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Cyclohexane oxidation catalyzed by manganese oxide octahedral molecular sieves—Effect of acidity of the catalyst

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ABSTRACT

Oxidation of cyclohexane is an important industrial process, its oxidation products, cyclohexanol and cyclohexanone are raw materials for adipic acid and caprolactam synthesis. Acid exchanged cryptomelane type manganese oxide octahedral molecular sieves (H-K-OMS-2) was used for liquid phase oxidation of cyclohexane with *t*-butyl hydroperoxide as an oxidant. The H^+ form of K-OMS-2 was synthesized by ion-exchange of K-OMS-2 with concentrated nitric acid. H-K-OMS-2 has been found to be an efficient catalyst for the oxidation of cyclohexane with a high conversion (∼60%). More than 90% selectivity for cyclohexanol and cyclohexanone was obtained. A turn over number (TON) of 73 was obtained in 24 h at 80 °C and if we consider only contributions of acidic manganese sites then the TON is 287. Effect of increase in number of acid sites of the K-OMS-2 was correlated with the increase in conversion. The reactions were carried out in a semi-batch reactor at 80 °C using acetonitrile as solvent. Effects of solvent, temperature, and amount of *t*-butyl hydroperoxide on conversion and selectivity were studied.

1. Introduction

The selective oxidation of relatively inert C–H bonds of alkanes is one of the most challenging problems. The products of these oxidation reactions are themselves important or they are used as valuable intermediates for fine chemical synthesis [1,2]. In particular, oxidation of cyclohexane to cyclohexanone (K) and cyclohexanol (A) (also known as K–A oil) are important because they are the key precursors for the production of adipic acid and caprolactam, which in turn are the starting materials for the synthesis of Nylon-66 and Nylon-6, respectively [3]. The significant industrial demand (∼10^6 ton/year in 2006) of K–A oil has stimulated various studies aiming to find milder, low-cost, and environmentally friendly conditions to find alternative processes for the classic industrial method. Current industrial process uses a soluble cobalt carboxylate catalyst to produce a mixture of cyclohexanone, cyclohexanol, and other products with less than 10% conversion and ∼70–90% selectivity for K–A oil. The reaction is carried out at 423–473 K and 8–15 bar of air pressure [4,5]. Apart from low (<10%) conversion and extreme reaction conditions, this process also produces several by-products, viz., mono- and dicarboxylic acids, esters, and other oxygenated materials.

Molecular oxygen has been used for cyclohexane oxidation with biomimetic metallo-porphyrin catalysts based on the iron complex present in cytochrome P-450 [6]. Use of Fe(III) and Cu(II) complexes as catalysts for oxidation of cyclohexane with molecular oxygen and *t*-butyl hydroperoxide (TBHP) as initiator were first investigated by Barton et al. [7] and later reinvestigated by Schuchardt et al. [8]. Transition metal aluminophosphates (MAPO) containing Mn(III), Co(III) and Fe(III) metal ions have also been used in cyclohexane oxidation with air as an oxidant. Mn-APO-36 is the most active catalyst among them [9]. Apart from low (<13%) conversion and severe conditions used for cyclohexane oxidation using molecular oxygen, they also have low selectivity for K–A oil, as many over-oxidation products are obtained.

Cyclohexane oxidation has been done with H_2O_2 catalyzed by biomimetic systems like dinuclear iron(III) complexes and ruthenium complexes [10,11]. Shul'pin et al. used a binuclear manganese(IV) complex and acetic acid mixture as a catalyst with H_2O_2 oxidant [12]. Cu^{2+}-phthalocyanine and Co^{2+}-perfluorophthalocyanine incorporated in faujasite and MCM-41 gave cyclohexanone and cyclohexanol as the only products [13]. However, these catalysts gave low H_2O_2 efficiency and suffered from metal leaching. Titanium based catalysts like Titanium silicalite-1 and Ti-MCM-41 when used with H_2O_2 gave only 15% and 7.0% conversion, re-

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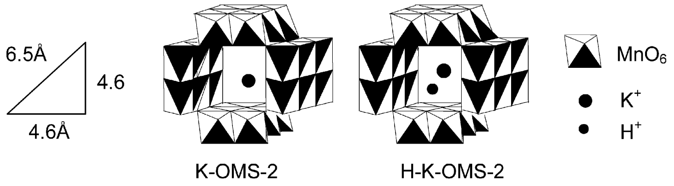


Fig. 1. Structure of OMS-2 catalysts.

spectively, for cyclohexane [14,15]. V- and Cr-MCM-41 gave higher activities compared to Ti-MCM-41, however all metallosilicates suffer from leaching of the metal and the observed catalytic activity is mainly due to the leached homogeneous metal species [15]. Although H_2O_2 is considered environmentally friendly as H_2O_2 produces water as the only by-product, a major disadvantage of H_2O_2 is its instability with respect to decomposition into oxygen and water, a process which is accelerated in the presence of transition metal complexes and metal oxides [16].

t-Butyl hydroperoxide has emerged as a class of oxidant with suitable properties for cyclohexane oxidation. Solubility of TBHP is much higher than H_2O_2 and molecular oxygen, and in certain polar solvents TBHP can be completely soluble. Leising et al. investigated the catalytic mechanism of cyclohexane oxidation with (μ-oxo)diiron(III) complexes using TBHP as an oxidant [17]. Amorphous microporous mixed oxides of Ti and Si, Ti-MCM-41, Ti-Beta, TS-1, metal-phthalocyanine (metal—Fe, Cu and Co) occluded in zeolite X and Y, and RuO_2-faujasite nano-composites have been studied for oxidation of cyclohexane using TBHP [18–21]. Recently, cobalt containing, three dimensional, mesoporous silicate, Co-TUD-1 has been reported to give excellent selectivity (72%) for the K–A oil and there was no leaching of metal, but the conversion was still low (10.3% in 18 h) [22].

The disadvantages like low conversion, leaching of metal, and over-oxidation products in the existing catalytic systems have led researchers to find a catalyst which can improve the conversion of cyclohexane under ambient conditions, with high selectivity for K–A oil. Earlier studies done by Wang et al. [23] and Xia et al. [24] in our research group have used manganese oxide octahedral molecular sieves like OMS-1, metal doped M-OMS-1 (M—Fe, Co, Cu, Cr), and K-OMS-2 for cyclohexane oxidation. The reactions were carried out in a closed vial under autogenous pressure using TBHP as an oxidant. A maximum conversion of 13.1% for cyclohexane and 77% selectivity for K–A oil was obtained in 40 h, at 80 °C, *t*-butyl alcohol as solvent, using Fe-OMS-1 as catalyst [23]. When K-OMS-2 was used as catalyst with TBHP as oxidant, at 60 °C, *t*-butyl alcohol as solvent, 13.0% conversion for cyclohexane and 92.3% selectivity for K–A oil was obtained.

