Research Article

Mesoporous Co_3O_4 as a New Catalyst for Allylic Oxidation of Cyclohexene

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Abstract

Mesoporous cobalt oxide was investigated for the liquid phase oxidation of cyclohexene using tertio-butylhydroperoxide (TBHP) as an oxidant. The results were compared with several series of supported cobalt catalysts to study the influence of the cobalt loading and solvents on the overall conversion and selectivity. Mesoporous cobalt was synthesized through the nanocasting route using siliceous SBA-15 mesoporous material as a hard template and cobalt nitrate as the cobalt oxide precursor. Supported cobalt oxide catalysts ($\text{Co}/\text{M}_x\text{O}_y$) were synthesized by the impregnation method using two loadings (1 and 5 wt.%) and Al_2O_3 , TiO_2 , and ZrO_2 as supports. Samples were characterised by means: elemental analysis, X-ray powder Diffraction (XRD), BET (surface area), UV-Vis DR Spectroscopy, and Transmission Electron Microscopy (TEM). The results obtained showed that the cobalt oxide retains the mesoporous structure of SBA-15, and in all $\text{Co}/\text{M}_x\text{O}_y$, crystalline Co_3O_4 , and CoO phases are observed. The mesoporous cobalt oxide is more active than the supported cobalt catalysts in the allylic oxidation of cyclohexene, with a conversion of 78 % of cyclohexene and 43.3 % selectivity toward 2-cyclohexene-1-ol. The highest activity of mesoporous cobalt oxide could be ascribed to its largest surface area. Furthermore, Co_3O_4 has both Lewis and Brønsted acidic sites whereas $\text{Co}/\text{M}_x\text{O}_y$ has only Lewis acidic sites, which could also explain its superior catalytic activity. Moreover, mesoporous cobalt oxide was more stable than supported cobalt catalysts. Therefore, this catalyst is promising for allylic oxidation of alkenes. Copyright © 2018 BCREC Group. All rights reserved

Keywords: Mesoporous Co_3O_4 ; Supported Cobalt; Cyclohexene; Allylic Oxidation

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1. Introduction

In the petroleum industry a large amounts of alkane and alkene are produced as by-products which can be oxidized to oxygenated derivatives and converted into value-added products, such

as: alcohols, ketones, aldehydes, and carboxylic acids [1].

During the allylic oxidation process, the reaction occurs on the C–H key in allyl of alkene to produce an alcohol and ketone and the C=C bond is retained [2,3]. When the reaction take place at C=C key, peroxide is generates. The oxidation of cyclohexene has been the research topic of a large number of investigations because of the importance of the obtained prod-

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ucts, like the cyclohexene oxide, 2-cyclohexene-1-one [4,5] and 2-cyclohexene-1-ol [5-8]. The 2-cyclohexene-1-ol (enol) can be converted to phenol without co-products. The 2-cyclohexene-1-one (enone) is extensively utilized in the synthesis of drugs, pesticides and adipic acid which is utilized in nylon-6 manufacture. The synthesis of fine chemicals uses cyclohexene oxide as a key intermediate owing to its high reactivity which is ascribed to the opening of the highly strained three-membered ring [9,10].

Although the homogeneous catalysts have a high activity in the oxidation reactions, however they have significant disadvantages in the recovery of the catalyst and the isolation of the product. In contrast, heterogeneous catalysts systems exhibit high activity, stability, and reusability. Various cobalt-substituted mesoporous materials have been investigated as catalysts for selective liquid phase oxidation [5,11-14].

Zhen *et al.* [15] reported that cobalt oxide in the form of nanocrystalline particles is a crucial factor for attaining high activity for combustion of VOCs, CO oxidation, and NO₂ decomposition [15]. Hence, the synthesis of nanostructured cobalt oxides especially with ordered mesoporous structure has been investigated [15,16]. Mesoporous Co₃O₄ has exhibited a higher catalytic activity in the combustion of VOCs than that obtained by a conventional Co₃O₄. To the best of our knowledge this is the first report investigating mesoporous Co₃O₄ as a catalyst for selective liquid phase oxidation.

