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A Comparative Study on the Acidic Properties and Catalytic Activities of TiO_2, SiO_2, Al_2O_3, SiO_2–Al_2O_3, SiO_2–TiO_2, Al_2O_3–TiO_2, and TiO_2–SiO_2–Al_2O_3

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Investigations are carried out to have a systematic comparison of the acidic properties and catalytic activities of single oxide TiO_2, SiO_2, Al_2O_3, their binary oxides and the ternary oxide TiO_2–SiO_2–Al_2O_3. The acidity distributions are measured by using butylamine titration technique and the test reactions selected for the catalytic activity measurements are alkylation of toluene with 2-propanol and the dehydration of 2-propanol. The single oxides have only low acid strength and are not at all active in catalyzing the alkylation reaction, but are marginally active in the dehydration of 2-propanol. However the binary oxides SiO_2–TiO_2 and Al_2O_3–TiO_2 of 10% by weight of TiO_2 are found to contain very strong acid sites $H_o \leqslant -8.2$ and are highly active catalysts in both the test reactions. But TiO_2–SiO_2–Al_2O_3 of 10% by weight of TiO_2 showed the highest acid amount and the highest activity in the aikylation and dehydration reactions compared to the binary oxides. The acid amount and the catalytic activity of the ternary oxide increased with the increase of TiO_2 content upto 50 mol% of TiO_2 and then decreased. The ternary oxide containing 80 mol% of TiO_2 is rich in weak acid sites. The increase of TiO_2 content does not affect the selectivity.

The utility of supported transition metal oxide catalysts like Cr_2O_3–SiO_2, MoO_3–SiO_2–Al_2O_3, and TiO_2–SiO_2–Al_2O_3 in certain acid-catalyzed oligomerization, polymerization, and a wide range of alkylation reactions are known.[1–8] The incorporation of transition metal oxides into SiO_2–Al_2O_3 is expected to alter the acidity distribution of the latter and hence its activity in various acid-catalyzed reactions. For instance, recently it has been found that TiO_2–SiO_2–Al_2O_3 is a highly active and regenerable alkylation catalyst.[8] Further investigations undertaken to study the effect of the pH of the coprecipitating solution on the acidic and catalytic properties of the ternary oxide revealed that the ternary oxide coprecipitated from a solution of pH 4 has optimum acid amount and acid strength and it even contains nearly double the acid amount of SiO_2–Al_2O_3[9].

The acidic properties of single oxides TiO_2, SiO_2, Al_2O_3, and their binary oxides are well studied.[10–16] However a systematic comparative study on the acidic properties and catalytic activities of these single oxides, the binary oxides SiO_2–Al_2O_3, SiO_2–TiO_2, Al_2O_3–TiO_2, and the ternary oxide TiO_2–SiO_2–Al_2O_3 in the isopropylation of toluene (a reaction catalyzed by solid acids with moderately strong acid sites) and the dehydration of 2-propanol (a reaction catalyzed by solid acids with relatively weak acid sites) are not previously attempted. Hence in the present paper we discuss the results of such a study. Besides we have prepared TiO_2–SiO_2–Al_2O_3 of varying TiO_2 content and almost the same silica to alumina molar ratio and studied the effect of titania content on the acidic and catalytic properties of the ternary oxide, the results of which are also included in this paper.

Experimental

Materials: The materials used are sodium silicate (Scientific Chemicals), aluminium sulfate (A. R. grade), titanium tetrachloride (KMML Chavara), 2-propanol (BDH), toluene (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 Metal Oxides: (a) Single Oxides: Single oxides such as Al_2O_3 and TiO_2 were prepared by the thermal decomposition of the respective hydroxides at 600 °C in air for 6 h. The hydroxides are precipitated from aqueous solutions of aluminium sulfate and titanium tetrachloride using 1 : 1 ammonia solution. The single oxide SiO_2 was prepared by precipitation from an aqueous solution of sodium silicate with dilute nitric acid followed by aging at 80 °C for 3 h and calcining at 600 °C for 6 h.

