Research Article

Oxidation of cyclohexene with hydrogen peroxide over nano-crystalline $Mn_xCe_{1-x}O_{2-\delta}$ catalyst

Rajib Mistri*, Bidyapati Kumar

Department of Chemistry, Achhruram Memorial College, Jhalda, Purulia

The liquid-phase catalytic oxidation of cyclohexene to produce cyclohexenol and cyclohexenone directly was attempted using Mn ion substituted in ceria in acetonitrile solvent with 30% H_2O_2 as oxidant under atmospheric pressure. Structural studies by XRD show indication of ionically dispersed metal over ceria. Among all the catalysts studied, the $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ catalyst prepared by the solution combustion method has shown more activity (95.3% conversion with 98.7% selectivity) than others. The influences of the amount of Mn loading, temperature, time, the concentration of H_2O_2 and solvent have also been investigated. The enhancement of activity in Mn^{2+} ion substituted ceria as compared to other catalysts has been attributed to Mn–O–Ce ionic interaction in the combustion synthesized catalyst. Ionic substitution also helps to get an active stable catalyst with lower risk of Mn-leaching compared to the impregnated catalyst.

1. Introduction

One of the most important current topics of catalysis research has been to find an efficient catalyst for the selective oxidation of cyclohexene [1–6]. Oxidation of cyclohexene generally yields various products such as cyclohexenol, cyclohexenone, cyclohexene oxide and cyclohexene peroxide etc. [7]. Allylic oxidation of cyclohexene gives the products such as cyclohexenol and cyclohexenone as major products along with cyclohexene oxide as the minor product, indicating the involvement of Fenton-type oxidation reactions [8]. But when the oxidation occurred on the double bond, it gives cyclohexene oxide or epoxide as major products along with cyclohexene diols as minor product [4]. Major formation of the allylic oxidation products show the preferential attack of the activated C–H bond over the C=C bond [9]. However, the selectivity towards these products depends on various parameters like reaction conditions, central metal ion, solvent, oxidizing agent, nature of the catalyst etc. [10–14]. Previously oxidation of cyclohexene oxidation was carried out by using inorganic oxidants such as permanganate and chromium oxide [15]. Among the oxidizing agents hydrogen peroxide was chosen as a clean oxidizing agent, since it is inexpensive, environmentally friendly and generates water as byproduct [16].

Various new efficient catalytic systems have been designed and developed for the oxidation of cyclohexene with hydrogen peroxide as an oxidant. Among the catalytic studies, transition metal complexes are used as very effective homogeneous catalysts for this oxidation reaction [17–20]. But decomposition or degradation is one of the major problems in the application of homogeneous transition metal complexes [21, 22]. On the other hand separation of the products from the reaction mixture is also a major problem in case of homogeneous catalysts. Decrease of degradation of homogeneous catalysts have been achieved by the methods such as covalent anchorage on polymers [23], using inorganic oxide as supports [24–26] and also entrapped inside a porous oxide framework [27]. However, deactivation of the metal based catalysts due to leaching of active metal from the catalyst is still challenging [28]. This can be controlled by adopting specific preparation procedure and incorporating with other supports [29].

Here we show that $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ prepared by a single step solution combustion method has a much higher selective oxidation activity towards cyclohexene to cyclohexenol and cyclohexenone than other catalysts at 70 °C in acetonitrile solvent and atmospheric pressure (Scheme 1).
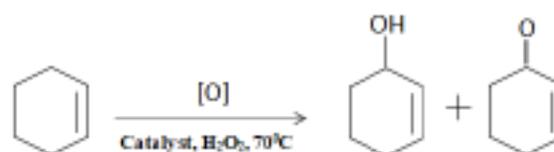
Scheme 1. Catalytic oxidation of Cyclohexene

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*Email ID: rajibmistri@yahoo.co.in

