Characterization of ZnO and Modified ZnO Catalysts for Anaerobic Oxidation of Cyclohexanol

Chaudhari S.M.¹, Waghulde A.S.¹, Samuel V.¹, Bari M.L.¹ and Chumbhale V.R.²
¹University Institute of Chemical Technology, North Maharashtra University, Jalgaon – 425001, INDIA
²Catalysis and Inorganic Chemistry Division, CSIR-National Chemical Laboratory, Pune-411008, INDIA

Abstract

Cyclohexanone is an important intermediate because of its use in the manufacture of e-caprolactum which is used for the production nylon 6. In the present work ZnO which acts as an amphoteric oxide is synthesized in the laboratory and characterized by XRD and BET surface area. This was modified by metal impregnation using aqueous solutions of sodium and boron salts qualitatively and quantitatively. The samples were calcined in the muffle furnace and were subjected to XRD investigation to check formation of new inorganic phases on impregnation. The ZnO and modified ZnO catalysts were screened using a downflow integral laboratory reactor at identical experimental parameters at atmospheric pressure. The effect of temperature, flow rate and type and quantity of metal loading on activity and selectivity of the title reaction studied. Activation energy, thermodynamic properties of parent and modified catalysts are evaluated. A rate equation has been applied. The inorganic phases responsible for dehydration and dehydrogenation of cyclohexanol are identical using JCPDS diffraction files.

Keywords: Anaerobic Oxidation, Cyclohexanol, XRD, BET surface area, ZnO

Introduction

Cyclohexanone is an important intermediate because of its use in the manufacture of e-caprolactum (via cyclohexanone oxime route) which is used as lactam for nylon 6. It also finds application as a solvent for cellulose acetate, nitro cellulose and natural and vinyl resins. Cyclohexene is used as an alkylating component and as a stabilizer for high octane gasoline. It also finds application in the manufacture of maleic acid, hexahydrobenzoic acid and cyclohexanecarbaldehyde. Cyclohexanone is manufactured by two processes – i. cyclohexane oxidation to cyclohexanone/cyclohexanol followed by dehydrogenation of cyclohexanol at 400-500°C and atmospheric pressure over Zn or Cu catalysts and ii. conversion of phenol into cyclohexanone via two step process after ring hydrogenation with nickel catalyst at 140-160 °C and 15 bar pressure followed by hydrogenation.

Metal oxides including binary and ternary systems have attracted a great attention because of their unique catalytic properties compared with those of individual metal oxides. Such behavior may arise from the interaction between the supported oxide and support, leading to structural and chemical changes. The performance of mixed oxide catalyst or metal oxide supported catalyst depends more or less extent on the structure and textural properties of the catalysts as well as their acid-base nature. The contribution of each of the factors to the catalytic performance depends on the nature of reaction. Recently researchers have studied the title reaction on different oxide systems. It is reported that different calcination temperatures, gas atmosphere exhibit substantial influence on activity and selectivity of La-promoted MgO catalyst for oxidative coupling of methane. In order to explore the possible favourable effect of different calcination temperature (in the atmosphere of static air) over selected catalysts the title reaction has also been studied in this perspective. Recently gas-phase oxidant –free oxidation of cyclohexanol over V₂O₅-MoO₃-M₂O (M=Na, K, Cs) is reported where the phase MoV₂O₇.5is identified favoring dehydration in cyclohexanol transformation by vapour phase and at ambient pressure. In the present work we are reporting modification of ZnO catalyst with Na₂O and B₂O₃ dopants qualitatively and quantitatively. The effect of temperature, weight hourly space velocity and quantity of dopants on activity, selectivity on the prominent reaction products (cyclohexene and cyclohexanone) is described. The Arrhenius activation energy and thermodynamic properties are also presented. A rate equation is applied.

Material and Methods

Materials: NaOH and H₂BO₃ were obtained from Loba Chemie and S. d. Fine chemicals for Na and B doping respectively.

