

Temperature-programmed reduction and acidic properties of molybdenum supported on MgO–Al₂O₃ and their correlation with catalytic activity

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Received 1 August 2003; received in revised form 5 December 2003; accepted 5 December 2003

Abstract

A series of catalyst with Mo loading from 2 to 14 wt.% on MgO–Al₂O₃ mixed oxide support was prepared by incipient wetness impregnation method. Pure MgO and Al₂O₃ were prepared by using Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O salt solutions and urea as hydrolyzing agent. MgO–Al₂O₃ (1:1) mixed oxide was prepared by co-precipitation of appropriate quantities of magnesium nitrate and aluminum nitrate salts. BET surface area, pore volume, pore size distribution, TPR, acidity and acid strength distributions of catalysts and supports were measured. MgO–Al₂O₃ (1:1) mixed oxide showed a bimodal pore size distribution. LTOC and TPR results show that an optimum 8% Mo on MgO–Al₂O₃ is sufficient to form MoO₃ monolayer. TPR technique can also be used as a vital tool to determine the monolayer coverage. HDS activity has been correlated with LTOC. Introduction of basic MgO in the lattice of Al₂O₃ moderates the strong acidity in MgO–Al₂O₃. Impregnation of acidic MoO₃ species further enhances the acidity favorable for HYC.

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Keywords: TPR; Acidity; Mixed oxides; Catalytic activity

1. Introduction

Hydrotreating of crude oil is an important process in refining industry. Processing of heavier feedstocks, which contain increased amount of sulfur, is increasing day by day and environmental regulations are becoming stringent. Fuels containing sulfur compounds are not only poisonous to catalysts used in reforming process and automobile catalytic converter but also such fuels on combustion produce sulfur oxide, thus causing serious environmental pollution. To reduce or eliminate the environmental pollution, the sulfur content in the fuel needs to be reduced to a lower level (<50 ppm). To meet the new challenges of environmental regulations and to process heavier feed stocks economically, highly active and selective catalysts are needed. Most of the hydroprocessing catalysts contain Mo, W promoted by Co and Ni metals supported on Al₂O₃. Support plays an important role to control the specific characteristics of a catalyst.

The textural and chemical properties of a support can be controlled by the method of preparation and by us-

ing different combinations of mixed oxides. Mixed oxide supports have emerged as a new class of support materials with enhanced activity and selectivity, in many cases, compared to conventional γ -alumina. Various combinations of mixed oxides such as TiO₂–Al₂O₃, SiO₂–Al₂O₃, ZrO₂–Al₂O₃, TiO₂–SiO₂, SiO₂–ZrO₂, etc. have been tried by several researchers to meet the requirement of the desired physico-chemical properties to suit a particular application [1–3].

The electronegativity of metal ions of oxides varies in the following order MgO < Al₂O₃ < TiO₂ < SiO₂. Larger the electronegativity stronger are the metal oxygen bonds. In other words, with decrease in electronegativity, metal–oxygen interaction becomes weaker, and hence, the co-ordination ability of lattice oxygen increases. As electronegativity of Mg ions is the lowest among the metal ions of other oxides studied thus the coordination ability of oxygen atom of MgO is the highest. In oxidative dehydrogenation of alkanes, reaction uses the lattice oxygen of catalyst/support. Hence, MgO has been found to be a suitable catalyst precursor in combination with other metal oxides like MoO₃ or V₂O₅ since last several years for dehydrogenation of alkanes [4,5].

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Klicpera and Zdrzil [6–9] reported that Mo supported on MgO has comparable HDS activity to Mo/Al₂O₃ catalyst under similar conditions. They also found strong synergistic effect between Co(Ni) and Mo in the HDS activity of MgO supported Co(Ni)–Mo sulfide catalyst. They showed that Co(Ni)–Mo/MgO catalyst exhibited about 1.5–2.5 times higher activity in HDS of benzothiophene than the corresponding reference commercial Al₂O₃ supported catalyst.