H^+-exchanged OMS-2 (H-K-OMS-2) (see Fig. 1) has been shown to be an excellent catalyst for alcohol oxidation, tetralin oxidation, imine synthesis, and 2-aminodiphenylamine synthesis [25–28]. K-OMS-2 (cryptomelane) are microporous tunnel structured manganese oxide. They contain one-dimensional tunnel structures formed by 2 × 2 edge and corner shared MnO_6 octahedra. The composition of K-OMS-2 is $KMn_8O_{16}\cdot nH_2O$ and the tunnels have dimensions of 4.6 Å × 4.6 Å. The average oxidation state of Mn in K-OMS-2 is ∼3.8 due to the presence of mixed valent Mn^{4+}, Mn^{3+}, and some Mn^{2+} ions in the framework [29,30]. The K^+ ions are present in the tunnel and they can be ion-exchanged with H^+ by ion-exchanging K-OMS-2 with nitric acid.

In this work we report the application of H-K-OMS-2 to improve the efficiency of the catalyst for cyclohexane oxidation using TBHP as oxidant. This paper explores the effect of increase in acidity of K-OMS-2 on conversion of cyclohexane. A property–activity relationship was established for the active sites of H-K-OMS-2. The effect of temperature and solvents were also studied.

2. Experimental

2.1. Catalyst synthesis

K-OMS-2 was prepared by refluxing a mixture of potassium permanganate and manganese sulfate in acidic medium according to procedures described in the literature [31]. Potassium permanganate solution in deionized water (0.4 M, 225 mL) was added to a mixture of manganese sulfate hydrate solution (1.75 M, 67.5 mL) and concentrated nitric acid (6.8 mL) to a 500 mL flask fitted with a reflux condenser. The dark brown slurry was refluxed for 24 h, then filtered and washed with deionized water several times. The catalyst was dried at 120 °C overnight before use. K^+ ions were then exchanged with H^+ ions by ion-exchanging K-OMS-2 with HNO_3 to obtain H-K-OMS-2. About 50 mL of concentrated HNO_3 was added to 2.0 g of K-OMS-2 and the slurry was stirred vigorously at 80 °C for 6 h. The product was filtered and washed with deionized water several times. The same procedure was repeated again for successive ion-exchange to obtain higher content of H^+ exchange in K-OMS-2. The product was dried at 120 °C for 12 h and then calcined at 280 °C for 6 h. The final material was named H-K-OMS-2(1) with the number in brackets indicating the number of times K-OMS-2 was exchanged with concentrated HNO_3.

2.2. X-ray powder diffraction studies

The structure of all these materials was studied by X-ray diffraction experiments. A Scintag 2000 PDS instrument with Cu$K\alpha$ radiation with a beam voltage of 45 kV and a beam current of 40 mA was used to collect the X-ray data. The X-ray patterns of the catalysts were compared to those of the standard OMS-2 materials (JCPDS file #29-1020).

2.3. Scanning electron microscopy

Scanning Electron Micrographs were taken on a Zeiss DSM 982 Gemini field emission scanning microscope with a Schottky Emitter at an accelerating voltage of 2 kV with a beam current of 1 µA. The images of K-OMS-2 and H-K-OMS-2 both showed a characteristic fibrous morphology of OMS-2 materials.

2.4. Chemical composition measurement

The chemical compositions of the synthesized catalysts were determined by an energy dispersive X-ray analysis (EDX) on a Philips PV 9800 EDX spectrometer using a SuperQuant program. This analysis provides a measure of the amount of H^+ in the tunnel of K-OMS-2 which were exchanged with K^+ cations.

2.5. Average oxidation state

The average oxidation state (AOS) of manganese in OMS-2 catalysts was determined by potentiometric titrations using methods described in the literature [32]. OMS-2 was dissolved in concentrated HCl to reduce all manganese to Mn^{2+} and was then titrated against $KMnO_4$ standard solution in presence of $Na_2S_2O_7$ solution to convert to Mn^{3+} complex to get the total amount of manganese. The AOS of manganese was then determined by reducing the solid to Mn^{2+} with $(NH_3)_2Fe(SO_4)_2$ and back titrating the excess Fe^{2+} with the $KMnO_4$ standard solution.

2.6. Measurement of acidic and basic sites in the catalyst

NH_3 and CO_2 chemisorption experiments were also conducted using a Micromeritics ASAP 2010 instrument (chemisorption attachment) to quantitatively measure the amount of strong acidic

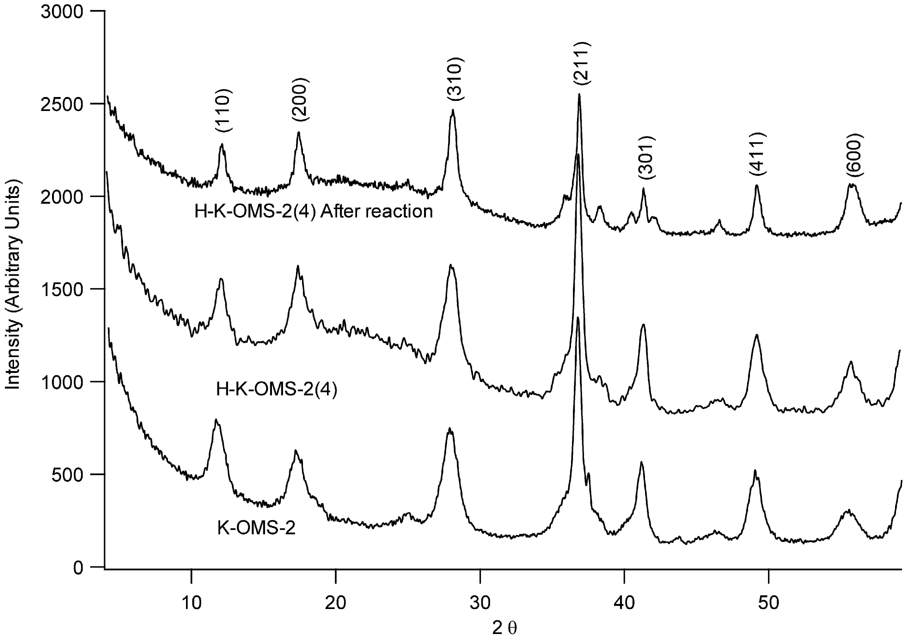


Fig. 2. XRD patterns of K-OMS-2, H-K-OMS-2 and regenerated H-K-OMS-2.