Preparation of catalyst: There are two preparation methods for ZnO in which zinc oxide sample can be prepared by thermal decomposition of Zn(NO₃)₂.6H₂O in flow of air at 500°C for 5h. Another way (which was also adopted in this work) of new high purity ZnO powder preparation is by adding 1M (NH₄)₂CO₃ (Aesar, 99.999%) solution drop by drop to Zn (NO₃)₂ (Aldrich, 99.999%) solution while stirring to precipitate ZnCO₃. The
precipitate was washed thoroughly with distilled, demonized water to removed residue NH$_4^+$ ions, filtered and oven dried at 393K for 48h, then stored in a desiccators. The zinc carbonate was decomposed to ZnO by calcinations in the muffle furnace at the heating rate of 2 °C/min and holding at 673K for 6h. The BET surface of ZnO is 28 M$^2$g$^{-1}$ 13, 14.

Modification of ZnO: Catalytic performance is highly depends on its preparation method. The modified catalysts prepared in the present work were by using wet impregnation method. The impregnation method is simple and is the most popular catalyst preparation method.

Modification of ZnO catalyst with Sodium: For the modification of ZnO with sodium NaOH solution was used. A calculated amount ZnO was immersed in a precursor solution of sodium. The obtained slurry is dried and calcined at the appropriate temperature (At 500°C for 6 h) in a muffle furnace at a heating rate of 10 ° K min$^{-1}$.

For the modification of ZnO with boron, H$_3$BO$_3$ solution was used. A calculated amount of ZnO was immersed in a precursor solution of boron. The obtained slurry is dried and calcined at the appropriate temperature (At 500°C for 6 h) in a muffle furnace at a heating rate of 10 ° K min$^{-1}$.

Table 1 describes the preparation method of the modified catalysts.

<table>
<thead>
<tr>
<th>Sr. No</th>
<th>Compound</th>
<th>Conc. (Wt %)</th>
<th>Addition of precursors salts in ml's</th>
<th>1 Wt</th>
<th>3 Wt%</th>
<th>6 Wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaOH</td>
<td>10</td>
<td>1.2</td>
<td>3.2</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>H$_3$BO$_3$</td>
<td>4</td>
<td>3.4</td>
<td>10.3</td>
<td>20.6</td>
<td></td>
</tr>
</tbody>
</table>

Catalyst characterization: The sample were thoroughly ground to fine powder using pestle and mortar and were subjected for XRD investigation. X-ray diffraction pattern of samples were recorded with Ringaku Dmax/III VC diffractometer using Ni-filtered CuKa ($\lambda$= 1.5406 A$^0$) radiation at scanning rate 2$^\theta$ min$^{-1}$ in the range 2$^\theta$ of 5 to 75.

XRD pattern of ZnO (Wurtzite structure): To characterize the ZnO products, X-ray power diffraction (XRD) experiment were performed on a D/max-RA XRD diffraction spectrometer with Cu Kα line at 1.5406 A$^0$. The XRD pattern for Wurtzite ZnO as shown in figure 1. The peak at 2 theta values 36.212$^0$ with a = 3.253 & c = 5.209 (d spacing 4.839 A$^0$ with plane 101), the peak is more intense at high temperature which are consistent with the values in the standard diffraction file of JCPDS (File No. 36-1451). XRD of ZnO confirmed Wurtzite structure. The presence of the (002) as the most intense peak for the sample synthesized preferred growth of catalyst$^{15}$.

Table 2 presents XRD data of Zn-Na-O (6 wt % loading of Na) 2θ, d value, and phase according to JCPDS data. The XRD pattern for Zn-Na-O (6 Wt% Na) having a cell parameters (a= 7.562 and c= 5.859) but as compare to 3 wt % there is an extra phase in 6 wt% of Na i.e. Na$_2$(Zn$_2$O$_3$) at intensity of 7 and varying lattice parameter ( a= 6.182 and c= 9.447 ). XRD pattern for 3 and 6 wt % of Na loading as shown in figure 2.
XRD pattern of Zn-B-O (3 & 6 Wt% B loading): Table 4 and 5 describe XRD data of Zn-B-O (3 wt % loading and 6 wt % loading) respectively. Catalyst (θ, d value, and phase according to JCPDS data). The XRD pattern for Zn-B-O (3 Wt% B) with phases occur ZnB₄O₇, Zn (BO₂)₂, ZnO (BO)₆ and β-Zn₅B₄O₁₁ but as compare to 6 wt % there is an varying Intensities as well as 2θ values with changing the position of peaks and phases occur after doping that phases and 2θ values are given below.

