Acidic Property and Catalytic Activity of TiO_2-SiO_2-Al_2O_3

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The acidity evaluations using butylamine titration have been carried out to correlate the surface acidic properties of TiO_2-SiO_2-Al_2O_3 catalysts with their alkylating activity. The acid amount of TiO_2-SiO_2-Al_2O_3 of silica to alumina molar ratio 16.4 and titania content 10.4% (by weight) is nearly double that of SiO_2-Al_2O_3 of the same silica to alumina molar ratio. The acid strength of TiO_2-SiO_2-Al_2O_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 SiO_2-Al_2O_3, SiO_2-MgO, SiO_2-ZrO_2, and Al_2O_3-B_2O_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 TiO_2-Al_2O_3,[2] TiO_2-ZnO,[3] SiO_2-ZnO,[4] SiO_2-TiO_2,[5,6] ZnO-Bi_2O_3, Al_2O_3-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 TiO_2-SiO_2-Al_2O_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 TiO_2-SiO_2-Al_2O_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 SiO_2-Al_2O_3 sample with that of these TiO_2-SiO_2-Al_2O_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 TiO_2-SiO_2-Al_2O_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 TiO_2-SiO_2-Al_2O_3 and SiO_2-Al_2O_3 were synthesized by coprecipiation 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 TiO_2-SiO_2-Al_2O_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 $m^2 g^{-1}$, 0.109 mmol g^{-1} for SiO_2 of surface area 289 $m^2 g^{-1}$, and 0.285 mmol g^{-1} for Al_2O_3 of surface area 190 $m^2 g^{-1}$ at $H_o \leqq +4.0$.[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 amounts[7] and the binary oxide SiO_2-Al_2O_3 is known to contain very strong acid sites ($H_o \leqq -8.2$).[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 TiO_2-SiO_2-Al_2O_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 SiO_2-Al_2O_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 SiO_2-Al_2O_3 are created on the surface of the ternary oxide Tisial. The large

Table 1. The Chemical Compositions and Acidity Distribution of Different TiO_2-SiO_2-Al_2O_3 Samples and SiO_2-Al_2O_3 (Calcined at 600 °C)

Sample	SiO_2/Al_2O_3 molar ratio	TiO_2 %(by wt)	Surface area $m^2 g^{-1}$	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-2	47.6	9.1	61.7	0.55	0.35	0.15	0.15	0.15	0.15	—	—
Tisial-4	16.4	10.4	100.0	0.63	0.63	0.63	0.63	0.63	0.63	0.15	0.15
Tisial-6	8.7	11.8	49.5	0.40	0.40	0.29	0.29	0.29	0.29	0.10	0.03
Tisial-7	8.3	11.1	46.0	0.40	0.40	0.28	0.28	0.28	0.28	0.09	0.03
Tisial-8	8.2	8.7	11.5	0.37	0.37	0.25	0.25	0.25	0.25	0.09	0.02
SiO_2-Al_2O_3	16.3	—	135.0	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.35

variations in the acid amounts of different Tisial samples could be attributed to the drastic change in the silica to alumina molar ratio (Table 1), caused by the change in pH of the coprecipitating solution. It is to be noted that the acid strength of TiO_2-SiO_2-Al_2O_3 coprecipitated from a solution of pH 2 is low, similar to that reported in the case of SiO_2-Al_2O_3 coprecipitated at pH 2.[11]

Effect of Calcination Temperature on Acidity Distribution: The Tisial-4 sample calcined at 150 °C is devoid of very strong acid sites (H_o<−5.6), but contains a large amount of weak acid sites (H_o>+3.3) and a limited quantity of moderately weak acid sites (H_o between +3.3 and −3) (Table 2). But on increasing the calcination temperature to 300 °C the amount of weak acid sites decreased and strong acid sites appeared. This could be due to the conversion of weak sites (Brønsted sites) to stronger Lewis sites caused by the loss of water molecules from the surface as in the case of silica-alumina. The Tisial-4 sample calcined at 600 °C is rich in very strong acid sites. But a further increase in the calcination temperature to 1000 °C rendered the sample negligibly acidic.

