Transition Metal-immobilized Silica Catalysts for Selective Oxidation of Cyclohexane with *t*-Butyl Hydroperoxide

Wimonrat Trakarnpruk
Department of Chemistry, Faculty of Science, Chulalongkorn University, Bangkok 10330

วิมลรัตน์ ตระการพฤกษ์
ภาควิชาเคมี คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย กรุงเทพ 10330
Tel: 0-2218-7577 E-mail: wimonrat.t@chula.ac.th

Abstract

Transition metal-immobilized silica catalysts, M/SiO_2 (M = Co, Cu, Mn, Cr and Ni) have been prepared by the sol-gel technique and characterized by means of X-ray diffraction, N_2-physisorption, ICP and FTIR. They have been used as heterogeneous catalysts for selective oxidation of cyclohexane to cyclohexanol and cyclohexanone with anhydrous *tert*-butylhydroperoxide (TBHP). All the M/SiO_2 catalysts prepared provided relatively high conversion and selectivity . The reaction mechanism was found to involve free peroxyl radicals. The Co/ SiO_2 was the most active catalyst and after calcination the conversion of cyclohexane was increased but selectivity to cyclohexanone was decreased.

Keywords: Cobalt, cyclohexane, oxidation, silica, *tert*-butylhydroperoxide, transition metals

1. Introduction

Oxidation of cyclohexane yields cyclohexanol and cyclohexanone. Cyclohexanol (A) and cyclohexanone (K) are the key intermediates in the production of adipic acid (Nylon-66) and caprolactam (Nylon-6). The oxidations were carried out with stoichiometric amounts of various homogenous reagents [1]. Homogeneous catalysis using soluble transition metal salts (such as cobalt naphthenate) is the only technology actually developed until now. In this process, the oxidation is carried out at 150 °C and 1-2 MPa pressure. This affords about 4% conversion and 70-85% selectivity to cyclohexanone and cyclohexanol. The conversion is limited to less than 10% to avoid overoxidation to unwanted products, since the primary products: cyclohexanone and cyclohexanol are more reactive than cyclohexane [2]. A combination of metal and boric acid was also reported [3] with acid as by-product. The process is low in energy efficiency, and generates plenty of by-products and waste. These homogeneous catalysts require tedious procedures in the separation of the catalysts and products. Heterogeneous catalysts offer advantages of a better control of reaction conditions, preventing catalyst self-destruction; higher catalyst stability; higher active site dispersion because of the high surface areas furnished by the support; and easier catalyst recovery and recycling. Heterogeneous catalysts include metal oxides, metal cations and complexes incorporated on inorganic matrixes. Some examples are as follows: V_2O_5-TiO_2 catalyst (8% conversion and 76% selectivity to cyclohexanol using acetic acid as solvent and acetone as initiator) [4]; Ce-MCM-41 (95% conversion based on oxidant with 82% selectivity to cyclohexanol at 100 °C) [5]; Cr-MCM-41 catalyst (99% conversion and 20% selectivity to cyclohexanone) [6], Cr-SiO_2 with H_2O_2 (100% conversion based on oxidant with 20% selectivity to cyclohexanone at 70 °C) [7]. Studies on Co-containing catalysts using O_2 as oxidant include Co/ZSM-5 (10% conversion and 97% selectivity to cyclohexanone and cyclohexanol) [8],

Co_3O_4 nanocrystals (7.6% conversion and 89% selectivity to cyclohexanone+cyclohexanol) [9]. Co-TUD-1 catalyst showed 9.5% conversion with 90% selectivity to cyclohexanone using TBHP [10]).

Sol-gel method has been commonly used to prepare metallosilicates due to the advantages of the superior homogeneity of metal distribution, high surface areas compared to impregnation method. In this work the transition metals-immobilized catalysts were prepared by sol-gel method and applied to oxidation of cyclohexane with TBHP as an oxidant. The stability and recyclability of the catalysts studied were also investigated.

2. Experimental

2.1 Syntheses of transition metal-immobilized silica catalysts

The catalysts were synthesized via sol-gel hydrolysis and polycondensation of transition metal salts with tetraethyl orthosilicate (TEOS). Nitrate salts of Cu, Mn, Cr and Ni were used except for Co. Acetate salt of Co was used because it was reported that this salt showed better activity in oxidation of alkyl aromatic compounds than nitrate salt [11].