### Table-4
<table>
<thead>
<tr>
<th>2 theta</th>
<th>D</th>
<th>Phase</th>
<th>I/I₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.280</td>
<td>7.2015</td>
<td>ZnB₄O₇</td>
<td>3</td>
</tr>
<tr>
<td>14.600</td>
<td>6.0619</td>
<td>ZnB₂O₇</td>
<td>3</td>
</tr>
<tr>
<td>15.500</td>
<td>5.7119</td>
<td>ZnB₄O₇</td>
<td>3</td>
</tr>
<tr>
<td>57.100</td>
<td>1.6117</td>
<td>Zn (BO₂)₂</td>
<td>3</td>
</tr>
<tr>
<td>66.340</td>
<td>1.4078</td>
<td>ZnO (BO₂)₆</td>
<td>8</td>
</tr>
<tr>
<td>67.980</td>
<td>1.3778</td>
<td>β-Zn₅B₄O₁₁</td>
<td>37</td>
</tr>
<tr>
<td>72.580</td>
<td>1.3014</td>
<td>β-Zn₅B₄O₁₁</td>
<td>4</td>
</tr>
</tbody>
</table>

In above table we observed that there is intensity is constant for first four to five phases and after it get increases but in case of 6 wt % of B there is intensity is continuously changes for each phase.

### Table-5
<table>
<thead>
<tr>
<th>2 theta</th>
<th>D</th>
<th>Phase</th>
<th>I/I₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.380</td>
<td>7.1435</td>
<td>ZnB₄O₇</td>
<td>3</td>
</tr>
<tr>
<td>14.660</td>
<td>6.0291</td>
<td>ZnB₂O₇</td>
<td>3</td>
</tr>
<tr>
<td>15.740</td>
<td>5.6253</td>
<td>ZnB₂O₇</td>
<td>3</td>
</tr>
<tr>
<td>66.480</td>
<td>1.4052</td>
<td>ZnO (BO₂)₆</td>
<td>7</td>
</tr>
<tr>
<td>68.040</td>
<td>1.3767</td>
<td>β-Zn₅B₄O₁₁</td>
<td>35</td>
</tr>
<tr>
<td>72.720</td>
<td>1.2992</td>
<td>β-Zn₅B₄O₁₁</td>
<td>4</td>
</tr>
</tbody>
</table>

Reactions procedure: 1g of catalyst (10-22 mesh size) was positioned in a down-flow integral fixed bed silica reactor (length 37cm; ID= 12 mm with thermocouple well of length 14 cm and ID= 6 mm) maintained at constant temperature. The catalyst was packed either side with porcelain beads and was activated in a flow of dry air at the rate of 25cc min⁻¹ at the desired temperature 500°C for 6 h. This was cooled till the desired reaction temperature in the flow of nitrogen at 20cc min⁻¹. The cyclohexanol was fed from the top of the reactor using pulse injection at desired rate. All reaction runs were carried out at ambient pressure. Liquid products were condensed in a receiver using ice cold trap and were analyzed by gas chromatograph (Model Agilent 7890 A) equipped with a CPCIL 8 CB column (30×0.5 mm i.d.) and FID. Figure 4 depicts the reactor assembly. All reactions runs were carried out at WHSV= 1.14 h⁻¹ and at ambient pressure.