In this paper, mesoporous Co₃O₄ was prepared via the nanocasting route using mesoporous SBA-15 silica as a mold and cobalt nitrate as a precursor through a solid-liquid route [17]. Mesoporous cobalt oxide was investigated for the liquid phase oxidation of cyclohexene using tertibutylhydroperoxide (TBHP) as an oxidant. The results were compared with several series of supported cobalt catalysts to study the influence of the cobalt loading and solvents on the overall conversion and selectivity.

2. Materials and Method

2.1 Catalysts Preparation

2.1.1 Mesoporous cobalt oxide (Co₃O₄)

Synthesis of the mesoporous silica SBA-15 was conducted in a way similar to that used by Zhao *et al.* [18]. The mesoporous cobalt oxide was obtained using the method given below, i.e. 1 mmole of the precursor Co(NO₃)_x.yH₂O was combined with 0.15 g of SBA-15 and the mix was then crushed for a short moment in an

agate mortar and pestle. Next, the admixture was placed in a melting pot that was put in a muffle furnace, where the temperature was raised from ambient temperature to 400 °C, at a rate of 1 °C/min; it was then maintained at the final value for the period of 5 hours. After that, the sample was cooled down back to ambient temperature. A 10 %wt. HF aqueous solution was used to remove the silica template. Centrifugation was used to recuperate the mesoporous cobalt oxide which was then washed with distilled water three times.

2.1.2 Supported Co/M_xO_y

The supports, such as: Al₂O₃ (Oxid C Degussa), TiO₂ (Titandioxid Degussa), and ZrO₂ (Aldrich), are all available on the market; they are in the form of a nanopowder (nanoparticles in the range from 10 to 50 nm). A preliminary treatment is required before the metal precursors are impregnated.

The chosen supports were mixed with water (an amount of 200 mL of H₂O with 100 g of support) in order to obtain a paste. This mixture was left to dry overnight at the temperature of 120 °C, and was then sifted in order to hold back only the particles with a diameter that is between 1 and 2.5 Å. After that, the support was calcined at the temperature of 400 °C under oxidative flow (20 % O₂, 80 % Ar, 60 mL/min) for a period of 4 hours. These oxides were next impregnated with an aqueous solution of Co(NO₃)₂.6 H₂O (Fluka) in order to get 1 and 5 %wt. of cobalt catalyst. First, the solvent was evaporated, next the solids were dried at the temperature of 120 °C overnight, and then they were calcined at 400 °C.

2.2 Catalysts Characterization

Instrumental analyses have been employed to investigate the physicochemical characteristics of the prepared catalysts. The metal content was checked by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) using an OPTIMA 2000 DV spectrometer. The surface areas and pore sizes were measured by nitrogen adsorption at 77 K on a Micrometrics Tristar 3000 apparatus after heat pre-treatment under vacuum for 6 hours at 250 °C. The acidity contents were determined by Fourier Transform Infra Red (FTIR) analysis of chemisorbed pyridine using a Nicolet Magna IR spectrometer. Details on the experimental procedure have been described in previous works [4,19].

Wide angle powder X-ray Diffraction (XRD) patterns were collected on a Bruker D5005 dif-

fractometer, using a Cu-K α radiation ($\lambda = 1.54$ Å). For small-angle analysis, the XRD patterns were collected on a Bruker AXS D5005 X-ray source; the signal was recorded for 2θ comprised between 0.7 and 5° . DRS spectra of the samples studied were recorded in the wavelength range 200-800 nm at room temperature, using a UV-Vis spectrophotometer (Perkin Elmer) with KBr as the reference. The size and dispersion of the Co particles were observed using Transmission Electron Microscopy (TEM) in conjunction with energy dispersive X-ray Spectroscopy (EDXS). Micrographs are obtained on a JEOL 2100 instrument (operated at 2200 KV with a LaB6 source and equipped with a Gatan Ultra Scan camera).

2.3 Catalytic Reactions

Tertiobutylhydroperoxide TBHP (Aldrich, 70 wt.% in H₂O) was used as an oxidant for the catalytic oxidation of cyclohexene in a two-neck glass round bottom flask fitted with a magnetic stirrer and a reflux condenser. Firstly, the solvent and TBHP were mixed and well agitated to achieve a phase transfer from water to organic phase.

