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Research paper

Selective Oxidation of Cyclohexane to KA Oil Over Ce-Alpo-18 Molecular Sieves

M. Esther Leena Preethi [1]*, A.Umasankari [1], C.H.Rekha [1], M.Palanichamy[2], T.Sivakumar[3], A.Pandurangan[3]

[1] *Department of Chemistry,Women's Christian College, Chennai-600 006*

[2] *Department of Chemical Engineering, HanseoUniversity, Seosan, 356- 706, South Korea.*

[3] *Department of Chemistry, Anna University, Chennai-600 025*

**Corresponding author E-mail: e.preethi.rajkumar@gmail.com*

Abstract

The novel catalysts Ce-AlPO-18 with Al/Ce = 25, 50, 75 &100 were synthesized using hydrothermal synthesis procedure. The newly synthesized catalysts were characterized using physico-chemical techniques such as, X-ray diffraction (XRD) which confirmed AEI structure, diffuse reflectance spectroscopy (DRS-UV) confirmed the presence of both Ce^{3+} and Ce^{4+} in the framework and Fourier transform infrared spectroscopy (FT-IR) confirmed the complete removal of template molecule. The synthesized catalysts were tested for the oxidation of cyclohexane using air as the oxidant in a solvent free system and the results were discussed.

Keywords: *AlPO-18; cerium; cyclohexane; hydrothermal synthesis; KA oil*.

1. Introduction

The present study of oxidation of cyclohexane to cyclohexanol and cyclohexanone is an industrially highly significant process [1]. The selective oxidation of cyclohexane is crucial to synthesize intermediate for the manufacture of Nylon 6 and Nylon 6, 6 [2]. Another reaction is cyclohexane with H_2O_2 which gave high selectivity to cyclohexylhydroperoxide and cyclooctane catalytic oxidation of cyclohexane have been carried out using variety of oxidants such as iodosylbenzene[3], alkyl Hydro peroxides[4] fenton's reagent[5], fenton like catalysts[6], m-chloroperbenzoic acid[7] and oxygen[8]. Molecular oxygen is possibly the best oxidant as it has proved to be efficient and could be easily harnessed from air. Of late many works have been carried out using molecular oxygen as oxidant and it proves its versatility and superiority over other oxidants[9]. The product of cyclohexane oxidation KA oil is used as a raw material to prepare adipic acid and caprolactum[10]. Of late, the oxidation of cyclohexane to cyclohexanol and cyclohexanone is developed in heterogeneous system. In recent years many porous metal containing molecular sieves with various metals have been synthesized and used as catalysts for cyclohexane oxidation [11, 12]. The transition metal cerium is known for its redox property and could be exploited for oxidation reactions. The AlPO-18 has got AEI type structure and with cerium in its framework could be tested for selective conversion. Of late the oxidation of cyclohexane was reported over Ce-AlPO-5 molecular sieves[13]. The current work elaborates on the synthesis of Ce-AlPO-18 catalysts with various Al/Ce ratios 25, 50, 75 and 100. The vapour phase oxidation of cyclohexane was carried over the synthesized catalysts in order to test its efficacy. Ce-ZSM-5 catalyst is also prepared and tested for its efficacy for the proposed oxidation reaction for comparison.

2. Experimental

2.1 Synthesis of Catalyst

Ce-AlPO-18catalyst synthesized using a hydrothermal process sing in the mole ratio xCe $(NO_3)_3.6H_2O$: 1.0 Al_2O_3: 1.0 P_2O_5: 1.6 DIPEA: 50 H_2O [9]. The source reagent were N, N-Diisopropylethylamine (DIPEA), cerium nitrate (Merck), aluminiumisopropoxide (Merck) and orthophosphoric acid (Merck). In the typical synthesis procedure cerium nitrate was dissolved in distilled water. The precursor gel was prepared by dissolving the required amount of aluminium isopropoxide and orthophosphoric acid in distilled water separately and stirred vigorously until a homogeneous solution was obtained. The homogeneous orthophosphoricacid was then added drop by drop with continuous stirring to the aluminium source. The precursor solution is then left for stirring for 30 minutes. The dissolved cerium nitrate solution was then added drop by drop followed by the addition of the organic template, DIPEA drop wise with stirring. There was slow dense gel formation and it was left for stirring**.** The pH of the reaction mixture was 8The dense gel was then poured into a Teflon lined autoclave and was kept in a hot air oven at 170 °C for 5 days. The Ce-AlPO-18 obtained was then cooled, filtered and dried to get the as-synthesized sample. It was then calcined at 600 °C for 6 hours to remove the occluded organic template molecules and to yield the microporous sample.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns of calcined Ce-$ALPO_4$-18 catalyst were collected on a Philips X'Pert model no. PW 3040/60, using Cu Kα radiation (λ = 1.5060 Å). The size and morphology of Ce-AlPO-18 catalyst were examined by scanning

electron microscopy using a Hitachi S-4200 electron microscope. The catalyst was examined by UV-Vis Diffuse reflectance spectroscopy. The DRS UV of Ce-AlPO-18(25) was recorded in the range of 200 to 800 nm using JASCO V-550 instrument. FT-IR spectra of the samples were recorded on a Nicolet (Avatar 360) instrument using the KBr pellet technique by making 50 scans at 2 cm^{-1} resolution. EPR analysis was done on a JEOL EPR spectrometer (JES FA200) operating in the X-band region. DPPH (g = 2.0037) was used as a reference to mark the g-value. The elemental composition of cerium in the catalyst was analysed by extracting the metal with con. HNO_3 using ICP-AES (Labtum Plasma 8440)

