

Influence of nature of support on the catalytic activity of supported molybdenum-oxo species in benzyl alcohol conversion

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Abstract

Supported catalysts containing 15 wt.% of molybdenum have been prepared by the incipient wetness impregnation method. CaO, MgO, Al₂O₃, Zr(OH)₄ and Al(OH)₃ have been used as supports for the preparation of supported Mo catalysts. Characterisation of all the materials prepared has been carried out through BET surface area measurement, X-ray diffractometry and FT-IR spectroscopy. Catalytic activity measurements have been carried out with reference to structure-sensitive benzyl alcohol conversion in the liquid phase. The percentage conversion of benzyl alcohol to benzaldehyde and toluene varied over a large range depending on the support used for the preparation of catalysts, indicating the importance of the support on catalytic activity of Mo catalysts. Al(OH)₃ has been found to be the best support for molybdenum among all the supports used. Support–metal interaction (SMI) has been found to play an important role in determining the catalytic activity of supported catalysts.

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1. Introduction

Even though MoO₃ as such is a very well-known catalyst, due to its instability at higher temperature, it is often used in a supported form. Supported molybdenum oxide catalysts have been used in petroleum, chemical and pollution control industries [1]. Earlier alumina, TiO₂, ZrO₂, SiO₂ and MgO were used as supports for molybdenum oxide by various authors and studied their various physico-chemical and catalytic properties [2–6]. It is a well-known fact that, in several reactions, catalysts based on multicomponent oxides exhibit a better performance than when component oxides were used separately [7]. The catalytic activity of a supported catalyst depends not only on the ion supported but also on the support. Even though various parameters are collectively responsible for the unique catalytic activity of the catalysts, SMI plays a major role [8–11]. It was earlier reported by Kim et al. that in the oxidation of methanol, TiO₂ supported molybdenum oxide catalyst is superior to other oxide

supports in the increasing order, MgO, SiO₂, Al₂O₃, ZrO₂ and TiO₂, when prepared by equilibrium adsorption method [12]. In our earlier work with varied amount of molybdenum supported on Al(OH)₃, it was observed that 15 wt.% molybdenum containing Al(OH)₃ converts 98% of benzyl alcohol to benzaldehyde and toluene [13]. In order to investigate the influence of the nature of the support on the distribution of the catalytically active species, we have used different types of supports like CaO, MgO, Zr(OH)₄, Al(OH)₃ and alumina. Molybdenum (15 wt.%) containing supports have been prepared and tested in the conversion of benzyl alcohol.

2. Experimental

2.1. Preparation of supports

Zr(OH)₄, Al(OH)₃ and CaO were obtained commercially and dried at 120 °C overnight prior to their use. MgO was prepared by treating commercial MgCO₃ at 350 °C. Alumina (Al₂O₃) was prepared by the calcination of commercial Al(OH)₃ at 750 °C for 5 h.

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2.2. Preparation of supported 15 wt.% molybdenum catalysts

Each support obtained as mentioned above was mixed with required amount of a solution of ammonium heptamolybdate at natural pH to obtain 15 wt.% molybdenum containing catalysts. Incipient wetness impregnation at natural pH was adopted to prepare these catalysts. The mixture was ground well for an hour and treated at 120 °C in an air oven overnight and finally calcined at 550 °C for 5 h. Since uncalcined Al(OH)₃ and Zr(OH)₄ were used as supports, these two supports containing Mo will be represented as Mo/Al(OH)₃ and Mo/Zr(OH)₄, respectively.

2.3. Characterisation

BET surface areas of all the materials were measured by N₂ adsorption at 77 K on a NOVA-1000 (VER: 3.7) instrument. The crystallographic phases of the supported catalysts were detected by recording powder X-ray diffraction patterns (PXRD) on a Philips X'pert Pro diffractometer with Cu K α ($\lambda = 1.5418 \text{ \AA}$) using a graphite monochromator to filter the K β lines. Data were collected at a scan rate of 2°/min with a 0.02° step size for 2θ ranging from 5° to 70°. To check the nature of molybdenum-oxo species, IR absorption spectra of the catalysts were recorded following the KBr pellet method in the range 4000–600 cm⁻¹ on a Jasco FT-IR-410 instrument.