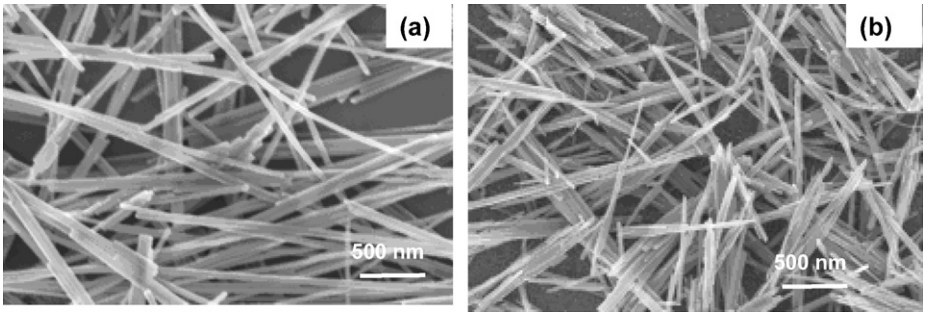


Fig. 3. SEM micrograph of K-OMS-2 and H-K-OMS-2.

and basic sites, respectively, in the materials. About 0.50 g of the material was first evacuated at 150 °C for 2 h to remove the adsorbed species from the surface to reveal acidic and basic sites followed by adsorption measurements at 35 °C at gas pressures from 100 to 700 mm Hg. After the first adsorption measurement, the material was evacuated at the analysis temperature (35 °C) for 1 h, and then a second adsorption measurement was done. The first measurement provides the total amount of gas adsorption resulting from physisorption, weak chemisorption, and strong chemisorption. The second measurement provides the amount of adsorption resulting from physisorption and weak chemisorption. The difference in the adsorption between the two measurements is the amount of strong chemisorption and gives a measurement of acid and basic sites.

2.7. Catalytic reactions

All experiments were carried out in a 50 mL round-bottom flask equipped with a reflux condenser, open to atmosphere, with a magnetic stirrer and placed in an isothermal paraffin oil bath. A typical reaction was carried out with 1 mmol cyclohexane, 1 mmol TBHP (70 wt% in water), 10 mL acetonitrile as solvent, and 0.050 g catalyst was added at the end. OMS-2 was heated at 120 °C overnight before being used in the reaction. After the reaction was over the catalyst was filtered and the products were analyzed. Leaching effects were studied by filtering off the catalyst after 4 h and the filtrate was then allowed to react further for additional 20 h and products were analyzed by periodic GC-MS sampling for the next 20 h.

Gas chromatography-mass spectroscopy (GC-MS) methods were used for identification and quantification of product mixtures. GC-MS analyses were done using an HP 5890 series II chromatograph with a thermal conductivity detector coupled with an HP 5971 mass selective detector. The column used was an HP-1 (nonpolar cross-linked siloxane) with dimensions of 12.5 m × 0.2 mm × 0.33 μm. Acetophenone was used as an internal standard for product analysis.

3. Results

3.1. Catalyst characterization

The X-ray diffraction patterns (Fig. 2) of as synthesized K-OMS-2, H-K-OMS-2, and regenerated H-K-OMS-2 show that the catalysts are pure phases and comparable to standard OMS-2 materials (JCPDS file #29-1020). The XRD patterns show that the catalyst retains its structure after successive ion-exchange with H^+ and that of regenerated H-K-OMS-2. The scanning electron micrograph shows a fibrous needle-like morphology of K-OMS-2 and the morphology is similar for the H-K-OMS-2 as shown in Fig. 3. The tunnel cation substitution has no effect on the morphology.

Table 1
Amount of H^+ exchange in the synthesized catalysts and AOS of Mn.

Catalyst	%K^+ exchanged with H^+[a]	AOS of Mn
K-OMS-2	0	3.82
H-K-OMS-2(1)[b]	38	3.62
H-K-OMS-2(2)	49	3.56
H-K-OMS-2(3)	58	3.51
H-K-OMS-2(4)	64	3.48

[a] %K^+ exchanged with H^+ was calculated based on the decrease in the wt% of potassium in EDAX data assuming that the amount of Mn does not change after the ion-exchange.

[b] The number in brackets indicate the number of times K-OMS-2 was ion-exchanged with concentrated HNO_3.

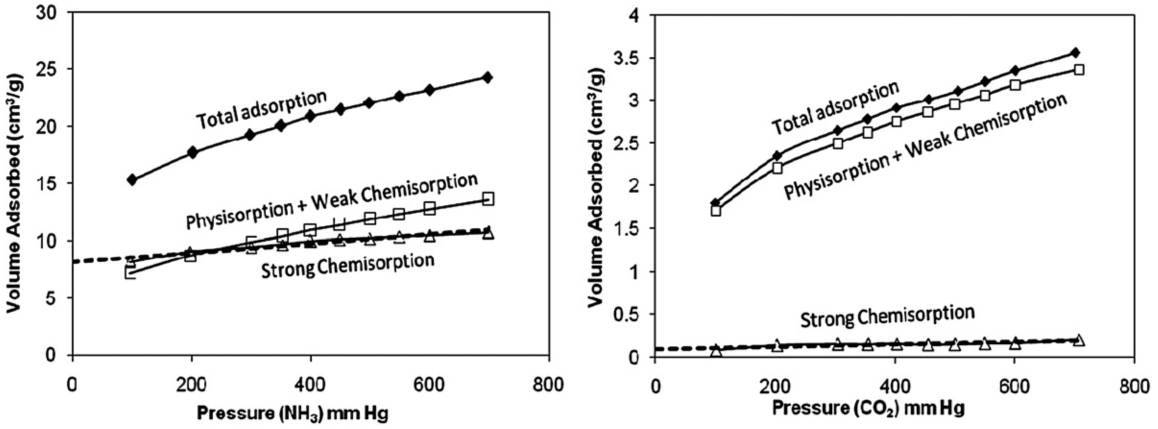
From the EDX analysis data the amount of K^+ cation in OMS-2 and in different H-K-OMS-2 materials was obtained as shown in Table 1. The percentage of K^+ exchanged with H^+ was calculated based on the decrease in the atomic % of K^+ assuming that the atomic % of Mn does not decrease in the ion-exchange process. When K-OMS-2 was ion-exchanged with concentrated HNO_3, 38% of K^+ was exchanged with H^+ after first exchange and 64% after four successive exchanges. The AOS measurement of manganese in various H-K-OMS-2 shows a decreasing trend as shown in Table 1. The average oxidation of Mn in as synthesized K-OMS-2 was 3.82 which decreased to 3.48 in H-K-OMS-2(4). The decrease in the AOS of Mn is indicative of an increase in Mn^{3+} ions in the framework due to ion-exchange.

