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Characterization and cracking activity of MoO₃-SiO₂ catalysts

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ABSTRACT

Pure silica and a series of MoO₃/SiO₂ catalysts with different MoO₃ loadings (2-16wt%) were prepared using the standard incipient wetness technique. The catalysts were characterized using XRD and FTIR techniques. The textural properties were determined from nitrogen adsorption at 77K. The acidic properties of these catalysts were measured by the amine titration method. The cracking of cumene was investigated over these catalysts. XRD data revealed the amorphous nature of the catalyst up to 6 wt % MoO₃ loading and the formation of crystalline MoO₃ phase on amorphous silica support were detected only for the catalyst with higher MoO₃ loading. Loading SiO₂ with higher MoO₃ (≥9wt%) leads to a significant change in texture, surface acidity and catalytic activity of the prepared catalysts. Catalysts with higher MoO₃ loading show much higher acid strength compared to the catalysts with lower MoO₃ loading (≤6 wt%). The cracking activity has been related to the strength of the acid sites presented on the catalyst surface. Cracking of cumene over the investigated catalyst necessitates the presence of strong acid sites. These sites are evidently Bronsted acid sites on which the cracking process probably proceeds via a carbonium ion mechanism. © 2008 Trade Science Inc. - INDIA

KEYWORDS

MoO₃/SiO₂;
 Characterization;
 Acidity and acid strength;
 Cracking of cumene.

INTRODUCTION

Over the past years a great deal of fundamental and applied research was focused on supported molybdena catalysts because of their numerous applications in petroleum refining, chemical production and pollution control industries^[1-3]. Presently oxidation reactions are playing an increasingly important role both in the production of materials needed and in the destruction of undesired products by total catalytic oxidation. MoO₃ is a principal component in catalysts for, allylic and alcohol oxidation and minority component in

many other oxidation catalysts such as those used for alkenes dehydrogenation^[4-5] and for aromatics and alkane oxidation^[6]. A renewed interest arose recently in the supported molybdena catalysts owing to their potential use in the partial oxidation of methane to formaldehyde^[6-7]. However supported molybdena catalysts also used as a catalytic material for a wide range of acid-catalyzed reaction^[9-10]. Different characterization techniques have been applied to investigate the acid properties of these catalysts. It has been found that the acidic properties and hence the catalytic activity of these catalyst systems are strongly dependent on the method

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of preparation, the thermal treatment, the presence of doping ions and MoO_3 /metal oxide weight ratio^[11-13].

In this study we examined the influence of chemical composition on the structural, acidic and textural properties of SiO_2 and $\text{MoO}_3\text{-SiO}_2$ catalyst. The cracking activity was related to some of the surface properties of the investigated catalysts.

EXPERIMENTAL

Catalyst preparation

Pure silica catalyst was precipitated by the sole addition of 1 M H_2SO_4 solution to an aqueous solution of sodium silicate at 333 K with continuous stirring.

The transparent white gel thus obtained was washed thoroughly till free from SO_4^{2-} and then dried for 10 h at 383 K and calcined in a muffle furnace at 773K for 6h.

A series of $\text{MoO}_3\text{-SiO}_2$ catalysts with varying compositions were prepared by impregnation using the standard incipient wetness technique. Thus, at a pH value of 9, 6g of SiO_2 was added to 40cm³ of an aqueous solution containing the appropriate amount of ammonium heptamolybdate to give the desired MoO_3 loading. Excess water was removed by drying the sample for 10h at 383K. The catalysts were calcined in an air circulation furnace for 8h at 773K.

The catalysts thus obtained were pure SiO_2 and $\text{MoO}_3\text{-SiO}_2$ containing 2,6,9,12, and 16 wt% MoO_3 and were designated as S, SM1, SM2, SM3, SM4 and SM5 respectively.

