The Acidic Property and Catalytic Activity of MoO_3-SiO_2-Al_2O_3

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The ternary oxide system MoO_3–SiO_2–Al_2O_3 was prepared by coprecipitation method. The pH of coprecipitation has been varied from pH=2 to pH=8 and its effect on the acidic properties of the ternary oxide acidic system was studied by butylamine titration. The MoO_3–SiO_2–Al_2O_3 prepared from highly acidic solution has low acid strength. The total acid amount of the ternary oxide decreased considerably at higher pH (>6) of coprecipitation. It was found that the total acid amount of MoO_3–SiO_2–Al_2O_3 containing 9.7% (by weight) of MoO_3 and silica to alumina molar ratio 16.6 is very high compared with that of SiO_2–Al_2O_3 of the same silica to alumina molar ratio. The acid strength of SiO_2–Al_2O_3 is reduced by the incorporation of MoO_3. Increase in calcination temperature increased the acid strength. The catalytic activity of MoO_3–SiO_2–Al_2O_3 was found to be very high for the alkylation of toluene with 2-propanol. The products are found to be *o*-cymene, *p*-cymene, and three isomers of diisopropyltoluenes. Reaction temperature >200 °C, higher liquid hourly space velocity, and higher alcohol content in the feed decreased the total conversion of 2-propanol to isopropyltoluenes. The acidic property and catalytic activity of MoO_3–SiO_2–Al_2O_3 are not considerably reduced up to four successive regeneration cycles.

Transition metal oxides as such are impractical acid catalysts due to their low acid strength and low value of acid amount. But binary oxides containing transition metal oxides and silica or alumina serve effective catalysts in various acid-catalyzed reactions.[1–5] Similarly many combinations of transition metal oxides viz. TiO_2–ZnO,[6] TiO_2–MoO_3,[7,8] TiO_2–V_2O_5,[8,9] ZnO–Fe_2O_3,[10] and WO_3–TiO_2[11] also have been found to show remarkable acidic properties and catalytic activities. The recent studies by K.V.C. Rao et al. on the ternary oxide sytem TiO_2–SiO_2–Al_2O_3 indicated their utility as acid catalysts in a wide range of alkylation reactions.[12] Also it has been found that the acidity distribution of this ternary oxide system depends on various parameters which include the pH of the solution from which the hydroxides of the component metals of the ternary oxides are coprecipitated, transition metal oxide content and calcination temperature.[13]

Even though MoO_3 supported on SiO_2–Al_2O_3 (Mosial) is also known to catalyze effectively certain oligomerization and polymerization reactions,[14–16] a systematic study on the synthesis of Mosial catalysts and their acidity distributions are not previously attempted. Thus in the present paper, we report the acidic and catalytic properties of a series of Mosial catalysts synthesized by changing the pH of the coprecipitating solution. The acidity distributions are evaluated using butylamine titration technique[17] and the alkylation of toluene with 2-propanol has been selected as the test reaction for comparing the activities of different Mosial catalysts. The effect of calcination temperature on the acidic and catalytic properties, and the effect of process parameters such as temperature and liquid hourly space velocity (LHSV) on the catalytic activity of alkylation are also studied. The regeneration studies on the catalyst have also been included.

Experimental

Materials: The materials used are sodium silicate (Scientific Chemicals), aluminium sulfate (A.R. grade), ammonium molybdate (BDH), 2-propanol (BDH), butylamine (SD Chemicals), nitric acid, and ammonia of chemically pure quality. The indicators used are Neutral Red (pK_a=+6.8), Methyl Red (pK_a=+4.8), Dimethyl Yellow (pK_a=+3.3), phenylazodiphenylamine (pK_a=+1.5), Crystal Violet (pK_a=+0.8), dicinnamylideneacetone (pK_a=−3.0), benzylideneacetophenone (pK_a=−5.6), and anthraquinone (pK_a=−8.2).

Preparation of MoO_3-SiO_2-Al_2O_3: To an aqueous solution of sodium silicate (260 g dm^{-3} of water), dilute nitric acid (1 : 1) is added at 90 °C under constant agitation, till the pH of

Table 1. Physicochemical Characteristics of Different Mosial Catalysts Calcined at 600 °C