Catalytic Activity: The ternary oxide system TiO_2-SiO_2-Al_2O_3 has been found to be a very effective catalyst in a wide range of alkylation reactions.[8,9] Our previous studies on the alkylation of toluene with 2-propanol have shown that the activity in terms of the conversion of 2-propanol to alkylaromatics of different catalysts is in the order Tisial-4>SiO_2-Al_2O_3>Tisial-6>Tisial-7>Tisial-8.[9] Since the acidity distribution of Tisial-4 sample varied with calcination temperature also, the catalytic activity in the isopropylation of toluene was studied with Tisial-4 catalysts calcined at different temperatures (Fig. 1). The optimum conversion of 2-propanol to alkylaromatics is given by the Tisial-4 sample calcined at 600 °C. But it has been found that with all the samples calcined at 600 °C studied, the amount of unreacted 2-propanol in the product mixture was found to be practically nil. However the amount of propylene produced as side product was high with the Tisial-4 catalyst calcined at 150 °C. This suggests that the isopropylation of toluene (aromatic alkylation) requires sites of high acid strength where as the dehydration of 2-propanol takes place even on the weakest acid sites. These results are in good agreement with the results observed by T. Yamaguchi et al.[12] where weak acid sites of

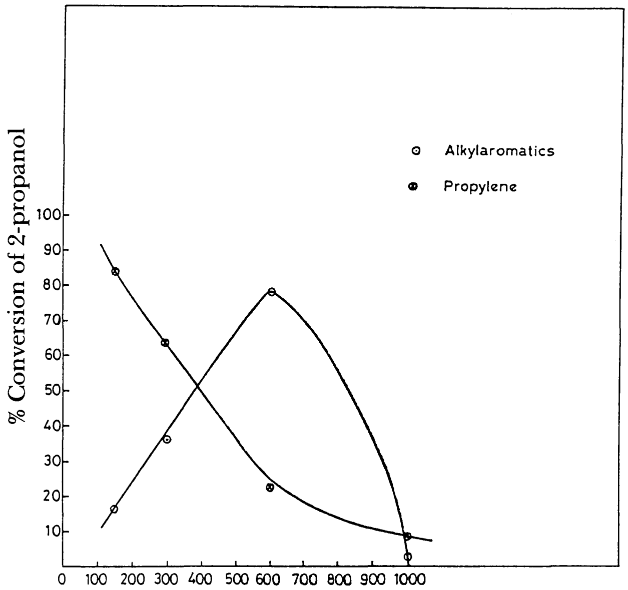

Fig. 1. The variation in the alkylating and dehydrating activities of Tisial-4 catalyst with calcination temperature.

Table 2. Acidity Distribution of Tisial-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	−5.6	−8.2
150	0.66	0.55	0.25	0.15	0.15	—	—	—
300	0.65	0.6	0.35	0.30	0.25	0.20	0.02	—
600	0.63	0.63	0.63	0.63	0.63	0.63	0.15	0.05
1000	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02

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

Number of regeneration cycles	Acid amount ($mmol\ g^{-1}$) at different pK_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

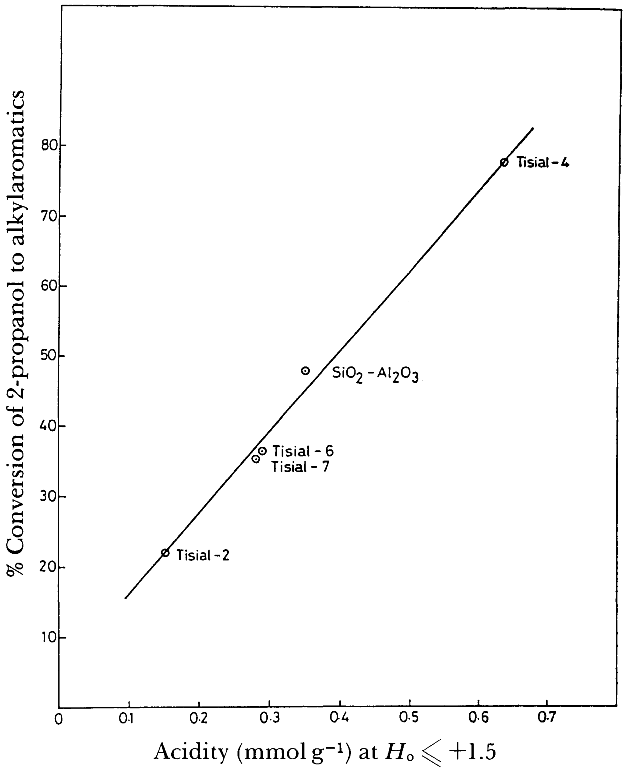

Fig. 2. The correlation of acidity with alkylating activity of different catalysts in the isopropylation of toluene with 2-propanol.

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 $H_o \leqq +1.5$. A linear activity to acidity correlation is obtained by plotting the acidity at $H_o \leqq +1.5$ of different samples of Tisial and SiO_2-Al_2O_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 SiO_2-Al_2O_3 are created on the surface of TiO_2-SiO_2-Al_2O_3. The pH of the coprecipitating solution plays vital role in governing the acidity distributions of TiO_2-SiO_2-Al_2O_3. Decrease in the pH of the coprecipitating solution (pH<4) decreased the acid strength and increase of pH (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 ($H_o \leqq +1.5$).

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