Murali Dhar and co-workers [10,11] reported that Mo/MgO catalysts have higher HDS and HYD activities in comparison to Mo/Al₂O₃ catalysts due to the increased dispersion of Mo on MgO support. A little work has been found in literature using MgO–Al₂O₃ mixed oxide as catalytic support for HDS reactions [12]. MgO is basic support while Al₂O₃ is amphoteric in nature. The acidic properties of MgO–Al₂O₃ mixed oxide can be controlled by using appropriate MgO and Al₂O₃ ratios [13].

In the present study for determination of the monolayer coverage of Mo on MgO–Al₂O₃ mixed oxide support, a series of different Mo content (2–14 wt.% Mo) catalysts were prepared. With an aim to understand the catalytic functionalities of MoS₂ and to study the support effect an optimum 8 wt.% Mo containing catalysts were also prepared supported on MgO, Al₂O₃ and MgO–Al₂O₃ mixed oxides.

The physico-chemical characterization like BET surface area, total pore volume, pore size distribution, temperature-programmed reduction, acidity and acid strength distribution are carried out and results are discussed in the light of hydrodesulfurization (HDS), hydrogenation (HYD) and hydrocracking (HYC) activity using model compounds.

2. Experimental

2.1. Catalyst preparation

MgO–Al₂O₃ (1:1) mixed oxide support was prepared by co-precipitation urea hydrolysis method. One molar aqueous solutions of Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O were taken in a round bottom flask. Aqueous solution of urea was added to the mixture as hydrolyzing agent and the whole mixture was refluxed at 90 °C for 4 h maintaining the pH at 10.5. The precipitate formed was washed, followed by drying and calcination at 823 K for 6 h. Pure MgO and pure Al₂O₃ were also prepared by the same method using their respective salts. The pH during the preparation was maintained at 10.5 for pure MgO and 7.2 for pure Al₂O₃.

A series of MoO₃ catalysts with Mo loading from 2 to 14 wt.% supported on MgO–Al₂O₃ (1:1) mixed oxide was prepared by incipient wetness impregnation method using ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O). The 8 wt.% Mo was also impregnated on pure Al₂O₃ and on pure MgO by the same method. The catalyst samples were dried at room temperature followed by drying at 383 K over night and finally calcined at 823 K for 6 h. All the reagents used were of analar grade.

2.2. Textural properties

BET surface area, total pore volume and pore size distribution were carried out using ASAP-2010 unit from Micromeritics (USA). Adsorption–desorption isotherms of N₂ were obtained at liquid N₂ temperature. For BET surface area relative pressure (P/P_0) was taken from 0.05 to 0.25. Total pore volumes were obtained from the volume adsorbed at relative pressure around 0.99. Pore size distributions were obtained from the adsorption branch of isotherms applying BJH pore model [14].

2.3. Low temperature oxygen chemisorption

A conventional glass static volumetric high vacuum system (10^{−6} Torr) was used for low temperature oxygen chemisorption (LTOC). The catalyst sample (~0.3 g) was sulfided in situ at 673 K for 2 h using hydrogen saturated with CS₂. Oxygen chemisorption measurements were carried out at 193 K. The temperature of the bath was maintained using a mixture of isopropyl alcohol and liquid nitrogen. Molybdenum metal dispersion was calculated using the following formula.

The dispersion (O/Mo) = atoms of O₂ uptake/atoms of Mo in the catalyst [15,16].

2.4. Temperature-programmed reduction

Temperature-programmed reduction (TPR) profiles of catalyst samples were obtained using TPD/TPR-2900 Micromeritics (USA) instrument. TPR profiles were taken from room temperature to 1273 K (10°/min) and then the temperature was kept isothermal for 30 min. Five percent hydrogen in argon mixture (50 ml/min) was used as reducing gas. The hydrogen consumption corresponding to the reduction of the metal oxide was computed from the area of calibrated TPR peak of standard Ag₂O.