Sample	pH of co-ppt	SiO_2/Al_2O_3 molar ratio	% MoO_3 (by weight)	Pore vol	Surface area
				cm^3 g^{-1}	m^2 g^{-1}
Mosial-2	2	48.2	11.5	0.54	52
Mosial-3	3	40.5	10.3	0.63	61.5
Mosial-4	4	16.6	9.7	0.67	83
Mosial-5	5	9.3	9.2	0.57	57
Mosial-6	6	8.8	6.4	0.36	38
Mosial-7	7	8.4	5.5	0.28	33
Mosial-8	8	8.1	5.3	0.04	8
SiO_2–Al_2O_3	4	16.3	—	1.20	135

the solution is reduced to one. Hot aluminium sulfate solution (100 g in 300 dm^3 of water) is added followed by the addition of ammonium molybdate solution (15 g in 100 dm^3 of water). Ammonia solution is added slowly, till the required pH is attained. The precipitations are carried out at different pH's (2,3,4,5,6,7,8, and 9) and are designated as Mosial-2, Mosial-3 and so on. A SiO_2–Al_2O_3 catalyst is also synthesized at pH 4 without molybdenum oxide. The precipitates are washed with distilled water till free from sulfate ion and are extruded as pellets. These are dried at 120 °C for 12 h and sintered at 600 °C. The Mosial-4 samples were also calcined at different temperatures viz. 150, 300, and 1000 °C.

The physical parameters such as surface area (BET) and pore volume, the silica to alumina molar ratio as well as molybdenum oxide contents of different Mosial catalyst (calcined at 600 °C) determined by chemical analysis are shown in Table 1.

Measurement of Acidity: The acid amounts and acid strength of samples were measured by titrating the 100—200 mesh powder, suspended in dry benzene with butylamine solution in dry benzene using the above mentioned indicators.

Measurement of Catalytic Activity: The isopropylation of toluene with 2-propanol were carried out in a fixed bed tubular reactor at 200 °C (LHSV 0.5 h^{-1}; toluene/2-propanol mole ratio 3; total reaction time 7 h) using all the catalysts synthesized. The effect of temperature on the alkylating activity of Mosial-4 catalyst has been studied at five different temperatures viz. 160, 180, 200, 220, and 240 °C (LHSV 0.5 h^{-1}; toluene/2-propanol mole ratio 3; total reaction time 3 h). Similarly the effect of LHSV on the alkylating activity of Mosial-4 is also studied at three different LHSV viz. 0.5, 1, and 2 (temperature 200 °C, toluene/2-propanol mole ratio 3; total reaction time 7 h). The reactor was fed under gravitational flow. The amount of catalyst used was 25 g which corresponds to 60 ml in volume. The reactor, experimental and analytical procedures of the product mixtures, and method of calculation of percentage yields of isopropyltoluene were the same as those employed in the previous work.[18]

To estimate the catalyst life for alkylation, the same catalyst (Mosial-4 calcined at 600 °C) is subjected to nine successive regenerations by passing air at 600 °C for 5 h, at the end of each alkylation experiment of 7 h.

The products are found to be *o*-cymene, *p*-cymene, and three isomers of diisopropyltoluenes (DIT).

Results and Discussion

The physical characteristics such as surface area and porosity are found to be optimum for the ternary oxide system coprecipitated from solution of pH 4 whereas these two parameters have been considerably reduced by the coprecipitation of the ternary oxide from highly acidic and highly alkaline solutions (Table 1). But the surface area of SiO_2–Al_2O_3 is comparatively high. The percentage of MoO_3 content decreased marginally and the silica to alumina ratio decreased drastically with the increase in the pH of coprecipitation.

Even though activated Al_2O_3 has moderately strong Lewis acid centers,[14] pure silica gel is inactive in demanding acid-catalyzed reactions as the acid strength value of surface SiOH groups is very low.[20] But several combinations of metal oxides each of which contains either SiO_2 or Al_2O_3 have been extensively used as useful catalysts in various acid-catalyzed reactions. Similarly transition metal oxides viz. TiO_2, MoO_3, etc. are impractical acid catalysts due to their low acid strength values, but serve as effective acid catalysts on combination with either SiO_2 or Al_2O_3.[1,3,4] The enhancement in the catalytic properties is attributed to increase in the acid strength and acid amount values of these binary oxides compared with the component single oxides. As reported recently, the incorporation of 10% (by weight) of TiO_2 into a SiO_2–Al_2O_3 support greately changed the acidity distribution of the latter.[13] Table 2 shows the acidity distribution of a series of MoO_3–SiO_2–Al_2O_3 samples calcined at 600 °C. The acidity distributions of all the Mosial samples differ greatly from that of SiO_2–Al_2O_3 as the latter possesses

Table 2. Acidity Distribution of Different Mosial Catalysts Calcined at 600 °C

Sample	Acid amount (mmol g^{-1}) at different pK_a's							
	+6.8	+4.8	+3.3	+1.5	+0.8	−3.0	−5.6	−8.2
Mosial-2	0.66	0.41	0.18	0.10	0.00	0.00	0.00	0.00
Mosial-3	0.61	0.48	0.32	0.14	0.05	0.00	0.00	0.00
Mosial-4	0.58	0.58	0.58	0.58	0.48	0.05	0.00	0.00
Mosial-5	0.55	0.55	0.55	0.55	0.46	0.10	0.00	0.00
Mosial-6	0.41	0.41	0.27	0.25	0.25	0.05	0.00	0.00
Mosial-7	0.37	0.34	0.22	0.21	0.21	0.02	0.00	0.00
Mosial-8	0.34	0.31	0.22	0.20	0.20	0.03	0.00	0.00