3.2. Acidic and basic sites in the catalyst

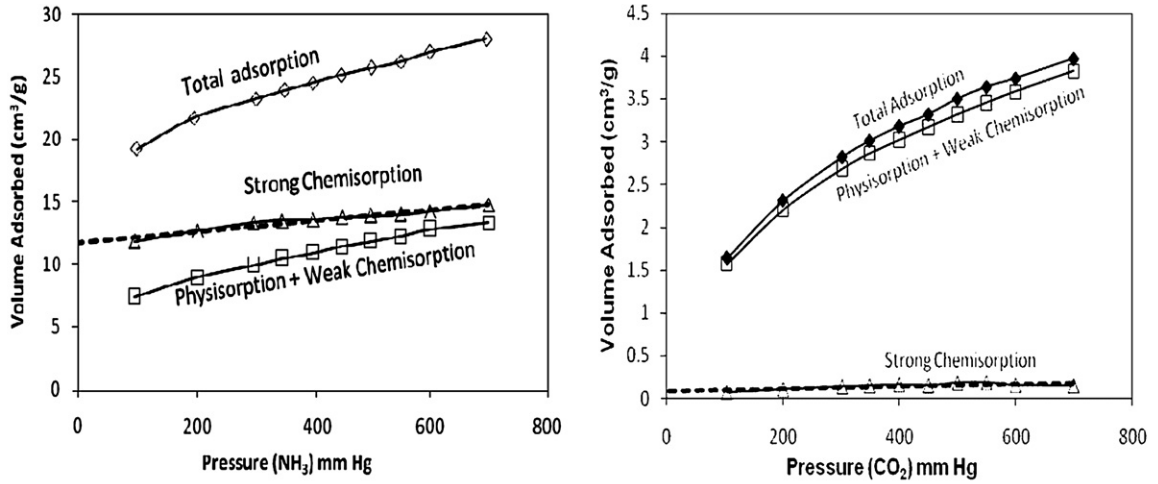
Isotherms of NH_3 and CO_2 chemisorption on the various OMS-2 are shown in Fig. 4. Extrapolation of the adsorption isotherms to zero gave a quantitative measure of the strong acidic sites and basic sites of the materials (Table 2). Here, each NH_3 and CO_2 molecule only adsorbs on one strong acidic and basic site respectively. K-OMS-2 has weak Brønsted acid sites, strong Lewis acid sites, and very weak basic sites and these results are in agreement with the literature [33,34]. The H^+ exchange increases the strong acidic sites, but the increase is mainly due to the presence of H^+ in the tunnels of H-K-OMS-2, which are Brønsted acid sites. As the percentage of H^+ exchange increases in H-K-OMS-2, the number of strong acidic sites also increases. However, the H^+ exchange decreases the number of basic sites in K-OMS-2 and H-K-OMS-2 is practically devoid of any basic sites.

3.3. Catalytic performance

K-OMS-2 and various H-K-OMS-2 were tested for their catalytic activity for cyclohexane oxidation using TBHP as an oxidant, the products obtained were cyclohexanol, cyclohexanone, and *t*-butyl cyclohexyl peroxide (TBCHP). A mass balance of 98% was obtained after the reactions. Table 3 shows the conversion of cyclohexane and selectivity of the products. The grinding of catalyst did not affect the conversion. In all reactions no unreacted TBHP was found after 24 h of reaction. We did not detect any cyclohexyl

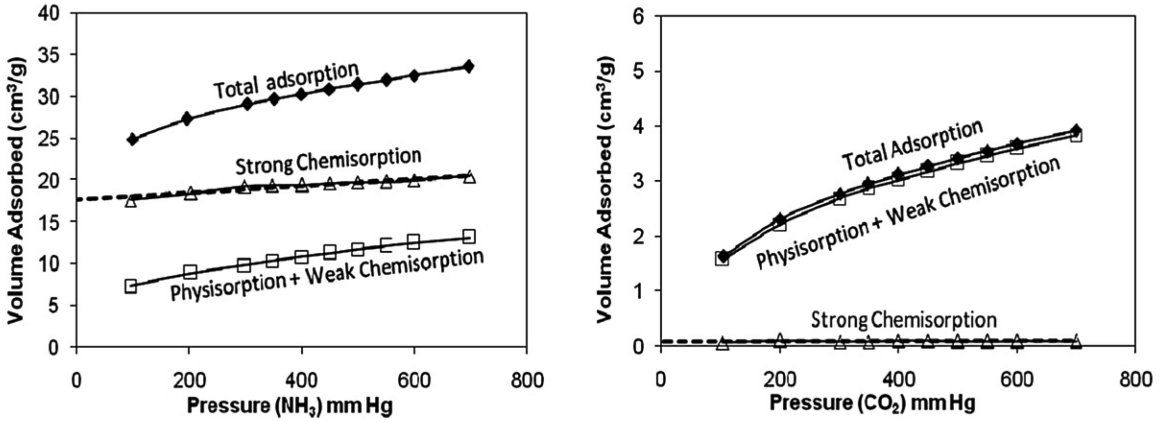


(a) K-OMS-2 NH_3 (b) K-OMS-2 CO_2

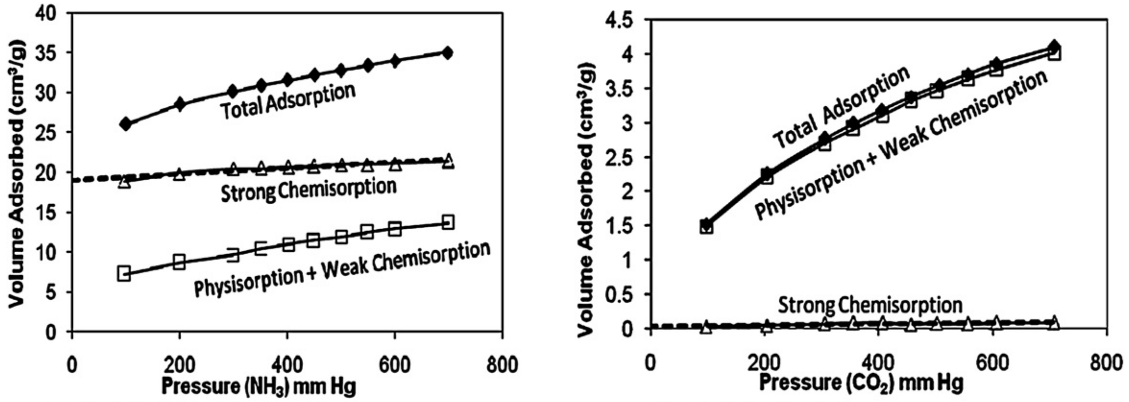


(c) H-K-OMS-2(1) NH_3 (d) H-K-OMS-2(1) CO_2

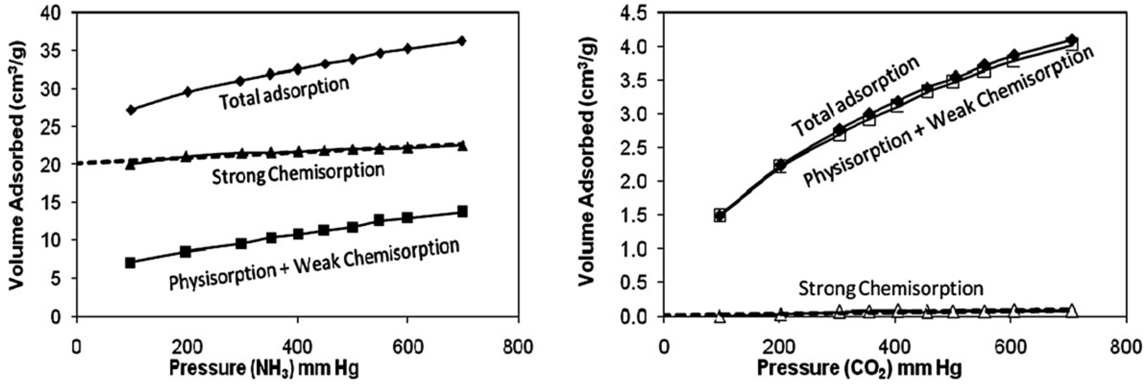
Fig. 4. (a–j) NH_3 and CO_2 chemisorption data for K-OMS-2 and H-K-OMS-2.