2.5. Acidity measurements

Microcalorimetric studies of adsorption of ammonia have been performed to determine total acidity and acid strength distribution using a Tian-Calvet type heat flux microcalorimeter (model C-80 Setaram, France) connected to a volumetric vacuum adsorption unit for sample treatment and probe molecule delivery. Samples were preheated at 723 K under vacuum for 4 h prior to microcalorimetric measurements. The heats evolved from sequential doses of ammonia onto the sample were measured at 448 K. The heat of adsorption generated for each dose was calculated from the resulting thermograms and the amount of ammonia adsorbed from the initial and final pressure. Sequential doses give the differential heat of NH₃ adsorption as a function of coverage (i.e. differential heat curves). It provides the information about the number and strength of acid sites on samples.

2.6. Catalytic activity

Catalytic activities were determined with a glass microreactor equipped with online GC at atmospheric pressure and at 673 K. Catalyst samples (0.2 g, particle size 18–40 mesh diluted with equal amount of quartz of same size placed between plugs of quartz wool) were sulfided in situ at 673 K for 2 h. Catalytic activities were measured using model compounds thiophene, cyclohexene and cumene for HDS, HYD and HCY activities, respectively.

3. Results and discussion

Pore size distribution curve of pure MgO, pure Al₂O₃ and MgO–Al₂O₃ mixed oxide are shown in Fig. 1. The BET surface areas of MgO and Al₂O₃ have been found to be 83 and 198 m²/g while that of MgO–Al₂O₃ has shown an intermediate value 170 m²/g. The total pore volume of three samples lies around 0.35 ml/g. Pure alumina has no micropores while MgO has about 15% and MgO–Al₂O₃ has 5%. Incorporation of MgO into the lattice of Al₂O₃ by urea hy-

drolysis method leads a bimodal type of pore size distribution. In MgO–Al₂O₃, the pores are centered around 45 and 90 Å diameter, whereas in the case of pure MgO and Al₂O₃ pore maxima are around 110 and 70 Å diameter, respectively. Wide range mesoporous distribution is observed in MgO–Al₂O₃ mixed oxide.

Temperature-programmed reduction profiles of catalyst samples with varying Mo content from 2 to 14 wt.% on MgO–Al₂O₃ mixed oxide support are shown in Fig. 2 and results are summarized in Table 1. All the Mo catalysts exhibit two distinct major peaks. The peak maxima (temperature of maximum reduction) of first peak (T_1), second peak (T_2), total hydrogen consumption obtained from TPR data and Mo dispersion calculated from LTOC values are also included in Table 1.

In Mo/MgO–Al₂O₃ series, the first peak maxima of all the catalyst samples that range from 845 to 887 K are mainly due to the reduction of octahedral species corresponding to the reduction of Mo⁶⁺ to Mo⁴⁺ state. The second peak maxima of all the catalyst samples are centered around 1200 K and are due to the reduction of tetrahedral species that correspond to the reduction of Mo⁴⁺ to Mo metal [17].