2.4. Catalytic activity

In a typical reaction, 5 ml of benzyl alcohol was refluxed for 6 h with 0.5 g of catalyst in a round bottom flask fitted with an ice-cold water condenser. After the stipulated time, the round bottom flask was cooled and the reaction mixture was separated from the catalyst by centrifugation. Components in the reaction mixture was analyzed by TLC first and later analyzed by a Netel gas chromatograph using a 10% SE 30 Chromosorb column. The products were further identified by ¹³C NMR, ¹H NMR and GC–MS.

3. Results and discussion

3.1. Surface area

The specific surface area of all supports and supported Mo catalysts determined by nitrogen physisorption is presented in Table 1. The surface areas of supports and supported molybdenum catalysts vary over a wide range. Among all the supports, the CaO support had the lowest surface area and Al(OH)₃ had the highest. The decrease in the surface area of Al(OH)₃ on calcination to 750 °C can be attributed to partial change from the γ phase to the more crystalline σ phase as shown by their powder XRD patterns.

Incorporation of molybdenum species reduced the surface area of all the supports, except for CaO supported catalysts where the increase was only marginal. The decrease in the surface area of Mo/Al(OH)₃, Mo/Al₂O₃ and Mo/Zr(OH)₄ compared to pure supports is due to the penetration of molybdenum species into

Table 1
Specific surface area of various supports and Mo supported catalysts

Support	Surface area (m ² /g)	Supported catalyst	Surface area (m ² /g)
Al(OH) ₃	191 (181)	Mo/Al(OH) ₃	139
Al ₂ O ₃	124	Mo/Al ₂ O ₃	109
Zr(OH) ₄	176 (32)	Mo/Zr(OH) ₄	22
MgO	43 (179)	Mo/MgO	136
CaO	8 (12)	Mo/CaO	16

Surface area of supports calcined at 550 °C are given in parenthesis.

the pores of the support, resulting in the dispersion of active species on the support [14]. This is confirmed by the absence of MoO₃ peaks in XRD of these supports. In the case of Mo/MgO there was an increase in the surface area compared to the MgO support obtained by the decomposition of MgCO₃ at 350 °C. However, this was not true when compared to 550 °C calcined MgO support. The change in the surface area of Mo/MgO is due to the formation of Mg(OH)₂ upon contact of MgO with water during incipient impregnation and its subsequent decomposition to high surface area MgO upon calcination [15].

The drastic decrease in the surface area of Mo/Zr(OH)₄ compared to the pure support can be attributed to the conversion of amorphous Zr(OH)₄ to ZrO₂ during calcination. Difference in the kind of phases present (monoclinic and tetragonal) in the presence of molybdenum species is also responsible for the decrease in surface area [16].

3.2. Powder X-ray diffraction

Powder X-ray diffraction patterns of all the supports and those containing 15 wt.% Mo are shown in Fig. 1. Mo/CaO showed a different crystallographic phase from that of the pure support. Apart from characteristic peaks of CaO the molybdenum containing CaO also showed a sharp peak at 28.8° which represents the compound CaMoO₄ (JCPDS No. 29-0351). Hence it can be inferred from X-ray diffraction patterns of CaO support and CaO supported molybdenum catalysts that CaO being basic in nature reacts with molybdenum species to form the compound CaMoO₄ [12]. Hence some of the peaks characteristic of CaO have disappeared and new peaks corresponding to CaMoO₄ appeared in the XRD pattern of the Mo/CaO catalyst.

Similarly, in the case of MgO, the PXRD showed peaks typical of MgO (JCPDS 01-1235) corresponding to d values of 2.1, 1.49 and 1.21 nm. Formation of α -MgMoO₄ in the Mo/MgO sample was indicated by a peak at $d = 3.1$ nm (JCPDS 31-0796) [17].

Aluminum hydroxide support (calcined at 550 °C) exhibited a diffraction pattern, typical of γ -alumina (JCPDS, Card No. 5-0508) [18]. Mo/Al(OH)₃ also exhibited a similar diffraction pattern, except for a slight deflection of the base line indicating the incorporation of molybdenum species in the support. Absence of peaks typical of crystalline MoO₃ at 2θ values of 27.3° and 25.6° indicates that these phases are not formed over the aluminum hydroxide support. This is in agreement with the fact that interaction between aluminum hydroxide support and