Normally, 20 mL of solvent and 5.5 mL of oxidant (TBHP) were blended into a closed erlenmeyer flask and magnetically agitated for a period of 24 hours. Next, the organic phase contained was isolated from the aqueous phase. The concentration of the TBHP that remained in the aqueous phase was determined by iodometric titration in order to control the phase transfer. The quantity of TBHP that remained in the aqueous phase was less than 10 % of the initial amount. After that, the TBHP-solvent mixture, 3 mL of cyclohexene, and 0.1 g of catalyst were admixed in the magnetic stirrer-glass reactor, at 343 K and stirred for a period of 6 hours.

Identification of the reaction products was done by comparing them with authentic ones. The course of the reactions was monitored by gas chromatography (GC), using a YL6500 GC system equipped with an Agilent HP-FFAP capillary column and a flame ionization detector (FID). The remaining TBHP was decomposed before the GC analysis by incorporating an excess of triphenylphosphine (Aldrich). Moreover, an iodometric titration was carried out at the end of the reaction (after 6 h) by analysing the organic phase, in order to control the remaining TBHP. The catalytic performances were reported in terms of cyclohexene conversion, selectivity towards products and turnover frequency. They are calculated following the

Equations (1-2).

$$\text{Conversion (\%)} = \frac{[C_6H_{10}]_0 - [C_6H_{10}]_t}{[C_6H_{10}]_0} \times 100 \quad (1)$$

$$\text{Selectivity(\%)} = \frac{\text{Moles of individual product}}{\text{Moles of total product}} \times 100 \quad (2)$$

3. Results and Discussion

3.1 Catalysts Characterization

3.1.1 N₂ Adsorption-desorption isotherms

N₂ adsorption-desorption isotherms and pore size distribution of Co₃O₄ are presented in Figure 1. The textural properties of Co₃O₄ and supported cobalt oxide catalysts are listed in Table 1. Figure 1 shows that Co₃O₄ has a jump at $P/P_0 = 0.8-1.0$ which is typical for mesoporous solids indicating that the mesoporous structure is retained in the nanocasting process via a solid-liquid route [20,21]. As shown in Table 1, mesoporous Co₃O₄ exhibits a larger surface area than those of supported catalysts.

It is important to note that the surface area of mesoporous Co₃O₄ synthesized in this work by the nanocasting pathway via a solid-liquid route is much higher than those of mesoporous Co₃O₄ synthesized by the nanocasting pathway via the solvent evaporation method [22,23]. The lower surface area of mesoporous Co₃O₄ as compared to SBA15 silica can partly be ascribed to the difference between the densities of the two materials, as reported for mesoporous MgO synthesized by the nanocasting pathway [24]. Bulk Co₃O₄ has a density of 6.11 g/cm³ while that of amorphous SiO₂ is 2.2 g.cm⁻³. It is reasonable to suppose analogous differences in the densities for the pore

Figure 1. N₂ adsorption-desorption isotherms and BJH pore size distribution of Co₃O₄

walls of the two mesoporous materials; therefore, the surface areas of mesoporous Co_3O_4 and SBA-15 silica are closer to each other when normalized with respect to the density. The lower surface area of mesoporous Co_3O_4 is also attributed to the partial loss of structural order, which is in agreement with the XRD results.

3.1.2 Acid properties of catalysts

Pyridine adsorption is still one of the most frequently used methods for evaluating the acidity of solids. The infrared spectrum in the region between 1400 and 1700 cm^{-1} has been determined for pyridine adsorbed on acidic solids. FTIR spectra of pyridine adsorbed on 5 wt% $\text{Co}/\text{Al}_2\text{O}_3$, 5 wt% Co/ZrO_2 , and 5 wt% Co/TiO_2 (not shown) showed only the 1455 cm^{-1} band which is typical of Lewis sites. No characteristic bands of pyridine adsorption on Brönsted acid sites were seen (formation of the pyridinium ion leading to two adsorption bands

at 1545 cm^{-1} and 1637 cm^{-1}) [25,26].

