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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 ~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

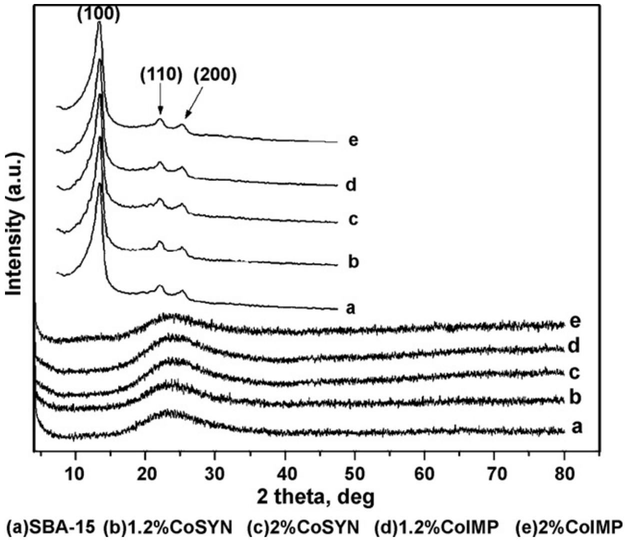

Fig. 1. Low and wide angle XRD patterns of Co-SBA-15 catalysts.