(b) Binary Oxides: The binary oxides SiO_2–Al_2O_3, SiO_2–TiO_2, and Al_2O_3–TiO_2 are obtained by the thermal decomposition of their hydroxides. The hydroxides were coprecipitated by adding 1 : 1 ammonia water to the mixed aqueous solutions of the metal salts, sodium silicate and aluminium sulfate for SiO_2–Al_2O_3, sodium silicate and titanium tetrachloride for SiO_2–TiO_2, and aluminium sulfate and titanium tetrachloride for Al_2O_3–TiO_2 till the pH of the final gel became 4. The precipitates were washed thoroughly to remove adhering anions such as chlorides and sulfates, extruded, dried (120 °C for 12 h) and calcined (600 °C for 6 h).

(c) TiO_2–SiO_2–Al_2O_3: The coprecipitation technique employed for the preparation of TiO_2–SiO_2–Al_2O_3 is referred elsewhere.[8] The coprecipitation was done by adding 1 : 1 ammonia water to the mixed aqueous solutions of sodium silicate, aluminium sulfate, and titanium tetrachloride till the pH of the final gel became 4. Six different samples of TiO_2–

Table 1. Amounts of Starting Materials Used for the Synthesis of Tisial with Different TiO_2 Contents and Their Physicochemical Characteristics (Calcined at 600 °C)

Sample	Amount of materials used			Composition		Surface area	Pore volume
	Sodium silicate	Titanium tetrachloride	Aluminum sulfate	SiO_2/Al_2O_3	TiO_2	$m^2\,g^{-1}$	$cm^3\,g^{-1}$
	g	ml	g	(mole ratio)	mol%		
Tisial-4A	270	5	105	16	2.3	120	1.05
Tisial-4B	265	10	102	15	4.3	108	0.87
Tisial-4C	260	20	100	16.4	8.4	100	0.71
Tisial-4D	220	50	85	17.3	19.8	90	0.60
Tisial-4E	175	120	70	17.4	50.0	66	0.42
Tisial-4F	120	200	40	17.0	80.0	41	0.28
SiO_2–Al_2O_3	260	—	100	16.4	—	135	1.20

SiO_2–Al_2O_3 of varying compositions viz.; Tisial-4A, Tisial-4B, Tisial-4C, Tisial-4D, Tisial-4E, and Tisial-4F were prepared by changing the starting quantities of sodium silicate, aluminium sulfate, and titanium tetrachloride as shown in Table 1. The precipitates were washed thoroughly to remove anions such as chlorides and sulfates, extruded, dried (120 °C for 12 h) and calcined (600 °C for 6 h). Tisial-4D, Tisial-4E, and Tisial-4F samples were also calcined at temperatures 150, 300, and 450 °C.

The physical characteristics such as surface area (for all the samples) and porosity (for binary oxides and ternary oxides) were measured and the chemical compositions were determined by chemical analysis.

Measurement of Acidity: The acidity distribution of different 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.[17)]

Measurement of Catalytic Activity: The alkylation of toluene with 2-propanol was done in a fixed bed tubular reactor (LHSV 0.5 h^{-1}, toluene/2-propanol mole ratio 3, total reaction time 7 h). The dehydration of 2-propanol was also done in the same reactor (LHSV 0.5 h^{-1}, total reaction time 7 h). The reactor, experimental and analytical procedures, and the method of calculation of percentage yields of alkylaromatics were the same as those employed in the previous work.[8,9)]

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

Results and Discussion

Acidic Properties of Various Mixed Oxide Catalysts: As the TiO_2 content increased, the physical parameters such as surface area and porosity of the ternary oxide TiO_2–SiO_2–Al_2O_3 decreased considerably (Table 1).