Catalyst characterization

XRD patterns of the calcined catalysts were made using a Siemens apparatus equipped with a Rigaku Geiger flux detector with Ni-filtered $\lambda=1.5405 \text{ \AA}$ at 40KV and 100mA with a scanning rate of 8° min^{-1} from $2\theta=10$ to $2\theta=80$. The infrared spectra were recorded at room temperature by means of a Mattson 5000 FT-IR spectrophotometer at 2cm^{-2} resolutions using KBr pressed disks containing 5Wt% catalyst powder. The textural properties of the prepared catalysts were measured from nitrogen adsorption studies at 77K using a conventional volumetric apparatus.

The acid amounts and acid strength of samples were measured by titrating of 100-200 mesh powder, suspended in dry benzene with n-butyl amine solution in dry benzene employing a series of Hammett indicators^[14]. The indicators used are methyl red ($\text{pK}_a=+4.8$),

Dimethyl yellow($\text{pK}_a=+3.3$), Crystal violet($\text{pK}_a=+0.8$), Dicinnamylideneacetone($\text{pK}_a=-3.0$), Benzylidene acetophenone($\text{pK}_a=-5.6$), and Anthraquinone($\text{pK}_a=-8.2$)

The catalytic cracking of cumene was carried out using a pulse microcatalytic system connected to a flame ionization detector(Hewlett- Packard 5890, gas chromatograph). Prior to any catalytic run, the catalyst(75mg) was activated by heating in dry air(40ml/min) for 2h at 773K and then in a current of nitrogen (60 ml/min) for 30min at the desired reaction temperature. Nitrogen was used as the carrier gas in all catalytic measurements and 2×10^{-3} ml sample of cumene was injected onto the catalyst in the form of a pulse using a microsyringe.

RESULTS AND DISCUSSION

The XRD patterns of $\text{MoO}_3/\text{SiO}_2$ catalysts calcined at 773 K are shown in figure 1. For comparison, the XRD pattern of pure silica (S sample) is also included in figure 1. Figure 1 reveals that silica calcined at 773K is an amorphous precursor with only a broad background peak, associated with SiO_2 . Figure 1 shows also the amorphous nature of the catalyst at lower MoO_3 loading. No diffraction lines characteristic of the MoO_3 phase were observed for the SM1 and SM2 catalysts (i.e. $\text{MoO}_3 \leq 6\text{wt}\%$). This may be attributed to the high surface area of SiO_2 ($337.2\text{m}^2/\text{g}$) which allowed the high dispersion of the MoO_3 species and inhibited the formation of MoO_3 crystallites.

Diffraction lines corresponding to MoO_3 were clearly observed for the SM3 catalyst ($\text{MoO}_3 \geq 9\text{wt}\%$), the intensity of this lines increasing with an increase in

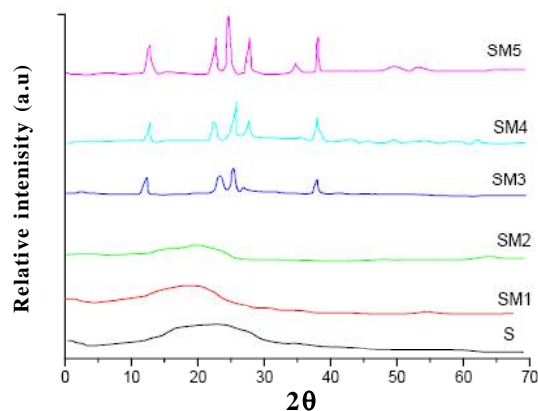


Figure 1 : XRD patterns for investigated catalysts

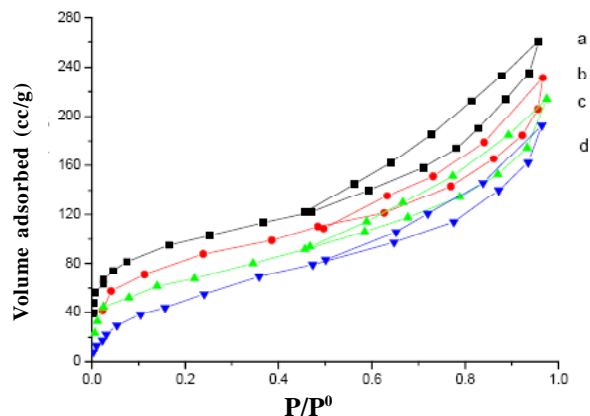


Figure 2 : Nitrogen adsorption/desorption isotherms at 77K for (a) S, (b) SM2, (c) SM4 and (d) SM5 catalysts