Table 3. Acidity Distribution of Mosial-4 Samples Calcined at Different Temperatures

Temperature of calcination/°C	Acid amount (mmol g^{-1}) at different pK_a's							
	+6.8	+4.8	+3.3	+1.5	+0.8	−3.0	−5.6	−8.2
150	0.64	0.48	0.24	0.15	0.00	0.00	0.00	0.00
300	0.61	0.52	0.32	0.30	0.05	0.00	0.00	0.00
600	0.58	0.58	0.58	0.58	0.48	0.05	0.00	0.00
1000	0.03	0.03	0.03	0.03	0.03	0.03	0.00	0.00

only too strong acid sites. Also it is well-known that MoO_3 is devoid of acid sites of strength $H_o<+4.8$.[5] Hence it is clear that new acidic sites which differ from those of MoO_3, SiO_2, Al_2O_3, and SiO_2–Al_2O_3 are created on the surface of the ternary oxide MoO_3–SiO_2–Al_2O_3.

However, the acidity distribution of MoO_3–SiO_2–Al_2O_3 system depends mainly on the pH of the final gel during coprecipitation. The Mosials prepared from highly acidic solutions contain mainly weak acid sites ($H_o>+1.5$) whereas a pH of 4 appears optimum in producing acid sites of fairly high acid strength and large acid amount. But further increase in pH decreased the total acid amount values even though the acid strength is not affected. The pH of the coprecipitating solution is shown to have pronounced effect on the compositions of ternary oxides prepared (Table 1). This change in composition, especially the drastic change in silica to alumina mole ratio can be a probable factor governing the acidity distribution.[13]

The acid strength of MoO_3–SiO_2–Al_2O_3 ($H_o \geqslant -3.0$) (Table 2) is comparatively lower than that of TiO_2–SiO_2–Al_2O_3 which is around $H_o=-5.6$.[13] The latter possesses even few acid sites of strength $H_o=-8.2$.[13] This can be probably due to the difference in the averaged electronegativity values of the component metal ions of these two ternary oxide systems.[21]

Effect of Calcination Temperature on Acidity Distribution: Table 3 shows that the Mosial-4 sample calcined at 150 °C is rich in weak acid site ($H_o \geqslant +3.3$) and does not contain any strong acid site. But on increasing the calcination temperature to 300 °C, moderately strong acid site appeared, which may be due to the conversion of weak acid sites to stronger Lewis sites, caused by the loss of water molecules. Mosial-4 sample calcined at 600 °C contains only moderately strong acid sites whereas further increase in calcination temperature to 1000 °C caused almost a complete destruction of acid sites.

Catalytic Activity: The enhancement in the catalytic activity of Mosial-4 and Mosial-5 compared with SiO_2–Al_2O_3 in the alkylation of toluene with 2-propanol (Fig. 1) can be due to the increased acid amount of the ternary oxide system (Table 2). Our earlier studies on TiO_2–SiO_2–Al_2O_3 have also shown that the transition metal oxide exerts a synergistic effect up on the alkylating activity of SiO_2–Al_2O_3.[18] When transition metal