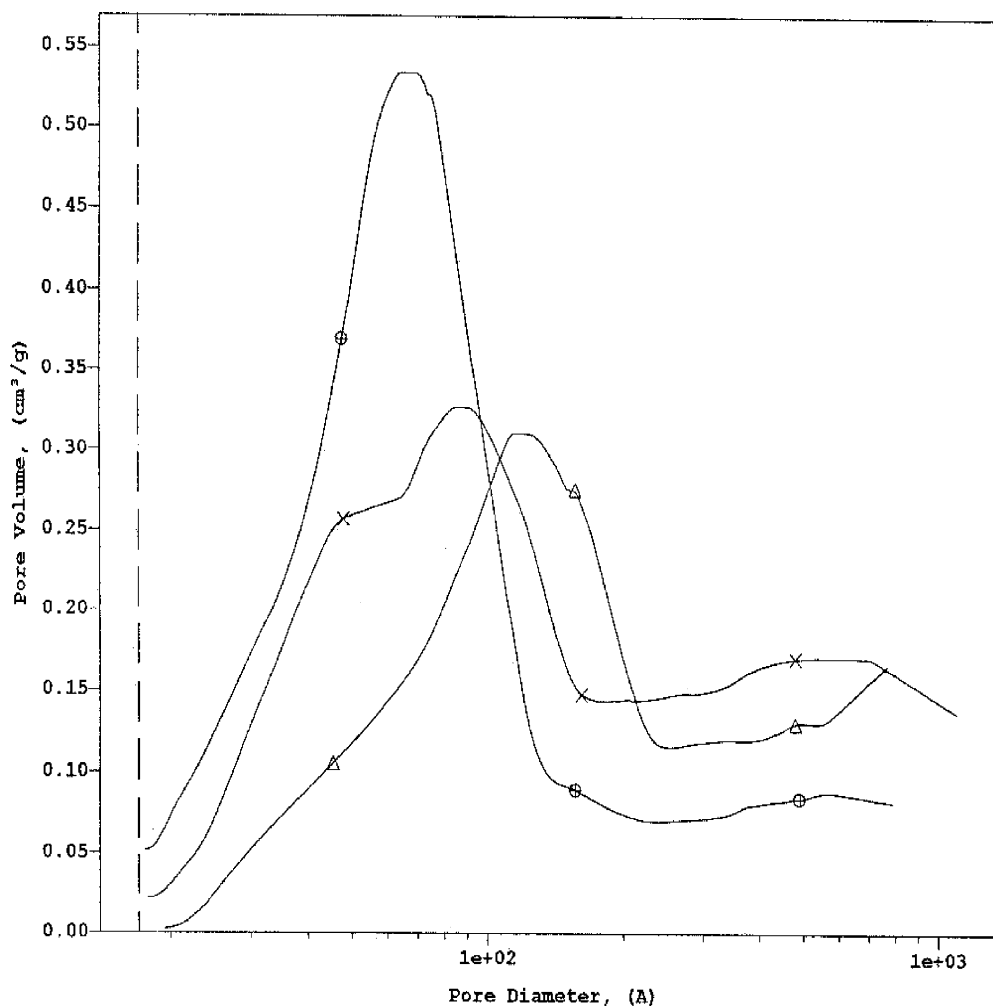


Fig. 1. BJH adsorption $dV/d\log(D)$ pore volume curves of pure Al₂O₃ (⊕), pure MgO (Δ) and MgO–Al₂O₃ mixed oxide (×).