The FT-IR spectrum of mesoporous Co_3O_4 showed both Lewis acid site bands and Brönsted acid site bands at 1446 and 1554 cm^{-1} , respectively. The data summarized in Table 1 indicate that mesoporous Co_3O_4 possesses significant Brönsted and Lewis acidity. The $\text{Co}/\text{Al}_2\text{O}_3$ sample was found to be more acidic (150 $\mu\text{mol.g}^{-1}$ at 150 °C) than Co/ZrO_2 (52 $\mu\text{mol.g}^{-1}$ at 150 °C) and Co/TiO_2 (6 $\mu\text{mol.g}^{-1}$ at 150 °C). The cobalt loading measured by ICP-AES is 1 or 5 wt% in all supported materials.

3.1.3 XRD characterizations

The XRD patterns of the samples are presented in Figure 2. The low-angle XRD pattern of Co_3O_4 (Figure 2a) shows one diffraction corresponding to (100) reflection which can be related with the hexagonal symmetry characteristic of mesoporous SBA-15 [27] showing that the mesoporous structure is retained in the nanocasting process via a solid-liquid route. It

Figure 2. XRD of mesoporous Co_3O_4 : Low angle (a) and Wide angle (b)

Table 1. Textural properties of supports, Lewis, and Brönsted acidity and metal content of catalyst

Catalyst	ICP-AES (wt.%)	Lewis acidity ($\mu\text{mol.g}^{-1}$)	Brönsted acidity ($\mu\text{mol.g}^{-1}$)	Textural properties of supports		
				Surface area ($\text{m}^2.\text{g}^{-1}$)	Pore size (nm)	Pore volume ($\text{cm}^3.\text{g}^{-1}$)
Co_3O_4	-	193	241	164	9	0.34
$\text{Co}/\text{Al}_2\text{O}_3$	1.07	-	-	-	-	-
	5.08	150	-	95	31	0.72
Co/ZrO_2	0.92	-	-	-	-	-
	5.07	52	-	35	30	0.26
Co/TiO_2	0.87	-	-	-	-	-
	4.76	6	-	43	26	0.27

is worth noting a certain degree of broadening of the reflections which indicate some loss in structural order.

Figure 2b shows the wide-angles XRD patterns; on the Co_3O_4 pattern the diffraction peaks at $2\theta = 19.08^\circ$, 31.38° , 36.88° , 44.88° , 59.38° , and 65.28° are ascribed to Co_3O_4 in the cubic phase with $\text{Fd}3\text{m}$ space group (JCPDS no. 42-1467) [28]. On all $\text{Co}/\text{M}_x\text{O}_y$ patterns (Figure 3), crystalline Co_3O_4 and CoO phases are observed and metallic Co is not detected. In addition, the diffraction peaks at $2\theta = 34.5^\circ$ and 42.4° could be attributed to CoO in the cubic form (JCPDS no. 71-1178) [29,30]. For 5 % $\text{Co}/\text{Al}_2\text{O}_3$, the diffraction peaks at $2\theta = 37^\circ$, 45° , and 66° are attributed to $\text{g Al}_2\text{O}_3$ [31] and for 5 wt% Co/ZrO_2 , the diffraction peaks at $2\theta = 28.17^\circ$, and 31.47° are ascribed to the presence of ZrO_2 in the monoclinic phase (JCPDS no. 37-1484), and the peak at 30.12° indicates the presence of zirconia in the face centered cubic form (JCPDS no. 49-1642). On Co/TiO_2 pattern, the simultaneous presence of rutile (JCPDS no. 21-1276) and anatase (JCPDS no. 21-1272) phases are detected indicating that TiO_2 is constituted of a mixture of titanium oxide in the quadratic and centered quadratic phases.