**Formulae**

\[
\% \text{ conversion of cyclohexanol} = \frac{\text{Moles of cyclohexanol fed} - \text{Moles of cyclohexanol in product}}{\text{Total moles of cyclohexanol fed}} \times 100
\]

\[
\% \text{ selectivity of cyclohexane} = \frac{\text{Moles of cyclohexane produced}}{\text{Conversion of cyclohexanol}} \times 100
\]

\[
\% \text{ selectivity of cyclohexane} = \frac{\text{Conversion of cyclohexanol produced}}{\text{Conversion of cyclohexanol}} \times 100
\]
Results and Discussion

X-Ray diffraction: The XRD profiles of sodium and boron modified ZnO showed that there is a formation of new phase of Na$_2$ZnO$_4$ on doping of 3wt% sodium (File No: 28-1193) at d = 1.3771 with I/I$_0$ = 42 and there is disappearance of Zn (BO$_2$)$_3$ phase (File No: 39-1126) on loading of 6wt% boron over ZnO.

Effect of reaction temperature on catalytic performance: The products of cyclohexanol transformation were cyclohexanone, (formed due to dehydrogenation) cyclohexene (formed due to dehydration) in prominence. However, small amounts of phenol, dicyclohexyl ether, benzene, and other minor products were obtained due to side reaction. These were termed as impurities. Figure 5 describes the effect of temperature on cyclohexanol conversion for ZnO, Zn-Na-O and Zn-B-O catalysts with low and high doping. The cyclohexanol conversion increased with increase in temperature from 150 to 250 steadily and after that it showed a significant increase at 300°C. As the amount of Na loading is increased from zero (for parent catalysts) to 6wt%, the conversion is increased linearly with doping amount at 180°C (from 9 to 67). At higher temperature the Zn-Na-O (3wt%) showed highest conversion of nearly 96 and it further dropped to 34 with loading amount of 6wt% Na. ZnO showed a linear increase in selectivity of cyclohexanone with the variation of temperature (figure 6), however, a reverse trend for cyclohexene selectivity was noticed (figure 7). There is a linear increase in conversion for low Na loading where as in case of higher loading the conversion is decrease. Both the loading amounts low and high show a similar trend with temperature in case of Zn-B-O catalysts. There is slight reduction in cyclohexanone selectivity (from 45 to 39%) for 3wt% doping but a significant increase in cyclohexanone selectivity is observed with 6wt% doping with absence of cyclohexene formation beyond a temperature of 180°C. This means that the complex nature of the catalyst enhances the dehydrogenation yielding cyclohexanone especially noted at higher temperature. ZnO showed a rise in cyclohexanone selectivity from 0.13% to 14% as the temperature increased from 180 to 280°C and for Zn-Na-O (3wt% Na loading) a drop in cyclohexanone selectivity from 80 to 11% was observed but as the loading amount is increased from 3 to 6wt% of Na, there was sharp reduction of cyclohexanone selectivity was noticed. ZnO nearly showed a constant selectivity for cyclohexene (79 to 76%). In the temperature range of 210–280°C cyclohexene selectivity was increased for low loading of Na and a decreasing trend (91 to 13%) was observed for higher loading for catalyst Zn-Na-O (6wt% Na loading).

This phenomenon is attributable to amphoteric nature of parent ZnO which show reverse phenomenon of doping of acidic salt on oxides$^{12}$. Higher loading of boron (6wt%) required a relatively higher temperature for cyclohexanol dehydration and it was only initiated beyond 200°C at low temperature (180°C) comparison of Na and B doping for comparable doping amount of 6wt% show that doping of basic alkali (sodium salt) prevailed cyclohexanone where as at the same temperature 6wt% boron showed nearly similar level of activity for dehydrogenation and dehydration (45 and 42% respectively) and beyond this temperature there is absence of cyclohexene formation for Zn-B-O (6wt%) loading. This is again a contradiction considering earlier work where in it is reported that acidic elements like phosphorus facilitated dehydration yielding cyclohexene.

