



STUDY OF STRUCTURAL AND CATALYTIC PROPERTIES OF COPPER SUPPORTED MIXED OXIDE CATALYSTS

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ABSTRACT

To explore structural and thermal stability of Cu/MoO₃/SiO₂, these mixed oxide systems were subjected to thermal treatments from 500^oC to 700^oC and were examined by FT-IR, TGA and X-ray diffraction techniques. Copper based molybdenum supported silica oxide catalyst was prepared by using tetraethyl orthosilicate with different loading of copper on MoO₃/SiO₂ catalyst such as 1-20wt% by sol-gel method. These catalysts were showed higher stability with nanocrystalline nature. We have also studied the catalytic activity of the prepared catalyst with oxidation of toluene with green oxidant hydrogen peroxide.

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INTRODUCTION

Solid-acid catalysts are generally categorized by their Brønsted and/or Lewis acidity, the strength and number of these sites, and the morphology of the support. Solid acid catalysts are important for the simplicity and versatility of process engineering and catalyst regeneration, decreasing reactor, plant corrosion problems, environmental safe disposal and industrially important reaction.

MoO₃/SiO₂ mixed oxide catalyst is well known heterogeneous acid catalyst, it possess both strong Lewis and Bronsted acid sites [Auroux *et al* 1990; M. Kawai *et al* 1981]. In case of dehydrogenation, dehydration, isomerization and transformation, supported molybdenum oxide has much attraction for use as solid acid catalysts. [C.C. Williams *et al.* 1991; M. Carbucicchio *et al.* 1980; K. Bruckman *et al.* 1993; T. Ono *et al.* 1987 ; X. Ma *et al.* 2004]. Synthesis of 1, 3-dioxolanes, using molybdenum containing heteropoly acid has been studied and proved to be very effective catalyst. [G. Li *et al.* 2005].

Now a days, there have been attracted much attention on the interaction of metal oxide and oxide as support, because supported metal oxide system has wide applicable in catalysis. Transition metals are widely used as supported oxide for various catalytic reactions. For petroleum hydrotreating reaction, molybdenum supported catalyst constitutes the most important catalysts.

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Molybdenum oxide is active compound often employed on supported oxide, i.e alumina, silica, titania or vanadium in many catalytic reactions. The efficiency of supported molybdenum oxide catalysts depends on dispersion of active phase which influenced by the method of preparation of catalyst and nature of supported oxide [Komandur V. R Chary *et al.* 2001].

In 2000, Benjaram M. Reddy *et al.* were studied the influence of support on the dispersion and the effect of calcinations temperature of supported oxide species. The catalyst were subjected to thermal treatments from 773 to 1073K and were examined by XRD, FT-IR, and XPS techniques.[Benjaram M. Reddy *et al.* 2000]

H. Nayebyzadeh *et al.*, investigated, the effect of calcination temperature on the synthesis of 20 mol % SrO/S-ZrO₂ was examined by solvent-free method. Strontium oxide promoted sulfated zirconia calcined at 500 °C temperature showed the highest percentage of tetragonal phases of zirconia.[H. Nayebyzadeh *et al.* .2013]

Researchers were reported about physicochemical surface and catalytic properties of NiO supported materials and effects of extent of NiO-loading, calcination temperature on its physicochemical surface and catalytic properties have been investigated. [S. A. El-Molla *et al.* 2009]

Solid acid catalysts were used as catalyst for different types of reactions. Cu –Mn oxide catalyst was selective for oxidation of toluene [Z. Ye, J.M. Giraudon *et al.* 2018]. Here, Manganese oxides were employed as catalyst in the selective oxidation of toluene to benzoic acid. Author gave 39% conversion of

toluene and 93% selectivity of benzoic acid was achieved [Xiaoqiang Li *et al.* 2006]. V_2O_5/TiO_2 catalyst was examined in the catalytic performance for the vapor phase oxidation of toluene to benzoic acid [Jun Miki *et al.* 1996].

To our knowledge there is no report on study of thermal properties and its catalytic activity on solid acid catalyst $Cu/MoO_3/SiO_2$ synthesized by sol-gel method by using TEOS and metal salts. These catalysts were characterized by FT-IR, TGA and x-ray diffraction techniques to study structural and thermal properties.