3.1.4 DR-UV-Vis analysis

Diffuse-reflectance UV-Vis spectroscopy is a sensitive tool that is frequently used to detect the environment of cobalt. Mesoporous cobalt oxide spectrum is characterized by the presence of six bands (Figure 4). The bands centered at about 410 nm and 720 nm are assigned to $\text{O}^{2-}\text{-Co}^{2+}$ and $\text{O}^{2-}\text{-Co}^{3+}$ charge transfer processes, respectively [32-34], indicating the formation of Co_3O_4 which in agreement with the XRD results. The peak intensity at 400 nm on

mesoporous Co_3O_4 was higher than that at 700 nm, which indicate the importance of Co^{2+} species on this catalyst. The bands at 320 nm, 520 nm, and 620 nm are ascribed to the presence of Co^{2+} in the tetrahedral coordination [35,36]. The absorption band at 248 nm can be assigned to NO_3^- ions present inside the pores [37].

The UV-vis-spectra of the catalysts supported cobalt $\text{Co}/\text{M}_x\text{O}_y$ (Figure 5) exhibit strong band at ~ 240 nm originating from the oxygen-to-metal charge transfer transitions [38]. The spectrums show a triplet at 320, 500, and 600 nm, characteristic of the presence of Co^{2+} ions in tetrahedral coordination. Two others bands at 400 and 670 nm could be assigned to octahedral Co^{3+} ion similarly to that in Co_3O_4 [34,39-32].

3.1.5 TEM characterizations

Figures 6 and 7 present TEM images of the cobalt based catalysts. Figure 6 shows, in accordance with the XRD and N_2 adsorption-desorption results, the mesoscopic order of Co_3O_4 , indicating that cobalt oxide retains the SBA-15 mesostructure. For 5 % $\text{Co}/\text{Al}_2\text{O}_3$ (Figure 7a) and 5 % Co/ZrO_2 (Figure 7b) of TEM analysis reveals an intensive agglomeration of cobalt particles on these samples and, then, a true reliable distribution cannot be given. The average size of these agglomerations is between 8 nm and 10 nm.

4. Catalytic Activity

4.1 Oxidation of Cyclohexene

The cyclohexene oxidation with tert-butyl hydroperoxide (TBHP) as oxidant was used to assess the catalytic activity of the as-prepared

Figure 3. X-ray diffraction (XRD) patterns of samples

Figure 4. DR-UV-vis spectra of Co_3O_4

catalysts. It should be noted that Al_2O_3 , ZrO_2 , and TiO_2 supports are inactive in this reaction.

The cyclohexene oxidation can give six products: cyclohexene epoxide (Epo); 2-cyclohexene-1-ol (enol); 2-cyclohexene-1-one (enone); cyclohexanol (ol); cyclohexanone (one); and cyclohexene-1,2-diol. A possible mechanism of cyclohexene oxidation has been proposed; it involves two main paths. The first one is a direct epoxidation, in the presence of redox catalysts, leading to the epoxide, which may be transformed into a diol in the presence of water and an

acidic medium. The second one is an allylic oxidation which, in the presence of Lewis acid sites and redox centers, may give 2-cyclohexene-1-ol (enol), 2-cyclohexene-1-one (enone), cyclohexanone, and cyclohexanol [43] as illustrated in the following catalytic scheme (Figure 8).

Our catalysts drive the reaction selectivity towards the allylic oxidation due to their strong acidity [4,25,44]. The orientation of the reaction towards the formation of 2-cyclohexene-1-ol as majority product indicates the preferential attack of the activated C–H bond over the C=C bond. It is important to mention that, the 2-cyclohexene-1-one, was only detected in presence of Co_3O_4 mesoporous oxide (Table 2).

From the results shown in Table 2 we note: The mesoporous cobalt oxide has a better activity with 78 % of conversion compared to $\text{Co/M}_x\text{O}_y$ catalysts. Co_3O_4 exhibits a larger surface area than those of supported catalysts (Table 1) which could explain the highest catalytic activity of this catalyst. Additionally, Co_3O_4 has both Lewis and Brönsted acidic sites

Figure 5. DR-UV-vis spectra of supported catalysts: (a) Co/Al₂O₃; (b) Co/ZrO₂; (c) Co/TiO₂

Figure 6. TEM images of mesoporous Co_3O_4

Figure 7. TEM photos of catalysts: 5 % Co/ Al₂O₃ (a), 5% Co/ZrO₂ (b)

whereas $\text{Co/M}_x\text{O}_y$ have only Lewis acidic sites (Table 1), which could also explain its superior catalytic activity, so it can be suggested that the presence of Brönsted acidic sites improves the catalytic activity in the cyclohexene oxidation.