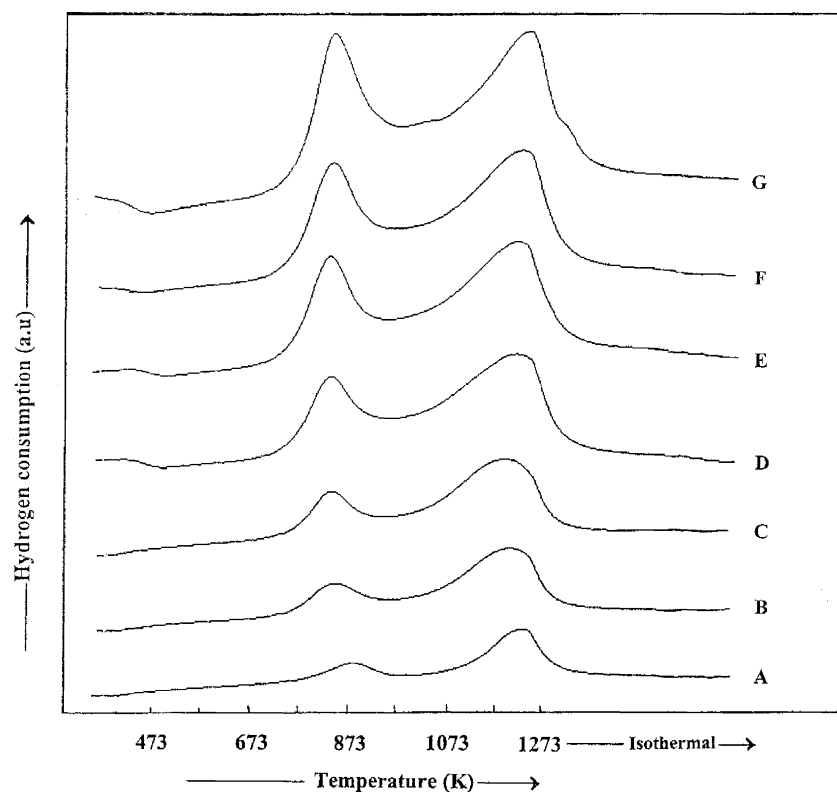


Fig. 2. Temperature-programmed reduction (TPR) profiles of: (A) 2 wt.% Mo; (B) 4 wt.% Mo; (C) 6 wt.% Mo; (D) 8 wt.% Mo; (E) 10 wt.% Mo; (F) 12 wt.% Mo; and (G) 14 wt.% Mo supported on 1:1 MgO–Al₂O₃ mixed oxide.

The first peak is continuously becoming sharper with Mo loading. It indicates that the rate of reduction of MoO₃ to MoO₂ increases and becomes easier with an increase in Mo content. The temperature of first reduction peak (T_1) K decreases with Mo loading up to 8 wt.% Mo and then it remains almost constant on further increase in Mo loading. It indicates that monolayer formation of MoO₃ on the support surface is complete up to 8 wt.% Mo loading. This fact is also corroborated by the studies on the dispersion of Mo metal on MgO–Al₂O₃ support calculated by LTOC values which remain constant up to 8 wt.% Mo loading and then decrease sharply. This also shows the completion of mono-

layer up to 8 wt.% Mo loading. Thus, the TPR studies are also indicative of the formation of MoO₃ monolayer on the surface of MgO–Al₂O₃ mixed oxide support. Similar to the first peak, second peak is also getting sharper with Mo content indicating an increase in reduction rate. The reduction of MoO₂ to Mo metal is also facilitated with increase in Mo content.

TPR profiles of Mo supported on pure MgO, Al₂O₃ and MgO–Al₂O₃ mixed oxide are shown in Fig. 3. The sharpness of the peaks show that the rate of reduction for both octahedral and tetrahedral species are higher in the case of Mo supported on MgO as compared to Al₂O₃, whereas

Table 1
TPR results and Mo metal dispersion of different catalysts

Catalyst	Peak max (K)		H ₂ cons. ⁺ (ml STP/g)	LTOC (μmol, STP/g)	Mo dispersion (O/Mo)
	T_1 (max. T_1)	T_2 (max. T_2)			
2 wt.% Mo/MA	887.5	1237.5	17.97	14.0	0.134
4 wt.% Mo/MA	849.3	1208.8	28.06	27.02	0.130
6 wt.% Mo/MA	846.0	1194.5	34.69	41.44	0.133
8 wt.% Mo/MA	840.8	1223.2	58.10	54.59	0.131
10 wt.% Mo/MA	840.8	1230.3	58.97	43.38	0.083
12 wt.% Mo/MA	840.8	1235.2	66.86	36.87	0.059
14 wt.% Mo/MA	842.5	1259.3	81.40	36.84	0.050
8 wt.% Mo/MgO	875.7	1240	86.62	91.21	0.219
8 wt.% Mo/Al ₂ O ₃	743	1123	55.70	58.04	0.139

MA: MgO–Al₂O₃; +: from TPR profiles.

the Mo supported on MgO–Al₂O₃ mixed oxide shows an intermediate rate of reduction. It indicates that the degree of dispersion of Mo supported on MgO is higher as compared to the same amount of Mo supported on Al₂O₃ and MgO–Al₂O₃. The reduction temperature of supported Mo is in the order, MgO > MgO–Al₂O₃ > Al₂O₃. This indicates a strong metal support interaction in Mo/MgO as compared to Mo/Al₂O₃ and Mo/MgO–Al₂O₃.