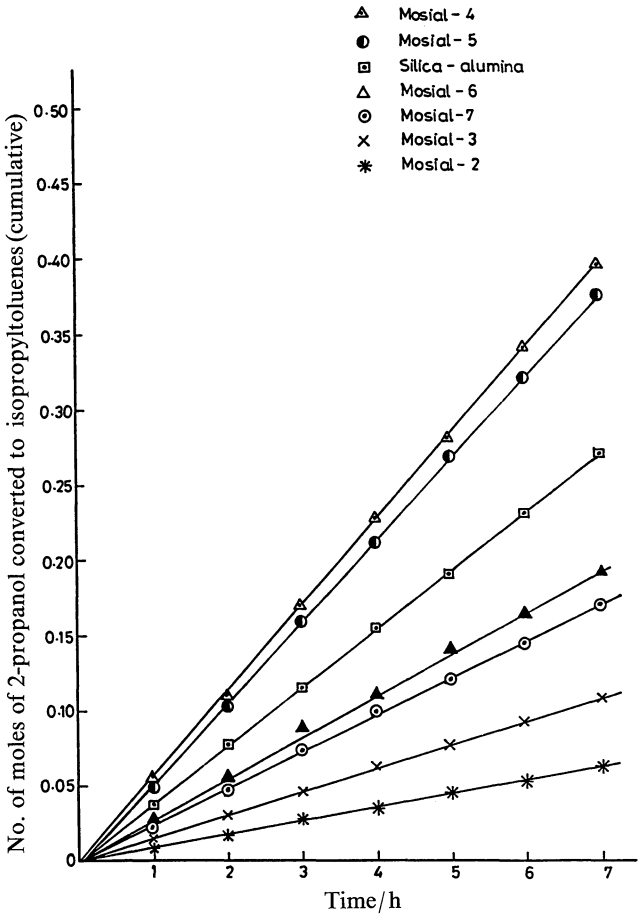


Fig. 1. Cumulative number of moles of 2-propanol converted to isopropyl toluenes over various Mosial catalysts. Reaction conditions: Reaction temperature: 200 °C; Liquid hourly space velocity: 0.5 h^{-1}; Toluene/2-propanol mole ratio: 3.

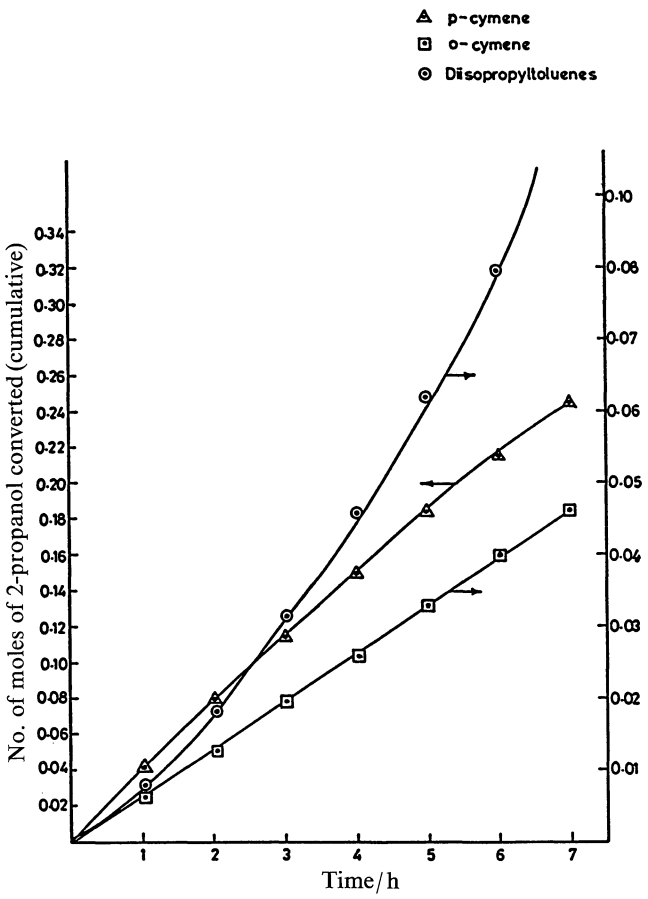


Fig. 2. Cumulative number of moles of 2-propanol converted to *o*-cymene, *p*-cymene, and diisopropyltoluenes over Mosial-4 catalyst. Reaction conditions: Reaction temperature: 200 °C; Liquid hourly space velocity: 0.5 h^{-1}; Toluene/2-propanol mole ratio: 3.

oxides are supported on SiO_2–Al_2O_3, $\overset{+}{M}$–H species are formed where M is the transition metal atom and these species are of suitable acid strength to initiate the alkylation reaction.[18] The $\overset{+}{M}$–H species interacts with the 2-propanol to produce $\overset{+}{M}$–$CH(CH_3)_2$ as shown in Scheme 1 which in turn forms a π-complex with the aromatic substrate, due to the low lying unoccupied d orbitals of the transition metal atom.[18] This π-complex on a π–σ rearrangement gives isopropyltoluenes.[18]

However Mosial-2, Mosial-3, Mosial-6, and Mosial-7 samples exhibited less alkylating activity (Fig. 1) which may be due to the low acid strength and low acid amount values respectively of the former and latter pairs (Table 2). But the rate of formation of isopropyltoluenes remained constant throughout the reaction time for all the catalysts studied (Fig. 1). Even though the product mixture is rich in *p*-cymene content which could be due to steric factors arising when the reacting species are adsorbed on adjoining sites,[22] the extent of formation of *p*-cymene decreased and a corresponding increase in the formation of diisopropyltoluenes was observed with the passing of reaction time (Fig. 2). Hence it could be depicted that the adsorbed *p*-cymene molecules are more prone to get further alkylated to produce diisopropyltoluenes.[18] However the rate of formation of *o*-cymene is unaffected by reaction time. These observations are in good agreement with the results obtained in the alkylation studies of toluene with 2-propanol over TiO_2–SiO_2–Al_2O_3.[18]

