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Novel and efficient cobalt encapsulated SBA-15 catalysts for the selective oxidation of cyclohexane

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ABSTRACT

Co-SBA-15 catalysts were synthesized by direct synthesis and post-synthetic impregnation methods at two different loadings of Co viz., 1.2 and 2 wt%. The structure of SBA-15 was found to remain intact even after the incorporation of Co in either of the two methods of catalyst preparation, which was confirmed by low-angle XRD. The existence of Co^{2+} species were confirmed by characteristic absorption bands of Co in the UV–vis spectra and XPS results. The encapsulation of Co in SBA-15 was found to be highly advantageous in yielding significant amounts of the desired products viz., cyclohexanone and cyclohexanol in the oxidation of cyclohexane in liquid phase without using any solvent under moderate pressure of O_2 at 433 K. The catalysts showed high turn over numbers towards the oxidation of cyclohexane to cyclohexanone and 2%CoSYN (2 wt% Co-SBA-15) catalyst showed a maximum of 9.4% conversion of cyclohexane and 78% selectivity towards the formation of cyclohexanone.

1. Introduction

The selective oxidation of saturated hydrocarbons by air/molecular oxygen especially under mild conditions has prime significance in the chemical industry and economical in the synthesis of various bulk and fine chemicals. Selective oxidation of cyclohexane is one such reaction the products of which viz., cyclohexanol and cyclohexanone are important intermediates in the manufacture of nylon-6 and nylon-66. Further these products are also very useful as solvents, stabilizers, homogenizers and in the synthesis of various insecticides, herbicides and pharmaceuticals [1,2]. The present commercial processes employ metal cobalt salt or metal-boric acid in the oxidation of cyclohexane at around 150 °C and 1–2 MPa pressure which showed $\sim$4% conversion of cyclohexane and 70–85% selectivity to cyclohexanone. Various other oxidants such as iodosobenzene [3], hydrogen peroxide [4] and alkylhydroperoxide [5] are used in presence of transition metal compounds as homogeneous catalysts for this reaction. However, the environmental limitation for the disposal of solid/liquid waste, the usage of solvent during the course reaction and the catalyst separation is one of the important problems in the homogeneous systems. In order to avoid these problems and make the processes green, heterogeneous catalysts are under intensive investigation [6,7]. Many catalysts like metal oxides, metal cations and complexes incorporated on inorganic matrixes such as silica, alumina, zirconia, active carbon, zeolites, Ti-containing mesoporous materials such Ti-MCM-41, TS-1, nanostructured amorphous iron oxide on TiO_2 surface and amorphous cobalt oxide, etc., are reported to show good activity towards oxidation of cyclohexane reaction [8–11]. Although there are a few reports of nano-cobalt in the oxidation of hydrocarbons [11], Co incorporated in SBA-15 offers additional advantages over other Co supported catalytic systems such as high surface area, uniform porosity and higher thermal stability over MCM-41. Thus, the present report elucidates the superior activity and stability of cobalt encapsulated SBA-15 catalysts in the selective oxidation of cyclohexane in presence of oxygen in the liquid phase and in particular the present system is solvent free.

2. Experimental

2.1. Preparation of catalysts

Cobalt from cobaltous chloride precursor in required amounts were taken to get 1.2 and 2 wt% Co in the final catalysts and designated as 1.2%CoSYN and 2%CoSYN, respectively. The synthesis procedure followed is same as that reported earlier for SBA-15 [12] and cobalt is introduced in the form of cobaltous chloride along with TEOS during the preparation process. The same

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Table 1
Structural characteristics of catalysts

Sl. no.	Catalyst	BET-surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Pore diameter (Å)
1	SBA-15	680	1.6	9.6
2	1.2%CoSYN	746	1.8	9.7
3	2%CoSYN	778	1.9	9.9
4	1.2%CoIMP	649	1.5	9.4
5	2%CoIMP	610	1.5	9.2

catalysts were made by wet impregnation method from aqueous solution of cobaltous chloride on SBA-15 calcined at 773 K and designated as 1.2%CoIMP and 2%CoIMP, respectively.