(e) H-K-OMS-2(2) NH_3 (f) H-K-OMS-2(2) CO_2



(g) H-K-OMS-2(3) NH_3 (h) H-K-OMS-2(3) CO_2



(i) H-K-OMS-2(4) NH_3 (j) H-K-OMS-2(4) CO_2

Fig. 4. (*continued.*)

Table 2
Chemisorption values of acidity and basicity in the OMS-2 samples.

Catalyst	Total acidity (mmol/g) STP	Acidity due to strong chemisorption only (mmol/g) STP	Total basicity (mmol/g) STP	Basicity due to strong chemisorption only (mmol/g) STP
K-OMS-2	0.65	0.36	0.077	4.1×10^{-3}
H-K-OMS-2(1)	0.99	0.69	0.070	3.4×10^{-3}
H-K-OMS-2(2)	1.09	0.79	0.068	3.2×10^{-3}
H-K-OMS-2(3)	1.14	0.85	0.062	1.5×10^{-3}
H-K-OMS-2(4)	1.18	0.90	0.061	0.76×10^{-3}

hydroperoxide (CHHP) among the products after 24 h of reaction unless otherwise noted and this was verified by addition of triphenylphosphine, as there was no increase in the cyclohexanol yield due to addition of triphenylphosphine [40]. H-K-OMS-2 is a highly selective oxidation catalyst and does not produce any dibasic acids under these conditions. The products of one of the first reaction we carried out were analyzed after esterification of the products but no dibasic acid was detected in the GC-MS. Therefore, for all the subsequent reactions we did not do the esterification of the products.

Table 3
Effect of various catalysts on conversion and selectivity.[a]

Entry	Catalyst	Time	Conversion[b] (%)	TON[c]	Selectivity[d] (%)		
					Cyclohexanol	Cyclohexanone	TBCHP[e]
1	K-OMS-2	24	25.3	37(141)	33.8	24.1	42.1
2	H-K-OMS-2(1)	24	45.2	65(251)	32.6	25.8	40.6
3	H-K-OMS-2(2)	24	47.3	68(263)	33.3	28.4	38.1
4	H-K-OMS-2(3)	24	49.8	71(277)	33.1	29.7	36.8
5	H-K-OMS-2(4)	24	51.6	73(287)	33.5	31.0	35.5
6	H-K-OMS-2(4)	72	59.9	85(333)	34.3	56.3	9.4
7	K-OMS-2	72	27.8	41(154)	34.0	24.3	41.7

[a] All reactions were done with 0.050 g of catalyst, 10 mmol cyclohexane, 10 mmol TBHP, 10 mL of acetonitrile, at 80 °C.

[b] Conversion (%) based on substrate $= \{1 - [(\text{concentration of substrate left after reaction}) \times (\text{initial concentration of substrate})^{-1}]\} \times 100$.

[c] Turnover number (TON): number of moles of cyclohexane converted per mole of catalyst. Number in parentheses is based on number of moles of acidic Mn sites only (from NH_3 chemisorption data).

[d] Selectivity (%) of product $= [(\text{concentration of product}) \times (\text{total concentration of all products})^{-1}] \times 100$.

[e] TBCHP—*t*-butyl cyclohexyl peroxide.

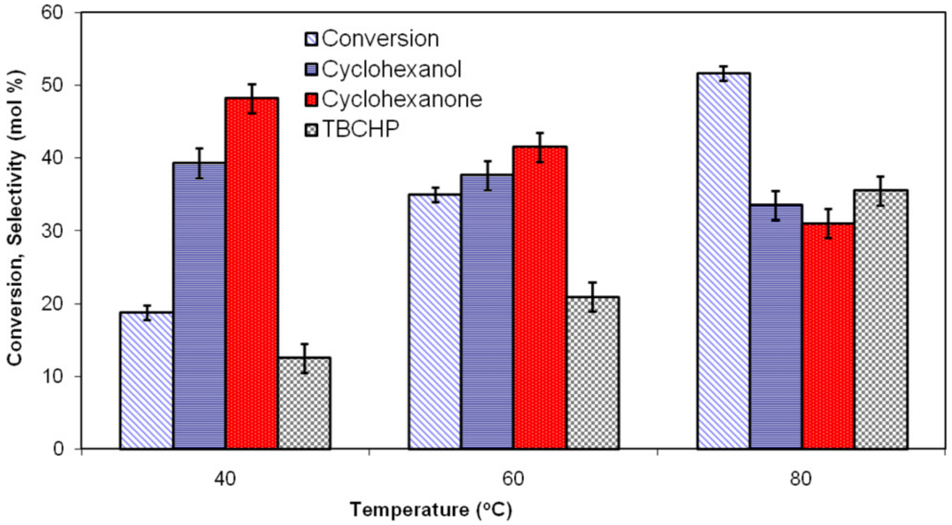


Fig. 5. Effect of temperature on conversion and selectivity.

Table 4
Effect of solvents on conversion and selectivity.[a]

Solvent	Dielectric constant	Temp. (°C)	Conversion (%)	TON	Selectivity (%)		
					Cyclohexanol	Cyclohexanone	TBCHP
Acetonitrile	36.6	60	35.0	50	37.6	41.5	20.9
t-Butyl alcohol	12.5	60	25.2	36	45.1	39.1	15.8
Acetone	20.7	60	8.0	11	35.8	48.1	16.1
Toluene	2.4	60	4.6	7	39.5	32.3	28.2

[a] All reactions were done with 10 mmol cyclohexane, 10 mmol TBHP, 0.050 g of H-K-OMS-2(4) catalyst, at 80 °C, for 24 h.

3.4. Effect of temperature

To study the effect of temperature on cyclohexane oxidation, reactions were done at 40, 60, and 80 °C using H-K-OMS-2(4) as catalyst and results are shown in Fig. 5. The conversion increases about three fold from 18.8% at 40 °C to 51.6% at 80 °C. The temperature was not increased beyond 80 °C, since the boiling point of cyclohexane is 80.7 °C and that of acetonitrile is 82 °C. With the increase in temperature the formation of TBCHP increases and the selectivity of K–A oil decreases.

3.5. Effect of solvents

Effects of various solvents were investigated at a reaction temperature of 60 °C with H-K-OMS-2(4) as a catalyst as shown in Table 4. For the purpose of good comparison the temperature was kept constant for all the solvents. Acetonitrile was found to be the best solvent under the conditions used for this reaction.