Single oxides TiO_2, SiO_2,and Al_2O_3 showed negligible amounts of acid sites stronger than acid strength H_o= +3.3. Also they possess very low value of total acid amount (Table 2). However, the binary oxide SiO_2–Al_2O_3 is a well-known solid acid of very high acid strength ($H_o \leqslant -8.2$) and hence is used as useful catalysts for various acid-catalyzed reactions in the field of petroleum chemistry.[17—21)] In good agreement with this, SiO_2–Al_2O_3 coprecipitated from a solution of pH 4 and which contains about 10% (by weight) of alumina was found to possess only strong acid sites (Table 3). Table 3 also shows that the binary oxides SiO_2–TiO_2 and Al_2O_3–TiO_2, both of which contain about 10% by weight of TiO_2 are rich in moderately strong acid sites (H_o

Table 2. The Acidity Distribution of Single Oxides (Calcined at 600 °C)

Oxide	Surface area	Acid amount ($mmol\,g^{-1}$) at different pK_a's							
	$m^2\,g^{-1}$	+6.8	+4.8	+3.3	+1.5	+0.8	−3.0	−5.6	−8.2
SiO_2	264	0.181	0.175	0.115	0	0	0	0	0
Al_2O_3	166	0.211	0.193	0.121	0.022	0	0	0	0
TiO_2	31	0.052	0.042	0.042	0	0	0	0	0

Table 3. The Physicochemical Characteristics and Acidity Distribution of Binary Oxides (Calcined at 600 °C)

Binary oxide	Composition $\frac{SiO_2}{Al_2O_3}$, $\frac{SiO_2}{TiO_2}$, $\frac{Al_2O_3}{TiO_2}$	Surface area	Pore volume	Acid amount ($mmol\,g^{-1}$) at different pK_a's							
	molar ratio	$m^2\,g^{-1}$	$cm^3\,g^{-1}$	+6.8	+4.8	+3.3	+1.5	+0.8	−3.0	−5.6	−8.2
SiO_2–Al_2O_3	16.4	135	1.21	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35
SiO_2–TiO_2	12.0	102	0.77	0.41	0.41	0.41	0.41	0.41	0.41	0.16	0.08
Al_2O_3–TiO_2	7.1	88	0.61	0.38	0.38	0.38	0.38	0.38	0.38	0.32	0.06

Table 4. Acidity Distribution of Tisial Sample of Varying TiO_2 Content (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
Tisial-4A	0.42	0.42	0.42	0.42	0.42	0.42	0.14	0.12
Tisial-4B	0.54	0.54	0.54	0.54	0.54	0.54	0.19	0.09
Tisial-4C	0.63	0.63	0.63	0.63	0.63	0.63	0.15	0.05
Tisial-4D	0.71	0.71	0.71	0.71	0.71	0.70	0.18	0.08
Tisial-4E	0.77	0.77	0.77	0.77	0.77	0.77	0.21	0.10
Tisial-4F	0.46	0.41	0.33	0.11	0.00	0.00	0.00	0.00

between +1.5 and −5.6) and they even contain very strong acid sites ($H_o \leqslant -8.2$). Even though binary oxides containing TiO_2 are known to posses strong acid sites due to which they serve as effective catalysts in the synthesis of aniline from phenol and ammonia, acid sites of strength $H_o = -8.2$ is never observed previously in the case of Al_2O_3–TiO_2.[21] Hence it may be concluded that the pH of coprecipitation governs the acidity distribution of these binary metal oxides similar to that reported in the case of ternary oxide containing SiO_2, Al_2O_3, and TiO_2. But the total acid amount value of TiO_2–SiO_2–Al_2O_3 containing about 10% by weight each of TiO_2 and Al_2O_3 is large compared with SiO_2–TiO_2 and Al_2O_3–TiO_2 (Table 4). Si–O–Si and Al–O–Al bond formation may occur in SiO_2–TiO_2 (when SiO_2 is the major component) and Al_2O_3–TiO_2 (when Al_2O_3 is the major component) respectively and could be a probable reason for the decreased acid amount values of these binary oxides in comparison with the ternary oxide TiO_2–SiO_2–Al_2O_3. That is, the number of bonds which can generate acid sites per unit surface area may be the highest in the case of TiO_2–SiO_2–Al_2O_3. However, the acid strength of a mixed metal oxide system depends on the averaged electronegativity values of the component metal ions.[10]