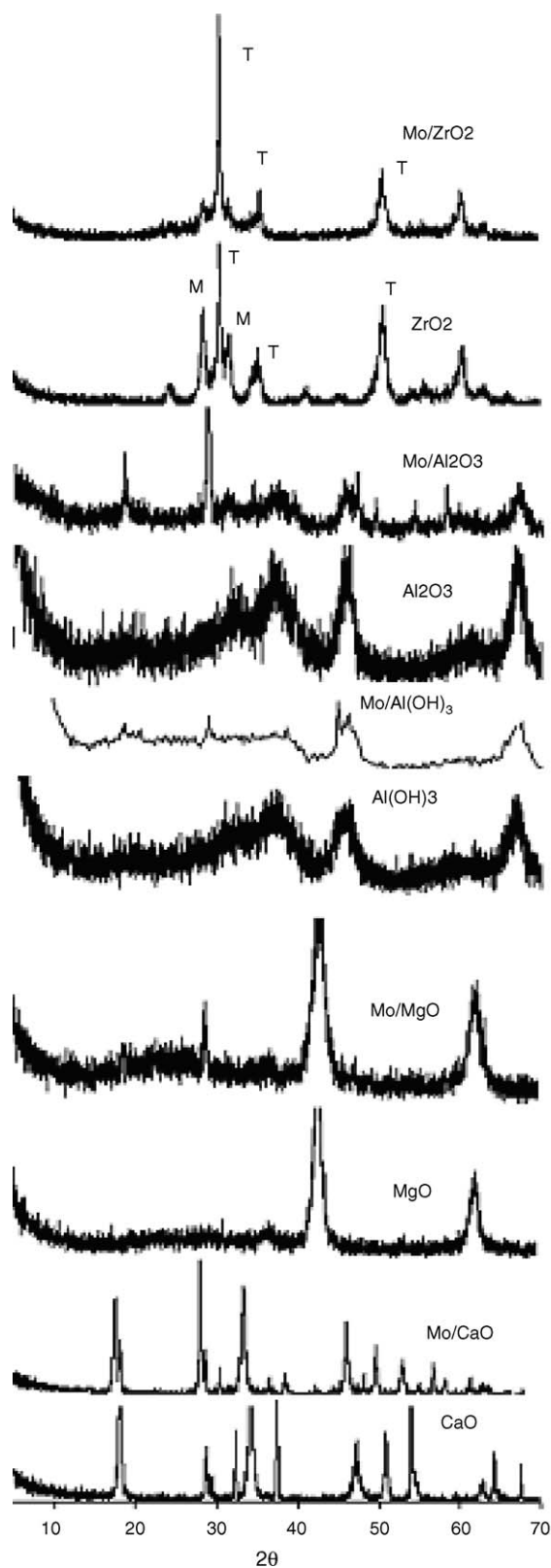


Fig. 1. Powder X-ray diffraction patterns of pure supports and supported Mo catalysts.

molybdenum-oxo species through hydroxyl groups prevents the formation of crystalline MoO_3 [19].

The X-ray diffraction pattern of the pure Al_2O_3 support (calcined at 750°C) exhibited peaks at 2θ values 37.1° , 45.8° and 67° . The peak at 37.1° indicates the presence of $\sigma\text{-Al}_2\text{O}_3$ (JCPDS 47-1292). Unlike Mo/Al(OH)_3 , $\text{Mo/Al}_2\text{O}_3$ catalyst exhibited a sharp diffraction peak at 28.8° . A survey of JCPDS files showed that the molybdenum species exist in the form of Mo_8O_{23} or Mo_4O_{11} . The difference in the crystallographic phases present in Mo/Al(OH)_3 and $\text{Mo/Al}_2\text{O}_3$ catalysts indicates that the concentration and nature of hydroxyl group on the support strongly influence the support–metal interaction.

Zr(OH)_4 is amorphous in nature at 120°C (JCPDS Card 37-1484) and during calcination at 550°C , mixed crystallographic phases of monoclinic ($2\theta = 24.1^\circ$, 28.4° , 31.4°) and tetragonal ($2\theta = 30.3^\circ$, 35.2° , 50.4°) are formed (JCPDS Card 37-1413 and 07-0337). There was no monoclinic phase of ZrO_2 in the Mo/Zr(OH)_4 catalyst. This indicates that incorporation of molybdenum into the zirconium hydroxide support has changed the crystalline structure of ZrO_2 present initially. Absence of peaks due to MoO_3 and $\text{Zr(MoO}_4)_2$ indicate that molybdenum species are well dispersed on the Zr(OH)_4 support. Hence it can be concluded from XRD patterns of catalysts that the extent of interaction of molybdenum-oxo species with the support varies significantly with the nature of the support. CaO and MgO react with molybdenum-oxo species to form the compound CaMoO_4 and MgMoO_4 , respectively, and Al_2O_3 gives polymolybdate. Among the five different supports used, aluminum hydroxide and zirconium hydroxide exhibited maximum dispersion of molybdenum-oxo species.