2.2. Characterization techniques

Low-angle X-ray diffractograms were recorded on a Philips PW 1840 powder diffractometer using Ni filtered Cu Kα radiation in the 2θ range of 0.5–6°. The N_2 adsorption–desorption measurements were performed at 77 K using automated gas sorption system (M/S. Quantachrome, USA) utilizing Brunner–Emmett–Teller (BET) calculation for surface area and Barrett–Joyner–Halanda (BJH) method for pore size distribution. Pore size distribution was obtained from the desorption branch of isotherms. Transmission electron micrographs were carried out in a Philips Tecnai G^2 FEI F12 electron microscope for probing particle size. The samples were ultrasonically dispersed in ethanol before loading onto a carbon-coated copper grid and then allowed to dry at room temperature before recording the micrographs.

The UV–vis diffused reflectance spectra were recorded on GBC UV–vis Cintra 10_e spectrometer with an integrating sphere reflectance accessory. The spectra were recorded in UV–vis region 200–900 nm at split width of 1.5 nm and scan speed of 400 nm/min.

The X-ray photoelectron spectra were obtained with a Kratos Axis 165 XPS electron spectrometer, by using the source of Mg Kα radiation (1253.6 eV). In order to remove charging shifts and deal with Fermi edge coupling problems, binding energies (BE) were scaled against the peak of the C–(C, H) component coming from contamination carbon (set to 285 eV) and the relative atomic sensitivity factors of 4.871 and 0.168 for Co 2p. The pressure of the analysis chamber was maintained at 5×10^{-10} mbar.

2.3. Oxidation of cyclohexane over Co-SBA-15 catalysts

Catalytic reaction of cyclohexane oxidation was accomplished in an autoclave (Parr instruments, USA) using 30 mL (277.5 mmol) of cyclohexane and 75 mg of Co-SBA-15. The reaction mixture was mechanically stirred at 433 K and 1 MPa of oxygen for 5–6 h. After reaction, the catalyst was filtered off and the product mixture was directly analyzed by GC (GC-17A, M/S. Shimadzu Instruments Corporation, Japan) equipped with a FID detector using ZB-5 capillary column (M/S. Zebron), having dimensions of 0.32 mm i.d. × 0.25 μm × 30 m long. The products were further confirmed by GC-MS analysis (QP-5050A, M/S. Shimadzu Instruments, Japan) with EI-mass detector. A blank cyclohexane oxidation reaction over SBA-15 in oxygen was also carried out under same reaction conditions. The activities of catalysts in terms of TON (turn over number) have been calculated as moles of substrate converted per mole of metal (Co) in the catalyst per hour.

3. Results and discussion

Table 1 presents the textural characteristics of SBA-15 and Co-SBA-15 catalysts. The surface areas of 1.2%CoSYN and 2%CoSYN catalysts are 746 and 778 $m^2\,g^{-1}$, respectively, whereas for Si-SBA-15 catalyst it is only 680 $m^2\,g^{-1}$. The substantial enhancement in the surface areas of 1.2%CoSYN and 2%CoSYN catalysts compared to the Si-SBA-15 may be due to the generation of certain amount of surface area by Co species existed in the pore walls of SBA-15. Similar trend was noticed in the case of Sn-SBA-15 catalysts [12]. The surface areas of 1.2%CoIMP and 2%CoIMP catalysts are lower than that of parent Si-SBA-15. The diminishing of surface area with increasing amount of Co loading may be due to blockage of pore mouths of certain pores during impregnation step.

There is a substantial enhancement in pore volume and pore diameter of 1.2%CoSYN and 2%CoSYN catalysts compared to Si-SBA-15. This may be due to differences in the bond lengths between the cations and oxygen. The Co–O bond length is longer than that of Si–O. The increased pore sizes of 1.2%CoSYN and 2%CoSYN catalysts suggest the incorporation of Co in the silica framework. The Co incorporated MCM-14 catalysts prepared by direct synthesis yielded the larger pore sizes which are rationalized by Co incorporated silica framework [13].

XRD studies of impregnated and directly synthesized Co-SBA-15 catalysts shown in Fig. 1, reveal only the diffuse peaks of noncrystalline silica and no characteristic peaks of cobalt oxides are detected, which is an indication of the formation of small crystallites of cobalt oxide well below the detectable limits of XRD (5 nm) or incorporated cobalt oxide is in the amorphous phase.