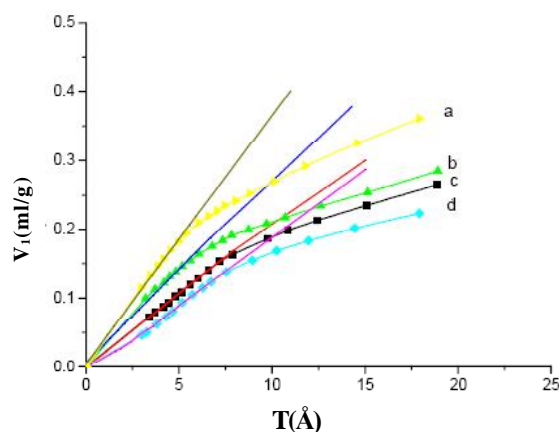


Figure 3 : V_1-t plots for nitrogen adsorption on some selected catalysts

TABLE 1 : Textural properties of $\text{MoO}_3\text{-SiO}_2$ catalysts

catalyst	S_{BET} (m^2/g)	S_t (m^2/g)	V_p (ml/g)	r (Å)
S	337.2	343.0	0.393	23.0
SM1	330.0	339.0	0.386	25.0
SM2	307.4	308.0	0.350	26.0
SM3	263.0	272.0	0.340	28.0
SM4	233.0	237.0	0.334	29.0
SM5	204.0	211.0	0.300	30.0

the MoO_3 content up to 16wt%.

In $\text{MoO}_3\text{-SiO}_2$ catalysts the Mo(VI) could be fixed on SiO_2 by the interaction of molybdic acid with the surface OH groups of SiO_2 on the basis of an acid – base interaction accompanied by the elimination of water. This would give Mo(VI) adsorbed on SiO_2 in a monolayer in tetrahedral coordination structure^[15]. At higher surface densities of these monomeric species, a two dimensional condensation with creation of Mo-O-Mo linkages and eventually the formation of surface

polymolybdate structure are results. It is interesting to note that even though the MoO_3 is in the crystalline form at higher MoO_3 loading, the silica support still retains its amorphous nature, leading to the relatively high surface area of the catalysts. The FTIR spectra of pure SiO_2 and the catalysts with MoO_3 content less than 9wt% (not illustrated) were similar (i.e. characteristic of silica). Thus a broad intense band at $\sim 1100\text{cm}^{-1}$, a less intense band at 818cm^{-1} and stronger band at 467cm^{-1} were obtained for this sample. All these bands in accordance with the literature^[16] are due to the vibrations of Si-O-Si and Si-O band of the silica. No indications of any absorption bands characterizing crystalline MoO_3 were observed. Catalysts with 12 and 16wt% MoO_3 loading show additional absorption bands at 995, 895 and 820cm^{-1} which may ascribed to freely isolated MoO_3 ^[17]. These results are in a good agreement with XRD observations quoted above.

Figure 2 shows the adsorption –desorption isotherms of nitrogen at 77K obtained for some selected catalysts. These isotherms are in shape between types II and IV of the classification adopted by Sing et al.^[18]. The specific surface areas are estimated by applying the BET equation^[19] adopting a value of 0.162nm^2 for the cross-sectional area of the nitrogen molecule. The total pore volume of each catalyst V_p (ml/g) was estimated from the uptake of nitrogen at the saturation vapor pressure. Another r (Å) important textural parameter, i.e. the mean pore radius was also calculated from nitrogen adsorption data using the relationship:

$$r = \frac{2V_p(\text{ml/g}) \times 10^4}{S_{\text{BET}}(\text{m}^2/\text{g})}$$

The textural parameters S_{BET} , V_p and r are listed in TABLE 1. To differentiate between the types of pores existing, the V_1-t method of de Boer and coworkers was used^[20]. The surface areas S_t (m^2/g) have been calculated from the slope of the linear part of V_1-t plots which passes through the origin. The V_1-t plots of selected catalysts are shown in figure 3 and the calculated areas(m^2/g) are compared with the S_{BET} areas in TABLE 1.