3.3. FT-IR

In Fig. 2(a) and (b) are given FT-IR patterns of supported 15 wt.% molybdenum catalysts and pure supports, respectively. The sharp bands at 854 cm^{-1} for Mo/MgO and at 809 cm^{-1} for Mo/CaO indicate the presence of $[\text{MoO}_4]^{2-}$ from CaMoO_4 and MgMoO_4 , respectively [20]. This observation is in agreement with XRD patterns of these samples.

The FT-IR spectrum of Mo/Zr(OH)_4 showed a band at 841 cm^{-1} due to molybdenum-oxo species. The shoulder band at 960 cm^{-1} is assigned to the terminal Mo=O stretching of the surface molybdenyl species like $[\text{O}_3\text{Mo=O}]^{2-}$ [21]. Even the $\text{Mo/Al}_2\text{O}_3$ sample showed the presence of Mo-O stretching band at 822 cm^{-1} [22]. Incorporation of molybdenum species in the aluminum hydroxide sample is indicated by the transmittance bands at 867 and 802 cm^{-1} . The difference in the infrared spectra of supported catalysts from the pure support is clear evidence for the incorporation of molybdenum species into the support and the interaction between them.

3.4. Catalytic activity

The results of catalytic activity studies performed on various supports and supported molybdenum catalysts are included in Table 2. The materials exhibited activity in the conversion of benzyl alcohol into three products namely, toluene, benzaldehyde