MATERIAL

Merck grade chemicals were used for synthesis of catalyst, tetraethyl orthosilicate (TEOS), isopropyl alcohol (IPA) and ammoniumheptamolybdate(AHM) as starting materials. Analytical grade metal salts i.e., copper acetate was used. All A.R. grade chemicals were used for synthesis.

METHOD

MoO_3/SiO_2 catalysts with varying copper oxide molar concentrations (1, 10 and 20 wt. %) was prepared. In a typical synthesis procedure, 20 wt. % MoO_3/SiO_2 mixed oxide catalyst was synthesized by dissolving 14.11 g AHM in 40 ml distilled water at about 80°C. This hot solution was added drop wise to the dry IPA solution of TEOS-40 with constant stirring. The resultant transparent greenish gel was air dried and calcined at 500 °C in muffle furnace for 10 h. Similarly varying concentration of catalysts with 1, 10 and 20 wt. % copper oxide loadings were prepared.

Apparatus and techniques

The synthesized catalysts were extensively characterized by various spectroscopic and non-spectroscopic methods including FT-IR, XRD, TGA techniques. The FT-IR spectra were recorded on Thermo Nicolet iS5IR instrument at ambient conditions using KBr pellets with a resolution of 4 cm^{-1} in the range of 4000-400 cm^{-1} and with 32 scans. The crystallite size of the catalyst was calculated by XRD using RigakuMiniflex diffractometer equipped with a Ni filtered $Cu K\alpha$ line radiation source ($\lambda = 1.54178 \text{ \AA}$) was used to recorded. The range of 2 θ angle is 20-80°.

Thermal analysis (TGA) of the prepared catalysts was performed on as a instrument TG/DTA-60Shimadzu instrument. The samples were heated from ambient temperature to 900°C under a nitrogen flow at flow rate of 20 $mL \text{ min}^{-1}$ and heating rate of 10 $K \text{ min}^{-1}$.

RESULTS AND DISCUSSION

FT-IR investigation of MoO_3/SiO_2 support and Copper loaded on MoO_3/SiO_2 solids calcined at different calcination temperatures

Fig. 1, 2, 3 and 4 demonstrates FT-IR spectrum of $Cu/MoO_3/SiO_2$ catalyst calcined at different temperatures 500°C, 600°C and 700°C has been recorded and the observed IR bands are presented in the Table 1. The IR band of $Mo=O$ in crystalline MoO_3 appears at 956 cm^{-1} due to stretching vibration mode in all the samples at various calcination temperatures. As the calcination temperature increased from 500°C to 700°C peaks were sharper. Frausen *et al.*, reported the formation of $ZrMoO_3$ compound by heating ZrO_2 and MoO_3 together at 820 K, which showed the IR bands at 980,

920 and 800 cm^{-1} [T. Frausen *et al.* 1976]. The FT-IR results in the present study also revealed the formation of $Cu/MoO_3/SiO_2$ catalyst and whose concentration was found to dependent on the calcination temperature employed. An interesting observation to be mentioned here is that calcination temperature does not affect the crystalline nature as well as intensity of peaks. The presence of copper modification was confirmed in spectrum between 400-750 cm^{-1} which was corresponding to stretching vibration of CuO .