In a Teflon-lined reactor, TEOS (40 mmol), metal salts (2 mmol, 5%mol based on TEOS) in 150 mmol ethanol was added 18 mmol of aqueous HCl (8 M) slowly and stirred for 5 min. Then the reaction mixture was left at room temperature for 3 days. The volatiles were removed by slow evaporation. Then it was dried at 110 °C for 24 h. The resulting solid material (M/SiO_2) was crushed and sieved (100 mesh). Only the Co/SiO_2 was selected for study of effect of calcination (as it was shown to be better catalyst than other metals), it was calcined under air at 500 °C for 5 h. This calcination temperature was chosen according to the reported work on synthesis of cobalt oxide nanoparticles [12].

The structure of the catalysts was analysed with Rigaku, DMAX 2002/Ultima Plus diffractometer equipped with a rotating anode using Cu-Kα radiation (Ni filter) between 2 and 30° (with a scanning rate of 2° min.$^{-1}$ The BET surface area, pore volume and pore size distributions were obtained from N_2 adsorption-desorption isotherm measured at 77K by a micromeritics adsorptometer, model Flowsorb 2300. For elemental analysis, the ICP analysis was carried out using a Plasma-1000 (Perkin Elmer) ICP-AES instrument. FT-IR spectrum (KBr disc) was recorded on a Nicolet FT-IR Impact 410 Spectrophotometer to obtain information of functional groups in the catalysts.

2.2 Oxidation of cyclohexane

The oxidation of cyclohexane was performed in a 60 ml Parr-type reactor. Cyclohexane, anhydrous *t*-butylhydroperoxide (TBHP, 6 M in decane), and catalyst (synthesized from 2.1) were added into the reactor. Then, the reactor was heated to 70 °C and stirred at 300 rpm with a magnetic stirrer. In cases of using $TBHP/O_2$ as oxidant, upon heating to the reaction temperature, the reactor was also charged with 1-3 atm of O_2. After a required time, the reaction mixture was filtered to remove the catalyst. The reaction mixture was added 25% H_2SO_4 and the reaction products were extracted with diethyl ether. The organic layer was neutralized with saturated $NaHCO_3$ and dried over anhydrous Na_2SO_4. The products were analyzed with a gas chromatography (a Shimadzu model CG-17A equipment with flame ionization detector and OV-1701 capillary column (30 m x 0.25 mm i.d.) and *n*-octane was used as internal standard. Cyclohexanone and cycloohexanol were identified by comparison with authentic standards. The percentage of each compound in the reaction mixture was estimated directly from the corresponding chromatographic peak areas. Blank experiment was also conducted in the absence of catalyst. Cyclohexyl hydroperoxide cannot be detected directly by GC as it decomposed to produce cyclohexanol and cyclohexanone. Therefore at the end of the oxidation reaction, cyclohexyl hydroperoxide was determined by treating the final reaction solution with an excess of triphenylphosphine (PPh_3) before the GC analysis. PPh_3 reduces the cyclohexyl hydroperoxide quantitatively to the corresponding cycloohexanol, giving triphenylphosphine oxide. The amount of cyclohexyl hydroperoxide was determined by comparing the concentrations of the cyclohexanol, measured before and after the treatment of the sample with PPh_3 [13]. Acid was analyzed by acid-base titration as follows: 0.2 g PPh_3 was added to 10 g reaction mixture, the solution was kept for 30 min before diluting with 25 mL deionized water and was refluxed for 1 h after adding 20 mL 0.1 M NaOH and then titrated with 0.1 M HCl. Values of conversion of cyclohexane reported are averaged from three experiments.

Experiments were also performed to confirm reaction mechanism, the reaction was conducted in the presence of radical scavenger (2,6-di-*tert*-butyl-4-methylphenol).

2.3 Catalyst recycling

Recycling tests of the catalyst were carried out by removing the catalyst from the reaction mixture, washed with acetone, dried and subjected to the next catalytic run. In addition, the filtrate was analyzed by to check leaching of metal into the reaction mixture.

2.4 Leaching test

Leaching of metal into the reaction mixture was tested. A hot reaction mixture was filtered after reaction and analyzed by ICP.

