

A Comparative Study on the Acidic Properties and Catalytic Activities of TiO_2 , SiO_2 , Al_2O_3 , $\text{SiO}_2\text{--Al}_2\text{O}_3$, $\text{SiO}_2\text{--TiO}_2$, $\text{Al}_2\text{O}_3\text{--TiO}_2$, and $\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3$

Kuzhunellil Raghavan Pillai SABU,* Kalur Vijayachandra C. RAO,
and Chandrathil Govindan Ramachandran NAIR†

Inter Disciplinary Research Group, Vikram Sarabhai Space Centre, Trivandrum 695022, India

†Department of Chemistry, University of Kerala, Trivandrum 695034, India

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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 $\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3$. 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 $\text{SiO}_2\text{--TiO}_2$ and $\text{Al}_2\text{O}_3\text{--TiO}_2$ of 10% by weight of TiO_2 are found to contain very strong acid sites $H_0 \leq -8.2$ and are highly active catalysts in both the test reactions. But $\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3$ of 10% by weight of TiO_2 showed the highest acid amount and the highest activity in the alkylation 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 $\text{Cr}_2\text{O}_3\text{--SiO}_2$, $\text{MoO}_3\text{--SiO}_2\text{--Al}_2\text{O}_3$, and $\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3$ in certain acid-catalyzed oligomerization, polymerization, and a wide range of alkylation reactions are known.^{1–8)} The incorporation of transition metal oxides into $\text{SiO}_2\text{--Al}_2\text{O}_3$ 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 $\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3$ 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 $\text{SiO}_2\text{--Al}_2\text{O}_3$ 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 $\text{SiO}_2\text{--Al}_2\text{O}_3$, $\text{SiO}_2\text{--TiO}_2$, $\text{Al}_2\text{O}_3\text{--TiO}_2$, and the ternary oxide $\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3$ 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 $\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3$ 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 $\text{SiO}_2\text{--Al}_2\text{O}_3$, $\text{SiO}_2\text{--TiO}_2$, and $\text{Al}_2\text{O}_3\text{--TiO}_2$ 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 $\text{SiO}_2\text{--Al}_2\text{O}_3$, sodium silicate and titanium tetrachloride for $\text{SiO}_2\text{--TiO}_2$, and aluminium sulfate and titanium tetrachloride for $\text{Al}_2\text{O}_3\text{--TiO}_2$ 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) **$\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3$:** The coprecipitation technique employed for the preparation of $\text{TiO}_2\text{--SiO}_2\text{--Al}_2\text{O}_3$ 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 $\text{TiO}_2\text{--}$

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Table 4. Acidity Distribution of Tisial Sample of Varying TiO₂ 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 ($H_0 \leq -8.2$). Even though binary oxides containing TiO₂ are known to possess strong acid sites due to which they serve as effective catalysts in the synthesis of aniline from phenol and ammonia, acid sites of strength $H_0 = -8.2$ is never observed previously in the case of Al₂O₃-TiO₂.²¹ 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 SiO₂, Al₂O₃, and TiO₂. But the total acid amount value of TiO₂-SiO₂-Al₂O₃ containing about 10% by weight each of TiO₂ and Al₂O₃ is large compared with SiO₂-TiO₂ and Al₂O₃-TiO₂ (Table 4). Si-O-Si and Al-O-Al bond formation may occur in SiO₂-TiO₂ (when SiO₂ is the major component) and Al₂O₃-TiO₂ (when Al₂O₃ 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 TiO₂-SiO₂-Al₂O₃. That is, the number of bonds which can generate acid sites per unit surface area may be the highest in the case of TiO₂-SiO₂-Al₂O₃. However, the acid strength of a mixed metal oxide system depends on the averaged electronegativity values of the component metal ions.¹⁰