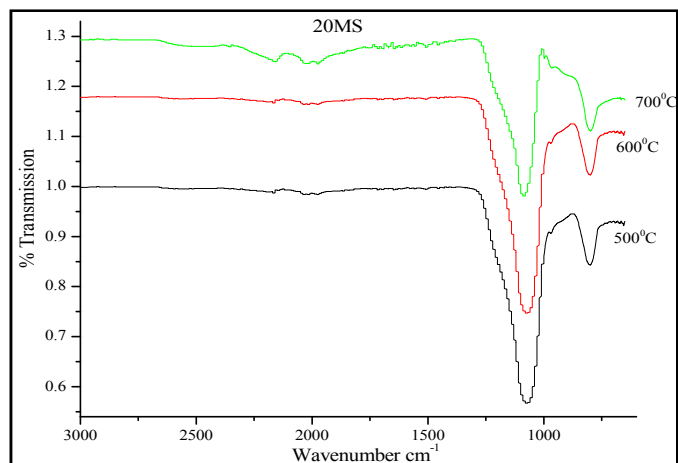


Fig 1 FT-IR spectra of 20 wt.% MoO_3/SiO_2 catalyst at different temperatures

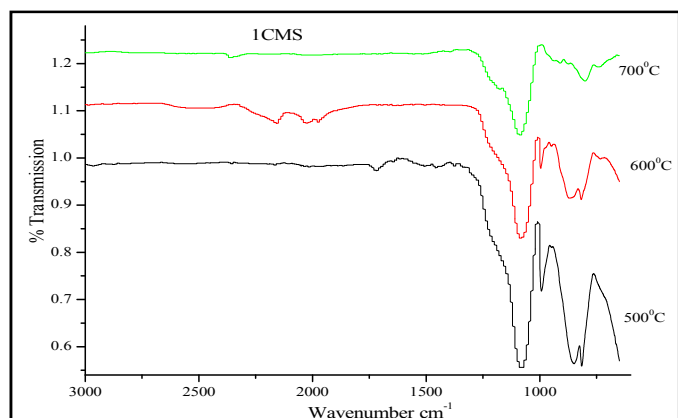


Fig 2 FT-IR spectra of 1 wt.% $Cu/MoO_3/SiO_2$ catalyst at different temperatures

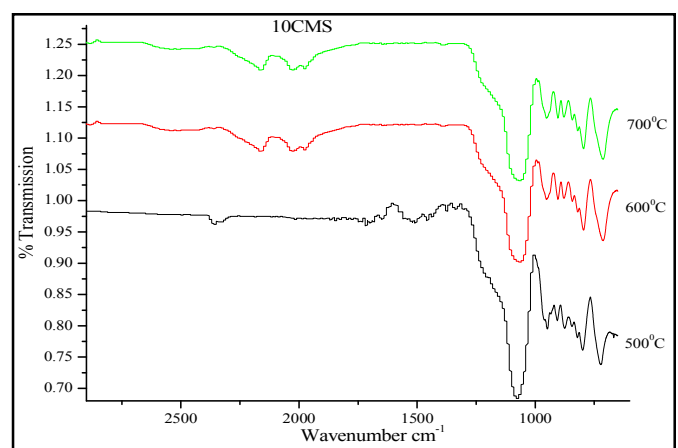


Fig 3 FT-IR spectra of 10 wt. % $Cu/MoO_3/SiO_2$ catalyst at different temperatures

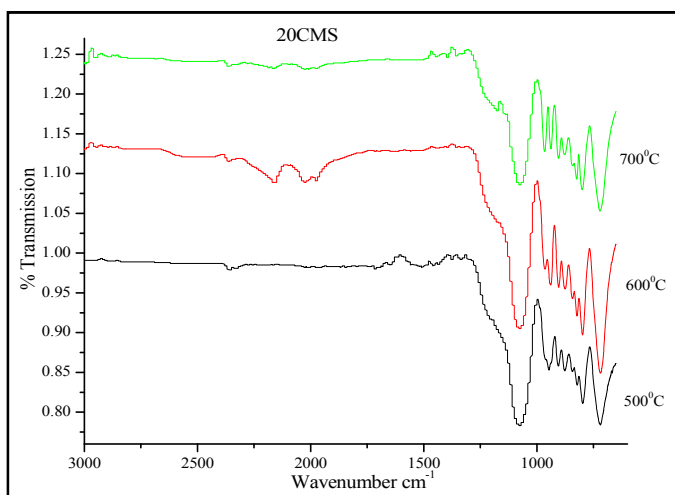


Fig 4 FT-IR spectra of 20 wt. % Cu/MoO₃/SiO₂ catalyst at different temperatures

The rest of the peaks were also similar with each other which indicated the formation of pure phase of CuO. Water from the environment gets adsorbed on the copper oxide surface creating two small peaks at 920 and 1020 cm⁻¹, as we increase the amount of Cu in the catalyst, the intensity of these peaks gets reduced.

XRD analysis of MoO₃/SiO₂ support and Copper loaded on MoO₃/SiO₂ solids calcined at different temperatures

The X-ray diffraction (XRD) patterns were studied for the identification of the crystalline phase present in prepared catalysts. XRD patterns of sol-gel prepared MoO₃/SiO₂ and various wt. % loading of Cu (1,10,20 wt.%) on MoO₃/SiO₂ calcined at various temperature (500, 600,700°C) catalysts were shown in fig. 5, 6, 7 and 8. The XRD studies reveals that the catalyst surface is heterogeneous. All the diffraction patterns exhibit broad peaks suggesting that the prepared mixed oxide catalysts are nanocrystalline materials. The XRD phases present in the prepared mixed oxide catalysts were identified with the help of JCPDS (Joint Committee on Powder Diffraction Standards) data files.