3. Results and discussion

3.1 Catalyst characterization

Table 1 presents textural characteristics of the M/SiO_2 catalysts. The BET surface area, pore volume and pore size of the catalysts were in the range of 363-418 m^2/g, 0.20-0.30 cm^3/g and 2.1-2.3 nm, respectively.

Table 1. Structural characteristics of M/SiO_2 catalysts

M	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Ni	364	0.30	2.3
Cr	418	0.20	2.1
Mn	363	0.20	2.1
Cu	430	0.24	2.3
Co	379	0.23	2.2

XRD patterns of the transition metals/SiO_2 were displayed in Fig. 1. A broad peak at low angle reflection revealed an amorphous phase and no characteristic peaks of metal oxide were detected. This is due to low amount of loaded metal (5 mol%), below detection limit of the XRD technique.

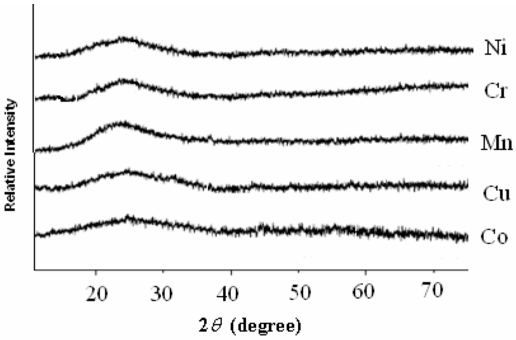


Fig. 1 XRD patterns of the M/SiO_2.

In Fig. 2, the typical silicate absorptions appear at about 1085, 800 and 550 cm^{-1} attribute to Si-O-Si bending and stretching vibrations in the Co/SiO_2. In the Cu/SiO_2, a band at 1393 cm^{-1} associated with the anti-symmetric NO_3-stretching vibration (from Cu nitrate starting material) was also observed. As the FTIR spectra of other M/SiO_2 (M = Ni, Cr and Mn) are similar to that of the Cu/SiO_2, so representative FTIR spectrum of the Cu/SiO_2 was shown in Fig. 2.

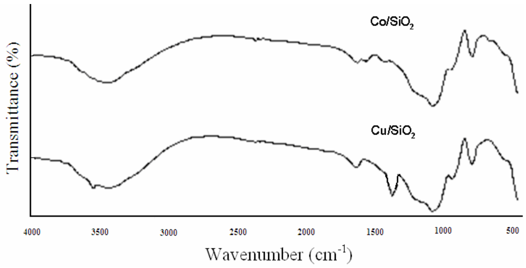
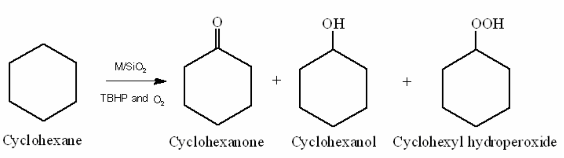


Fig. 2 FTIR spectra of the Co/SiO_2 and Cu/SiO_2.

3.2 Oxidation of cyclohexane over M/SiO_2 catalysts

The performance of the M/SiO_2 catalysts was tested in oxidation of cyclohexane with TBHP. The major oxidized products detected are cyclohexanone and cyclohexanol, with trace amount of cyclohexyl hydroperoxide (about 2.0-3.1%) (equation 1).



(1)

Effect of type of transition metal

The results on oxidation of cyclohexane over different transition metal immobilized silica catalysts are shown in Table 2 under the same reaction condition. The reaction carried out in the absence of the catalyst showed no oxidized product. Among different transition metal immobilized on silica, the activity order demonstrated by %conversion is: Co > Cu > Mn > Cr > Ni and the order of selectivity to cyclohexanone follows the same trend except Ni > Cr (probably due to experimental error).

Table 2 Oxidation of cyclohexane over M/SiO_2 using TBHP

Catalyst	%Conv.[a]	%Sel.[b]	
		cyclohexanone	cyclohexanol
none	-	-	-
Ni	11.3	64	36
Cr	13.0	60	40
Mn	16.2	68	32
Cu	17.2	73	27
Co	23.5	76	24

Reaction condition: cyclohexane 18 mmol, catalyst 0.05 g, TBHP (6 M in decane) 12 mmol, temperature 70 °C, time 24 h

[a] Conversion (conv.) is based on GC.

[b] Selectivity (sel.) is expressed as percentages of cyclohexanone and cyclohexanol. Cyclohexyl hydroperoxide (2.0-3.1%) was not included.