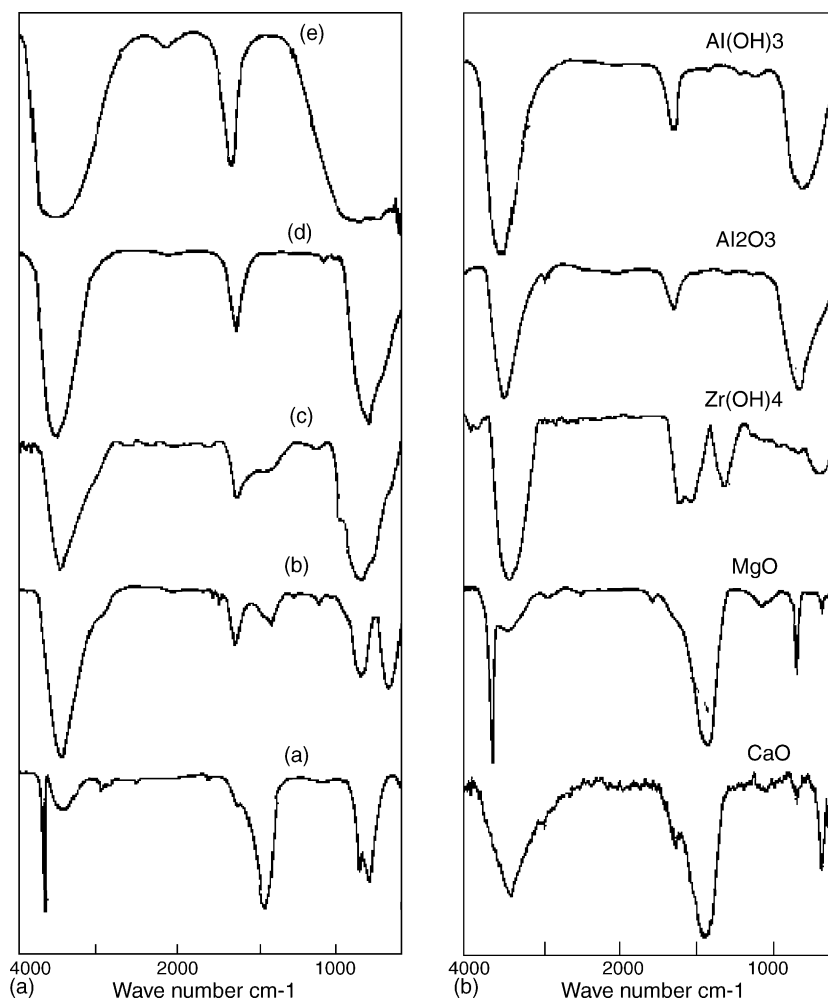


Fig. 2. (a): FT-IR patterns of supported Mo catalysts. (a) Mo/CaO; (b) Mo/MgO; (c) Mo/Zr(OH)₄; (d) Mo/Al(OH)₃; (e) Mo/Al₂O₃. (b) FT-IR patterns of pure supports CaO, MgO, Zr(OH)₄, Al(OH)₃ and Al₂O₃.

via hydride transfer reaction and dibenzyl ether via dehydration. The three products were formed noticeably to different extents.

As far as the catalytic activities of pure supports are concerned, the % conversion of benzyl alcohol varied significantly over different supports. The pure supports in general exhibited poor and almost no activity for benzaldehyde and toluene formation, respectively. Earlier it was reported that the disproportionation of benzyl alcohol to benzaldehyde and toluene takes

place over strong acid sites [23]. Absence of disproportionation products over the pure supports at the outset infers the absence of any such active centers on their surfaces. Among the pure supports, only Al(OH)₃ and Al₂O₃, gave the dehydration product of benzyl alcohol, i.e. dibenzyl ether (DBE) to an observable extent [24,25]. This indicates the presence of catalytically active weak Lewis/Bronsted acid sites on the surface of these supports [12,26,27]. Higher yield of DBE over Al₂O₃ compared to

Table 2
Conversion of benzyl alcohol into various products

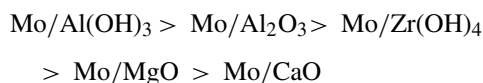
Support/catalyst	Toluene (%)	Benzaldehyde (%)	DBE (%)	Benzyl alcohol (%)	Total conversion (%)
Al(OH) ₃	0.6	4.4	38.5	56.5	43.5
Al ₂ O ₃	1.8	6.8	59.6	31.8	67.3
Zr(OH) ₄	–	3.8	–	96.2	3.8
MgO	–	1.7	–	98.3	1.7
CaO	–	1.5	–	98.5	1.5
Mo/Al(OH) ₃	41.0	51	6.0	18	98
Mo/Al ₂ O ₃	30	34	–	36	64
Mo/Zr(OH) ₄	24	17	–	59	41
Mo/MgO	7	14	–	79	21
Mo/CaO	–	2	–	98	2

Note: All the supported catalysts contain 15 wt.% molybdenum. DBE: dibenzyl ether; amount of catalyst: 0.5 g; benzyl alcohol: 5 ml; time of reflux: 6 h.

Al(OH)₃ calcined at 550 °C indicates that during calcination at 750 °C new acid sites are created.

Only Al(OH)₃, Al₂O₃ and Zr(OH)₄ supported catalysts resulted in the formation of significant amount of toluene and benzaldehyde as products. In the presence of 15 wt.% molybdenum, alumina did not yield any DBE. DBE selectivity drastically reduced even for the Al(OH)₃ supported catalyst compared to the pure support (i.e. 39–6%). On the other hand, presence of 15 wt.% molybdenum on Al(OH)₃, Al₂O₃ or Zr(OH)₄ increased the yield of toluene and benzaldehyde.

It is noteworthy that Mo on basic supports such as MgO and CaO exhibited very low activity. The catalytic activity of various Mo containing supports was found to be in the following decreasing order:



It can be learned from the results listed in Table 2 that, in spite of the molybdenum content being equal in all the supported catalysts, there was observable change in their catalytic activity which reflects the importance of supports. Mo/Al(OH)₃ catalyst was highly active compared to other supported Mo catalysts towards benzyl alcohol conversion. Between Al(OH)₃ and Al₂O₃ supports, the former was found to be a better support than the latter for molybdenum species. This difference in catalytic activity can be explained on the basis of support–metal oxide interaction (SMI) as follows.