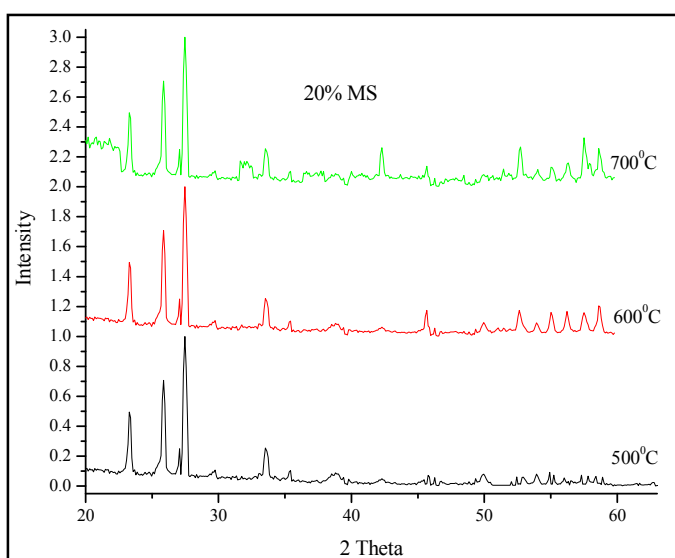


Fig 5 XRD spectra of 20 wt. % MoO₃/SiO₂ catalyst

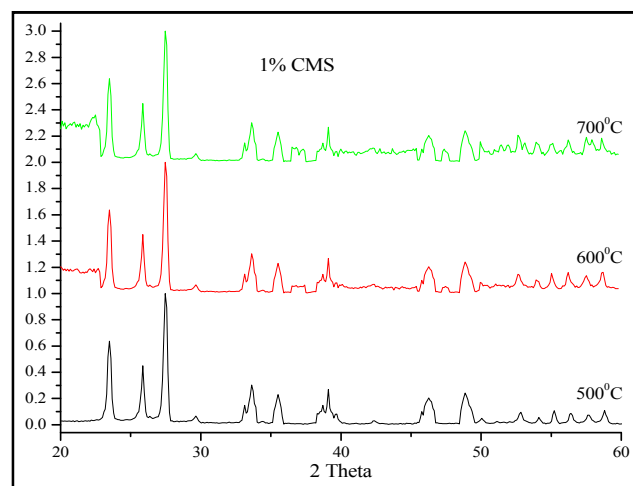


Fig 6 XRD spectra of 1 wt. % Cu/MoO₃/SiO₂ catalyst

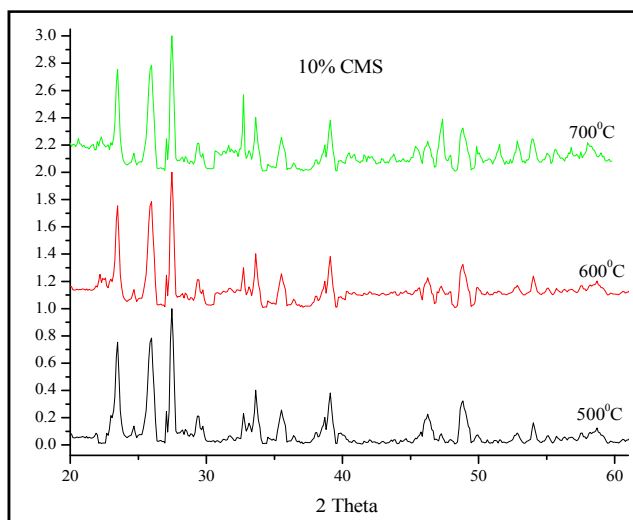


Fig 7 XRD spectra of 10 wt. % Cu/MoO₃/SiO₂ catalyst

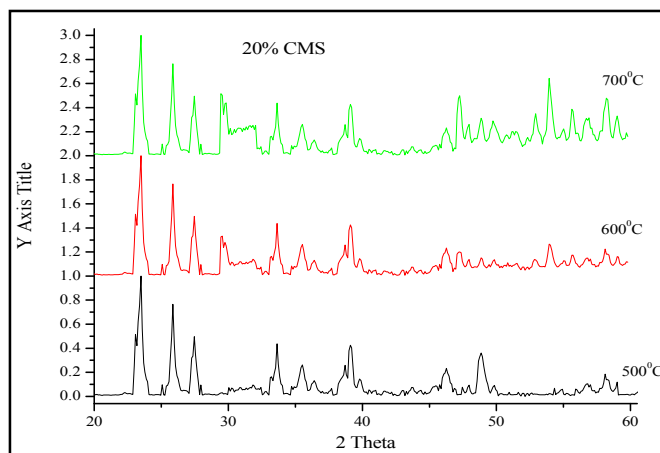


Fig 8 XRD spectra of 20 wt. % Cu/MoO₃/SiO₂ catalyst

The above figures indicated that with increase in calcination temperature after loading copper oxide content over MoO₃/SiO₂ support, the intense peak slightly reduces and broadening was observed. With increasing temperature, catalyst showed more and more sharp peaks. At 500°C temperature, all the prepared Cu/MoO₃/SiO₂ catalysts exhibit clear formation of CuO and α-MoO₃ phases with decrease in crystallite size and same also observed at 600°C and 700°C.

The influence of calcination temperature on crystallite size was presented in the table 1. All the peaks become stronger and

sharper and decrease the crystallite size with increasing the calcination temperature.