As the Co/SiO_2 showed the best catalytic performance therefore it was chosen for study of reaction condition.

Effect of reaction time

Cyclohexane conversion using the Co/SiO_2 is given in Fig. 3 as a function of time (6-24 h). It can be seen that the conversion is increased with increasing reaction time. Fig. 4 shows product selectivity as a function of time. The initial oxidized products were both cyclohexanol and cyclohexanone. The prolonged reaction times resulted in increasing cyclohexanone and subsequently decreasing cyclohexanol, this suggested further oxidation of cyclohexanol to cyclohexanone. At 6, 12, 18 and 24 h, the conversion is 6.3, 13.8, 17.5 and 23.5%, whereas the selectivity to cyclohexanone is 44, 49, 58, and 76%, respectively. In this work cyclohexyl hydroperoxide was also detected in little amount (~ 2-3% based on total products).

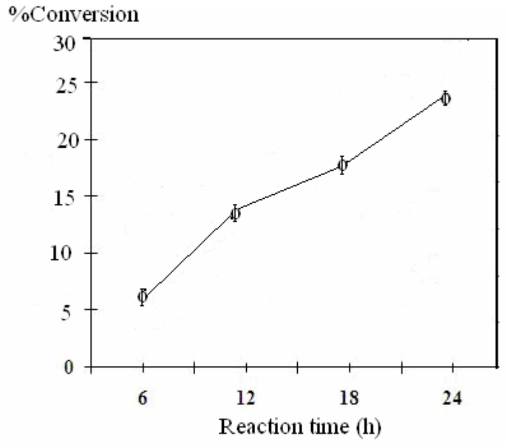


Fig. 3 Effect of reaction time on conversion of cyclohexane over the uncalcined Co/SiO_2 catalyst.

Condition: cyclohexane 18 mmol, Co/SiO_2 0.05 g, TBHP (6 M in decane) 12 mmol, temperature 70 °C

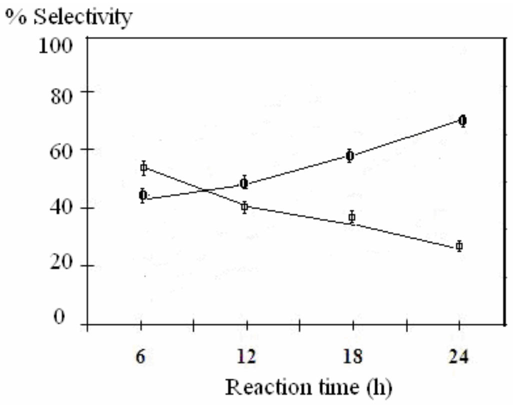


Fig. 4 Effect of reaction time on selectivity between cyclohexanone and cyclohexanol the uncalcined Co/SiO_2 catalyst.

(0 = cyclohexanone, □ = cyclohexanol)

Condition: cyclohexane 18 mmol, Co/SiO_2 0.05 g, TBHP (6 M in decane) 12 mmol, temperature 70 °C

Effect of calcination

As the Co/SiO_2 was the most active catalyst in this work, it was chosen for the more detailed study. Its activity was compared to the calcined sample. After the Co/SiO_2 was calcined at 500 °C for 5 h, its surface area was increased from 379 to 395 m^2/g.

The oxidation of cyclohexane was performed over the calcined Co/SiO_2 catalyst under the same reaction condition as used in the uncalcined catalyst. The result in Fig. 5 shows that the conversion of cyclohexane from the calcined catalyst is higher than that of the uncalcined catalyst (in Fig. 3). However the comparison of the product selectivity (Fig. 6) showed that the selectivity to cyclohexanone is lower compared to the uncalcined catalyst (in Fig. 4).

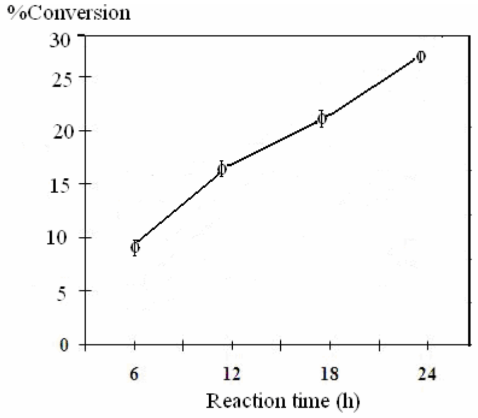


Fig. 5 Effect of reaction time on conversion of cyclohexane over the calcined Co/SiO_2 catalyst.

