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# Surface Characterization and Catalytic Activity of Cobalt Promoted MoO<sub>3</sub>/SiO<sub>2</sub> Solid Acid Catalysts

# Vinod B. Mane<sup>1</sup>, Jayamala M. Deshmukh<sup>1</sup>, Shobha A Waghmode<sup>2</sup> and Sharda P. Dagade<sup>\*1</sup>

## <sup>1</sup>Department of Chemistry, Bharati Vidyapeeth Deemed University, Pune-411038. MS (India) <sup>2</sup>Abasaheb Garware College, University of Pune, Pune, MS (India)

**Abstract:** Cobalt promoted (loading 0.5, 5, and 10%) on molybdenum-silica mixed oxide catalysts were prepared by sol-gel method using ammonium heptamolybdate (AHM) and ETS-40 (silica source). Synthesized gel was dried at room temperature and calcined at 773K. The resultant materials were characterized by XRD, TGA, FT-IR, SEM-EDX, and acidity measurement techniques. The catalytic activity of these materials was studied over oxidation of cyclohexanol using  $H_2O_2$  as oxidant. The mild reaction conditions, easy workup and short reaction times are responsible for the better conversion and selectivity. **Keywords:** mixed oxide, sol gel, calcination, cyclohexanol, oxidation.

### Introduction

The molybdenum oxide as such or in supported form is widely used as catalysts in number of reactions. Particularly, molybdenum oxide supported on silica is a well-known solid acid catalyst which possesses both strong Lewis and Bronsted acidity<sup>1,2</sup>. The oxidation of alcohols to corresponding ketones is of significant importance in the fine chemicals and pharmaceutical industries. Supported molybdenum oxide catalysts are widely used in various catalytic processes<sup>3-7</sup>. These catalysts are normally obtained by impregnating the catalytically active molybdenum oxide species on an inorganic oxide support for the purpose of increasing the catalytic activity, selectivity and life of the catalysts.

Dongare et al reported that molybdenum promoted silica exhibits strong acidity and excellent catalytic properties for various organic synthesis and transformation reactions in the liquid phase<sup>8</sup>. There are several methods reported in the literature for the synthesis of metal-supported catalysts. Ion exchange results in small metal particles at low metal loading<sup>9,10,11</sup>. Impregnation can be termed wet or dry, depending whether the volume of the impregnating solution is greater than or equal to the pore volume of the support.

Oxidation of cyclohexanol to cyclohexanone is a significant step in the syntheses of adipic acid and caprolactam. These intermediates are important in the manufacture of nylon 6 and nylon 66 and also as plasticizers and food additives<sup>12</sup>. Commercially cyclohexanol and cyclohexanone are oxidized to adipic acid using copper and vanadium salts dissolved in excess amount of HNO<sub>3</sub> as catalysts<sup>13</sup>. In order to produce fewer by-products and develop more environmentally friendly procedures to oxidize cyclohexanol, a variety of metal catalysts have been investigated<sup>14-16</sup>. This has included precious metals<sup>17,18,19</sup>.

The most common methods still use toxic, corrosive and expensive oxidants such as chromium(VI) and manganese complexes, stringent conditions of high pressure or temperatures and use of strong mineral

acids<sup>20,21a,21b</sup>. Oxidation over metal catalysts using eco-friendly oxidants such as  $H_2O_2$  and  $O_2$  are preferred now for environmental and economical benefits. The heterogeneous oxidation of alcohols with an environmentally suitable oxidant,  $H_2O_2$ , is quite an interesting objective for the industrial fields.

Alan L. Chaffee et al studied that preparation and characterization of mesoporous silica supported cobalt oxide as a catalyst for the oxidation of cyclohexanol. They reported that lowest cobalt content exhibited highest catalytic activity due to the better accessibility of the reactants to the active sites<sup>24</sup>.

The molecular structure of molybdenum oxide on different supports has also been extensively studied by various techniques over the past decade. Considering the importance of the catalyst, we have prepared Co (II) supported on  $MoO_3$  /SiO<sub>2</sub> composites by sol-gel method.