3.6. Effect of amount of TBHP

All the reactions in this paper were done at a substrate to oxidant ratio of one. To study the effect of amount of TBHP on cyclohexane oxidation, reactions were done with 10, 15, 20, and 25 mmol of TBHP keeping the number of moles of cyclohexane constant, as shown in Table 5. The conversion of cyclohexane increases with increase in amount of TBHP, however the efficiency of TBHP decreases.

3.7. Catalyst stability and heterogeneity of reaction

The reusability of the catalyst was tested. The catalyst was recovered by filtration after the reaction and was regenerated by a simple regeneration procedure, by washing with acetone and drying at 120 °C overnight restored the original activity. The regenerated catalyst was reused 3 times without any appreciable loss of

Table 5
Effect of amount of TBHP on conversion and selectivity.[a]

Amount of TBHP (mmol)	Conversion (%)	TON	TBHP efficiency[b] (%)	Selectivity (%)		
				Cyclohexanol	Cyclohexanone	TBCHP
10	51.6	73	51.6	33.5	31.0	35.5
15	52.3	74	34.9	29.8	35.4	34.8
20	54.8	78	27.4	28.8	39.7	31.5
25	55.5	79	22.2	25.8	42.3	31.9

[a] All reactions were done with 10 mmol cyclohexane, 0.050 g of H-K-OMS-2(4) catalyst, 10 mL acetonitrile solvent, at 80 °C, for 24 h.
[b] TBHP efficiency based on number of moles of cyclohexane converted per mole of TBHP.

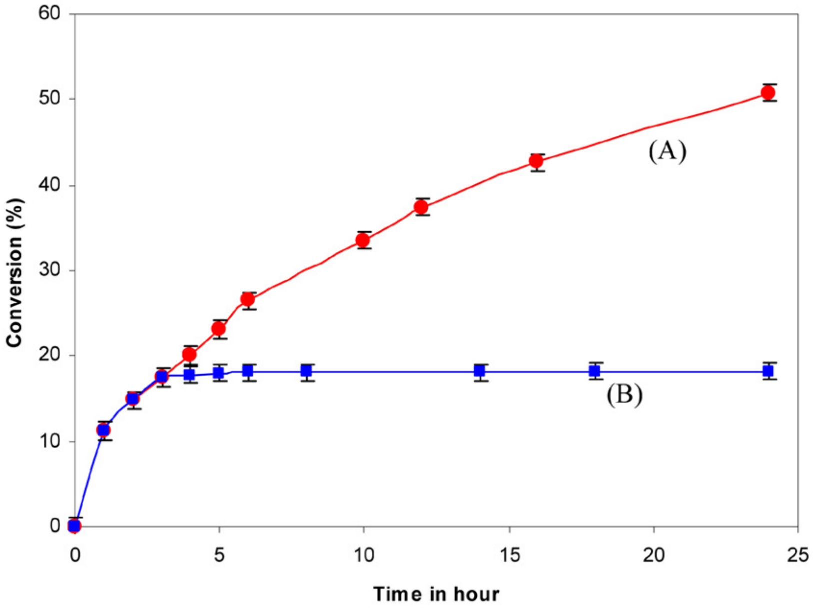


Fig. 6. Conversion of cyclohexane as a function of time with H-K-OMS-2(4) catalyst.

activity as shown in Fig. 8. The powder X-ray diffraction (XRD) data were collected for the catalyst after four runs as shown in Fig. 2. Crystallinity was retained even after three runs and that the intensities did not show any obvious change. Crystallinity was retained for H-K-OMS-2(4) after reaction as shown by XRD data. The conversion was 47.0% after the second run and 46.9% after the fourth run as compared to 51.6% for the fresh catalyst (Fig. 8).

In order to obtain the evidence that this process is a heterogeneous catalytic reaction, the solid catalyst was removed by filtration after 3 h of reaction and the reaction was allowed to continue for another 20 h. The analysis of the products show that there was no further conversion of cyclohexane after the catalyst was removed as shown in Fig. 6. There was no metal or H^+ leaching in the solution and the chemical composition of the catalyst remained the same as verified by EDX data.

4. Discussion

4.1. Catalyst characterization

The NH_3 chemisorption study gave the quantitative analysis of the acidic sites. If we consider contributions from only strong chemisorption, then concentration of strong acidic sites in K-OMS-2 is 0.36 mmol/g, which increases to 0.69 mmol/g in H-K-OMS-2 (1), and 0.90 mmol/g in H-K-OMS-2(4). This increase is due to the presence of Brønsted acid sites (H^+ in the tunnels of H-K-OMS-2) in the H^+-exchanged material. The increase is consistent with the amount of H^+ present in the materials. Both Lewis and Brønsted sites have important roles to play in the oxidation of cyclohexane. The CO_2 chemisorption data for strong chemisorption show that the concentration of basic sites decreases from 4.1×10^{-3} mmol/g in K-OMS-2 to 0.76×10^{-3} mmol/g in H-K-OMS-2(4). These results indicate that H-K-OMS-2 has very weak basic sites and this may be due to a change in the surface properties due to ion-exchange with H^+.

The calculated AOS of Mn is 3.875 and the experimentally determined value is 3.82. The AOS of 3.875 comes from the fact that in K-OMS-2 for every seven Mn^{4+} there is one Mn^{3+}. The Mn in K-OMS-2 is in an octahedral environment with coordination number of Mn being six, but the structure also has some oxygen vacancies. The AOS results show a decrease in the average oxidation state of Mn due to H^+ ion-exchange. H^+ has a smaller ionic radius than K^+ and this causes a distortion in the OMS-2 structure. Some of the Mn^{4+} sites are converted to Mn^{3+} sites due to a distortion of the geometry of cryptomelane from tetragonal to monoclinic. In monoclinic geometry Mn^{3+} fits better than Mn^{4+} because of the larger ionic radius of Mn^{3+} compared to Mn^{4+} [36,37]. This increase in Mn^{3+} sites plays a key role in cyclohexane oxidation.