The results of low-angle powder XRD patterns of calcined Si-SBA-15 and Co-SBA-15 catalysts prepared by post-synthetic impregnation and direct synthesis are shown as inset in Fig. 1. Three well-resolved and two poorly resolved diffraction peaks are observed which are indexed to the (1 0 0), (1 1 0), (2 0 0), (2 1 0) and (3 0 0) reflections of the *p*6*mm* space group [14] for all the Co-SBA-15 catalysts irrespective of the method of preparation. In other words, the hexagonally ordered SBA-15 structures are intact

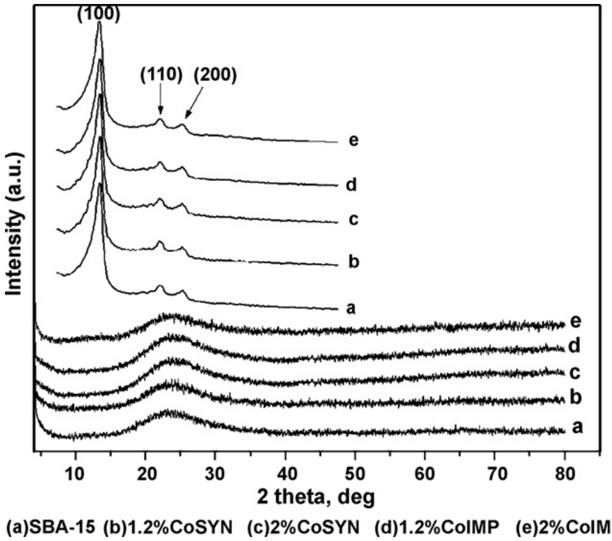

Fig. 1. Low and wide angle XRD patterns of Co-SBA-15 catalysts.

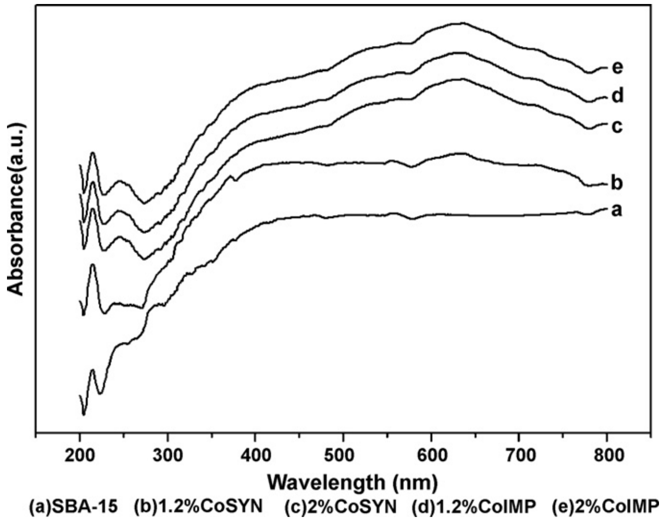

Fig. 2. UV–vis spectra of the catalysts.

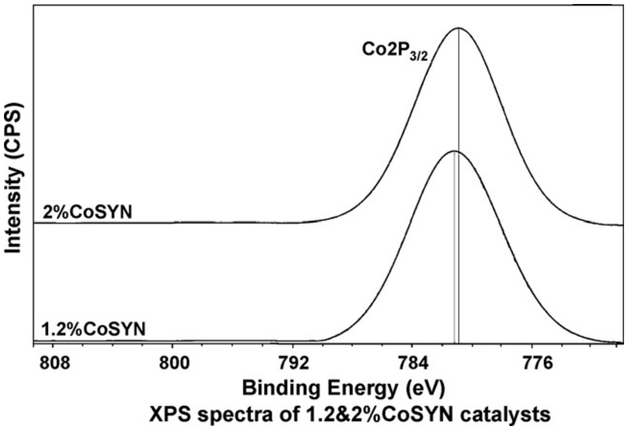

Fig. 3. XPS of 1.2%CoSYN and 2%CoSYN catalysts.

even after the incorporation of Co in either of the two methods [15].

Fig. 2 depicts the UV–vis spectra of SBA-15 and Co-incorporated SBA-15 catalysts. Si-SBA-15 shows no absorption at all in the wavelength region of 400–800 nm as can be seen from the straight-line pattern of the sample in this figure. Whereas a broad improperly resolved peak could be seen in both the spectra of Co-containing samples. However, the intensity of this peak is much lower but broader in case of 1.2%CoSYN as compared to 2%CoSYN sample. The absorbance in this region viz., 550–700 nm is reported to be characteristic for tetrahedrally co-ordinated Co^{2+} [16] which suggests the presence of certain amount of tetrahedrally coordinated Co^{2+} in the frame work of SBA-15 even in the impregnated catalysts. The results of TPR further confirmed the presence of framework Co species.