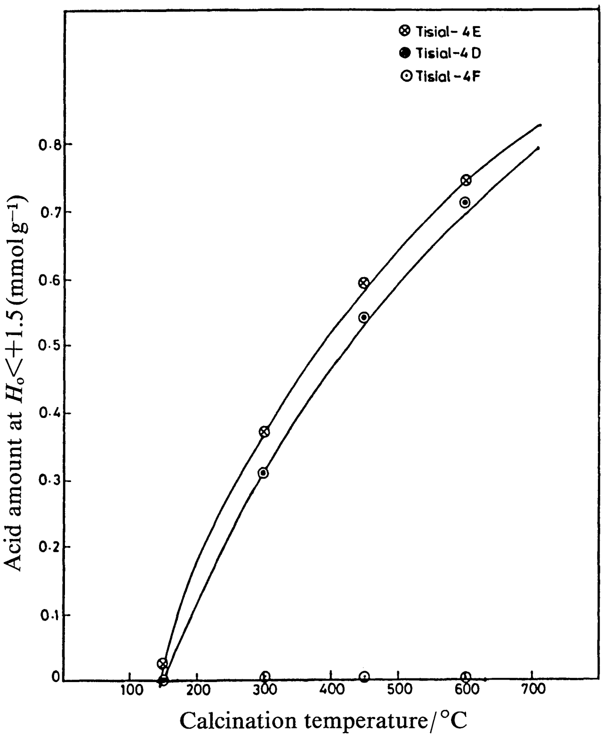

Fig. 1. The effect of calcination temperature on the acidity distribution of Tisial-4D, Tisial-4E, and Tisial-4F.

The Effect of TiO_2 Content on the Acidity Distribution of TiO_2-SiO_2-Al_2O_3: The acidity distribution of TiO_2–SiO_2–Al_2O_3 of varying TiO_2 content shows that the total acid amount increased with the increase of TiO_2 content and the maximum acid amount is shown by the sample containing 50 mol% of TiO_2 (Tables 3 and 4). Further increase in TiO_2 content decreased both the acid amount and acid strength. TiO_2–SiO_2–Al_2O_3 containing 80 mol% of TiO_2 (Tisial-4F) is rich in very weak acid sites. As the silica to alumina molar ratio is the same in all these Tisial samples, it may be assumed that the probability for the formation of Si–O–Al type bonds are the same, but the probabilities for the formation of Si–O–Ti and Al–O–Ti type bonds are different. The highest acid amount shown by Tisial-4E is due to the maximum number of Si–O–Ti and Al–O–Ti bonds on the surface of the ternary oxide, which are known to generate acidic sites. But the titania rich Tisial-4F may be rich in Ti–O–Ti bonds as substantiated by the existence of acid sites with low acid strength on the surface of this sample, which is the characteristic of TiO_2. Also Fig. 1 shows that with the increase in calcination temperature, the strong acid sites do not appear in Tisial-4F whatever be the calcination temperature, as in the case of TiO_2.[11]

Catalytic Activity. i) Alkylation of Toluene with 2-Propanol: The single oxides SiO_2, TiO_2, and Al_2O_3 are not effective in demanding the alkylation of toluene. However, the catalytic activity in the conversion of 2-propanol to alkylaromatics is fairly high for the binary oxides SiO_2–Al_2O_3, SiO_2–TiO_2, and Al_2O_3–TiO_2 (Fig. 2). Among them, SiO_2–TiO_2 showed the highest activity and SiO_2–Al_2O_3 showed the least activity. But TiO_2–SiO_2–Al_2O_3 is more active for the conversion of 2-propanol to alkylaromatics than any of these binary oxides. The enhanced activity of TiO_2–SiO_2–Al_2O_3 catalysts could be attributed to the very large acid amount at a suitable acid strength ($H_o \leqslant +1.5$) for the alkylation.[22] This is evident from the linear activity to acidity correlation obtained by plotting the acidity at $H_o \leqslant +1.5$ of different binary oxides and the ternary oxide against their isopropylating activity (Fig. 3).