2. Materials and Methods

2.1 Preparation of catalyst

We have synthesized the catalysts by single step solution combustion method in an open muffle furnace kept in a fume hood with exhaust by the combustion of the corresponding metal nitrate salts with oxalyl dihydrazide $[C_2H_6N_4O_2(ODH)]$ as the fuel. Oxalyl dihydrazide was prepared by the dropwise addition of diethyl oxalate $(C_2H_6N_4O_2$, Sisco Research Laboratories Pvt. Ltd., 99%) to ice-cooled aqueous solution of hydrazine hydrate $(N_2H_4.2H_2O$, Qualizens Fine Chemicals, 99%) as reported in [30]. Solution combustion synthesis (SCS) for the preparation of $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ involves combustion of the metal salts $(NH_4)_2Ce(NO_3)_6$, $Mn(NO_3)_2,3H_2O$ with ODH, taken in a molar ratio 0.90 : 0.10 : 2.26, at the temperature of ignition of the redox mixture ($\sim$350 °C). In a typical preparation, 5 g of $(NH_4)_2Ce(NO_3)_6$ (Loba Chemie, 99%), 1.145 mL 10% $Mn(NO_3)_2.3H_2O$ (Merck India, 99%) solution and 2.5122 g of ODH are dissolved in 30 mL of double distilled water in a borosilicate dish. The solution is then transferred to the preheated muffle furnace maintained at $\sim$350 °C. Initially the solution boils with frothing and foaming followed by complete dehydration when the surface gets ignited and burns with a flame yielding a voluminous solid product within a minute. We have also prepared $Mn_xCe_{1-x}O_{2-\delta}$ (x = 0.03, 0.07, 0.10 and 0.15) catalysts in a similar manner.

In order for comparison, we have also prepared $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ by the incipient wetness impregnation (IWI) methods. For the preparation of the impregnated catalyst, the support (combustion made CeO_2) was first dried and then impregnated with an appropriate volume of the aqueous solution of manganese nitrate, corresponding to the support pore volume. The sample was then dried overnight at 100 °C, crushed and calcined at 500 °C for 3 h in air to get the catalyst.

2.2 Characterization of catalysts

The synthesized materials have been characterized by XRD. X-ray powder diffraction patterns were collected in a Rigaku diffractometer fitted with a horizontal goniometer mounted on a rotating anode. These data were recorded at 4 kW (40 kV, 100 mA) at $1°$ min^{-1} with a step size of $0.02°$ in the range 20 to 80 degrees. The rotating anode has Cu anode with effective wavelength of 1.5418 Å. There is a diffracted beam monochormator (Graphite crystal) which takes care of K_β lines and fluorescence.

2.3 Catalytic test

The oxidation of cyclohexene by H_2O_2 was carried out in the temperature range RT$-$80 °C at atmospheric pressure. In a typical experiment, 50 mg of catalyst was added to a liquid mixture containing 10 mL of acetonitrile, 2.45 mL of 30 wt% H_2O_2 (24 mmol) and 0.865 mL of cyclohexene (8 mmol) in a 250 mL two-necked round bottomed flask. For uniform mixing, the contents were stirred continuously during the course of reaction by a magnetic stirrer. The reaction system consisted of two liquid phases—an organic phase containing cyclohexene and acetonitrile, and an aqueous phase containing acetonitrile and 30% H_2O_2.

The reaction compositions were analyzed using a gas chromatograph (Nucon 5765, New Delhi) using a fused silica capillary column (EC5) of 30 m $\times$ 0.25 mm $\times$ 0.25 μm film thickness from Alltech and equipped with a FID detector. The injector and detector temperatures were 220 °C and 240 °C. The initial and final column temperatures were 110 °C and 150 °C, respectively with a temperature programmed rate of 80 °C min^{-1}. The quantitative analysis was done by standard sample injection.

Catalyst recycling was carried over the most active SCS and its corresponding IWI catalysts only. After each experiment, the reaction mixture was allowed to settle. Then the solution was filtered and the solid residue was washed thoroughly with the solvent. After washing, the solid residue was dried at 100 °C for overnight. This was used as catalyst for the next cycles to check the recycling ability of the catalysts.