The V_1-t plots indicate the predominance of a micropore structure in all catalysts investigated.

Inspection of the textural data listed in TABLE 1 reveals the following:

1. The values of S_t areas are in fair agreement with those of the S_{BET} areas indicating that the correct choice of the reference t-curve was made.

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TABLE 2 : Acidic and catalytic parameters of catalysts investigated

Catalyst	Acid amount (mequiv/g) at different PK _a 's						Cracking % at 723K	ΔE Kcal/mole
	+4.8	+3.3	+0.8	-3.0	-5.6	-8.2		
S	0.42	0.28	0.18	0.00	0.00	0.00	Nil	--
SM1	0.60	0.40	0.34	0.00	0.00	0.00	Nil	--
SM2	0.64	0.54	0.38	0.00	0.00	0.00	Nil	--
SM3	0.58	0.44	0.50	0.08	0.06	0.00	18	24.0
SM4	0.44	0.40	0.68	0.20	0.08	0.00	26	18.6
SM5	0.34	0.30	0.40	0.28	0.14	0.00	31	12.5

- Pure SiO₂ and SiO₂ containing 2wt% of MoO₃ (samples S and SM1) exhibited almost the same textural parameters.
- A slight decrease in both surface area and total pore volume was found on increasing the MoO₃ content up to 6wt%. However, appreciable changes occurred on increasing the degree of loading with MoO₃, e.g. a 20%, 31% and 40% decrease in surface area respectively occurred for catalysts SM3, SM4, and SM5 relative to the surface area of pure SiO₂. The slight variation in the textural properties of the catalysts containing not more than 6wt% MoO₃ may be attributed to high dispersion of the small molybdena species on the silica surface. At high MoO₃ loading (MoO₃ ≥ 9wt%), the crystalline molybdenum oxide clusters are formed that cover the amorphous silica support, reducing the surface area and the total pore volume of the catalyst.
- A change in mean pore radius with chemical composition is less pronounced.

Amine titrate experiments were carried out using a series of Hammett indicators to determine the acidity and acid strength of the catalysts. The results are given in TABLE 2. The pure silica catalyst shows the lowest acidity. The acidity increased gradually upon the addition of MoO₃ to SiO₂ reaching a maximum at SMS catalyst. Weak acid sites with PK_a values of ≤ +4.8 to ≤ +0.8 were exhibited by pure silica catalyst. The amount of acid sites in this PK_a range was found to increase with increasing MoO₃ loading up to 6wt%.

Strong acid sites with PK_a values of ≤ -3.0 to ≤ -5.6 were observed for the catalysts containing more than 6 wt % MoO₃, indicating the formation of new acid sites stronger than those of the catalysts had MoO₃ content ≤ 6wt%. The catalyst with 16 wt % MoO₃ loading shows maximum acidity as well as the highest acid strength. At low MoO₃ content (≤ 6.0 wt%) the molybdenum species may interact with neighboring hydroxyl groups on

the SiO₂ surface to form undetectable molybdate species, which may represent an additional source of weak acid sites. An increase in the amount of the weak acid sites in that range would be expected in this case. On increasing the MoO₃ loading to a higher level (>6.0wt%), the MoO₃ crystallites formed may generate stronger acid sites and more acidity as compared with the other catalysts containing low MoO₃ level (<6.0wt%)^[3,21].

