

Acidic Property and Catalytic Activity of $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$

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The acidity evaluations using butylamine titration have been carried out to correlate the surface acidic properties of $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ catalysts with their alkylating activity. The acid amount of $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ of silica to alumina molar ratio 16.4 and titania content 10.4% (by weight) is nearly double that of $\text{SiO}_2\text{-Al}_2\text{O}_3$ of the same silica to alumina molar ratio. The acid strength of $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ coprecipitated from a solution of pH 2 and the acid amount of the same ternary oxide coprecipitated from solutions of higher pH (>6) are low.

Binary metal oxides such as $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{SiO}_2\text{-MgO}$, $\text{SiO}_2\text{-ZrO}_2$, and $\text{Al}_2\text{O}_3\text{-B}_2\text{O}_3$ have been used as solid acid catalysts since their surface acidic properties are well-known.¹⁾ Later many other combinations of metal oxides, viz $\text{TiO}_2\text{-Al}_2\text{O}_3$,²⁾ $\text{TiO}_2\text{-ZnO}$,³⁾ $\text{SiO}_2\text{-ZnO}$,⁴⁾ $\text{SiO}_2\text{-TiO}_2$,^{5,6)} $\text{ZnO-Bi}_2\text{O}_3$, $\text{Al}_2\text{O}_3\text{-MgO}$,⁷⁾ have been found to show remarkable acidic properties and catalytic activities, in various acid catalyzed reactions. But the surface acidic properties and catalytic activities of ternary oxide systems have not been studied elaborately. These systems, especially $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ (Tisial) synthesized by coprecipitation technique are found to be very efficient and regenerable catalyst in a wide range of alkylation reactions.^{8,9)}

In the present paper, we report the acidity distribution of a series of $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ catalysts (synthesized by coprecipitation method) the activities of which have been studied for the isopropylation of toluene with 2-propanol. Also a comparison of the acid amounts and acid strengths of a synthetic $\text{SiO}_2\text{-Al}_2\text{O}_3$ sample with that of these $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ have been made. The change in the acidity distribution of the ternary oxide with subsequent use in the isopropylation of toluene and regenerations is also investigated. The effect of calcination temperature on the surface acidic characteristics of $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ is also discussed in the light of the observed results.

Experimental

Materials: The materials used are sodium silicate (Scientific chemicals), aluminium sulfate (A. R. grade), titanium tetrachloride (obtained from KMML Chavara), toluene (BDH), benzene (BDH), 2-propanol (BDH), butylamine (SD chemicals), nitric acid, and ammonia of chemically pure quality. The indicators used are neutral red ($pK_a=+6.8$), methylred ($pK_a=+4.8$), dimethyl yellow ($pK_a=+3.3$) phenylazodiphenyl amine ($pK_a=+1.5$) crystal violet ($pK_a=+0.8$), dicinnamylideneacetone ($pK_a=-3.0$), benzylideneacetophenone ($pK_a=-5.6$), and anthraquinone ($pK_a=-8.2$).

Preparation of Ternary Oxides: Samples of $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ and $\text{SiO}_2\text{-Al}_2\text{O}_3$ were synthesized by coprecipitation method as referred elsewhere.⁹⁾ The coprecipitations were carried out at different pH's (2, 4, 6, 7, and 8) and were designated as Tisial-2, Tisial-4, and so on. The $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ sample was coprecipitated from a solution of

pH 4. The precipitates were washed, extruded, dried (120 °C for 12 h), and calcined (600 °C for 6 h). The Tisial-4 sample was also calcined at different temperatures viz 150, 300, and 1000 °C.

Measurement of Acidity: The acid amounts and 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). 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, and the method of calculation of percentage yields of alkylaromatics were the same as those employed in the previous work.⁹⁾

Results and Discussion

The acid strength of single oxides such as TiO_2 , SiO_2 , and Al_2O_3 are generally weak ($H_o>+3.3$) with low acid amount values: 0.057 mmol g⁻¹ for TiO_2 of surface area 38.5 m² g⁻¹, 0.109 mmol g⁻¹ for SiO_2 of surface area 289 m² g⁻¹, and 0.285 mmol g⁻¹ for Al_2O_3 of surface area 190 m² g⁻¹ at $H_o\leq+4.0$.⁷⁾ This renders them impractical as acid catalysts. On the other hand, a combination of any two of these three single oxides are strong acids with fairly high acid amounts⁷⁾ and the binary oxide $\text{SiO}_2\text{-Al}_2\text{O}_3$ is known to contain very strong acid sites ($H_o\leq-8.2$).¹⁰⁾ The creation of new acidic sites, on the surface of binary oxides which differ from those of component single oxides is well known.⁷⁾ The acid amount at a certain acid strength per unit surface area of the ternary oxide $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$ (Tisial) (Table 1) is larger than the sum of the acid amounts divided by the sum of the surface areas of the component oxides. Also when comparing the acidity distribution of $\text{SiO}_2\text{-Al}_2\text{O}_3$ and Tisial-4, it can be seen that the latter possesses nearly double the acid amount of the former. In addition, almost the entire acid amounts of Tisial-4 is distributed between acid strengths of $H_o=-3$ and $H_o=-5.6$. Thus our results indicate that new acidic sites which differ from those of TiO_2 , SiO_2 , Al_2O_3 , and $\text{SiO}_2\text{-Al}_2\text{O}_3$ are created on the surface of the ternary oxide Tisial. The large