Table 1 Effect of calcination temperature on crystallite size of prepared catalysts

Compound	Temperature	Crystallite size
20 wt. % MoO ₃ /SiO ₂	500 ^o C	79.9
	600 ^o C	39.65
	700 ^o C	37.47
1wt. %Cu/ MoO ₃ /SiO ₂	500 ^o C	52.4
	600 ^o C	40.48
	700 ^o C	24.07
10wt. %Cu/ MoO ₃ /SiO ₂	500 ^o C	50.87
	600 ^o C	48.3
	700 ^o C	30.65
20wt. %Cu/ MoO ₃ /SiO ₂	500 ^o C	89.8
	600 ^o C	38.55
	700 ^o C	37.51

This can be ascribed by more agglomerated crystals formation. From the table data, it was confirmed that all the prepared mixed oxide catalysts were nanosized having crystallite size ranges between 24-79 nm.

Thermogravimetric analysis (TGA)

In order to study the thermal stability of the prepared mixed oxide catalysts thermal analysis was carried out. The prepared catalysts were subjected to TGA analysis before calcination. Thermal analysis (TGA) of prepared catalysts was performed in nitrogen atmosphere at a heating rate of 100 C/min and 0.01 scan rates in the range of ambient to 800^oC. The TGA graphs of 20 wt.% MoO₃/SiO₂ and 10 wt. % Cu/MoO₃/SiO₂ as shown in fig. 9 and 10.