The present study deals with preparation and characterization of cobalt promoted solid acid catalyst having molybdenum silica support using the cobalt acetate as a precursor via sol gel method. The characterization of surface properties of these catalysts by using various spectral techniques and catalytic activity of these catalysts for the oxidation of cyclohexanol has been investigated by using environmental friendly hydrogen peroxide  $(H_2O_2)$  as oxidant.

#### Experimental

#### Materials

XRD was carried out on a Rigaku Miniflex X-ray diffractometer with Cu K $\alpha$  radiation source ( $\lambda$ = 1.54178 A<sup>0</sup>) scanning rate of 0.02 <sup>0</sup>/s was applied to record the pattern in the 2 $\Theta$  range of 20- 80<sup>0</sup>. The FT-IR spectra obtained with a Nicolet iD5 spectrometer (4000-400 cm<sup>-1</sup>) using KBr pellet technique. Thermogravimetric analysis (TGA) was conducted on a Shimadzu (Simultaneous DTA-TGA System, DTG-60) under nitrogen flow and then it was heated up at a rate of 10 K/min to 1100<sup>0</sup>C. Scanning Electron Microscope image and EDX (JEOL-JSM 6360A) were obtained at accelerating voltage 20 KeV. Sample were deposited on a sample holder with an adhesive carbon foil and sputtered with gold. Acidity of the prepared catalysts was tested by using titrimetric method.

#### Synthesis of Co/Mo/SiO<sub>2</sub> catalysts

Co (II) supported on Mo/SiO<sub>2</sub> catalyst was prepared by sol-gel process to obtain the catalyst with high surface area as well as for uniform distribution of Co/Mo on silica support. Ethylsilicate-40 (CAS Registry No. 18954-71-7) was used as a silica source for the first time because of its higher silica content as well as low cost as compared to tetraethyl orthosilicate, which is generally preferred silica source for sol-gel synthesis of silica support in catalysis<sup>16</sup>. 250 g of ethylsilicate-40 was mixed with 250 mL of dry isopropyl alcohol under constant stirring. 5.225 g of cobalt acetate was dissolved in 100 mL of isopropyl alcohol and was added to ethyl silicate solution under vigorous stirring. 20.31 g of Ammonium Heptamolybdate (AHM) was dissolved in 100 mL of water and was added to the above solution under constant stirring. A viscous gel was obtained which was further stirred for another two hours and was kept overnight. A transparent solid product was obtained which was air dried and heated in an oven at 110°C for 12 hours. The product was further calcined at 450°C for 12 hours.

#### Catalytic oxidation of cyclohexanol

A typical oxidation reaction was performed in a round bottomed flask fitted with water cooled condenser using 30% aqueous  $H_2O_2$  as the oxidant. To the mixture of Cyclohexanol (1mmol),  $H_2O_2$  (10mmol), and Acetonitrile (10ml), the Co/Mo/SiO<sub>2</sub> (10%) catalyst was added in the flask. The reaction mixture was heated at a constant temperature of 80<sup>o</sup>C with continuous stirring. The progress of the reaction was monitored by making use of TLC and GC equipped with a flame ionization detector (FID) and a capillary column. Samples of the reaction mixture were withdrawn at regular time intervals and in each case the catalyst was filtered off or removed by centrifugation prior to the GC examination. Products were identified by comparing them with authentic samples and further confirmed by GC (Shimadzu GC-2014), while substrate conversion as well as product yield was determined.

#### **Results and Discussion**

#### **FT-IR Analysis:**

The FTIR spectra of the Co/Mo/SiO<sub>2</sub> calcined at  $500^{\circ}$ C for 5 h are shown in fig.1. A strong and wide absorption band, caused by the stretching vibration of the O-H bond, appears at 3488 cm<sup>-1</sup> (Fig.1).