The activities of the catalysts towards cumene cracking at 723 K and at N₂ flow rate of 30 ml/min as a function of MoO₃ content are listed in TABLE 2. Formation of benzene as the only liquid product, while toluene and ethylbenzene are always absent, is strong evidence of the fact that cumene cracking on the investigated catalysts proceeds through a carbonium ion mechanism. On this basis it is interesting to compare cracking activities of the catalysts with the results of surface acidity measurements. Pure silica, SM1 and SM2 catalysts exhibited no cracking activity (TABLE 2) which may be due to their low acid strength and low acid amount values respectively relative to the other catalysts.

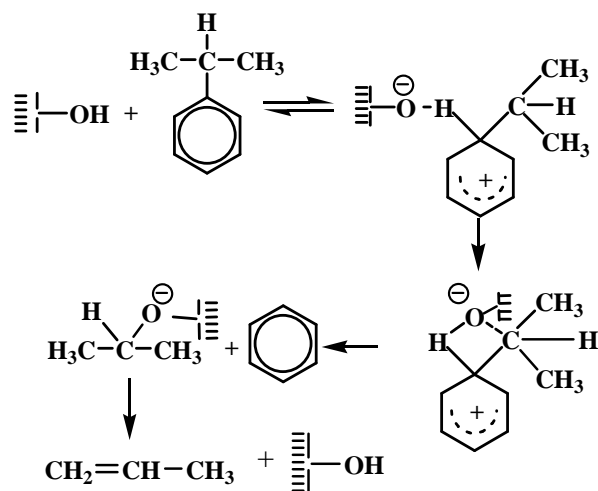
Only those catalysts had strong acid sites in PK_a range ≤ -3.0 to ≤ -5.6 exhibited cracking activities which found to increase with the increase of the amount of acidity in this particular PK_a range.

Cumene cracking takes place on relatively strong acid sites of the catalysts^[22]. On the other hand it appears that the extent of the surface was not an important parameter in the cracking process. Moreover the cracking ability was found to increase with a decrease in the surface area.

The kinetic data obtained for the cumene cracking over SM3, SM4 and SM5 catalysts at different reaction temperatures (713-735K) at N₂ flow rates varying from 20 to 60 ml/min were found to obey the Bassett-Habgood equation^[22]. Liner plots (not illustrated) were obtained indicating that the cracking process over these catalysts follows a first order reaction. The activation energies were calculated from Arrhenius plots and are listed in TABLE 2. It is evident that the activation energy of cracking process decreased with increasing amount of acid sites with PK_a ≤ -3.0 to ≤ -5.6.

These results indicate that the cracking of cumene necessitates the presence of strong acid sites. These sites are evidently Bronsted acid sites on which the cracking probably proceeds via a carbonium ion mechanism^[24]. The detection of benzene as the only

cracking product supported this fact. In this mechanism, the cumene molecule is initially adsorbed at a Brønsted acid site on the catalyst surface to give the corresponding carbonium ion. This carbonium ion can either regenerate the initial proton and the cumene molecule or crack to give benzene in the gas phase plus a propyl carbonium ion which remains adsorbed on the catalyst surface. The propyl cation then desorbed giving propylene and regenerating the Brønsted acid site as shown in SCHEME 1.



SCHEME 1

CONCLUSION

The characteristics of MoO₃/SiO₂ catalysts under our operational conditions may be briefly described as follows:

1. MoO₃ is highly dispersed on the SiO₂ surface and causes no significance change in the texture properties of silica support up to 6wt % of MoO₃.
2. The catalysts with lower MoO₃ loading (≤6wt%) do not possess any activity for cumene cracking probably due to the lack of acid sites with sufficient strength.
3. Catalysts with higher MoO₃ loading (≥9wt%) have significant activity for cumene cracking which is strongly dependent on MoO₃ content. The cracking activity seems to be closely related to the presence of strong acid sites. The activation energy of the cracking process decreased with increasing the amount of acid sites with pK_a values of ≤-3.0 to ≤-5.6.

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