The strong metal support interaction observed in the case of Mo/MgO catalyst is because of the poor electronegativity of Mg ions in MgO, leading to a weak Mg–O bond and hence the co-ordination ability of oxygen of MgO support to Mo metal is higher causing strong metal (Mo)–support interaction. Electronegativity of metal ions present in Al₂O₃ is greater than MgO. Metal ions present in MgO–Al₂O₃ mixed oxide have an average effective electronegativity that lies in between to its component metal ions separately.

Theoretically, 8% Mo (~12% MoO₃) should need 56.02 ml STP H₂ for complete reduction to Mo metal. Actually, this proceeds in sequences of reduction, i.e. MoO₃ → MoO₂ requiring 18.67 ml STP/g H₂ corresponding to first TPR peak and MoO₂ → Mo needing 37.36 ml STP/g for the second peak. MgO support is also reduced consuming ~20 ml STP/g H₂ with peak maxima at 764 K (Fig. 3). A higher H₂ consumption in 8% Mo/MgO was therefore observed (Table 1). Assuming around 56 ml/g STP H₂ contributed by MoO₃ for complete reduction, the extra hydrogen consumption may be due to reduction of MgO support itself. Some other unidentified Mg species seems to be formed below 764 K as indicated by small peaks in TPR profile (Fig. 3), which account for the rest hydrogen consumption (~10 ml STP/g).

The H₂ consumption in TPR profiles with fixed 8 wt.% Mo should be basically the same on different supports

provided the support is not reduced. However, the metal support interactions are different on different supports. In 8 wt.% Mo/MgO, the first TPR peak maxima corresponding to MoO₃ → MoO₂ is observed at 876 K. The reaction was studied at 673 K on catalyst after sulfidation at 673 K where catalytically active species MoO₂ (MoS₂) are available as sulfidation is thermodynamically favorable than reduction [18].

The hydrogen consumption in reduction up to first TPR peak is indicative of formation of MoO₂ species only. This H₂ consumption does not have direct correlation with hydrogen available for hydrogenation on metal sites during the reaction in post sulfided (reduced) catalyst. Thus, low hydrogenation rate in Mo/MgO (Table 2) as compared to MgO/Al₂O₃ and Mo/MgO–Al₂O₃ cannot be explained on the basis of TPR results alone. However, a good correlation has been found with HDS activity and LTOC (Mo dispersion). The 8% Mo/MgO has shown highest LTOC indicating large population of metal sites available at the surface for desulfurization in presence of H₂. This has also reflected in the highest value of HDS activity for this catalyst (Table 2). About 8% Mo/Al₂O₃ and 8% Mo/MgO–Al₂O₃ have lower values of LTOC and the HDS activity also falls accordingly. Moreover, HDS may involve hydrogenation and hydrogenolysis.

Microcalorimetric results on the acidity and acid strength distribution of supports and their respective Mo catalysts are shown in Table 3. Differential heats versus ammonia coverage for supports and Mo catalyst are illustrated in Figs. 4 and 5, respectively. Al₂O₃ has a total acidity 0.336 mmol/g and shows a heterogeneous distribution of acid sites. MgO does not show any acidity, as it is basic in nature but incorporation of equal stoichiometric amounts of MgO into Al₂O₃ matrix through co-precipitation creates moderate acidity.