Figure 1: FT-IR spectra of A) MoO<sub>3</sub>/SiO<sub>2</sub>, B) Co(0.5%)/MoO<sub>3</sub>/SiO<sub>2</sub>, C)Co(5%)/MoO<sub>3</sub>/SiO<sub>2</sub>, D) Co(10%)/MoO<sub>3</sub>/SiO<sub>2</sub>

However a weak absorption band appears at 1611.54 cm<sup>-1</sup> due to flexural vibration of the O-H bond. Absorbed water and hydroxyl on the sample surface contribute to these absorption bands. A strong absorption band, caused by the vibration of the chemical bond of Si-O-Si, is present at approximately 1085.50 cm<sup>-1</sup>. This condition also indicates a certain interaction between molybdenum and supported matrix. However, in the 10% Co/Mo/SiO<sub>2</sub> sample, the vibration of the chemical bond of Si-O-Si moves toward the low intensity and causes a strong absorption band observed at around 1084cm<sup>-1</sup>. Same effect was observed in 0.5 and 5% samples. This indicates the interaction between cobalt and molybdenum species. After loading of Co on Mo/SiO2, some new features observed in Fig.1.The band due to MoO<sub>3</sub> (950cm<sup>-1</sup>) did not appear exactly at the usual frequency in the case of low loading molybdenum. This may be due to the interference of silica. This interference was vanished, after increasing Mo loading. The simultaneous and consecutive increase in the bands assigned at 990, 860 and 650 cm<sup>-1</sup> may be due to the decomposition of Mo=O=Si bonds and the formation of MoO<sub>3</sub>. 10% Co/Mo/SiO<sub>2</sub> exhibits two additional bands at 660 and 570 cm<sup>-1</sup>. These latter bands can be ascribed to Co- O vibrations in the cobalt oxide lattice<sup>25,26</sup>.

#### **XRD** analysis:

The X-ray powder diffraction patterns of  $Co/Mo/SiO_2$  calcined at  $500^{\circ}C$  were measured. XRD was utilized to analyze the crystallite size (Fig. 2). X-ray diffraction is the powerful tool to study the phase composition.



Figure 2: XRD graph of A) Mo/SiO<sub>2</sub>, B) Co (0.5%), C) Co (5%), D) Co (10%)

The result indicates that slight variations in the spectrum of Co/Mo/SiO<sub>2</sub> (0.5, 5, 10%) compared with  $Mo/SiO_2^{15}$ . The Mo/SiO<sub>2</sub> catalyst dispersion characteristic peak appears at approximately at  $2\theta$ =27.3°, which is the characteristic peak of MoO<sub>3</sub>. The characteristic peak of the Co/Mo/SiO<sub>2</sub> dispersion appears at approximately  $2\theta$ =23°. This peak is almost unchanged compared with undoped SiO<sub>2</sub>. However, the peak of the Co/Mo/SiO<sub>2</sub> catalyst was slightly sharper than Mo/SiO2. The resulting diffraction pattern can be matched with a crystal structure database and the phases present can be identified. CoMoO<sub>4</sub> phase is observed at 33.5° and 39.1° (JCPDS file no. 21-0868). As we increase the Co content then intensity of the band also increases.

From a more detailed analysis of the XRD data it is also possible to estimate the average crystallite size using the Debye-Scherrer equation: the FWHM (full width at half maximum) is inversely proportional to the crystallite size. Table 1 showed the crystallite size was around 30 nm in all compositions of the catalysts which confirm the formation of nanosized crystalline catalysts.

Sr. No.	Catalyst	Crystallite Size (nm)	Acidic strength (mmol/g)
1.	Mo/SiO <sub>2</sub>	30.82	1.843
2.	Co/Mo/SiO <sub>2</sub> (0.5%)	29.33	2.736
3.	Co/Mo/SiO <sub>2</sub> (5%)	20.58	2.984
4.	Co/Mo/SiO <sub>2</sub> (10%)	30.50	3.421

Table 1. Comparative data of XRD, and acidic strengths of prepared nanoceria catalysts.

#### SEM and EDX analysis:

The SEM images and EDX analysis of the prepared mixed oxide catalysts were carried out and the results were shown in Figure 3. EDX analysis showed the presence of Co, Mo, and Si in the synthesized catalysts. The scanning electron micrograph analysis depicted the cubic nature of the particles with mean particle size of about 500 nm.