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Table 3. Acidity Distribution of Tisial-4. Samples After Different Number of Regenerations

Number of regeneration cycles	Acid amount (mmol g ⁻¹) at different p <i>k</i> _a 's							
	+6.8	+4.8	+3.3	+1.5	+0.8	-3	-5.6	-8.2
0	0.63	0.63	0.63	0.63	0.63	0.63	0.15	0.05
3	0.61	0.61	0.61	0.61	0.61	0.61	0.13	0.03
9	0.30	0.30	0.30	0.30	0.30	0.30	0.05	0.00

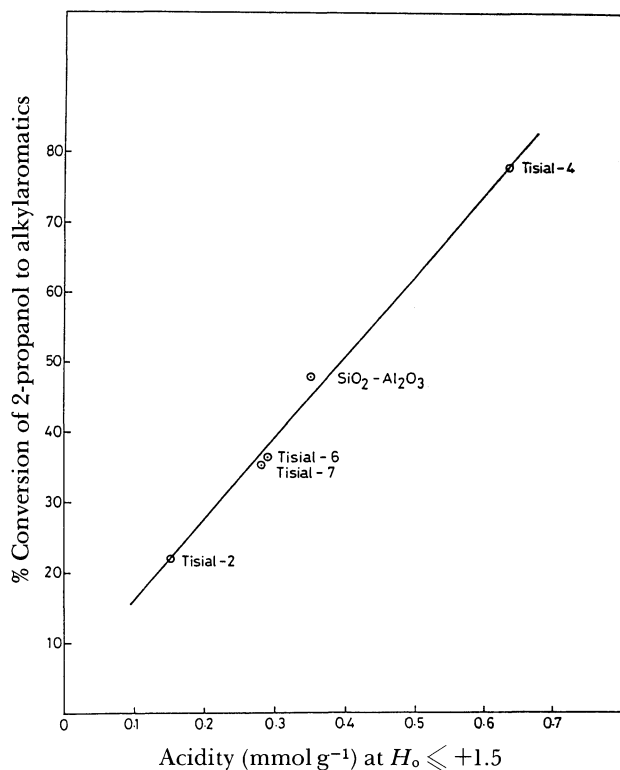


Fig. 2. The correlation of acidity with alkylating activity of different catalysts in the isopropylation of toluene with 2-propanol.

different solid acids were active in the dehydration of 4-methyl-2-pentanol. Also on comparing the acidity with activity, it appears that the isopropylation of toluene requires acid sites of strength $H_0 \leq +1.5$. A linear activity to acidity correlation is obtained by plotting the acidity at $H_0 \leq +1.5$ of different samples of Tisial and $\text{SiO}_2\text{-Al}_2\text{O}_3$ against their isopropylating activity (Fig. 2).

The Regenerability of Tisial-4: It has been found (Table 3), that even after three regeneration cycles the acidity distribution of Tisial-4 was remaining unchanged. But after nine successive regeneration cycles, the total acid amount of these catalyst had been reduced by more than 50%. These results are in good agreement with the activity decrease of Tisial-4 with repeated use in the isopropylation of toluene.¹¹⁾

Conclusion

New acidic sites which differ from those of TiO_2 , SiO_2 , Al_2O_3 , and $\text{SiO}_2\text{-Al}_2\text{O}_3$ are created on the surface of $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$. The pH of the coprecipitating solution plays vital role in governing the acidity distributions of $\text{TiO}_2\text{-SiO}_2\text{-Al}_2\text{O}_3$. Decrease in the pH of the coprecipitating solution ($\text{pH} < 4$) decreased the acid strength and increase of pH ($\text{pH} > 6$) decreased the acid amount. The acid strength increased with the increase in calcination temperature. The aromatic alkylation requires sites of high acid strength ($H_0 \leq +1.5$).

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