3. Results and Discussion

3.1 XRD studies

Powder XRD patterns of SCS made $Mn_xCe_{1-x}O_{2-\delta}$ catalysts as well as the IWI catalyst are shown in Figure 1. All the diffraction lines can be indexed to the fluorite structure of Ceria (Fm3m) only [31] [JCPDS card no. 34–0394]. Thus other than the solid solutions phase no other peak(s) due to manganese oxide or metal are detected in XRD. This again points to Mn^{2+} ion substitution for Ce^{4+} in CeO_2 matrix. The corresponding IWI catalyst in which MnO is dispersed over ceria also shows no peak due to this phase in the XRD pattern. Thus, MnO crystallites in the IWI catalyst are so finely distributed over ceria that they escape XRD analysis. A much slower scan might have shed more light on the evolution of different Mn-phase(s).
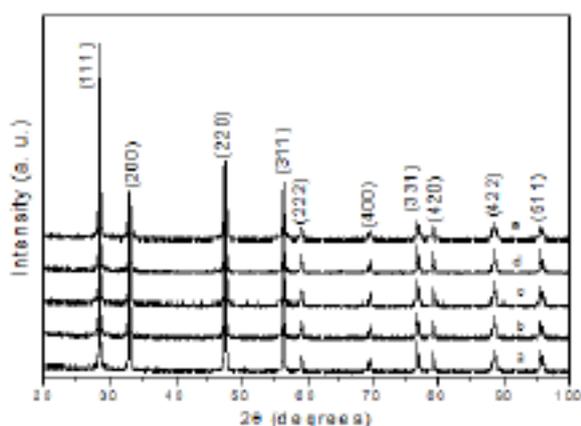
Figure 1. XRD patterns of (a) $Mn_{0.05}Ce_{0.95}O_{2-\delta}$, (b) $Mn_{0.07}Ce_{0.93}O_{2-\delta}$, (c) $Mn_{0.10}Ce_{0.90}O_{2-\delta}$, (d) $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ aged and (e) $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ IWI

4. Activity studies

4.1 Screening of catalysts

Table 1 lists cyclohexene oxidation activities of all the catalysts investigated here. The $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ catalyst shows much higher reactivity ($\sim 95\%$ conversion) and selectivity (99%) to cyclohexenol and cyclohexenone than the other catalysts after 3 h. The effect of varying catalyst loading of on the reaction is also investigated (Table 1). The enhanced oxidation activity over $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ catalyst indicates promoting effect of ceria in the combustion synthesized catalyst.

Table 1: Cyclohexene oxidation activities of different catalyst.

Catalyst	Amt. of cat. (mg)	Conv. (%)	Products (%)			Sel. (%)
			Cyclo-hexe-nol	Cyclo-hexe-none	By-pro-duct*	
$Mn_{0.03}Ce_{0.97}O_{2-\delta}$	50	86.4	26.6	53.9	5.9	93.2
$Mn_{0.05}Ce_{0.95}O_{2-\delta}$	50	95.3	26.8	67.3	1.2	98.7
$Mn_{0.07}Ce_{0.93}O_{2-\delta}$	50	95.6	25.9	65.2	4.5	95.3
$Mn_{0.10}Ce_{0.90}O_{2-\delta}$	50	88.3	23.7	59.1	5.5	93.8
$Mn_{0.15}Ce_{0.98}O_{2-\delta}$	50	86.4	21.5	53.5	13.3	86.8
$Mn_{0.05}Ce_{0.95}O_{2-\delta}$	30	92.3	26.1	63.8	2.4	97.4
$Mn_{0.05}Ce_{0.95}O_{2-\delta}$	70	93.2	25.5	63.6	4.1	95.6

Reaction condition: 0.865 mL cyclohexene + 10 mL MeCN + 2.450 mL H_2O_2 + 70 °C + 3 h;

*byproducts are mainly cyclohexene oxide and a little bit of cyclohexenediols.

The $Mn_{0.03}Ce_{0.97}O_{2-\delta}$ sample and 30 mg $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ catalyst are also found to be already very active. But a conversion of 95.3% with 98.7% selectivity was observed for 50 mg $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ catalyst which is higher than other catalysts. Although the 7 atom% metal loaded catalyst ($Mn_{0.07}Ce_{0.93}O_{2-\delta}$) showed slightly higher conversion than the $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ catalyst, the latter showed higher selectivity than the former. Any further increase in manganese content and amount of catalyst caused a decrease in the cyclohexenol and cyclohexenone formation. The lower activity of higher loaded (> 5 atom%) catalysts indicate that as manganese loading increased, percentage of MnO phase increased and manganese dispersion decreased resulting in reduced activity and selectivity. Hence we chose $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ as the best formulation for further investigation.