#### Figure 3: SEM images Co/Mo/SiO<sub>2</sub>

This image showed global and uniform particles which are coherent together. The EDX data of  $Co/Mo/SiO_2$  in Fig.3 shows two intense and prominent peaks of Molybdenum and silica and other comparatively smaller peak of cobalt at 6.9 keV. These results confirmed the existence of Co atoms in the solid catalysts. Therefore, it may be concluded that Co ions are uniformly dispersed among the crystallites of molybdenum and silica.

#### Acidity measurement:

Titrimetric experiments were carried out to determine the acid strength of the  $MoO_3/SiO_2$  catalyst. The  $MoO_3/SiO_2$  catalyst showed the lowest acid strength at 1.843 mmol/g indicating the presence of weaker acidic strength. Addition of metal content to the  $MoO_3/SiO_2$  support by sol gel technique increased the acidic strength of the catalyst which was given in table 1, with respect to the acid strength. The catalyst with 10% Co loading on  $Mo/SiO_2$  catalyst showed highest acid strength (3.421 mmol/g).

#### Thermal analysis:

TGA data of all the catalysts were depicted in fig. 4. In the 0.5% Co/Mo/SiO<sub>2</sub> the step I start from 29.57 -170.14<sup>o</sup>C which showed 12.288% weight loss due to vaporization of physically adsorbed water. Above 170.14<sup>o</sup>C and upto 547.21<sup>o</sup>C gradually weight loss was observed. The weight loss in this region can be considered as a result of dehydroxylation of hydroxyl group present in the catalyst. In step III corresponds to decomposition of AHM via intermediates into MoO<sub>3</sub>. In case of 5% Co/Mo/SiO<sub>2</sub>, temperature start with 34.55 - 207.02<sup>o</sup>C where weight loss observed due to loss of adsorbed water and silica precursor, which extends upto 508.97<sup>o</sup>C. After 508.97<sup>o</sup>C there is formation of MoO<sub>3</sub> from AHM to various intermediates. In case of 10% Co/Mo/SiO<sub>2</sub> the heating upto 421.28<sup>o</sup>C, the major weight loss was occurred i.e. 24.165%. The weight loss in this region can be considered as a result of loss of water and decomposition of MoO<sub>3</sub>.



Figure 4: TGA curves of (0.5%, 5%, and 10%) Co loading on Mo/SiO<sub>2</sub>

The result showed that after calcination temperature  $i.e.500^{\circ}$ C the remarkable weight loss occurs. Therefore utilizing 500°C as the catalyst calcination temperature in the present study was suitable.

#### Catalytic activity:

A typical oxidation reaction of cyclohexanol to cyclohexanone was carried out by using  $H_2O_2$  as oxidant over Co/Mo/SiO<sub>2</sub> mixed oxide catalyst. The reaction studied at various parameters such as temperature, time, solvent and amount of catalyst.

#### Study of the effects of various reaction parameters

#### **Effect of Temperature:**

The effect of the reaction temperature was studied by adding the Co/Mo/SiO<sub>2</sub> (10%) catalyst to the reaction mixture involving cyclohexanol (1mmol), aqueous  $H_2O_2$  (10mmol) and 10 ml Acetonitrile. The oxidation reaction was carried out at various temperatures 60°, 80°, and 100°C respectively for 4 hrs and then progress of reaction was monitored by TLC and GC. At 60°C, the conversion of cyclohexanol was 70%. The conversion increases considerably when the temperature of the reaction was increased to 80°C. It showed increase in selectivity to 100% and also conversion of cyclohexanol to 100%. As temperature increases further to 100°C, the conversion was decreased as compared to 80°C. Overall the reaction was optimized at 80° C and for further study the temperature was kept constant which was shown in table 2.