2.3 Catalytic tests

The vapour phase oxidation of cyclohexane was carried out in a fixed-bed vertical downward flow glass reactor of internal diameter 2 cm. About 0.5 g of the catalyst was placed at the center of the reactor, and it was supported on either side with a thin layer of quartz wool and ceramic beads. The reactor was heated to the requisite temperature using a temperature-programmed furnace. The catalyst was activated before each reaction at 500 °C for 6 h. The reactant was fed into the reactor using a syringe infusion pump. The products were collected in the receiver flask and analyzed using a gas chromatograph (Shimadzu 17A) equipped with a DB-5 capillary column (30 m × 0.25 mm × 0.25 μm) and a flame ionization detector. The products were also identified using a GC-MS (Perkin Elmer Clarus 500) with helium as the carrier gas at a flow rate of 1 ml/min.

3. Results and Discussion

3.1. XRD Analysis

The XRD patterns of the calcined Ce-AlPO-18(25) with different Al/Ce ratios are shown in Figure 1. Show that the synthesized different ratio Ce-AlPO-18 have the typical structure of AEI type structures and the intense (110), (022), (210) and (211) peaks are located at 2θ= 9.28A°, 5.72 A°, 4.16 A° and 1.96 A° respectively. The 3-dimensional structure based on the six member rings, with an average pore size ≈ 3.8 Å[14].

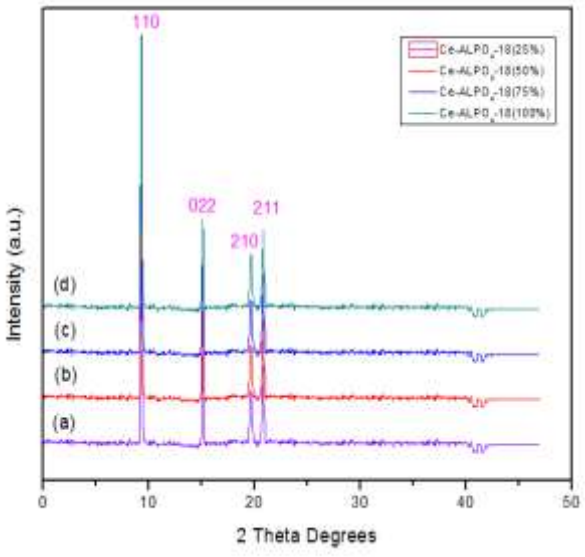

Fig. 1: XRD of (a) Ce-AlPO-18(25), (b) Ce-AlPO-18(50), (c) Ce-AlPO-18(75) and (d) Ce-AlPO-18(100)

3.2. DRS-UV

The DRS-UV-visible spectrum (See Fig. 2) has been recorded in order to know the information about O2-- Ce3+ and O_2-- Ce^{4+} charge transfer transitions. Lowering of symmetry and strain development at cerium sites can also be inferred. The oxygen storage capacity of cerium which is a prerequisite for our study requires the reduction of Ce^{4+} to Ce^{3+} whose charge transfer transition takes place in the region of 588 nm. A small hump is observed in that region. It has been already reported that 4f-5d transition occur in the range of 200-250 nm due to isolated Ce^{3+} ion in framework. The O_2-- Ce^{4+} charge transfer transitions peak is noticed at 297 nm. This confirms the presence of both Ce^{3+} and Ce^{4+} in the framework. The very slight hump noticed at 370 nm could be attributed to the extra framework cerium oxide particles [15].

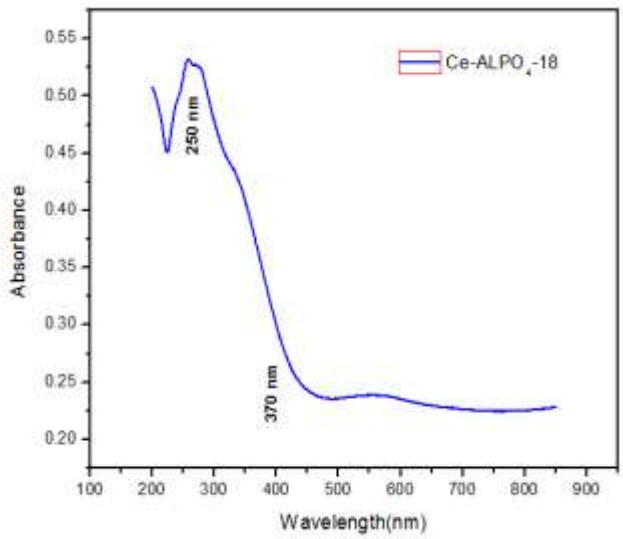

Fig. 2: DRS UV spectrum of Ce-AlPO-18(25)