Effect of Temperature: The conversion of 2-propanol to isopropyltoluenes increased as the reaction temperature increased from 160 to 200 °C (Fig. 3). Further increase in temperature decreased the conversion. But the unreacted alcohol in the product mixtures is practically nil, irrespective of the reaction temperature (Fig. 3). This shows that the dehydration of 2-propanol is possible over Mosial-4 even at lower temperatures. As shown in Scheme 1, both the dehydrated product (propylene) as well as the alkylated product (isopropyltoluenes) may be formed from the same intermediate, $\overset{+}{M}$–isopropyl.[23] The increase in the reaction temperature from 160 °C to 200 °C may enhance the interaction between the entity $\overset{+}{M}$–isopropyl and the toluene molecule due to the effective diffusion of the latter molecules into the interior surfaces of the catalysts pellet.[23]

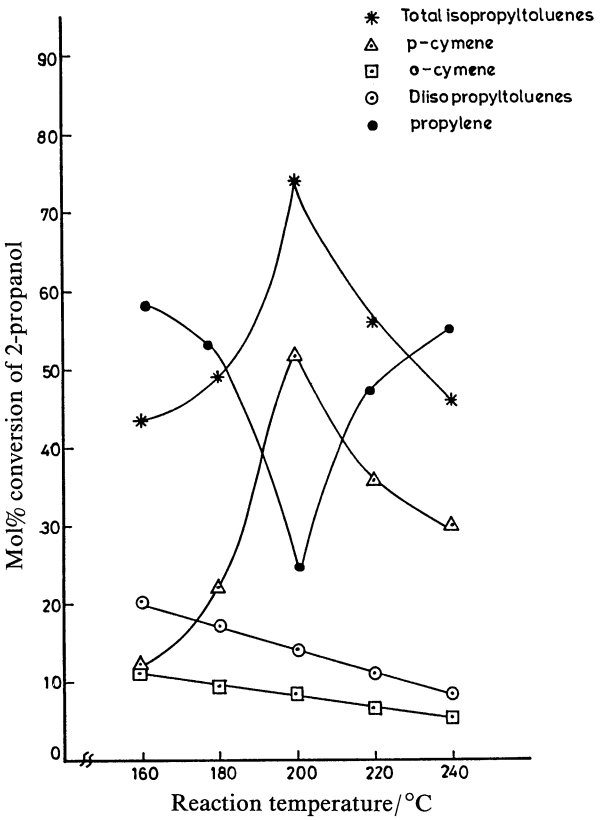
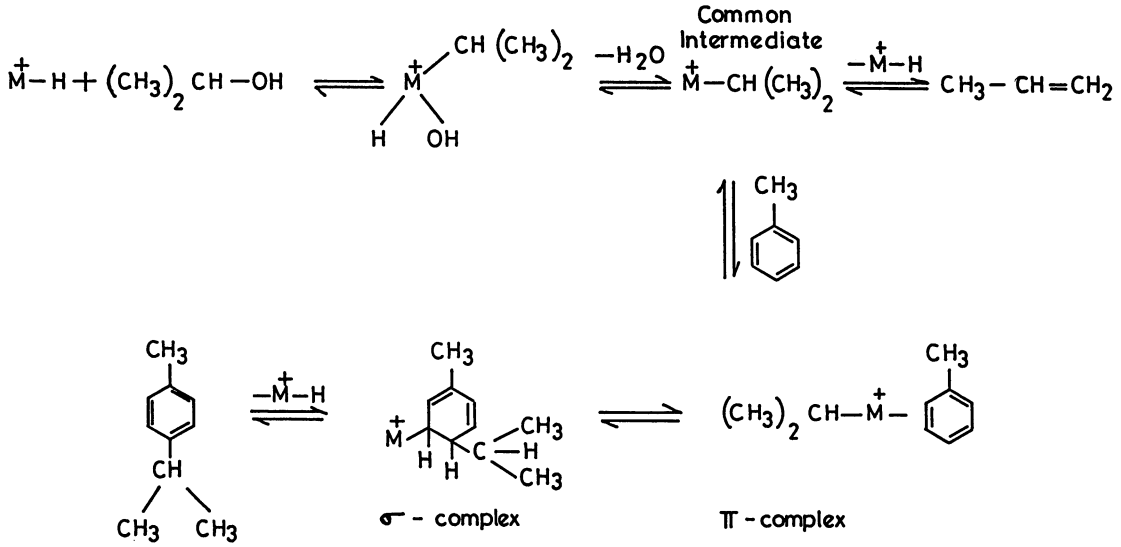


Fig. 3. Effect of reaction temperature on the conversion of 2-propanol to isopropyltoluenes over Mosial-4 catalyst. Reaction conditions: Liquid hourly space velocity: 0.5 h^{-1}; Toluene/2-propanol mole ratio: 3.



Scheme 1. The mechanism of alkylation of toluene with 2-propanol over MoO_3–SiO_2–Al_2O_3 catalyst.