During calcination of Al(OH)₃, the acid–base strength of hydroxyl groups are altered [28]. The hydroxyl groups in Al(OH)₃ are more basic in nature compared to those in Al₂O₃. There exists interaction between more number of hydroxyl groups present in Al(OH)₃ which are more basic and metal solution which is acidic in nature [29,30]. This type of interaction of molybdenum species which is more electronegative through hydroxyl groups creates Lewis acid sites due to the increased electronegativity of support through the inductive effect [31]. But in the case of Al₂O₃, due to lower density and acidic nature of hydroxyl groups, this kind of interaction is weak compared to the Al(OH)₃ support.

Mo is present either in the form of monomeric MoO₄²⁻ or heptamolybdate (Mo₇O₂₄⁶⁻) or both, based on the pH and concentration of the aqueous salt solution [32,33]. It was reported earlier by many authors that at lower Mo loading and at basic pH monomeric species interacts with the support and at higher loading heptamolybdate species is involved [34–36].

In the case of Mo/Zr(OH)₄, conversion of benzyl alcohol to toluene and benzaldehyde occurred but not in the case of the pure support. Among all the supports discussed in this paper, molybdenum-oxo species interact with Al(OH)₃ and Zr(OH)₄ in such a way that molybdenum species is well dispersed on the surface of these supports, which is further corroborated by the absence of any compound formation like Al₂(MoO₄)₃, Zr(MoO₄)₂ and crystalline MoO₃. The higher number of hydroxyl groups with adequate basic strength is responsible for the unique interaction between Mo species and Al(OH)₃/Zr(OH)₄ supports. This in turn resulted in higher level

of dispersion which is responsible for high catalytic activity of Al(OH)₃ and Zr(OH)₄ supported molybdenum catalysts compared to their pure supports.

The present study interrogates the exact role of support and metal oxide species towards its catalytic activity. The supports and the MoO₃ behave differently when used independently in the benzyl alcohol reaction. CaO, MgO and Zr(OH)₄ supports were inactive in the reaction. When MoO₃ obtained by the calcination of precursor (ammonium heptamolybdate) at 550 °C is used as a catalyst, it turned completely black at the end of the reaction and the products were inseparable. However, when Mo species supported on various supports, due to the interaction of Mo-oxo species with the support, the support–metal oxide system behaved altogether in a different manner.

In the case of pure supports CaO and MgO, the lack of required nature of hydroxyl groups prevented the extensive interaction with the molybdenum-oxo species which in turn influences the catalytic activity. However, due to the high aqueous solubility of CaO and MgO, being strongly basic in nature, their acid–base interaction with the precursor resulted in the formation of CaMoO₄ and MgMoO₄ [37]. X-ray diffraction and FT-IR studies support the fact that CaMoO₄ and MgMoO₄ phases are formed on Mo/CaO and Mo/MgO, respectively.

The difference in the SMI and the consequent formation of well-dispersed metal ion species or crystalline compound drastically influenced the catalytic activity. Further the SMI in the selected materials accounts for the fact that those supports, which exhibited good catalytic activity in the benzyl alcohol conversion had uniform distribution of the active centres whereas the inactive materials exhibited non-homogeneous distribution or crystallites of metal–support species. The surface areas of former materials were also found to be generally high.

Thus the present studies over CaO, MgO, Al₂O₃, Zr(OH)₄ and Al(OH)₃ supported Mo shows that the presence of molybdenum species is not the only criterion for increased catalytic activity but the metal–support interaction plays a key role. These results by and large indicate that the nature of SMI was significantly different and hence created catalytic centers with different activities. It is noteworthy that the observed change and difference in the catalytic activity of supports and Mo supported catalysts exhibited a good correlation with the structural changes on Mo incorporation. It can be concluded that Al(OH)₃ supported molybdenum catalysts is a better catalyst in the benzyl alcohol conversion over the other supported catalysts mentioned in the present study due to SMI.

4. Conclusions

Catalytic activity of supported molybdenum catalysts depends on the type of the support to a greater extent. The acido-basic nature of the support influences the support–metal interaction. The higher the base strength of hydroxyl groups on the surface of the support, the higher its interaction with the metal-oxo species. Benzyl alcohol can be converted to benzaldehyde and toluene over aluminum hydroxide/alumina/zirconium hydroxide supported molybdenum catalysts. However, due to SMI, Al(OH)₃ supported 15 wt.% molybdenum catalysts are a

more ideal system for the disproportionation of benzyl alcohol than other supports like CaO, MgO, Zr(OH)₄ and Al₂O₃.

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