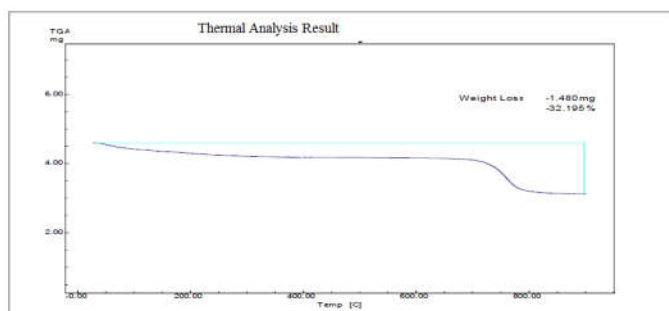


Fig 9 TGA graph of 20 wt. MoO₃/SiO₂catalyst

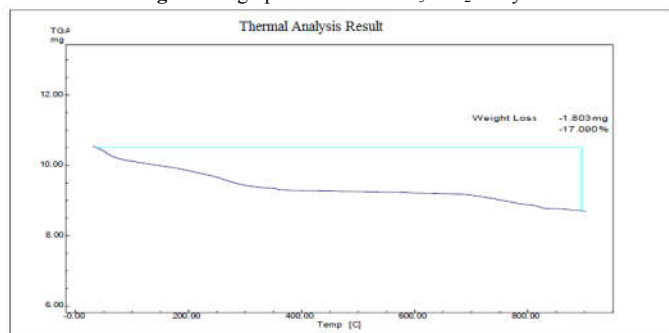


Fig 10 TGA graph of 10 wt.% Cu/MoO₃/SiO₂catalyst

From the TGA profiles of the representative catalysts, it was clear that the weight loss found due to physically adsorbed water and decomposition of the residual organics and nitrates was finished below 500^oC temperature. Hence copper supported catalysts were calcined at 500^oC contain only metal oxides without any impurity. Up to 800^oC no further weight loss was observed which confirmed the thermal stability of prepared catalysts. Most importantly, the TGA results suggest that the optimum temperature for calcination of prepared all

the catalysts were 500^oC where no weight loss was observed. Therefore, 500^oC temperature was used for the calcination temperature and thermal stability of the prepared catalysts.

By comparing the weight loss of two samples (20 wt.% MoO₃/SiO₂ catalyst showed major weight loss upto 32.195% while other catalysts 10 wt. % Cu/MoO₃/SiO₂ gives 17.090% weight loss. The percent weight loss of MoO₃/SiO₂ of Cu/MoO₃/SiO₂ was showed in below table 2.

Table 2 Observed percent weight loss of prepared catalysts

Sr. No	Catalyst	Weight loss (%)
1.	20 wt.% MoO ₃ /SiO ₂	32.195
2.	10 wt. % Cu/MoO ₃ /SiO ₂	17.090

Catalytic activity

Oxidation reaction was carried out in a two necked round bottom flask fitted with water condenser kept in a thermostatic oil bath at a temperature of 120^oC. The catalyst was activated before its use in the oxidation reaction. To the mixture of toluene (1mmol), 30% H₂O₂ (10 mmol) and 15 wt.%Cu/MoO₃/SiO₂ catalyst (0.4 g) was used for the reaction. Reaction was monitored by GC and samples of the reaction were withdrawn at regular time intervals. Products were identified by comparing them with authentic sample and further confirmed by GC (Shimadzu). Heterogeneous catalyst can be easily removed by simple filtration of reaction mixture and then reactivated by simple washing with solvent and then reused without noticeable loss of reactivity.

Influence of reaction parameters

The catalytic activities of Copper loaded on MoO₃/SiO₂ solid catalyst samples were determined by using toluene conversion at varied reaction temperatures, the catalytic reaction being conducted in an oil bath under solvent free condition.

The effect of the reaction temperature was studied by adding the CMS (15 wt. %) catalyst to the reaction mixture involving toluene (1 mmol), 30% H₂O₂ (10mmol) under solvent free condition. Temperature showed drastic effect on the course of the reaction, and 29.91% of the substrate was converted when the reaction was carried out at 100^oC. The conversion increases considerably when temperature of reaction mixture was increased to 120^oC. Results showed increase in selectivity, highest selectivity towards benzaldehyde (93.56%) as major product and other byproduct benzoic acid was obtained. There was not much change in conversion with further increase in temperature. The conversion decreased below reflux temperature (100^oC). Hence 120^oC was found to be suitable for the conversion of toluene. Results indicated that catalysts were active towards oxidation and proved that CMS catalysts were catalytically active and can be used to study different types of acid catalyzed reactions.

CONCLUSION

The FTIR results in the present study revealed the formation of Cu/MoO₃/SiO₂ catalyst and whose concentration was found to dependent on the calcinations temperature employed. XRD data indicated that all the peaks become stronger and sharper and decrease the crystallite size with increasing the calcinations temperature. At lower calcinations temperatures copper interacts strongly with molybdenum-silica oxide support. In thermogravimetric analysis 20% MoO₃/SiO₂ catalyst showed major weight loss upto 32.195% while other

catalysts 10% Cu/MoO₃/SiO₂ gives 17.090% weight loss. In this work, catalytic activity was investigated on the oxidation of toluene with 30% H₂O₂. The results proved that sol-gel synthesized Cu supported on MoO₃/SiO₂ solid acid catalyst (CMS) was very efficient and stable for oxidation of toluene and found suitable catalyst for different types of acid catalyzed reactions. Under the similar reaction conditions, synthesized 15 wt.% of CMS catalyst gave maximum conversion as well as selectivity.

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