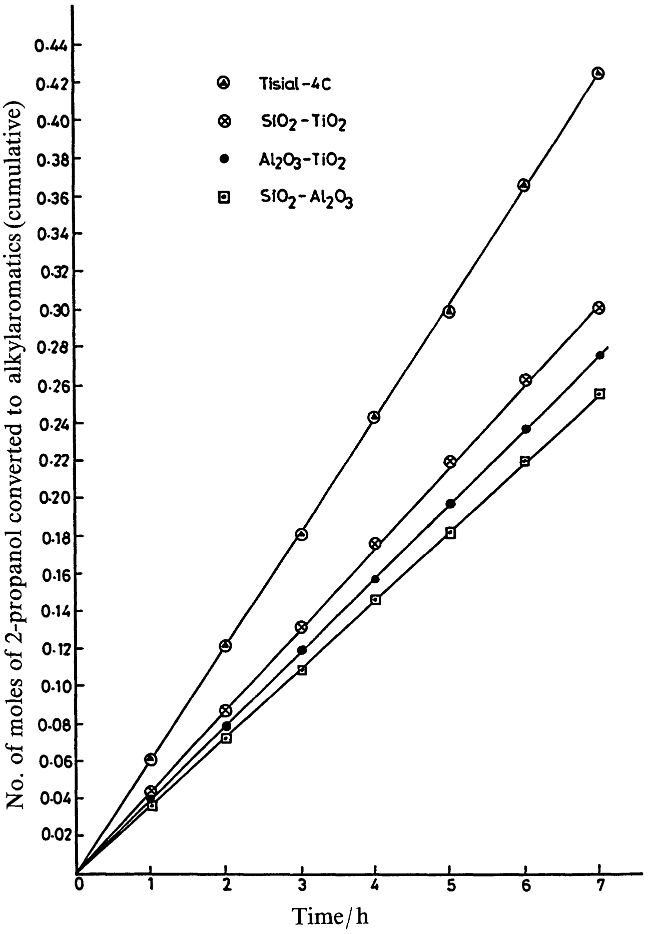

Fig. 2. Comparison of the catalytic activity of TiO_2–SiO_2–Al_2O_3 (Tisial) with that of binary oxides in the alkylation of toluene with 2-propanol. Reaction conditions; reaction temperature: 200 °C; LHSV: 0.5; toluene/2-propanol (mole ratio): 3.

With the increase in TiO_2 content, the alkylating activity of the ternary oxide system also increased (Fig. 4). But the Tisial-4F which is rich in weak acid sites are ineffective in catalyzing the alkylation of toluene.