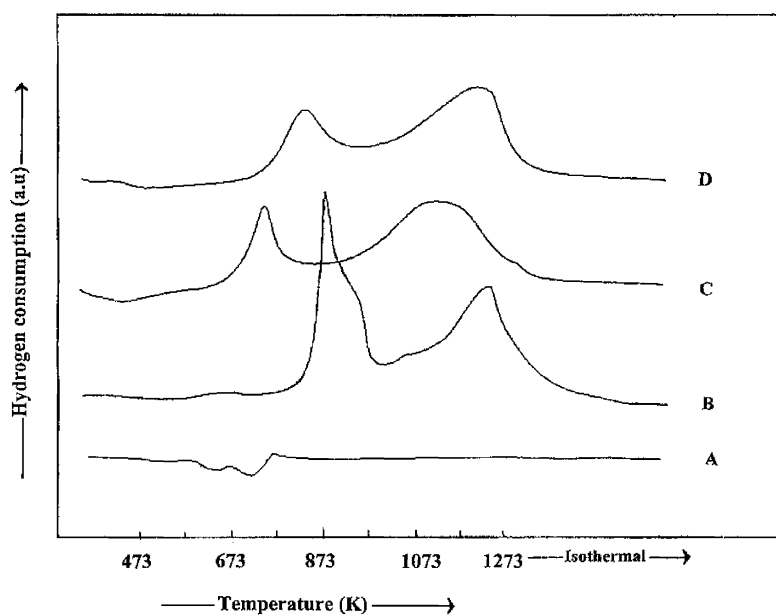


Fig. 3. Temperature-programmed reduction (TPR) profiles of: (A) pure MgO; (B) 8 wt.% Mo/MgO; (C) 8 wt.% Mo/Al₂O₃; and (D) 8 wt.% Mo/MgO–Al₂O₃.

Table 2
Catalytic activities of supported Mo catalysts

Catalyst	r_{HDS} (mol/h g _{cat})	r_{HYD} (mol/h g _{cat})	r_{HYC} (mol/h g _{cat})
8 wt.% Mo/MgO	52.6×10^{-3}	15.6×10^{-3}	23.65×10^{-3}
8 wt.% Mo/Al ₂ O ₃	23.56×10^{-3}	36.4×10^{-3}	32.34×10^{-3}
8 wt.% Mo/MgO–Al ₂ O ₃	11.78×10^{-3}	30.5×10^{-3}	36.25×10^{-3}

Table 3
Acidity and acid strength distributions of oxide supports and catalysts

Samples	Total acidity (mmol/g _{cat})	Acid strength distribution (mmol of NH ₃ /g _{cat})		
		Strong	Medium	Weak
Al ₂ O ₃	0.336	0.085	0.105	0.146
MgO	0.000	–	–	–
MA	0.290	Nil	0.125	0.165
8% Mo/MgO	0.209	0.00	0.145	0.064
8% Mo/Al ₂ O ₃	0.402	0.170	0.120	0.112
8% Mo/MA	0.339	0.100	0.160	0.079

MA: MgO–Al₂O₃; strong >100 kJ/mol; medium: 100–75 kJ/mol; weak: <75 kJ/mol.

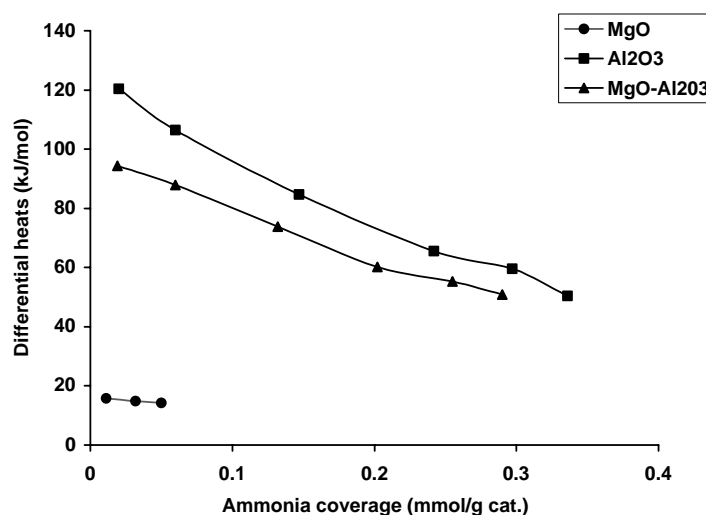


Fig. 4. Differential heats vs. ammonia coverage for MgO, Al₂O₃ and MgO–Al₂O₃ support samples.