The catalytic behavior of $\text{Co/M}_x\text{O}_y$ towards cyclohexene oxidation was found to enhance with cobalt loading. When the Co content increased (from 1 to 5 %), the 2-cyclohexen-1-ol selectivity decreased slightly with concomitant formation of other oxidized products with com-

parable amounts: cyclohexene-1,2-diol (1.7 %), cyclohexene epoxide (2.4 %), cyclohexanol (3.7 %) and cyclohexanone (5.3 %).

These results could be explained in terms of the Lewis acidity of the catalysts. It is well established in the literature that the acidity jointly with the redox properties of the metal determine the selectivity of the catalyst towards oxidation products [45]. Moreover, the contribution of Lewis acid sites in the oxidation of cyclohexene has many times been stressed in the literature [45-47].

Figure 8. Different pathways for cyclohexene oxidation reaction

Table 2. Oxidation of cyclohexene with different catalysts

Catalyst	wt. (%)	Conv. (%)	Selectivity (%)						TBHP consumption (%)
Co_3O_4	/	45	6	50	32	0	12	0	75
		78 ^a	0 ^a	43 ^a	41 ^a	0 ^a	16 ^a	0 ^a	81
$\text{Co/Al}_2\text{O}_3$	5.08	13	2	87	0	4	5	2	16
		44 ^a	4 ^a	48 ^a	0 ^a	27 ^a	12 ^a	9 ^a	53
Co/ZrO_2	1.07	5	2	96	0	0	2	0	14
	5.07	7	3	96	0	1	0	0	16
Co/TiO_2	0.92	3	0	98	0	0	2	0	16
	4.76	11	0	95	0	2	1	2	14
Co/TiO_2	0.87	5	0	97	0	0	1	2	16

TBHP = 39.73 mmol (5.5 mL); Solvent: heptane (20 mL); C_6H_{10} = 29 mmol (3 mL); Catalyst = 0.1 g $T = 70^\circ\text{C}$.

^a: solvent: acetic acid

The results reveal (Table 1) that all Co/M_xO_y systems seem to have the following relative order of Lewis acidity: Co/Al₂O₃ > Co/ZrO₂ > Co/TiO₂. This Lewis order of acidity is in agreement with the catalytic activity of our samples and also with other results previously reported in the literature [48]. On other hand, TBHP as oxidant promotes the allylic oxidation pathway and minimizes the epoxidation, particularly under the highly acidic properties of catalysts [49].

It is well known that the nature of solvents used has a major impact on the reaction kinetics and product selectivity in the oxidation of cyclohexene. The oxidation reaction was carried out in polar protic solvent (acetic acid) in presence of Co₃O₄ and 5 %Co/Al₂O₃ the most acidic catalyst among the 5 %Co/M_xO_y catalysts (Table 2). It has been found that 2-cyclohexene-1-ol was formed as the major product with high conversion (78 %) and selectivity (43.3 %) over mesoporous Co₃O₄. Obviously, the catalyst surface prefers to adsorb the more polar molecules, such as ketone and alcohol molecules, which are able to block the active sites of the catalyst. Then, the polar solvent could wash out the other products from the surface and consequently the oxidant and cyclohexene would have more chance to reach the active sites [50,51]. Moreover, the acetic acid acts as an oxidizing agent (formation of the peracetic acid complex) [19].

4.2 Reusability of the Catalyst

The catalytic stability of mesoporous Co₃O₄ and 5 % Co/Al₂O₃ in cyclohexene oxidation is studied (Table 3). The catalyst was reused for a

new run after it was separated from the reaction mixture through filtration, washed with water and dried at 100 °C.

For mesoporous Co₃O₄, the activity of the refreshed catalyst after the first cycle remains the same as that of fresh catalyst and decreases of 21.8 % and 34.6 % for the 3rd and 4th runs, respectively. It is also noted that the selectivity changes slightly, the appearance of the diol after the first cycle is probably due to the presence of the water framework, adsorbed during the course of the reaction. In contrast, 5 %Co/Al₂O₃ loses its activity under recycling. The deactivation of the catalyst is probably related to frequent inhibition processes found in oxidation reactions such, as the adsorption of oxygenated species on the catalyst surfaces [3].