The product mixtures obtained are rich in *p*-cymene

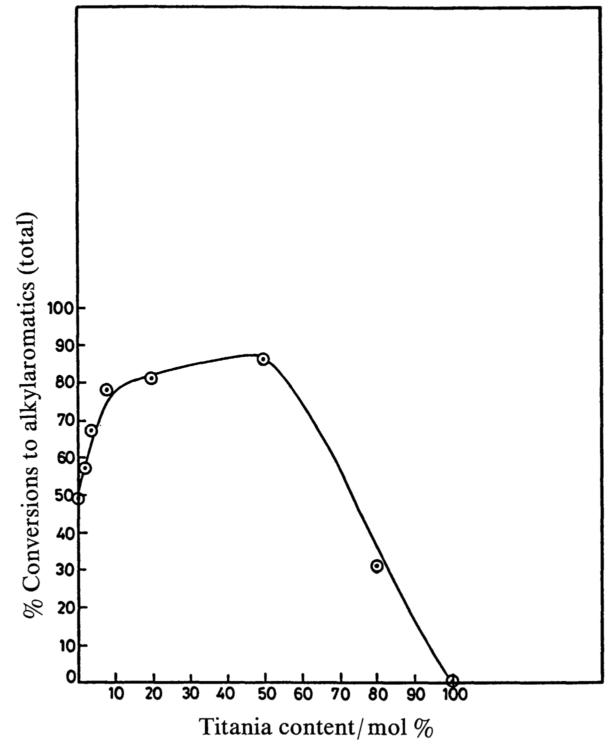

Fig. 4. Effect of titania content of Tisial on the conversion of 2-propanol to alkylaromatics. Reaction conditions; reaction temperature: 200 °C; LHSV: 0.5; toluene/2-propanol (mole ratio): 3.

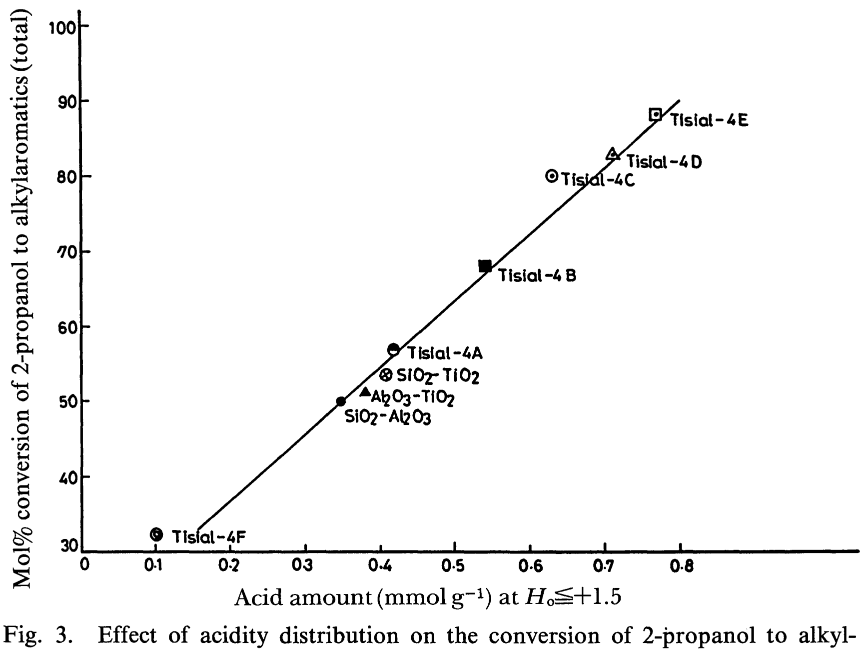

Fig. 3. Effect of acidity distribution on the conversion of 2-propanol to alkylaromatics. Reaction conditions; reaction temperature: 200 °C; LHSV: 0.5; toluene/2-propanol (mole ratio): 3.