The Effect of TiO₂ Content on the Acidity Distribution of TiO₂-SiO₂-Al₂O₃: The acidity distribution of TiO₂-SiO₂-Al₂O₃ of varying TiO₂ content shows that the total acid amount increased with the increase of TiO₂ content and the maximum acid amount is shown by the sample containing 50 mol% of TiO₂ (Tables 3 and 4). Further increase in TiO₂ content decreased both the acid amount and acid strength. TiO₂-SiO₂-Al₂O₃ containing 80 mol% of TiO₂ (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 TiO₂. Also Fig. 1 shows that with the increase in calcination temperature, the strong acid sites do not

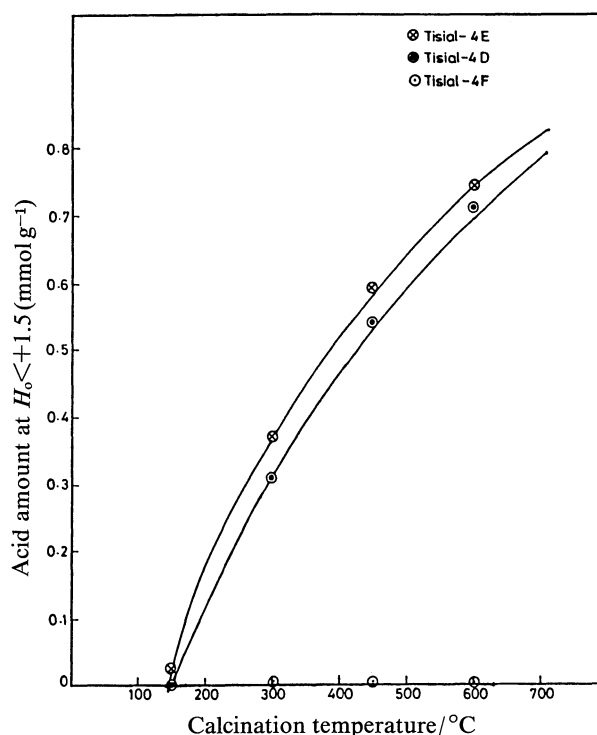


Fig. 1. The effect of calcination temperature on the acidity distribution of Tisial-4D, Tisial-4E, and Tisial-4F.

appear in Tisial-4F whatever be the calcination temperature, as in the case of TiO₂.¹¹

Catalytic Activity. i) Alkylation of Toluene with 2-Propanol: The single oxides SiO₂, TiO₂, and Al₂O₃ 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 SiO₂-Al₂O₃, SiO₂-TiO₂, and Al₂O₃-TiO₂ (Fig. 2). Among them, SiO₂-TiO₂ showed the highest activity and SiO₂-Al₂O₃ showed the least activity. But TiO₂-SiO₂-Al₂O₃ is more active for the conversion of 2-propanol to alkylaromatics than any of these binary oxides. The enhanced activity of TiO₂-SiO₂-Al₂O₃ catalysts could be attributed to the very large acid amount at a suitable acid strength ($H_0 \leq +1.5$) for the alkylation.²² This is evident from the linear activity to acidity correlation obtained by plotting the acidity at $H_0 \leq +1.5$ of different binary oxides and the ternary oxide against their isopropylating activity (Fig. 3).