A comparison of comparable doping (3wt% loading) of sodium and boron for cyclohexanone and cyclohexene selectivity is depicted in figure 8 (a molar ratio of cyclohexanone / cyclohexene produced per hour). A remarkable observation is that Zn-Na-O (3wt% Na loading) showed cyclohexanone / cyclohexene molar ratio of almost 45 at lower temperature of 180°C and there is enhancement in dehydrogenation performance as compared to parent as well as boron modified ZnO catalysts. This is also observed at 210°C. With increase of Na doping the ratio is decreased where as on doping of boron there is linear decrease (figure 8). This means that a doping of merely 3wt% of sodium over ZnO facilitates energy efficient conversion of cyclohexanol to cyclohexanone at a temperature of 180°C and it is at higher level than boron modified ZnO irrespective of loading amounts as depicted in figure 6 and 7.

![Graph of temperature Vs % selectivity of cyclohexanone](image-url)  
Figure 5: Effect of temperature on cyclohexanol conversion  
Figure 6: Graph of temperature Vs % selectivity of cyclohexanone
The reaction rate constant \(k_r\) were calculated by using following expression: **Arrhenius activation energy**: 

\[
\ln k_r = \frac{E_a}{RT} - \frac{1}{2} \frac{\Delta H}{R} \frac{1}{T} \ln T
\]

Where, \(F\) = reactant feed passed in mole per hour, \(W\) = weight of catalyst in gram, \(X\) = Fractional conversion (%).

From the data, the plots of \(-\ln k_r vs 1/T \ 'K\) were drawn. The Arrhenius activation energies from the slopes of the plots were calculated (Slope = \(\frac{E_a}{2.303 RT}\)).

**Thermodynamic properties**: Thermodynamic activation parameters such as enthalpy \(\Delta H\), entropy \(\Delta S\) and free energy \(\Delta G\) are important for any chemical transformation. These deduced by using the following relations

\[
\Delta H = E_a - RT \text{cal/g mole}
\]

\[
\Delta S = \left[ \Delta H + \frac{2h}{k \ln k_r} \right] / T
\]

Where, \(\Delta H\) = Change in enthalpy Kcal/mole, \(\Delta S\) = Change in entropy Cal/° mole, \(K\) = Boltzmann constant i.e. \(1.3805 \times 10^{-23}\), \(k_r\) = Rate constant of reaction at optimum reaction temperature, \(h\) = planks constant i.e. \(6.625 \times 10^{-34}\).

\[
\Delta G = \Delta H + T\Delta S
\]

Where, \(\Delta G\) = Gibbs free energy Kcal/mole

*Figure 7*: Graph of Temperature Vs % selectivity of cyclohexene

*Figure 8*: Cyclohexanone/Cyclohexene molar ratio

*Figure 9*: The Arrhenius plot of ZnO (parent) catalyst

*Figure 10*: The Arrhenius plot of Zn-Na-O (3 wt %) catalyst

*Figure 11*: The Arrhenius plot of Zn-B-O (6 wt %) catalyst
The complex nature of Zn-B-O (6wt %) showed higher activation energy than ZnO. Free energy zero indicates feasibility of the reaction in presence of these catalysts. Enthalpy and entropy positive values are indicative of bond rearrangement in the cyclohexanol transformation.

Reaction scheme: Dehydrogenation of cyclohexanol to cyclohexanone over modified oxide is given below. In this reaction when cyclohexene is reacting with air we give cyclohexanol with water as byproduct further hydrogen reduction take place we give cyclohexanone. From cyclohexanol reaction we get other two products that are phenol & dicycloether. On the other hand water molecule reduction take place from cyclohexanone and gives Bycyclo-ene-hexanone as product. All the reactions are reversible reaction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$\text{Ea Kcal/gmol}$</th>
<th>$\Delta H\text{ Kcal/g mol}$</th>
<th>$\Delta S\text{ (e.u) Cal/ mol}$</th>
<th>$\Delta G\text{ Kcal / mol}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>27.35</td>
<td>26.44</td>
<td>0.05836</td>
<td>$6.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>Zn-Na-O (3 Wt %)</td>
<td>23.57</td>
<td>22.66</td>
<td>0.05002</td>
<td>$5.6 \times 10^{-5}$</td>
</tr>
<tr>
<td>Zn-Na-O (6 Wt %)</td>
<td>19.26</td>
<td>18.35</td>
<td>0.04050</td>
<td>$4.5 \times 10^{-5}$</td>
</tr>
<tr>
<td>Zn-B-O (3 Wt %)</td>
<td>18.99</td>
<td>18.088</td>
<td>0.03992</td>
<td>$4.20 \times 10^{-5}$</td>
</tr>
<tr>
<td>Zn-B-O (6 Wt %)</td>
<td>33.059</td>
<td>32.157</td>
<td>0.07098</td>
<td>$8.03 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