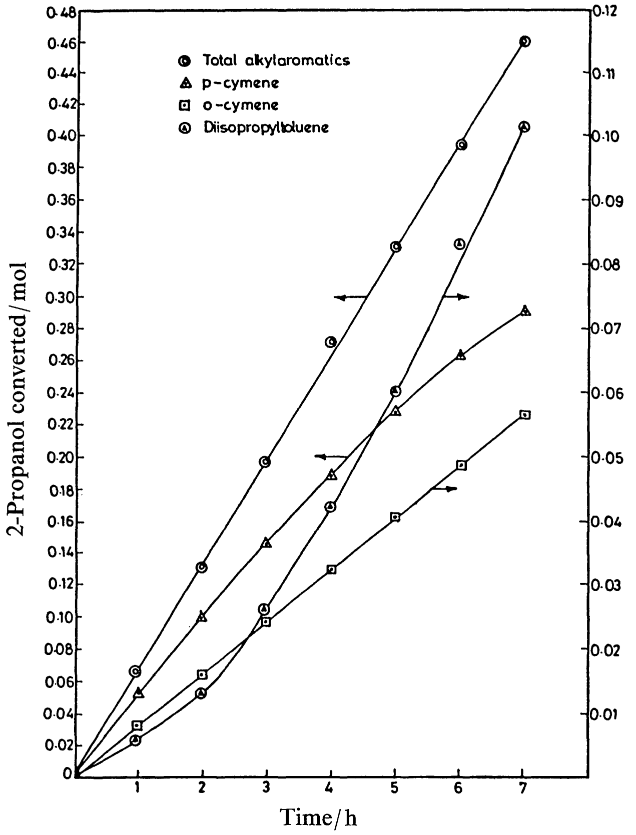

Fig. 5. Cumulative formation of *p*-cymene, *o*-cymene, and diisopropyltoluenes with reaction time over Tisial-4E. Reaction conditions; reaction temperature: 200 °C; LHSV: 0.5; toluene/2-propanol (mole ratio): 3.

content for all the catalysts studied, as illustrated in Fig. 5 for Tisial-4E, which is found to be the most active alkylation catalyst included in the present study. The conversion to *p*-cymene decreased and a corresponding increase in the formation of diisopropyltoluenes is observed with the passing of reaction time. However, the conversion to *p*-cymene remained constant throughout the reaction time.

Even though the alkylating activity of TiO_2–SiO_2–Al_2O_3 increased considerably with increase in TiO_2 content (upto 50 mol% of TiO_2), the selectivity to different products is not altered. This is evidenced from the product patterns obtained at different reaction times, (Table 5) when Tisial-4C of 8.5 mole% of TiO_2 and Tisial-4E of 50 mol% of TiO_2 are used as catalysts.

ii) Dehydration of 2-Propanol: In the dehydration of 2-propanol to propylene, the single oxides TiO_2, SiO_2, and Al_2O_3 showed marginal activity (Fig. 6), whereas the binary oxides are found to show better catalytic activity. However, the ternary oxide system is the most active catalyst for the dehydration and the enhanced activity can be due to the large acid amount values. On plotting the total acidity at $H_0 \leqslant +6.8$, of single oxides, binary oxides, and ternary oxide against their dehydrating activity, a linear correlation is obtained (Fig. 7). This suggests that even the weakest acid sites are efficient in demanding the dehydration of 2-propanol.