4.2 Temperature effect

The effect of temperature on the oxidation of cyclohexene was studied by varying the temperature from 35 °C to 80 °C over the catalyst (50 mg) with other parameters kept constant and the results are shown in Figure 2. Selection of this particular temperature range is due to the fact that at higher temperatures the decomposition of H_2O_2 predominates [32]. At room temperature (35 °C)
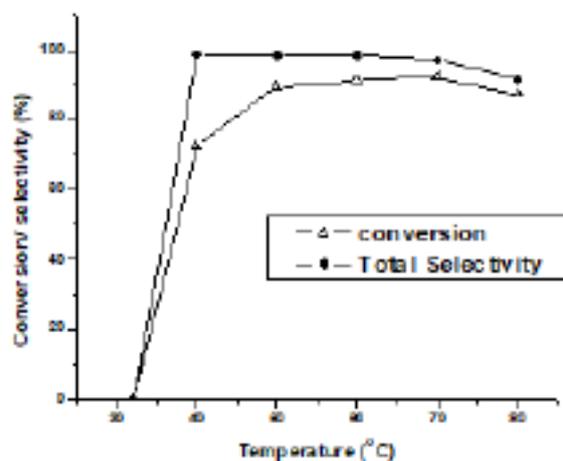

Figure 2. Conversion of cyclohexene/selectivity of cyclohexenol and cyclohexenone as a function of temperature over $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ catalyst. Reaction condition: 50 mg catalyst + 0.865 mL cyclohexene + 10 mL MeCN + 2.450 mL H_2O_2 + 3 h.

cyclohexene was not oxidized, showing no reactivity of the catalyst. But an increase of the reaction temperature by just 5 °C leads to a conversion of $\sim 31\%$ with total selectivity of $\sim 90\%$ to cyclohexenol and cyclohexenone. Further 10 °C raise in temperature increases the conversion ($\sim 80\%$) and selectivity remains similar. The conversion is maximum (95%) between 60–70 °C with $\sim 99\%$

selectivity. It decreases marginally to $\sim 88\%$ when reaction temperature was increased to 80 °C. The above data indicates that the competition between the products and byproduct occurs above 70 °C. Hence, the reaction temperature higher than this optimum temperature is in favour of byproduct formation in addition to the self-decomposition of hydrogen peroxide resulting to a relatively lower conversion. Thus 70 °C has been chosen as the most suitable temperature for the selective oxidation of cyclohexene under our reaction conditions.

4.3 Effect of reaction time

The cyclohexene conversion over $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ as a function of reaction time at 70 °C is presented in Figure 3. The oxidation starts at ~ 30 min over the catalyst, progresses linearly to $\sim 80\%$ upto 120 min and maximum activity ($\sim 95\%$ conversion) and selectivity (99%) is reached beyond ~ 180 min. This is why we chose 3 h as reaction time in our studies.
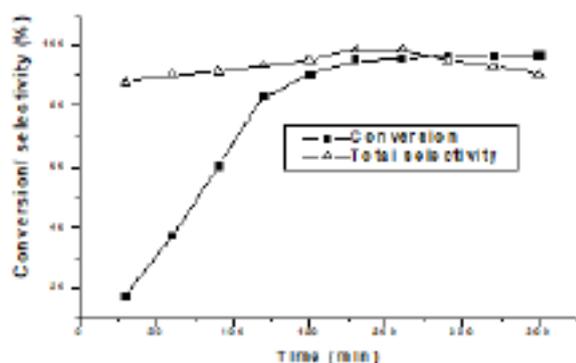

Figure 3. Conversion of cyclohexene/selectivity of cyclohexenol and cyclohexenone as a function of time over $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ catalyst. Reaction condition: 50 mg catalyst + 0.865 mL cyclohexene + 10 mL MeCN + 2.450 mL H_2O_2 + 70 °C.

4.4 Influence of H_2O_2 concentration

Cyclohexene oxidation was carried out by adding H_2O_2 to the reaction mixture in one lot at the reaction temperature. To study the effect of varying the amount of H_2O_2, the reaction was carried out with 50 mg of catalyst and the amounts of H_2O_2 from 8 mmol to 40 mmol while keeping other conditions unchanged. The results are shown in Figure 4. In absence of H_2O_2, cyclohexene was not oxidized which indicates that the catalyst cannot oxidize cyclohexene in presence of air (O_2) only. Percentage conversion and total selectivity for cyclohexene oxidation reaches a maximum value with 24 mmol of H_2O_2 and then these