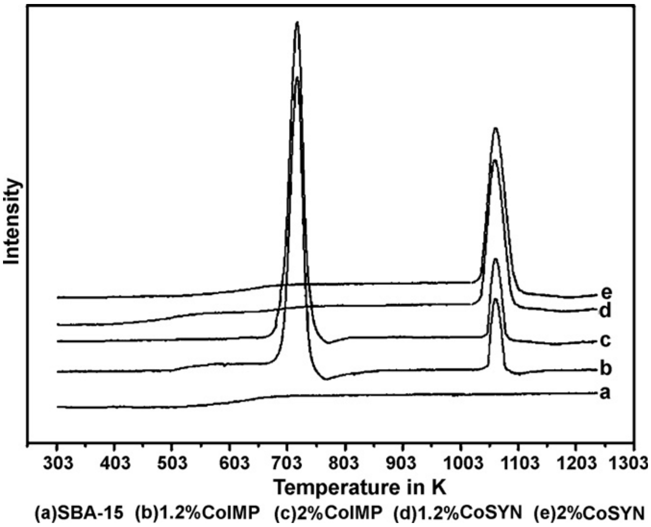

Fig. 5. TPR spectra of the catalysts.

Fig. 3 illustrates the Co 2p XP spectra obtained for 1.2%CoSYN and 2%CoSYN catalysts after calcination at 773 K for 8 h, are characterized by binding energies of Co $2p_{3/2}$ component at 783.4 and at 785.8 eV, respectively. No other peaks, either from cobalt or from the siliceous SBA-15 carrier, are split or broadened, indicating the absence of differential charge effects.

TEM images of Co-SBA-15 are shown in Fig. 4. The characteristic hexagonal channels of SBA-15 are clearly visible in Fig. 4a and b but are smeared and dark due to the encapsulation of cobalt. The size of Co particles appear to be ~10–12 nm close to the pore dia of SBA-15 as can be seen from the TEM images.

Fig. 5 depicts the reduction behavior of the catalysts in the hydrogen TPR (temperature-programmed reduction) carried out in the temperature range from 303 to 1173 K. A clear distinguishing behavior of the impregnated to the direct synthesis Co-SBA-15 catalysts can be observed from the TPR patterns. The TPR (a) pattern shows a straight-line profile recorded for bare SBA-15 showing the absence of any reducible species. The impregnated Co-SBA-15 catalysts showed two peaks at temperature maxima of 703 and 1053 K. The highly intense peak is at 703 K and minor peak at 1053 K. On the other hand, Co-SBA-15 catalysts prepared by

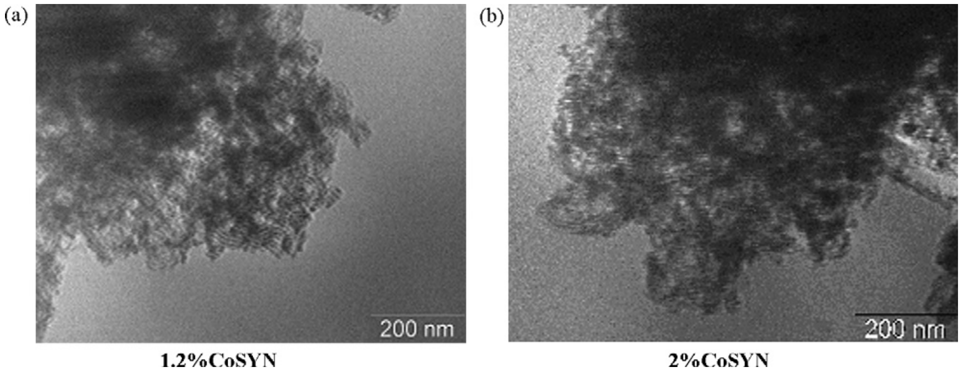

Fig. 4. TEM image of Co-SBA-15 catalysts.

Table 2
Activity results of cyclohexane oxidation at 433 K, 6 h of reaction and 1 MPa of O_2

Sl. no.	Catalyst	% Conversion of CyH	% Selectivity to Cyone	% Selectivity to CyOH	% Selectivity to others[a]
1	1.2%CoSYN	6.3	76	19	5
2	2%CoSYN	9.4	78	17	5
3	1.2%IMP	1.2	74	18	6.8
4	2%IMP	1.5	73	16	9.5
5	SBA-15	–	–	–	–

[a] Others = adipic acid; valeraldehyde; traces of olefins.

direct synthesis showed only a single high temperature maximum at 1053 K.