Leaching of the metal into solution was checked by AAS analyses of the supernatant solution (Table 3). We found that a negligible amount of cobalt was leached into solution when mesoporous Co₃O₄ was used as catalyst, so it is not the likely reason for the catalyst deactivation. In contrast, a higher metal leaching (3.61 %) was observed for Co/Al₂O₃.

In order to confirm that mesoporous Co₃O₄ acts truly as a heterogeneous catalyst, it was separated by filtration from the reaction mixture and the reaction was allowed to continue on the remaining filtrate solution for another 2 h under the same reaction conditions; no further conversion of cyclohexene was observed, showing that the oxidation of cyclohexene over mesoporous Co₃O₄ is purely heterogeneous.

In order to investigate the causes for the decrease in the activity during the recycling experiment, the spent Co₃O₄ catalysts were characterized by XRD and N₂ physisorption.

Table 3. Recycling results of the catalysts

Catalyst	wt. (%)	Conv. (%)	Selectivity (%)						wt% Co ^a

Co ₃ O ₄	1 st	78	6	49	33	0	12	0	0.29
	2 nd	78	2	44	25	0	31	8	0.35
	3 rd	61	0	38	21	0	28	13	0.19
	4 th	51	0	41	23	0	24	12	0.16
5% Co/Al ₂ O ₃	1 st	44	4	48	0	26	13	9	2.1
	2 nd	37	0	46	0	26	16	15	3.61
	3 rd	31	0	45	0	24	14	17	3.46
	4 th	12	0	46	0	24	11	19	1.04

TBHP = 39.73 mmol (5.5 mL); Solvent: Acetic acid (20 mL); C₆H₁₀ = 29 mmol (3 mL); Catalyst = 0.1 g T = 70
a: cobalt content (wt%) leached into solution

It can be seen from Figure 9 that the XRD patterns of fresh and spent catalysts are similar, indicating that the ordered structure of Co_3O_4 is not affected during the recycling experiment, showing that the catalytic system can be reused without loss of catalyst's structure.

In contrast, the textural properties of Co_3O_4 catalysts are affected during the recycling experiment (Table 4), the BET surface area and the pore volume decrease, which is attributed to clogging catalyst pores by carbonaceous species that makes them inaccessible for nitrogen adsorption. These carbonaceous species, formed inside the catalyst porosity through secondary reaction between the reaction products, block the pore access of the catalyst, leading to a deactivation during the reuse. The spent catalyst can be easily regenerated by calcination in air at 500 °C.

5. Conclusions

This study demonstrates that mesoporous Co_3O_4 is more active than supported cobalt oxide catalysts for allylic oxidation of cyclohexene with TBHP as an oxidant. The superior catalytic activity of mesoporous Co_3O_4 could be explained by its larger surface area compared to

those of supported materials ($\text{Co}/\text{M}_x\text{O}_y$). Indeed, a high surface area often leads to a greater activity due to an increased dispersion of active sites.

Additionally, Co_3O_4 has both Lewis and Brönsted acidic sites whereas $\text{Co}/\text{M}_x\text{O}_y$ have only Lewis acidic sites, which could also explain its higher catalytic activity. Indeed, a high surface area often leads to a greater activity due to an increased dispersion of active sites. Moreover, mesoporous cobalt oxide is more stable than supported cobalt catalysts and it can be regarded as self-supported nanoscale catalysts; it does not need any support, as required by normal nanoparticle catalysts. Therefore, this catalyst is promising for allylic oxidation of alkenes.

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Figure 9. XRD patterns of fresh and used catalysts

Table 4. Textural properties of fresh and used catalysts

Catalyst	Surface area ($\text{m}^2\cdot\text{g}^{-1}$)	Pore size (nm)	Pore volume ($\text{cm}^3\cdot\text{g}^{-1}$)
Fresh Co_3O_4	164	9	0.34
Co_3O_4 after the 1 st run	144	8.3	0.22
Co_3O_4 after the 2 nd run	50	5.6	0.15

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