3.3. FT-IR

The FTIR spectrum of Ce-AlPO-18 is given in Fig. 3bands 500 cm^{-1}, 700 cm^{-1}, 1100 cm^{-1}, 1300 cm^{-1}, 3500cm^{-1}. A broad absorption band in the range at 3500cm^{-1} was ascribed to the -OH stretching vibration of water and The stretching vibration of Ce-O is seen at 700 cm^{-1}[16]. The band at 1250 cm-1 to 950 cm-1 is due to the asymmetric stretching, the band in the range of 790 to 650 cm-1is due to symmetric stretching vibration and the band in the range of 500 to 450 cm-1 is due to the M-O bending vibration of MO_4 in the framework of the AlPO-18[17].

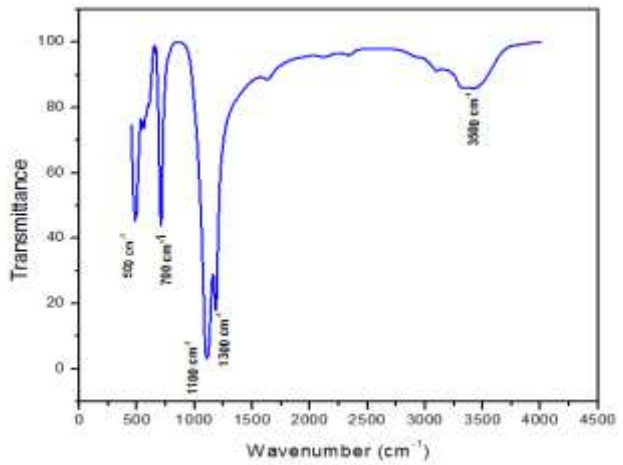

Fig. 3: FTIR spectrum of Ce-AlPO-18(25)

The bending vibration of -OH is observed in 1620 cm^{-1}. There is no band in the range of 3000-2850 cm^{-1} corresponding to the C-H stretching which rules out the presence of template molecule which is proved to be completely removed during calcinations.

3.4 Effect of Various Catalysts for the Conversion of Cyclohexane

The direct oxidation of cyclohexane in air is carried out over all the synthesized catalysts Ce-AlPO-18(25, 50, 75 and 100) and also with Ce-ZSM-5 and the results are given in Table 1. It has been observed that the percentage conversion of the cyclohexane increases as the amount of cerium increases in the catalysts. This is also confirmed by the low conversion of cyclohexane over Ce-ZSM-5. The main product is the KA oil (ketone and alcohol mixture), which is the raw material for the synthesis of adipic acid. Among the product formed cyclohexanol predominated in selectivity. The other product obtained in very less quantity was found to be cyclohexylhydroperoxide, which is the intermediate compound which led to the formation of the KA oil. The vapour phase oxidation of cyclohexane in air without catalyst was carried out and the product analysis confirmed that there was no conversion observed for cyclohexane. This result confirms that the presence of catalyst is prerequisite for this oxidation reaction. The formed cyclohexanol escapes out of the channel of the AEI of Ce-AlPO-18 before it can form cyclohexanone. The diamagnetic cyclohexanol move away from the active site so that further oxidation could take place. A significant amount of cyclohexanone is also formed as the product.

Table 1 Effect of different catalysts on percentage conversion of cyclohexane

Catalyst	#Ce (wt%)	T (ºC)	^Cane Conv. (%)	Selectivity (%)		
				^Col	^Cone	^Chpo
Ce-AlPO-18(100)	0.23	200	38	26	69	05
Ce-AlPO-18(75)	0.33	200	40	45	33	23
Ce-AlPO-18(50)	0.57	200	53	80	4	15
Ce-AlPO-18(25)	1.8	200	71	76	19	05
Ce-ZSM-5	0.14	200	37	50	13	37

#Analysed by ICP-AES
^Cane Conv.: cyclohexane conversion
^Col: cyclohexanol
^Cone: cyclohexanone
^Chpo: cyclo hexyl hydroperoxide
Reaction condition: catalyst weight 0.5g, temperature 200 ºC; feed rate 3mLh^{-1}, air flow rate 6mLmin^{-1}

4. Conclusion

The Ce-AlPO-18 catalysts with various Al/Ce ratios (25, 50, 75 and 100) were successfully synthesized. XRD confirmed all the synthesized catalysts are in AEI framework type. The FTIR confirmed the presence of cerium in AlPO-18 framework. The DRS-UV and ESR confirmed the presence cerium in both +3 and in +4 oxidation state. The catalyst Ce-AlPO-18(25) is found to be most active among the catalysts tested this may be due to the availability of more active sites. The product obtained was KA oil.

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