Cobalt oxide (Co_3O_4) is reduced in two steps, which could be ascribed to the successive reduction of Co_3O_4 to CoO at 580 K and the subsequent reduction of CoO to metallic Co at 615 K [17]:

$$Co_3O_4 + H_2 \rightarrow 3CoO + H_2O$$

$$CoO + H_2 \rightarrow Co + H_2O$$

The former major peak of the impregnated Co-SBA-15 catalysts centered at 703 K can be attributed to the reduction of Co_3O_4 to CoO and the later minor peak at a temperature maximum of 1053 K is due to the reduction of CoO to metallic Co. As it is reported [16], Co species reduced below 773 K can be attributed to the surface species. The low intensity high temperature maxima at 1053 K may probably be attributed to the reduction of some strongly interacted cobalt oxide species with the support [18]. Hence, it can be concluded that the Co species in the impregnated Co-SBA-15 catalysts is the adsorbed surface species which is predominant and remaining small portion is highly interacted species with the SBA-15 support or this small portion of Co may be present in the silica framework of SBA-15.

In the case of Co-SBA-15 catalysts prepared by direct synthesis (Fig. 5) only a narrow reduction peak at a temperature maximum of 1053 K is seen which suggests that cobalt is in the divalent state and there is strong interaction between CoO and silica SBA-15 or it may be present in the silica framework. Lou et al. [16] synthesized Co-SBA-15 catalysts by direct synthesis using pH adjusted method and reported that cobalt oxide reduced at about 800 °C (1073 K) is the framework species. Framework Co species has also been reported [19] for the directly synthesized Co-MCM-41 catalysts at a temperature maximum of 978 K. The variation in the reduction behavior of Co in silica framework varies with the other parameters such as preparation temperature, pressure and the chemicals. The absence of this low temperature maximum in the Co-SBA-15 prepared by direct synthesis further confirms the incorporated Co species in the silica framework of SBA-15.

Oxidation of cyclohexane to cyclohexanone and cyclohexanol is one of the industrially important reactions. Cyclohexane is the lightest cyclic alkane, whose C–C bond strength is equal to that of its corresponding linear alkane, and the high symmetry of cyclohexane suggests a small number of possible product species. Oxidation of cyclohexane is exothermic with $\Delta H = -294$ kJ/mol and can reach an autocatalytic runaway state if temperatures exceed 150 °C (300 °F). The maximum conversion reported for this reaction is ~20% under oxygen pressure. The oxidation of cyclohexane primarily yields cyclohexanone and cyclohexanol as shown in the scheme. Further oxidation of these two products leads to adipic acid which is a high valuable product and is the major intermediate in the synthesis of nylons. In the present investigation, cyclohexanone and cyclohexanol are the major products obtained in the oxidation of cyclohexane, the results of which are presented in Table 2. Adipic acid and valeraldehyde are the minor products accounting for ~5% of the total products formed and trace amounts of olefins are also observed in the reaction.

The maximum conversion of cyclohexane and the selectivity of cyclohexanone obtained are up to ~9.4% and 78% respectively over 2%CoSYN catalyst. Table 2 presents the variation in the activity levels and the product distribution over the two Co-catalysts studied at 433 K and 1 MPa pressure in oxygen in 6 h. The reaction below this temperature is found to be too low (<2% conversion of cyclohexane). It can be observed from Table 2 that 2%CoSYN shows slightly higher activity over the 1.2%CoSYN catalyst. The wet impregnated catalysts show very low conversion and bare support, i.e., SBA-15 showed no conversion of cyclohexane when tested under similar conditions.