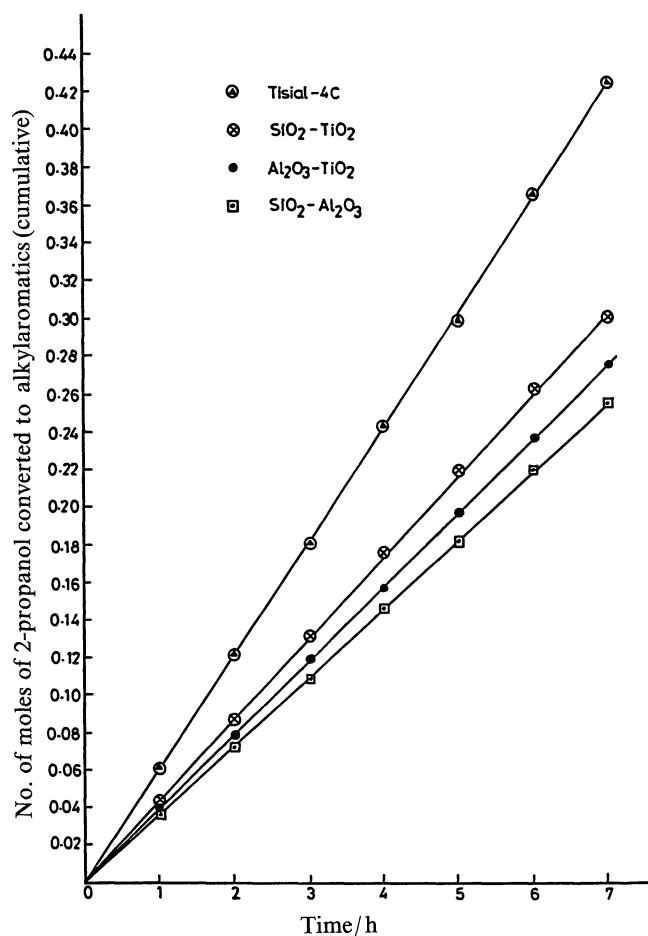


Fig. 2. Comparison of the catalytic activity of TiO₂-SiO₂-Al₂O₃ (Tisial) with that of binary oxides in the alkylation of toluene with 2-propanol. Reaction conditions; reaction temperature: 200 °C; LHSV: 0.5; toluene/2-propanol (mole ratio): 3.

With the increase in TiO₂ content, the alkylating activity of the ternary oxide system also increased (Fig. 4). But the Tsial-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

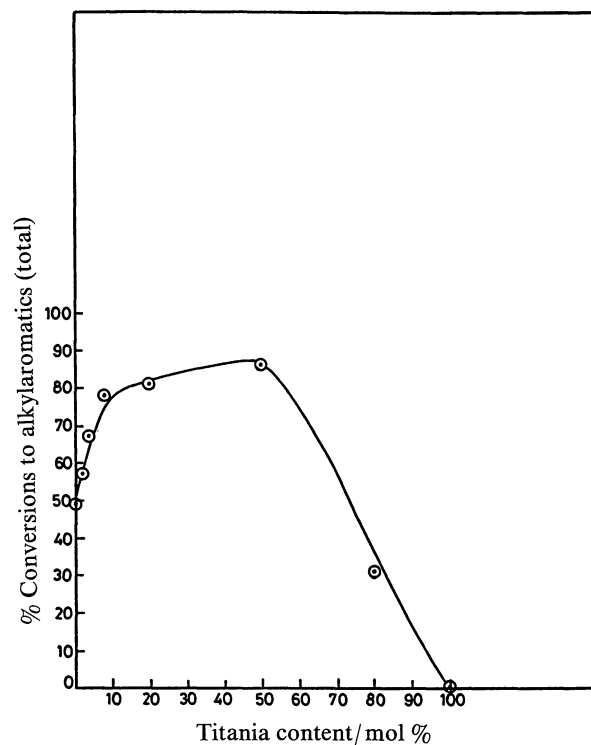


Fig. 4. Effect of titania content of Tsial on the conversion of 2-propanol to alkylaromatics. Reaction conditions; reaction temperature: 200 °C; LHSV: 0.5; toluene/2-propanol (mole ratio): 3.