starts decreasing. The distribution of allylic oxidation products shows the same trend but the cyclohexene oxide percentage shows a gradual increase [4]. Even though the theoretical molar ratio of cyclohexene to H_2O_2 for the oxidation reaction is 1 : 1 and concentration of H_2O_2 was 8 mmol, here the results show that H_2O_2 needed was triple its stoichiometry. This can result from the fact that not all the H_2O_2 can take part in the oxidation due to its unavoidable self-decomposition under the reaction conditions [33].
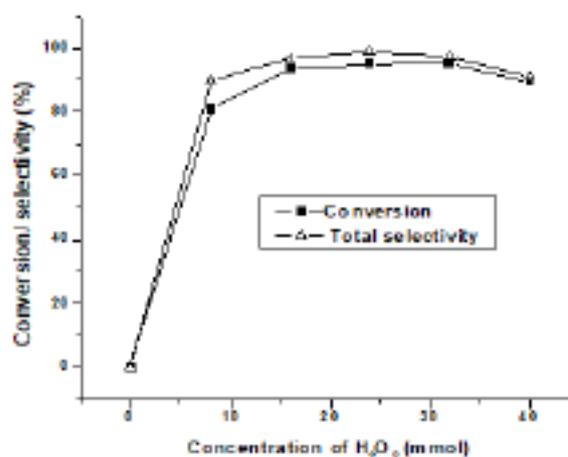

Figure 4. Conversion of cyclohexene/selectivity of cyclohexenol and cyclohexenone as a function of H_2O_2 concentration over $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ catalyst. Reaction condition: 50 mg catalyst + 0.865 mL cyclohexene + 10 mL MeCN + 70 °C + 3 h.

4.5 Effect of solvent

The cyclohexene oxidation was carried out using various solvents such as acetonitrile, methanol, ethanol and toluene over $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ catalyst and the results are presented in Figure 5. Acetonitrile is found to be the best solvent for cyclohexene oxidation with highest conversion of 95.3% and selectivity of 98.7%. Toluene showed lowest cyclohexene conversion (70%) but the selectivity (93%) was very high. Using ethanol or methanol as a solvent, comparatively lower conversion is observed.

In this study, it is believed that the solvent acetonitrile acted as a 'media' serving homogeneity for the liquid phase(s). Cyclohexene and hydrogen peroxide are both soluble in acetonitrile and the reaction products; viz., cyclohexenol and cyclohexenone are not only soluble in the reaction mixture but also can be displaced from the surface of catalyst as they are formed. Acetonitrile, an aprotic solvent, can also activate H_2O_2.

The $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ prepared by IWI method ($Mn_{0.05}Ce_{0.95}O_{2-\delta}$ IWI) gives a conversion of $\sim$ 81% with $\sim$ 92% selectivity than the same catalyst prepared by SCS method. These values are quite lower compared to those of the SCS catalyst.
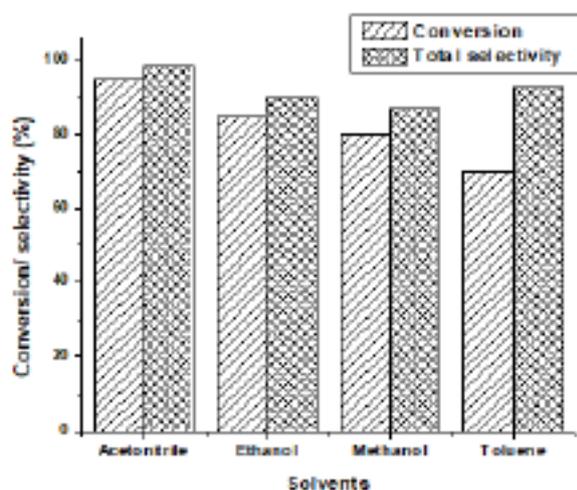

Figure 5. Solvent effects on cyclohexene oxidation activities over $Mn_{0.05}Ce_{0.95}O_{2-\delta}$. Reaction condition: 50 mg catalyst + 0.865 mL cyclohexene + 2.450 mL H_2O_2 + 70 °C + 3 h.

To check the stability and recycling ability of the SCS catalyst, the used catalyst was separated from the reaction mixture and dried in air at 110 °C, and then oxidation experiments were performed under the typical reaction conditions used here. The results show that the $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ catalyst maintains its activity after three consecutive cycles without any appreciable loss of conversion and selectivity.

The result of ageing experiments over both SCS and IWI catalysts show a decreasing trend for the IWI catalyst, whereas the SCS catalyst more or less maintains its activity (Figure 6). The loss of activity of the IWI catalyst during ageing is likely due to leaching of MnO from the catalyst.