Condition: cyclohexane 18 mmol, calcined Co/SiO_2 0.05 g, TBHP (6 M in decane) 12 mmol, temperature 70 °C

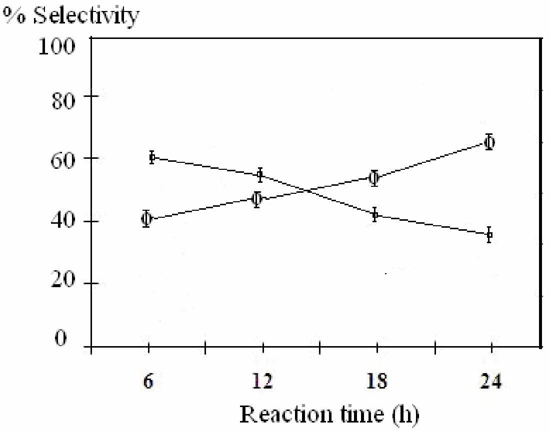


Fig. 6 Effect of reaction time on selectivity to cyclohexanone and cyclohexanol over the calcined Co/SiO_2 catalyst. (0 = cyclohexanone, □ = cyclohexanol)

Condition: cyclohexane 18 mmol, calcined Co/SiO_2 0.05 g, TBHP (6 M in decane) 12 mmol, temperature 70 °C

The conversion and selectivity to cyclohexanone are compared and summarized in Table 3.

Table 3 Oxidation of cyclohexane over the uncalcined and calcined Co/SiO_2 catalysts

Catalyst	Time (h)	%Conv.	%Sel. cyclohexanone
calcined	6	8.3	40
	12	16.0	45
	18	20.7	55
	24	27.5	64
uncalcined	6	6.3	44
	12	13.8	49
	18	17.5	58
	24	23.5	76

Reaction condition: cyclohexane 18 mmol, catalyst 0.05 g, TBHP (6 M in decane) 12 mmol, temperature 70 °C

The change in catalytic performance might be due to existence of Co_3O_4 phase after calcination, as shown in the XRD pattern in Fig. 7, the diffraction peaks at (2θ, °) 31.4, 36.8 and 38.6, matching with cubic Co_3O_4 phase (JCPDS-43-1003). The higher activity resulted from the Co_3O_4 in the calcined catalyst is in agreement with the result obtained from cobalt oxide on titania in oxidation of cyclohexane [14].

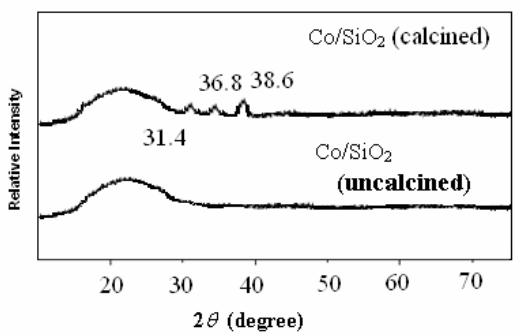


Fig. 7 XRD pattern of the Co/SiO_2 (calcined) and (uncalcined).

Effect of oxygen pressure

In order to enhance the catalytic activity of the calcined Co/SiO_2 catalyst, oxygen gas in the system was increased by pressurized O_2 in the range of 1-3 atm, along with the TBHP under the same reaction condition. The result was shown in Table 4. It was found that the conversion can be increased slightly when 1 atm. oxygen was fed in the reaction mixture. At 2-3 atm O_2, the increase in conversion was more significant. The higher concentration of O_2 in the system was from the decomposition of TBHP and also from the fed O_2, which then reacted with cyclohexane. However the product selectivity was unchanged.

Table 4 Effect of O_2 pressure over calcined Co/SiO_2

Pressure	%Conv.	%Sel.	
(atm)		cyclohexanone	cyclohexanol
0	27.5	64	36
1	27.7	64	36
2	28.3	65	35
3	29.0	65	35

Conditions: cyclohexane 18 mmol, calcined Co/SiO_2 0.05 g, TBHP (6 M in decane) 12 mmol, time 24 h, temperature 70 °C.