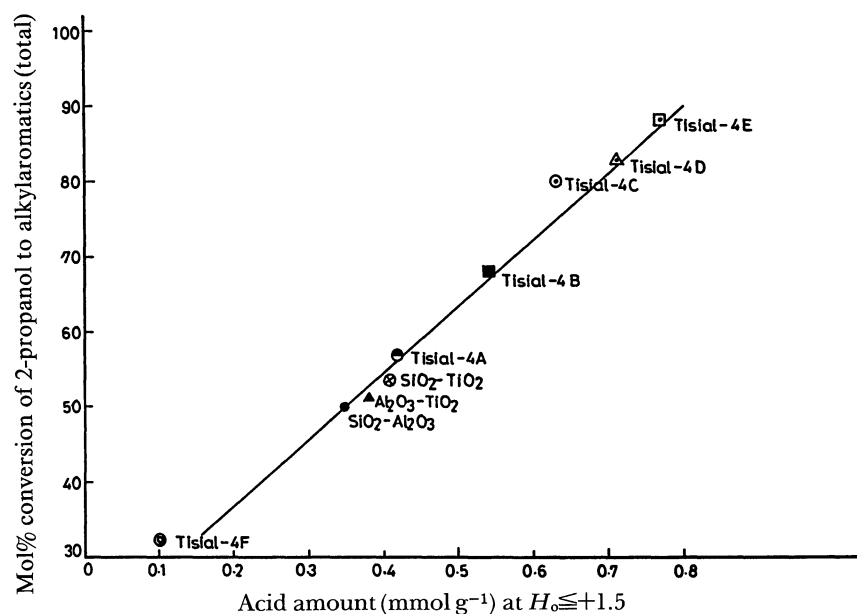


Fig. 3. Effect of acidity distribution on the conversion of 2-propanol to alkylaromatics. Reaction conditions; reaction temperature: 200 °C; LHSV: 0.5; toluene/2-propanol (mole ratio): 3.

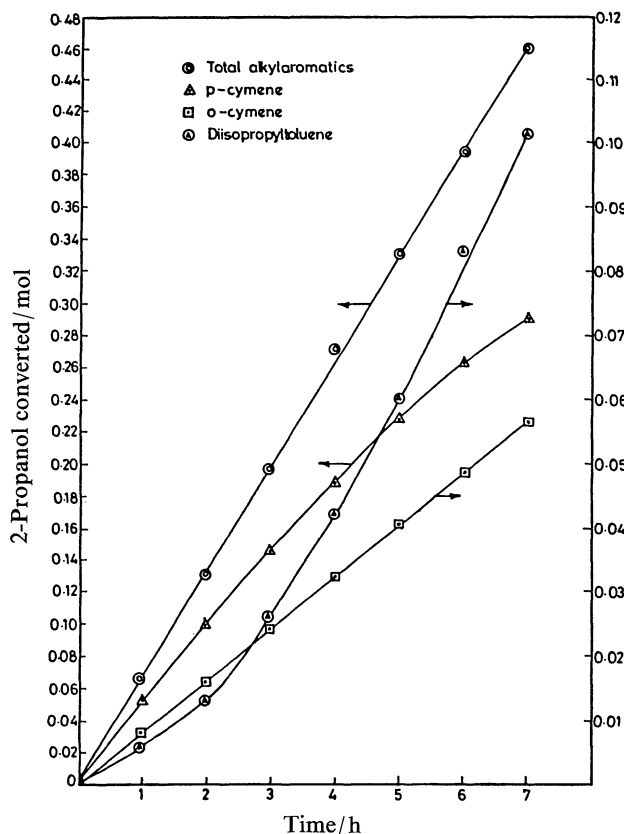


Fig. 5. Cumulative formation of *p*-cymene, *o*-cymene, and diisopropyltoluenes with reaction time over Tisial-4E. Reaction conditions; reaction temperature: 200°C; LHSV: 0.5; toluene/2-propanol (mole ratio): 3.