Fig. 6 shows the variation in the conversion of cyclohexane with time over Co-SBA-15 catalysts. The conversion increased with time over both the catalysts and a steady state is attained with in ~5–6 h of reaction. Fig. 7 is a plot showing the turn over numbers and yields of the products viz., cyclohexanone and cyclohexanol over the two Co-incorporated SBA-15 catalysts studied for the oxidation of cyclohexane. Though, the yields of the products are higher over 2%CoSYN catalyst, the turn over number which indicates the number of moles of cyclohexane converted by a mole of cobalt in

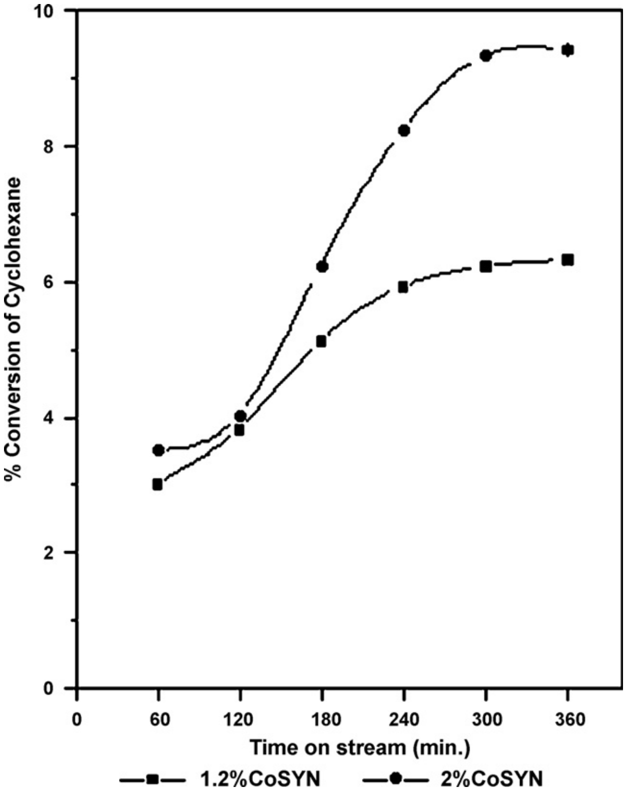

Fig. 6. Time on stream activities of Co-SBA-15 catalysts towards the oxidation of cyclohexane.

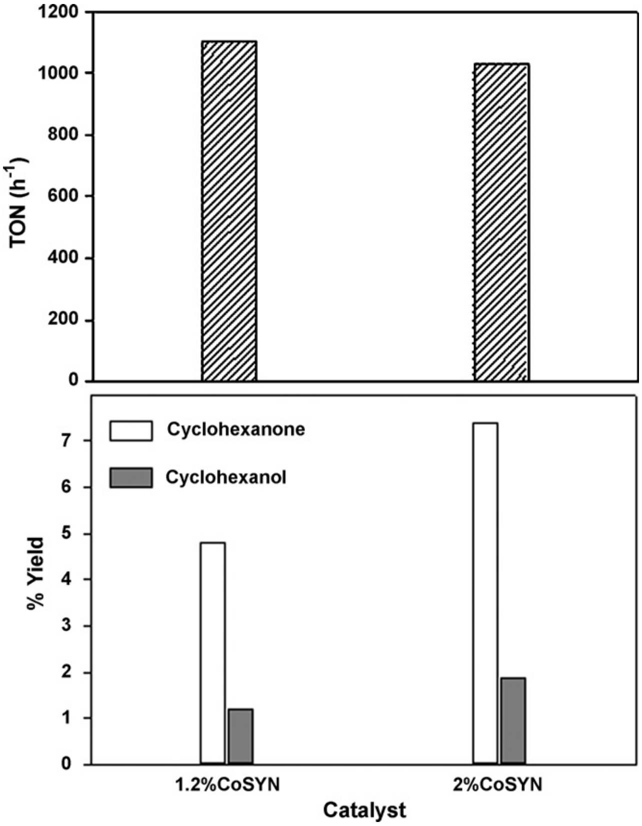

Fig. 7. A comparison of activities of Co-SBA-15 catalysts towards the oxidation of cyclohexane.

the catalyst shows equivalent higher activity of 1.2%CoSYN catalysts towards the oxidation of cyclohexane.

4. Conclusions

Encapsulation of Co in SBA-15 structure is successfully achieved. The structure of SBA-15 remained intact even after the incorporation of Co as observed from the low-angle XRD characteristics. Highly stable cobalt species in the SBA-15 framework could be observed from TPR peaks. Co-SBA-15 catalysts showed significantly high turn over numbers and good yield towards the formation of cyclohexanone from the oxidation of cyclohexane under a moderate oxygen pressure of 1 MPa. 2%CoSYN yielded a maximum of 9.4% cyclohexanone from cyclohexane oxidation at 433 K.

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