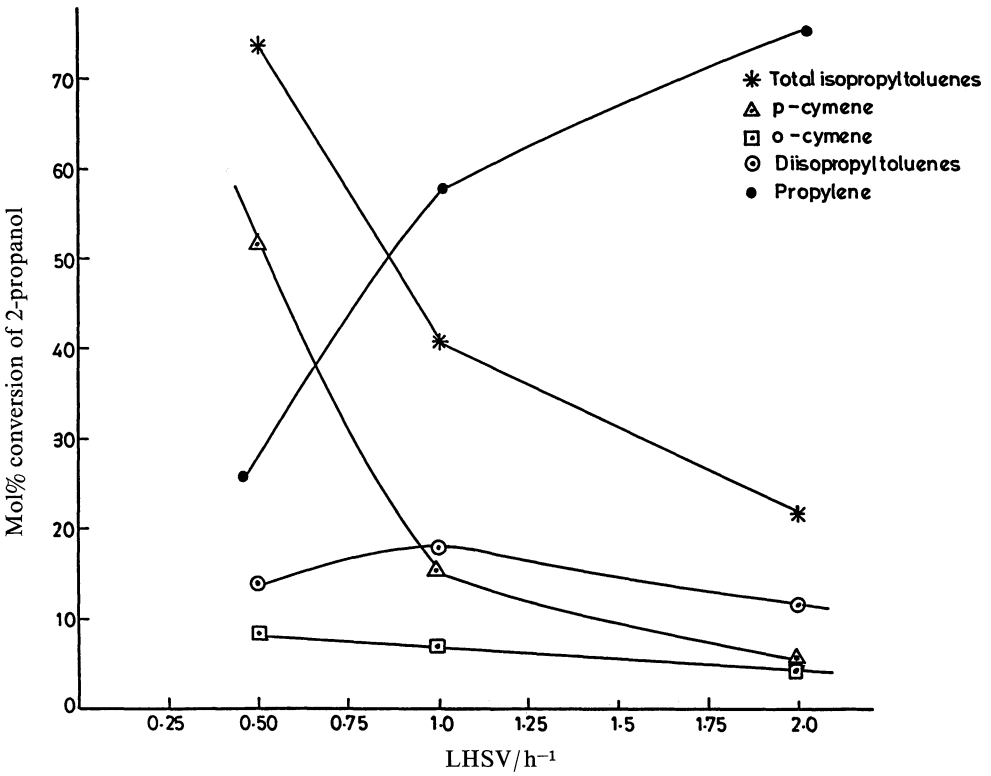


Fig. 4. Effect of liquid hourly space velocity on the conversion of 2-propanol to isopropyltoluenes over Mosial-4 catalyst. Reaction conditions: Reaction temperatures: 200 °C; Toluene/2-propanol mole ratio: 3.

However, at very high reaction temperatures (>200 °C), the formed isopropyltoluene molecules may undergo dealkylation to toluene which could be a probable reason for the decreased conversions. Similarly, the dealkylation of formed cymene molecules at reaction temperatures >200 °C has been observed by us earlier over TiO_2–SiO_2–Al_2O_3 catalyst in the alkylation of toluene with 2-propanol.[18] The *o*-cymene formation decreased marginally with the increase in reaction temperature whereas the optimum formation of *p*-cymene is observed at 200 °C. However in the product mixture, the para-isomer content is more irrespective of the reaction temperature studied, which could be due to the steric factors arising between the reacting species as discussed previously.[22] Hence it may be presumed that the interaction between an adsorbed toluene molecule and the adsorbed alkylating moiety leads to the formation of the para-isomer whereas the interaction of the latter with a free unadsorbed toluene in the gaseous state results in the formation of ortho-isomer.[18] Also it could be depicted that the formation of cymene molecules via the former route take place on the interior surface of the catalyst pellet, the rate of which is enhanced by the effective diffusion of the toluene molecules into the pores of the catalyst pellet.[23] Hence the marginal decrease in the formation of *o*-cymene and increase in the formation of *p*-cymene with increase in reaction temperature. These observations are also in line with those of alkylation reactions carried out over ion-exchanged zeolites.[24]

Increased formation of diisopropyltoluene is observed at lower reaction temperatures. This may be due to the high residence time of cymene molecules formed at lower temperatures, resulting in further alkylation.[18] Multialkylations are generally favored at lower reaction temperature.[25]

Effect of LHSV: As the LHSV increased from 0.5 to 2, the conversion of 2-propanol to isopropyltoluenes decreased drastically (Fig. 4). However unreacted 2-propanol has not been observed in the product mixture in all cases. It may be assumed that at higher LHSV, because of the less effective diffusion of the toluene molecules into the interior surface of the catalyst pellet, the $\overset{+}{M}$–isopropyl species formed there leads to propylene formation and hence the decreased conversions to *p*-cymene and marginal increase in the formation of *o*-cymene.[23] Also at higher LHSV, the formed cymene molecules may get further alkylated by $\overset{+}{M}$–isopropyl species, even before desorbing out from the reaction site, causing increase in the formation of diisopropyltoluenes.