The reaction 1 and 2 takes place in parallel with each other and $K_1$ and $K_2$ are the corresponding rate constants. Let’s assume these two reactions to be first order irreversible reactions. Hence, overall rate of reaction is given as

$$\frac{1}{y_1} = K_1y_1 + K_2y_2$$

$$\frac{1}{y_2} = K_3y_2$$

The performance equation of fixed bed reactor is given as,

$$\frac{W}{F_{in}} = \int_{0}^{X_a} \frac{d_{in}}{d_{out}} dx$$

Substituting equation (3) in (4) we have

$$\frac{W}{F_{in}} = \frac{X_a}{1 + \frac{1}{X_a}}$$

where $C_a = \frac{C_{in}}{(1 + X_a)}$ concentration of $A$ in feed as (moles/ liter)

At low temperature (180°C), the dehydrogenation was in the order-Zn-Na-O (6 wt %) > Zn-B-O (3 wt %) > Zn-B-O (6 wt %) > Zn-Na-O (3 wt %) > ZnO.

Conclusion

At low temperature (180°C), the dehydrogenation was in the order-Zn-Na-O (6 wt %) > Zn-B-O (3 wt %) > Zn-B-O (6 wt %) > Zn-Na-O (3 wt %) > ZnO.
This means that at low temperature trend is no effective dehydrogenation over ZnO catalyst, however, on modification with sodium (6 wt % doping) enhanced the dehydrogenation activity to a considerable extent (Cyclohexanone/cyclohexene mole ratio was = 44.71)

At higher temperature of 280°C, the trend for dehydrogenation was noted as- Zn-Na-O (3 wt %) > Zn-B-O (6 wt %) > Zn-B-O (3 wt %) > ZnO > Zn-Na-O (6 wt %)

Higher loading of Na facilitated energy efficient conversion for cyclohexanone. This also holds well for doping boron as higher loading of boron (6 wt %) showed an enhancement of selectivity ratio of cyclohexanone/cyclohexene by a factor of 1.82 with a reduction in temperature (of 40°C). This means that doping of boron and sodium, facilitated dehydrogenation rather than dehydration and this could be attributable to complex nature of catalyst surface at higher loading.

The comparable loading of sodium and boron revealed that sodium is more favorable for dehydrogenation than boron and more over it showed energy efficient conversion for dehydrogenation. This is facilitated due to Na\textsubscript{2}ZnO\textsubscript{2} phase. The disappearance of Zn(BO\textsubscript{3})\textsubscript{2} phases for higher boron loading facilitated the suppression of impurities formation to a considerable extent that are formed due to undesirable reaction pathways at identical experimental conditions.

From reaction data, the order of reaction was determined to be first order reaction.

References

1. *The Merck Index*, 7\textsuperscript{th} Edn (Merck and Co, Rahway, N J, USA), (1960)
12. Vyawahare Y.K., Chumbhale V.R., Pardhy S.A., Samuel V., Aswar A.S., Gas-phase oxidant-free oxidation of cyclohexanol over V\textsubscript{2}O\textsubscript{5}/MoO\textsubscript{3}-M\textsubscript{2}O (M = Na, K, Cs) catalysts, *IJCT*, 17, 43-49 (2010)