4.2. Mechanism of catalytic activity

The results presented clearly indicate the enhanced catalytic activity of H-K-OMS-2 as compared to K-OMS-2. This enhanced activity results from creation of new active sites in the catalyst, and the presence of both Lewis and Brønsted acid sites. When the reaction was done with K-OMS-2, 25.3% conversion was obtained, which increased to 45.2% with H-K-OMS-2(1) as catalyst. The increase in Mn^{3+} sites increases the formation of t-$BuO^{\bullet}$ (Eq. (2b), Scheme 1), which propagates the reaction with formation of cyclohexyl radical (Eq. (3), Scheme 1), thereby increasing the conversion

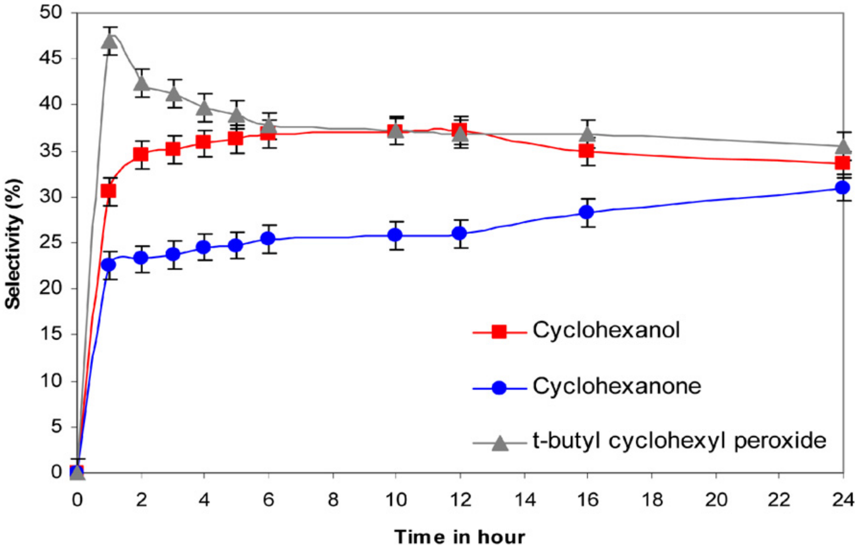


Fig. 7. Selectivity of products as a function of time with H-K-OMS-2(4) catalyst.

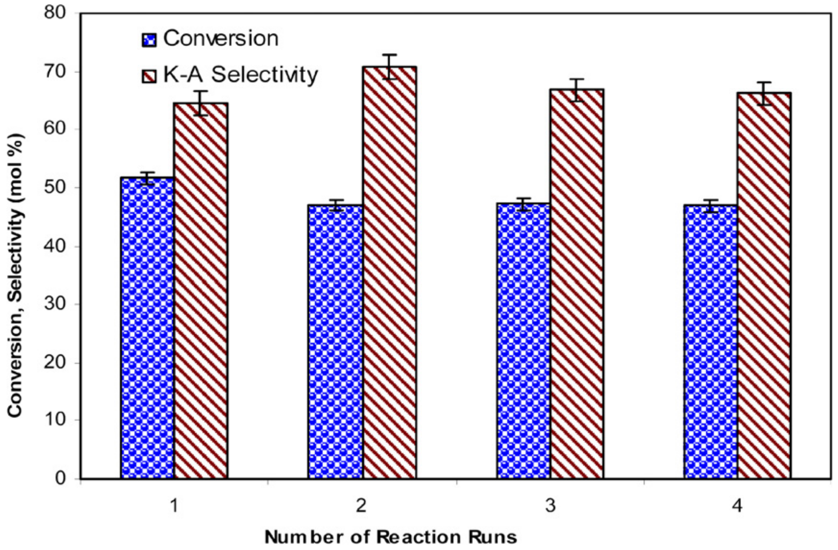
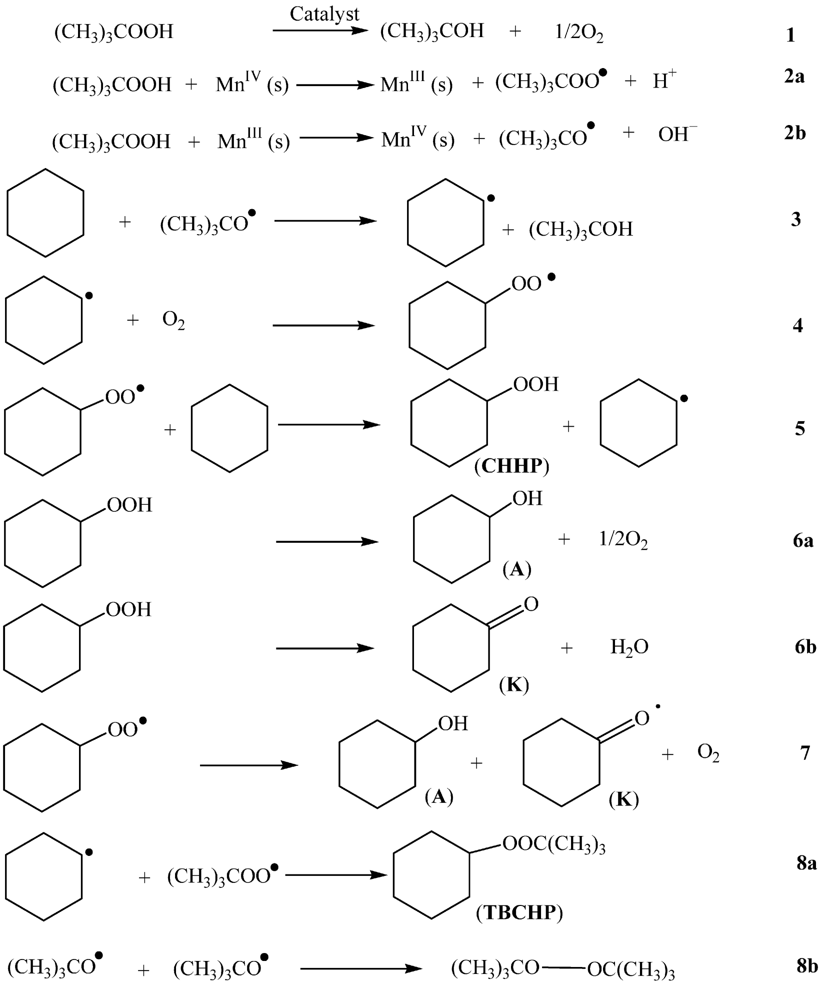


Fig. 8. Catalytic performance of fresh and regenerated H-K-OMS-2(4) catalyst.

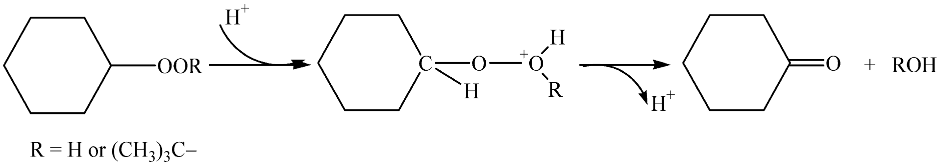
of cyclohexane. The selectivity of TBCHP decreases with increase in H^+ content in the catalyst (Table 3). This shows that the Brønsted acid sites in H-K-OMS-2 play a role in decomposition of TBCHP. Other data that support the role played by Brønsted acid sites is the increase in selectivity of cyclohexanone from 31.1% to 56.3% and decrease in selectivity of TBCHP from 35.4% to 9.4%, when the reaction was continued for 72 h (Entry 6, Table 3). However, when the reaction was done with K-OMS-2 for 72 h (Entry 7, Table 3) there was only a small decrease in the TBCHP selectivity. We propose an acid catalyzed conversion of TBCHP to cyclohexanone over the Brønsted acid sites as shown in Scheme 2 similar to conversion of CHHP to cyclohexanone as suggested by Vanoppen et al. [40]. The increase in conversion of cyclohexane from 51.6% in 24 h to 59.9% in 72 h might be due to the residual reactivity of radicals still present in the reaction mixture. Since the selectivity of cyclohexanol is not affected with increasing time, oxidation of cyclohexanol to cyclohexanone is limited, although OMS-2 is a very good catalyst for alcohol oxidation [25]. This might be due to unavailability of the active site for cyclohexanol oxidation.