Conclusion

The binary oxides SiO_2–TiO_2 and Al_2O_3–TiO_2 copre-

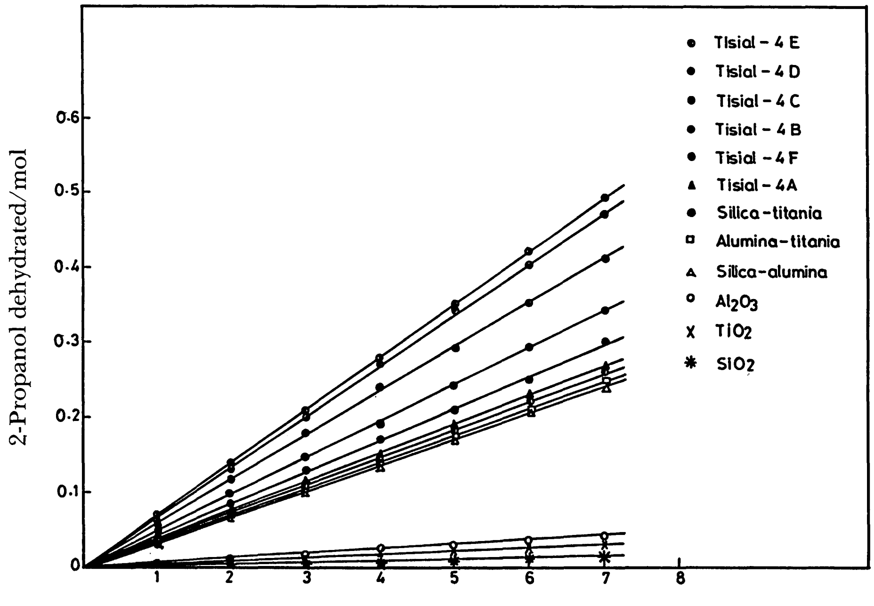

Fig. 6. Comparison of dehydrating activity of different catalysts (The cumulative number of moles of 2-propanol converted to propylene with reaction time is given). Reaction conditions; reaction temperature: 200 °C; LHSV: 0.5; toluene/2-propanol (mole ratio): 3.

Table 5. Conversions (mol%) of 2-Propanol to Alkylaromatics at Different Reaction Times over Tisial-4C (8.4 mol% of of TiO_2) and Tisial-4E (50 mol% of TiO_2)

Reaction time	Tisial-4C					Tisial-4E				
h	*o*-Cymene	*p*-Cymene	DIT	*o*/*p*	DIT/*o*+*p*	*o*-Cymene	*p*-Cymene	DIT	*o*/*p*	DIT/*o*+*p*
1	9.8	64.0	7.0	0.153	0.95	10.4	68.0	7.2	0.153	0.092
2	9.7	57.3	13.5	0.169	0.20	10.4	62.3	13.0	0.166	0.180
3	9.7	54.0	17.4	0.179	0.27	10.4	60.2	17.0	0.174	0.240
4	9.7	50.6	19.4	0.191	0.32	10.4	54.5	21.0	0.190	0.320
5	9.6	47.3	21.6	0.200	0.37	10.4	52.4	23.6	0.200	0.370
6	9.7	45.8	22.8	0.205	0.40	10.4	47.0	30.0	0.220	0.500

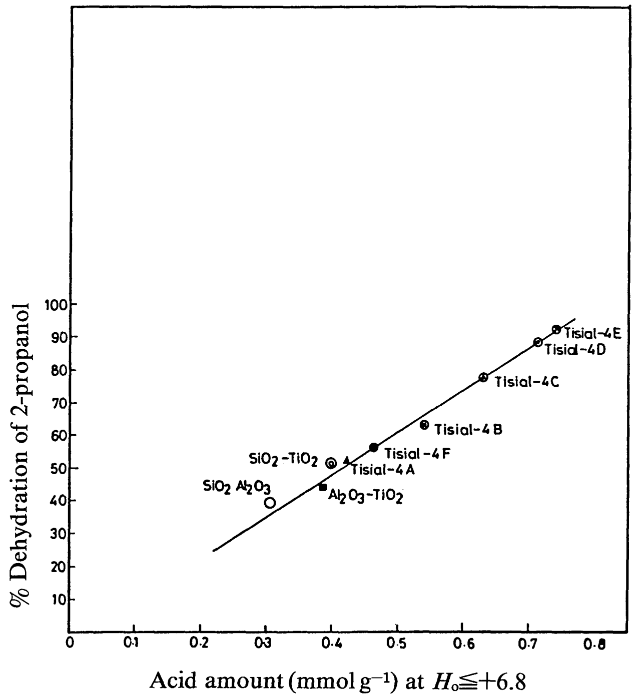

Fig. 7. Effect of acidity distribution on the dehydration of 2-propanol to propylene. Reacton conditions; reaction temperature: 200 °C; LHSV: 0.5.

cipitated from a solution of pH 4 exhibited acid strength of $H_0=-8.2$ and are found to be highly active catalysts in the alkylation of toluene with 2-propanol and the dehydration of 2-propanol, even though the single oxides are ineffective catalysts due to their low acid strength. However, the corresponding activity of TiO_2-SiO_2-Al_2O_3 is the highest. The acid amount of the ternary oxide system TiO_2-SiO_2-Al_2O_3 increased with the increase of TiO_2 content upto 50 mol% of TiO_2 and then decreased, without altering the selectivity.

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