems that oxidation of cyclohexene using O₂ as oxidant proceeds via a classic Haber–Weiss radical-chain sequence mechanism as shown in scheme 1.

According to the literature,^{33,34} the oxidation of cyclohexene with molecular oxygen initially forms 2-cyclohexene-1-hydroperoxide as shown in scheme 1 (step a). 2-Cyclohexene-1-hydroperoxide is not stable and can form 2-cyclohexene-1-ol (step c) or decompose to 2-cyclohexene-1-ol and 2-cyclohexene-1-one in the presence of catalyst (step g). The conversion of cyclohexene is controlled by the rate of step a in scheme 1.

Table 3. Effect of space velocity on the conversion of cyclohexene and selectivity of 2-cyclohexene-1-one + 2-cyclohexene-1-ol formation^a.

Space velocity (h ⁻¹)	Conversion (%)	Selectivity (%)
3837	35.2	34.4
3176	44.9	47.1
3027	62.3	65.9
2878	73.7	35.3
2217	43.7	30.9

^aCatalyst = 5 wt.% NiO/MCM-41 nanocomposite, T = 280 °C, catalyst volume ≈ 1.5 mL, catalyst weight = 1 g, reaction time = 3 h, P = 1 atm.

Initiation: **Propagation:** **Termination:**

Scheme 1. The classic Haber–Weiss radical-chain sequence mechanism proposed for the oxidation of cyclohexene by NiO/MCM-41 nanocomposites, based on the research of Weiner, etc.^{31,32}

As shown in table 2, with increasing reaction temperature from 220°C to 310°C, the conversion of cyclohexene increases, which indicates that high temperature is of advantage to step a in scheme 1.

4. Conclusions

The present work showed the results of synthesis, characterization and application of NiO nanoparticles supported on mesoporous MCM-41 in the oxidation of cyclohexene with air, in the absence of any solvent, reducing agent and co-catalyst. The catalysts possess particular nanostructure and excellent function

and can be easily separated after the reaction, which endow mesoporous MCM-41-supported NiO with a bright future in industrial applications. In view of the conversion percent of cyclohexene and selectivity of the 2-cyclohexene-1-ol/2-cyclohexene-1-one, the optimum condition is 5 wt.% NiO/MCM-41 nanocomposites in $P = 1$ atm, $T = 280^\circ\text{C}$ and space velocity of 3027 h^{-1} .

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