Oxidation of cyclohexane was studied as a function of time (Fig. 6). The conversion of cyclohexane shows a continuous increase with time. The selectivity of TBCHP constantly decreases, whereas the selectivity of cyclohexanol increases in the beginning, reaching a maximum at 12 h and then there was a slight decrease (Fig. 7). The selectivity of cyclohexanone increases continuously as TBCHP gets converted to cyclohexanone. We detected formation of CHHP in the first two hours, and the reported cyclohexanol selectivity is after treating the reaction mixture with triphenylphosphine. No CHHP was detected after 24 h.

Cyclohexane oxidation using TBHP as oxidant proceeds via a radical mechanism as shown in Scheme 1. The homolytic decomposition of TBHP generates t-BuOO$^\bullet$ and t-BuO$^\bullet$ (Eqs. (2a) and (2b)) [17]. TBHP can also decompose over transition metals to form t-butyl alcohol and oxygen (Eq. (1)), which is an unwanted process. t-Butoxy radicals abstract hydrogen from cyclohexane forming cyclohexyl radicals which react with molecular oxygen from air (Eqs. (3) and (4)). The formation of CHHP is an important step in cyclohexane oxidation. This is an unstable peroxide and dissociates via two separate processes to give cyclohexanol and cyclohexanone (Eqs. (6a) and (6b)). Cyclohexanol is produced from CHHP by a decomposition pathway on Mn active sites with evolution of oxygen and cyclohexanone is pro-



Scheme 1. Proposed mechanism of cyclohexane oxidation.



Scheme 2. Acid catalyzed pathway for formation of cyclohexanone from peroxides.

duced by a dehydration process over Brønsted acid sites [38]. Cyclohexanol and cyclohexanone can also be produced via a Russell termination reaction (Eq. (7)) [39]. We have observed the formation of TBCHP, which is the product of another termination step (Eq. (8a)). However, TBCHP is a stable peroxide and decomposes very slowly. We also obtained bis(*t*-butyl) peroxide in small quantity (<2%) resulting from another termination reaction (Eq. (8b)).

4.3. *Effect of temperature*

The effect of temperature on cyclohexane oxidation is shown in Fig. 5. As expected, the conversion of cyclohexane shows a sharp increase from 18.8% at 40 °C to 51.6% at 80 °C. However, the selectivity of cyclohexanone decreases and that of cyclohexanol increases with increase in temperature. As the temperature increases, the rate of decomposition of TBHP increases, and that leads to increased formation of TBCHP. At 40 °C we also detected 2.7% of CHHP as determined from triphenylphosphine treatment and the reported selectivity of cyclohexanol is after triphenylphosphine treatment. However, no CHHP was detected at 60 °C and 80 °C after 24 h of reaction. These data suggest that at lower temperature the dehydration of CHHP (Eq. (6b)) takes precedence over decomposition (Eq. (6a)). The high conversion of cyclohexane at 80 °C suggests that this is the optimum temperature for the reaction under these conditions, although the selectivity for K–A oil was less than that at 60 °C. We did not observe any over oxidation product like hexanoic acid and adipic acid as reported in some literature [41,42].

It is possible that at lower temperature the TBHP is adsorbed in the pores and the decomposition is slow. However, there are no diffusion problems for either the reactant or the products. The diagonal length of the tunnels of H-K-OMS-2 is 6.5 Å. The kinetic diameter of TBHP and cyclohexane is 4.7 Å and 5.1 Å, respectively, and that of cyclohexanone, cyclohexanol, and TBCHP are not more than 6.0 Å.

4.4. Effect of solvent

The nature of solvent in cyclohexane oxidation is known to have an effect on conversion and selectivity of the products. Among all the solvents used for the reactions, acetonitrile was found to be the best solvent. Acetonitrile which is a polar aprotic solvent has the highest polarity and dielectric constant [35] among the four solvents tested for the reaction and which helps in solvation of TBHP, intermediate compounds, and radicals. *t*-Butyl alcohol which is a polar protic solvent gave better selectivity for K–A oil as a protic medium helps in formation of cyclohexanol and cyclohexanone from CHHP, but the conversion for cyclohexane was only 25.2%. This might be due to a stronger interaction of the solvent with the active sites and thereby reducing the access of substrate and oxidant to the active sites. Acetone which is aprotic and less polar than acetonitrile gave only 8.0% conversion and toluene which is non-polar gave the lowest conversion (4.6%).

4.5. Effect of amount of TBHP

When the amount of TBHP was increased (keeping all other factors constant) the conversion of cyclohexane increases. Increase in the amount of oxidant helps in generating more radicals and thereby increasing the conversion. The selectivity of cyclohexanone increases with increase in TBHP amount and selectivity of cyclohexanol decreases. This might be due to oxidation of cyclohexanol to cyclohexanone in the presence of excess amounts of TBHP. The presence of an excess amount of TBHP also leads to termination reactions (Eq. (8b), Scheme 1) and thereby decreases the efficiency of TBHP.

4.6. Stability of catalyst and heterogeneity of reaction

When catalyst was removed after 3 h of reaction, there was no further conversion of cyclohexane as shown in Fig. 6. These data show that the reaction does not take place in the absence of catalyst. This also proves that there was no leaching of manganese into solution, and the reaction is truly heterogeneous. The chemical composition of the catalyst remained the same after the reaction. The H^+ content of the catalyst also remained the same as verified by the NH_3 chemisorption study. The regenerated catalyst showed only a little decrease in the conversion of cyclohexane even after the fourth run as shown in Fig. 8.

5. Conclusions

A highly efficient catalytic process for cyclohexane oxidation has been demonstrated. Successive ion-exchange with concentrated nitric acid leads to a very high H^+ content in K-OMS-2 and 64% of H^+-exchange was achieved after four exchanges. The use of H^+-exchanged K-OMS-2 shows a marked improvement in conversion of cyclohexane as compared to K-OMS-2. A maximum conversion of 59.9% for cyclohexane with 90.6% selectivity for K–A oil was obtained using H-K-OMS-2(4) as a catalyst in 72 h. A turn over number (TON) of 73 was obtained in 24 h at 80 °C and if we consider only contributions of acidic manganese sites then the TON is 287. These manganese oxide based materials gave higher conversion for cyclohexane compared to other non-noble metal catalysts. The introduction of Brønsted acid sites and increase in Mn^{3+} sites in the H^+-exchanged material plays an important role in cyclohexane oxidation and contributes in achieving higher conversion and higher selectivity for the desired product. The proposed mechanism supports the dual active site participation in the oxidation process. Acetonitrile was found to be the best solvent among those tested for this reaction.

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