Effect of reaction temperature

In order to shorten the reaction time, temperature was increased from 70 °C to 90 and 120 °C and the reaction time was set to 6 h. It was reported that Co_3O_4 with an average particles size of 50 nm showed 7.6% conversion and 56% selectivity to cyclohexanone in 6 h at 120 °C [9]. The result shown in Table 5 revealed that the conversion was increased with temperature, however it was found that the selectivity to combined cyclohexanone and cyclohexanol was decreased. This might be due to over-oxidation of cyclohexanol and cyclohexanone to by-products, resulting in formation of acid (adipic acid) [9]. The increase of acid with increasing of the reaction temperature indicates that, at higher temperature, the rate of oxidizing the cyclohexane to desired products was slower than that of oxidizing cyclohexanone/cyclohexanol to form by-products.

In this work the activity of the calcined Co/SiO_2 was higher than those obtained using Co-substituted AlPO which gave 5.8% conversion, 41% cyclohexanone, 36% cyclohexanol and 4% acid at 130 °C for 8 h or MCM-41 [15].

Table 5 Oxidation of cyclohexane over calcined Co/SiO_2 at different temperatures in 6 h

T(°C)	%Conv.	%Sel.		
		cyclohexanone	cyclohexanol	acids
70	8.3	40	60	0
90	11.6	50	47	3
120	14.0	51	41	8

Conditions: cyclohexane 18 mmol, calcined Co/SiO_2 0.05 g, TBHP (6 M in decane) 12 mmol.

3.3 Recycling and leaching test of catalyst

The uncalcined and calcined Co/SiO_2 catalysts were chosen for study of leaching test. After reaction the catalyst was separated by filtration, washed with acetone and dried. It was used for the recycling study under the same reaction conditions. The result was shown in Table 6. The conversion of cyclohexane decreased slightly for three consecutive cycles but the product selectivity was unchanged. Analysis of the reaction mixture with ICP did not show any metal leaching (below 0.3 ppm).

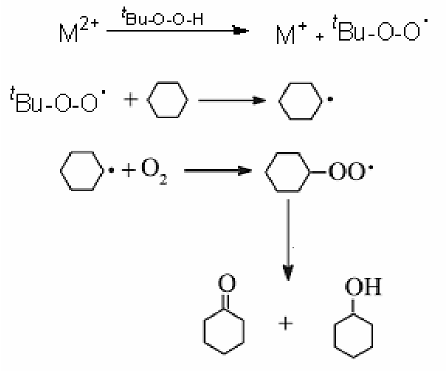
Table 6 Recycling of the uncalcined and calcined Co/SiO_2 catalysts

Catalyst	Run	%Conv.	%Sel.	
			cyclohexanone	cyclohexanol
uncalcined	1	23.5	76	24
	2	23.0	76	24
	3	22.5	75	24
calcined	1	27.5	64	36
	2	27.1	64	36
	3	26.7	64	36

Reaction condition: cyclohexane 18 mmol, catalyst 0.05 g, TBHP (6 M in decane) 12 mmol, temperature 70 °C, time 24 h

3.4 Reaction mechanism

In order to test whether the mechanism occurs via radical, radical trap (2,6-di-*tert*-butyl-4-methylphenol or BHT) was added along with the reactants. The results show that for all catalysts, no product was detected. This reveals that the oxidation of cyclohexane to cyclohexanone and cyclohexanol is a free radical mechanism as shown in scheme 1 [16]. In the case of the calcined Co/SiO_2, the same mechanism was revealed. In this work TBHP acts as a radical initiator and as source of molecular oxygen.



Scheme 1. Proposed mechanism of cyclohexane oxidation with TBHP.

4. Conclusions

The prepared M/SiO_2 catalyzed oxidation of cyclohexane selectively to cyclohexanone and cyclohexanol using TBHP at 70 °C for 24 h. The activity order is: Co > Cu > Mn > Cr > Ni. Effect of calcination was studied on the Co/SiO_2 which showed the highest activity. The uncalcined Co/SiO_2 catalyst provided relatively higher selectivity to cyclohexanone than that of the calcined Co/SiO_2 catalyst. Both uncalcined and calcined catalysts were recyclable and can be reused three times with only a slight decrease of the activity, and exhibited practically the same selectivity as that of the fresh catalyst. The oxidation of cyclohexane is considered to undergo via a free-radical mechanism.

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