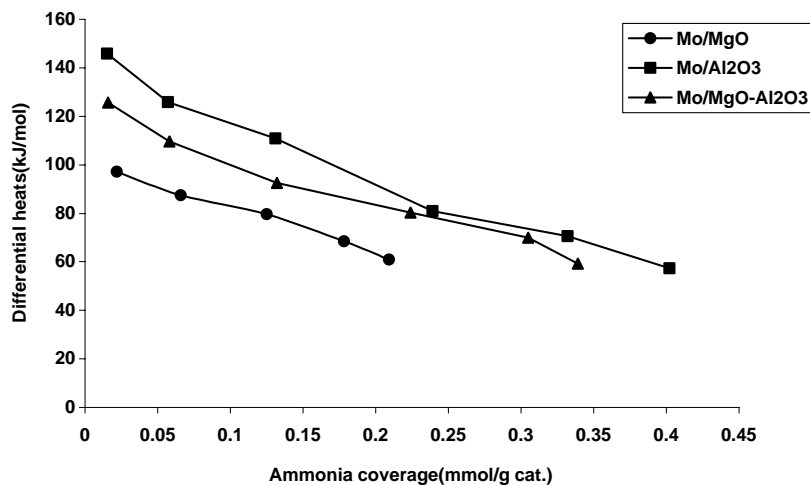


Fig. 5. Differential heats vs. ammonia coverage of 8 wt.% Mo supported catalysts.

MgO–Al₂O₃ does not have strong acid sites but shows an increase in medium and weak acid sites as compared to Al₂O₃. It seems to follow the rule that strong acid sites are neutralized first when an acidic support is mixed chemically with basic one. Generation of medium and weak acid sites in MgO–Al₂O₃ mixed oxide are due to redistribution of charges which depends upon the structure of mixed oxide [19]. It was noticed that incorporation of 8 wt.% Mo onto the surface of oxide supports improves the total acidity and its distribution. MgO does not have inherent acidity but incorporation of 8 wt.% Mo creates acidic sites on the surface of MgO. In general, acidity depends upon the average electronegativity of ions present. Addition of Mo onto surface of oxides improves average electronegativity of metal ions present in it. Comparison among Mo supported catalysts shows that Mo/Al₂O₃ catalyst has the highest total acidity and strong acid sites than Mo/MgO–Al₂O₃ and Mo/MgO.

HYC activities do not seem to be affected by hydrogen consumption of catalysts as hydrocracking is a function of acidity and is strongly controlled by acidic properties of catalyst. The HYC activities are nearly equal for supported Al₂O₃ and MgO–Al₂O₃ catalysts. Mo/MgO catalyst also show some HYC activity due to the presence of acid sites of moderate strength induced by the incorporation of acidic MoO₃ on basic MgO.

4. Conclusions

Incorporation of Al₂O₃ to MgO increases BET surface area significantly without affecting the total pore volume and also introduces bimodal pore size distribution. At least a 8% Mo on MgO–Al₂O₃ mixed oxide has been found to be sufficient to form a MoO₃ monolayer on the surface. This has been established by two independent techniques, viz. TPR and LTOC. TPR technique can also be used effectively as an additional tool to determine the monolayer coverage of MoO₃ on the support. TPR studies reveal that there are strong metal support interactions in the case of MgO as compared to Al₂O₃. Mo/MgO has the highest HDS activity

among Mo supported on Al₂O₃ and MgO–Al₂O₃. Incorporation of basic MgO into the lattice of amphoteric Al₂O₃ in the MgO–Al₂O₃ catalysts introduces moderate acidity neutralizing the strong acid sites of alumina. Addition of Mo on MgO, Al₂O₃ and MgO–Al₂O₃ enhances the acidity of these oxides due to the acidic nature of MoO₃ species. An increase in acidity is noticed from weak to strong acid sites with the increase in electronegativity of the metal ion of an oxide.

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