Temperature	% Conversion of Cyclohexanol	% Selectivity of Cyclohexanone
60	70	84
80	99.95	100
100	99.95	100

Table 2: Effect of temperature	on oxidation	of cyclohexanol
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Reaction condition; catalyst (10% Co/Mo/SiO<sub>2</sub>)-0.2g, Reaction Time- 4h, Solvent-Acetonitrile (10ml), Cyclohexanol: H<sub>2</sub>O<sub>2</sub> ratio- 1:10

#### Effect of Cobalt loading on Mo/SiO<sub>2</sub> Catalyst for cyclohexanol oxidation:

It can be seen that the 10% Co/Mo/SiO<sub>2</sub> sample exhibited the highest activity of the catalysts examined. This is more interesting and active due to higher cobalt loading on Mo/SiO<sub>2</sub> (Fig. 5). Aggregation of cobalt oxide particles, mostly on the external surface indicated that much of the cobalt was available for the reaction. To check the effect of cobalt oxide on catalytic activity, the same reaction was carried out with Mo/SiO<sub>2</sub> and also in absence of any solid substrate. In both cases the conversion was negligible after 24 h.



Figure 5: Effect of Cobalt loading on Mo/SiO2 Catalyst for cyclohexanol oxidation

Reaction condition; catalyst (Co/Mo/SiO<sub>2</sub>)-0.2g, Reaction Time- 4h, Cyclohexanol:  $H_2O_2$  ratio- 1:10 Temperature-80<sup>0</sup>C

#### Effect of Solvent:

The reaction was carried out using benzene, acetonitrile and DMSO solvents to improve conversion of cyclohexanol and selectivity of cyclohexanone shown in table 3. The maximum cyclohexanone selectivity i.e. 100% was achieved with acetonitrile. By changing the solvent resulted in the lowering of cyclohexanone selectivity. The DMSO showed higher selectivity (87.45%) but the conversion was less (37.25%). With benzene the conversion (90%) as well as selectivity also increased but less than the acetonitrile used as solvent. The selectivity of cyclohexanone also depends on the type of solvents used for the reaction. As DMSO was more polar than acetonitrile but still results are good with acetonitrile. It might possible that partial decomposition of  $H_2O_2$  was more in acetonitrile than DMSO<sup>27</sup>.

Table 3:	Effect of	Solvent	on oxidation	of c	vclohexanol

Solvents	% Conversion Cyclohexanol	% Selectivity of Cyclohexanone
DMSO	37.25	87.44
Acetonitrile	99.95	99.99
Benzene	99.83	99.99

Reaction condition; catalyst (10% Co/Mo/SiO<sub>2</sub>)-0.2g, Reaction Time- 4h, Cyclohexanol: H<sub>2</sub>O<sub>2</sub> ratio- 1:10 Temperature-80<sup>o</sup>C

#### Effect of oxidant ratio:

The reaction of oxidation of cyclohexanol to cyclohexanone was carried out at various amounts of oxidant  $H_2O_2$ . The results are shown in figure 6 in the form of bar diagram. The reaction were carried out under previously optimized conditions and changing the volume of  $H_2O_2$  from 5 mmol to 20mmol while keeping the substrate constant. Without oxidant only 25% conversion was observed but in the presence of oxidant higher conversion was observed. The conversion increases from 80 to 100% upon changing the  $H_2O_2$  amount from 5 to 20 mmol. Therefore 10mmol oxidant was selected for the oxidation reaction.



Figure 6: Effect of amount of oxidant on conversion of cyclohexanol.

#### Conclusion

Successfully synthesized cobalt supported on molybdenum (VI)/ silica by sol-gel method and formation of catalysts confirmed by FT-IR, XRD, SEM, EDX techniques and investigated their performance as catalysts in the oxidation of cyclohexanol. It was indicated that  $Co/Mo/SiO_2$  (10%) has been successfully utilized for the catalytic oxidation of cyclohexanol with eco-friendly hydrogen peroxide as an oxidant. Important factors which affect the conversion as well as selectivity were temperature, reaction time, solvents and amount of oxidant. At optimum conditions the conversion of cyclohexanol and selectivity was 100%. In addition, the commercial availability and low cost of the reagent, high yields of the products, mild reaction conditions, easy workup and short reaction times are noteworthy advantages of this method.

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