Effect of Toluene/2-Propanol Mole Ratio in the Feed: The conversion of 2-propanol to isopropyltoluenes decreased considerably with the increase in the alcohol content in the feed (Fig. 5). However at these conditions, the dehydration of 2-propanol to propylene predominated, which suggests that large excess of toluene in the feed suppresses the formation of propyl-

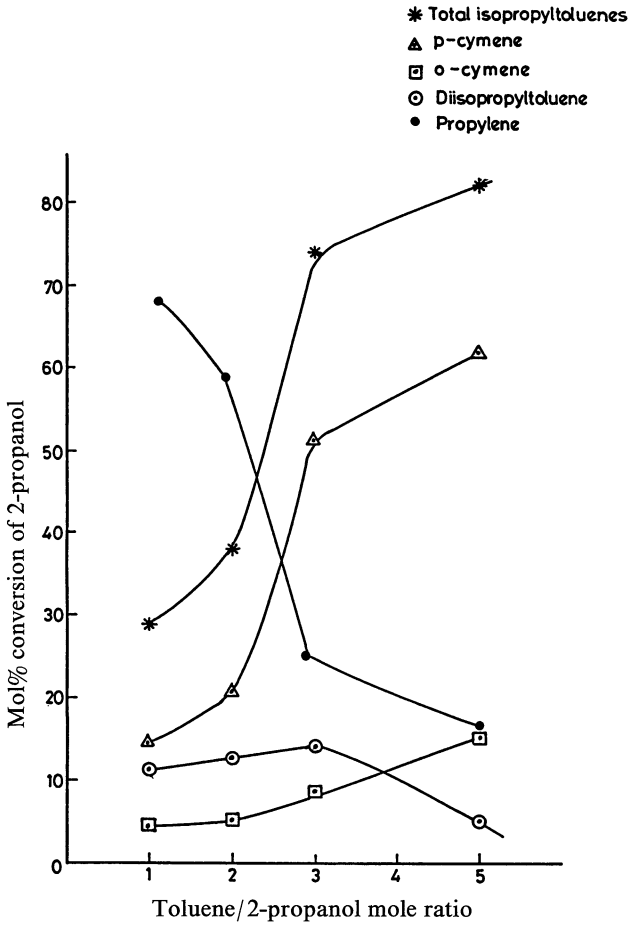


Fig. 5. Effect of toluene/2-propanol mole ratio on the conversion of 2-propanol to isopropyltoluene over Mosial-4 catalyst. Reaction conditions: Reaction temperature: 200 °C; Liquid hourly space velocity: 0.5 h^{-1}.

ene from $\overset{+}{M}$–isopropyl, causing increased conversions to isopropyltoluenes. Similarly, increased conversions to isopropylbenzene have been observed by K. H. Chandavar et al.[26] in the isopropylation of benzene at higher benzene to alcohol mole ratio.

Also the large excess of the aromatic substrate in the feed decreased the formation of diisopropyltoluene and caused marginal increase in the conversion to *o*-cymene (Fig. 5).

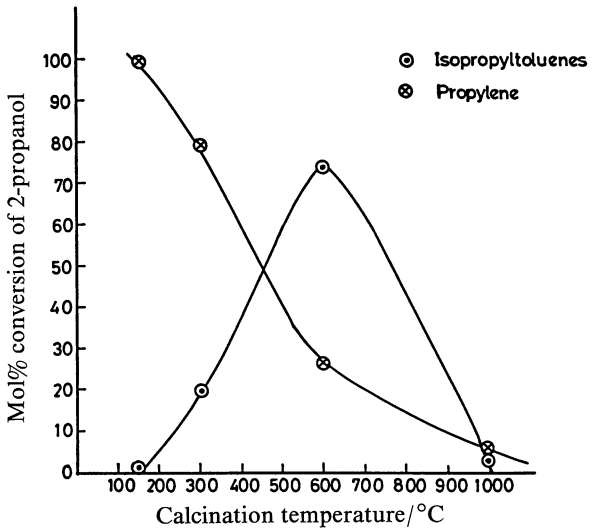


Fig. 6. Effect of calcination temperature on the alkylating activity of Mosial-4 catalyst. Reaction conditions: Reaction temperature: 200 °C; Liquid hourly space velocity: 0.5 h^{-1}; Toluene/2-propanol mole ratio: 3.

Effect of Calcination Temperature: The optimum conversion of 2-propanol to isopropyltoluenes is given by Mosial-4 samples calcined at 600 °C (Fig. 6) which has a high acid strength value and fairly large acid amount (Table 3). Even though the samples calcined at lower temperatures are less active in catalyzing the alkylation of toluene, they served as effective catlaysts in the dehydration of alcohol molecules which is evidenced by the quantity of propylene produced (Fig. 6).