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 $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ 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 $H_0 \leq +6.8$, 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 $\text{SiO}_2\text{-TiO}_2$ and $\text{Al}_2\text{O}_3\text{-TiO}_2$ copre-

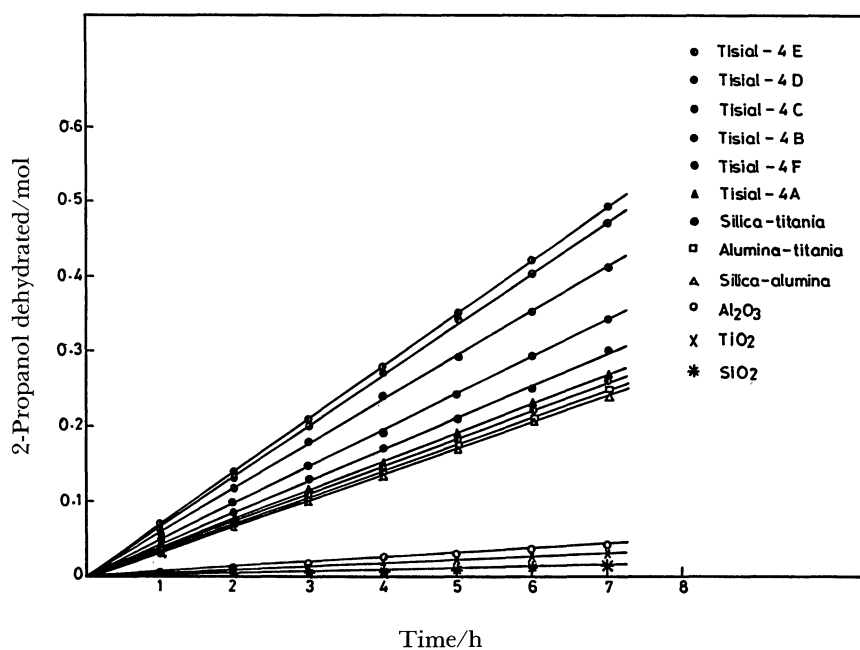


Fig. 6. Comparison of dehydrating activity of different catalysts (The cumulative number of moles of 2-propanol converted to propylene with reaction time is given). Reaction conditions; reaction temperature: 200°C; LHSV: 0.5; toluene/2-propanol (mole ratio): 3.

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

Reaction time h	Tisial-4C					Tisial-4E				
	<i>o</i> -Cymene	<i>p</i> -Cymene	DIT	<i>o/p</i>	DIT/ <i>o+p</i>	<i>o</i> -Cymene	<i>p</i> -Cymene	DIT	<i>o/p</i>	DIT/ <i>o+p</i>
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

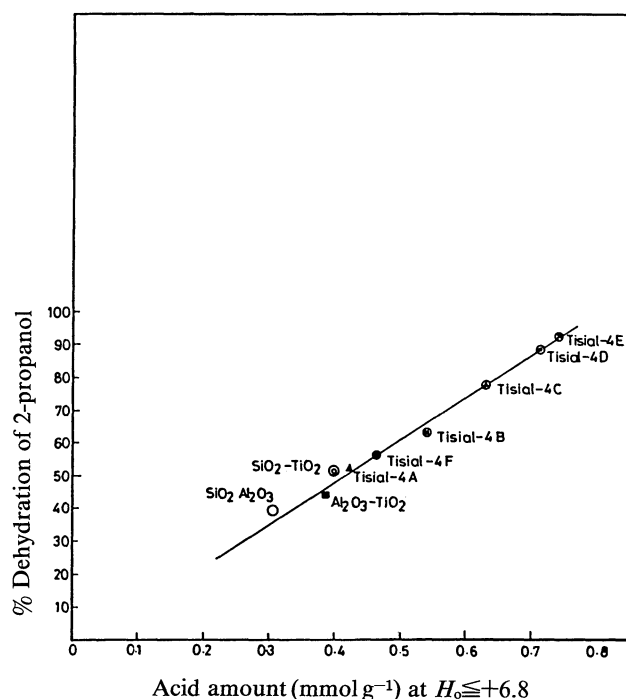


Fig. 7. Effect of acidity distribution on the dehydration of 2-propanol to propylene. Reaction conditions; reaction temperature: 200 °C; LHSV: 0.5.

precipitated 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 $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ is the highest. The acid amount of the ternary oxide system $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ 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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