The different catalytic activity of SCS and IWI catalysts is related to phase composition of the support oxide. In case of $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ made via combustion route, there is no MnO phase (as revealed from XRD study) and it shows better catalytic behavior than the corresponding IWI catalyst that contains very finely distributed MnO over ceria. Thus, Mn^{2+} in the ceria lattice sites (as in $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ catalyst) is more active than MnO (as in $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ IWI catalyst) towards cyclohexene oxidation. This higher activity of combustion synthesized catalyst compared to

the impregnated catalyst can then be attributed to Mn–O–Ce ionic interaction in the $Mn_xCe_{1-x}O_{2-\delta}$ catalyst. The loss of activity of IWI catalyst during ageing is most likely due to leaching of MnO from the catalyst. The SCS catalyst contains Mn^{2+} ion sites in the ceria lattice which is difficult to be leached out from the catalyst surface and hence its activity remains unaltered during ageing in the reaction atmosphere.
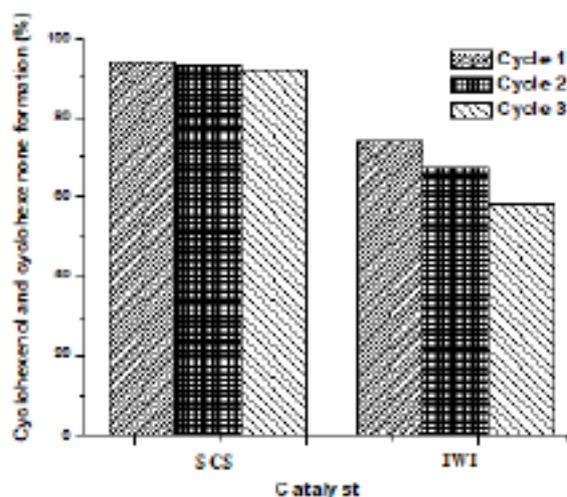

Figure 6. Effect of cycling on cyclohexene oxidation activities of $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ catalyst prepared via (a) solution combustion (SCS), (b) impregnation (IWI). Reaction condition: 50 mg catalyst + 0.865 mL cyclohexene + 2.450 mL H_2O_2 + 10 mL MeCN + 70 °C + 3 h.

Cyclohexene oxidation generally proceeds through a radical pathway in presence of a peroxide oxidant, in which the homolytic cleavage of the oxidant is involved [8,34]. To examine the mechanism involved in the present case, we performed the oxidation in presence of a radical scavenger (quinone). The radical scavenger was added to the reaction mixture after 1 h of reaction and the progress of reaction was monitored. Cyclohexene oxidation was found to be totally stopped after addition of the scavenger. Therefore, we believe that cyclohexene oxidation over the reported catalysts in this study proceeds via a radical mechanism [35]. Hydroxide radical is first produced that subsequently abstracts hydrogen from the reactant to produce cyclohexenyl free radical. This radical is then trapped by O_2 and/or combine with hydroperoxide radical to form cyclohexenyl peroxide intermediate which eventually leads to the formation of cyclohexenol and cyclohexenone.

5. Conclusions

In this study, solution combustion synthesized single phase $Mn_{0.05}Ce_{0.95}O_{2-\delta}$ is shown to be a highly efficient catalyst for the oxidation of cyclohexene in acetonitrile solvent at 70 °C than the other catalysts investigated. The conversion of cyclcohexene achieved over this catalyst is $\sim 95\%$ and the selectivity of cyclohexenol and cyclohexenone was almost $\sim 99\%$. XRD study indicates ionic substitution of manganese in ceria. The high activity can thus be attributed to active Mn^{2+} ion sites and Mn–O–Ce ionic interaction in the $Mn_xCe_{1-x}O_{2-\delta}$ catalyst. Since Mn is incorporated as Mn^{2+} ion in the structure of ceria, the possibility of its leaching is diminished. The ageing and recycling experiments confirm this since there was no loss of activity of the SCS catalyst due to these treatments. On the other hand, the activity of the IWI catalyst is lower due to presence of MnO crystallites over the ceria support where leaching of the active phase is easier as observed in the ageing experiment where a decreasing activity trend is observed.

Acknowledgements

Conflict of interest

The authors have no affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

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