The Regenerability of Mosial-4: The acidity distribution of Mosial-4 is negligibly affected by four or five successive regeneration cycles (Table 4). Correspondingly, the alkylating activity of the sample also is almost unaffected which is evidenced from (Fig. 7). However further regeneration cycles reduced alkylating activity.

Conclusion

The total acid amount of MoO_3–SiO_2–Al_2O_3 containing 9.7% by weight of MoO_3 and silica to alumina molar

Table 4. Effect of Successive Regeneration Cycles on the Acidity Distribution of Mosial-4

No. of regeneration cycle	Acid amount (mmol g^{-1}) at different pK_a's							
	+6.8	+4.8	+3.3	+1.5	+0.8	−3.0	−5.6	−8.2
0	0.58	0.58	0.58	0.58	0.48	0.05	0.00	0.00
1	0.58	0.58	0.58	0.58	0.48	0.05	0.00	0.00
2	0.57	0.57	0.57	0.57	0.48	0.04	0.00	0.00
3	0.55	0.55	0.55	0.55	0.48	0.04	0.00	0.00
4	0.53	0.53	0.53	0.53	0.46	0.04	0.00	0.00
5	0.49	0.49	0.49	0.49	0.44	0.03	0.00	0.00
6	0.44	0.44	0.44	0.44	0.40	0.02	0.00	0.00
7	0.38	0.38	0.38	0.38	0.36	0.02	0.00	0.00
8	0.32	0.32	0.32	0.32	0.10	0.00	0.00	0.00
9	0.27	0.27	0.27	0.27	0.10	0.00	0.00	0.00

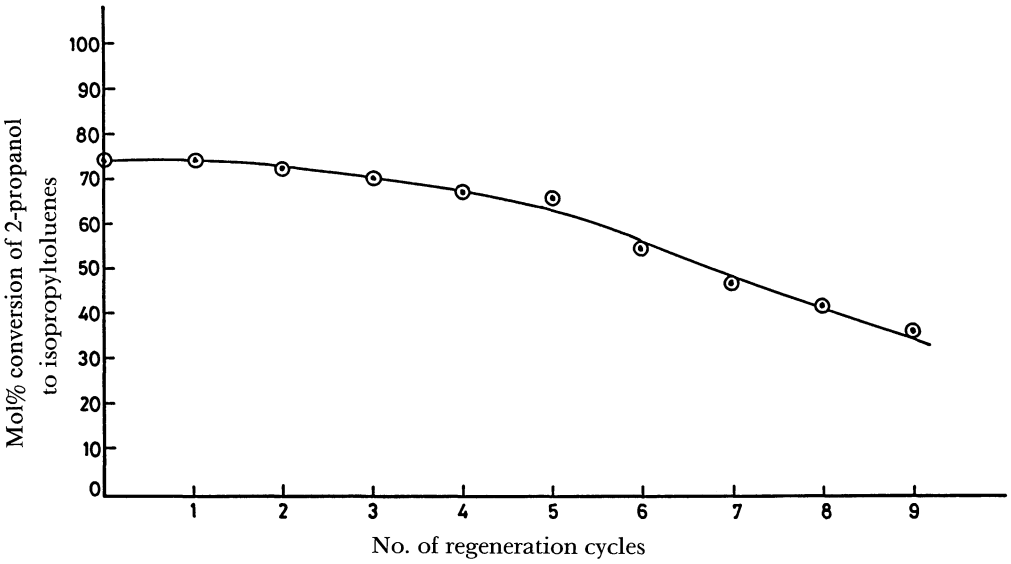


Fig. 7. Effect of successive regeneration cycles on the alkylating activity of Mosial-4 catalyst. Reaction conditions: Reaction temperature: 200 °C; Liquid hourly space velocity: 0.5 h^{-1}; Toluene/2-propanol mole ratio: 3.

ratio 16.6 is very high compared to that of SiO_2–Al_2O_3 of the same silica to alumina molar ratio. The acid strength of SiO_2–Al_2O_3 is reduced by the incorporation of MoO_3. Also the ternary oxide system coprecipitated from highly acidic solution has low acid strength and that coprecipitated from highly alkaline solution has low acid amount. The catalytic activity of MoO_3–SiO_2–Al_2O_3 for the alkylation of toluene with 2-propanol is very high compared with that of SiO_2–Al_2O_3. However reaction temperatures >200 °C, higher liquid hourly space velocity and higher alcohol content in the feed decreased the total conversion of 2-propanol to isopropyltoluenes. The acidic property and catalytic activity of MoO_3–SiO_2–Al_2O_3 are not considerably reduced up to four successive regeneration cycles.

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