

Solid Super Acids: Preparation and Their Catalytic Activities for Reaction of Alkanes

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Preparation of solid super acid catalysts was attempted by treatment of metal oxides with NH_4F , FSO_3H , SbCl_5 , SbF_5 , and $\text{FSO}_3\text{H-SbF}_5$. All treatments with these reagents enhanced the acidic properties of the metal oxides. Among them, SbF_5 was the most effective. Conversions of several alkanes proceeded at room temperature or below, over the metal oxides treated with SbF_5 . The conversion rates of alkanes were in the order: cyclohexane \approx methylcyclopentane $>$ hexane $>$ pentane \approx 2-methylbutane $>$ butane \approx 2-methylpropane $>$ propane \gg 2,2-dimethylpropane \approx ethane \approx methane. The acid strengths were $-13.75 \geq H_0 > -14.52$ for $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ and $-13.16 \geq H_0 > -13.75$ for $\text{SbF}_5\text{-TiO}_2\text{-SiO}_2$ and $\text{SbF}_5\text{-Al}_2\text{O}_3$. The ir spectra of pyridine adsorbed on $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ showed that both Brönsted and Lewis acid sites were present on the surface when $\text{SiO}_2\text{-Al}_2\text{O}_3$ was treated with SbF_5 at low temperatures below 100°C , but only Lewis acid sites when treated at 300°C . The reaction mechanisms are discussed on the basis of the acidic properties, product distributions, and a tracer study.

INTRODUCTION

Liquid super acids have been extensively investigated by the Olah's group, and many interesting phenomena which occurred only in super acid solutions have been observed (1-4). One of the distinct phenomena is the formation of carbonium ions which result from addition of a proton to alkanes. The carbonium ions are easily converted into the carbenium ions with evolution of a hydrogen molecule as well as methane, ethane, etc. The carbenium ions undergo skeletal rearrangement and finally yield the isomerized alkanes. Therefore, a liquid super acid is capable of acting as a catalyst for skeletal isomerization of alkanes at low temperatures.

Because of the great advantages of heterogeneous catalysts over homogeneous ones, a number of attempts have been made to prepare solid super acids which should also be active for the skeletal isomerization of alkanes, and most of them are patented. Beside the patents, Magnotta *et al.* reported that a complex of AlCl_3 with cross-linked polystyrenesulfonic acid catalyzed

cracking and isomerization of hexane at 85°C (5, 6). Olah *et al.* presented Nafion-H as a solid super acid (7-9). Ono *et al.* reported that mixtures of aluminum halide with metal sulfate and with metal chloride showed a high activity for isomerization of pentane (10-12). Tanabe and Hattori briefly reported that various metal oxides treated with SbF_5 exhibited activity for the conversion of butane and 2-methylpropane (13).

The surface properties of solid super acids and the reaction mechanisms catalyzed by solid super acids, however, have not been investigated yet. In this paper, some attempts to prepare solid super acids are described, and the surface properties and the catalytic activities of the resulting catalysts for the reactions of several alkanes are examined. The reaction mechanisms for the formation of surface carbenium ions are discussed on the basis of the surface properties and product distributions.

EXPERIMENTAL METHODS

Preparation of catalyst. Catalysts were

prepared by treatment of various metal oxides with NH_4F , FSO_3H , SbCl_5 , SbF_5 , and $\text{FSO}_3\text{H-SbF}_5$. The metal oxides used and their preparation methods are summarized in Table 1. All the metal oxides were calcined at 500°C for 3 hr in air before treatment.

(1) NH_4F -treated catalysts: Silica-alumina (I) and Al_2O_3 (I) were treated with a 0.54 *N* aqueous NH_4F solution. They were washed with deionized water, dried, and calcined at 500°C . The amounts of F in the catalysts were calculated from the differences in F concentration of aqueous NH_4F solutions before and after the treatment. The concentration of F in the solution was determined by titration with 0.1 *N* aqueous $\text{Th}(\text{NO}_3)_4$ solution, alizarine S was used as an indicator. The amounts of F in the resulting F- SiO_2 - Al_2O_3 and F- Al_2O_3 were 1.6 and 5.5 wt%, respectively.

(2) FSO_3H -, SbCl_5 -, SbF_5 -, or $\text{FSO}_3\text{H-SbF}_5$ -treated catalysts: A metal oxide was outgassed at 500°C in a Pyrex glass reactor. After cooling to room temperature, the sample was exposed to the vapor of FSO_3H , SbCl_5 , SbF_5 , or $\text{FSO}_3\text{H-SbF}_5$ for 10 min, followed by evacuation for 10 min. In most cases, the procedure of exposure and evacuation was repeated three times at

room temperature, and final evacuation was performed at 50°C . The amount of SbF_5 on the sample was determined by weight increase of the resulting catalyst.

ir spectroscopy. For the *ir* study of pyridine adsorbed on the SbF_5 - SiO_2 - Al_2O_3 (II) catalyst, the sample was prepared in an *in situ* cell by repeated exposure of the disk of SiO_2 - Al_2O_3 to the vapor of SbF_5 and evacuation as described above. Pyridine was adsorbed at room temperature, followed by outgassing at 100°C .

Acid strength. Indicators used for determination of the acid strength were *p*-nitrochlorobenzene ($\text{p}K_a = -12.70$), *m*-nitrochlorobenzene ($\text{p}K_a = -13.16$), 2,4-dinitrotoluene ($\text{p}K_a = -13.75$), and 2,4-dinitrofluorobenzene ($\text{p}K_a = -14.52$) (14). All indicators are colorless or slightly yellow, and turn into yellow in their acid forms. The vapor of the indicator which was stored in a sealed glass tube was directly admitted to the sample through a breakable seal by heating the all-glass system at 50°C . Acid strength was determined by visual observation of the color change of an indicator adsorbed on the sample. By this method, only the strongest acid sites could be determined.

TABLE 1

Preparation of Base-Metal Oxides

Metal oxide	Starting material	Method	Remarks
SiO_2	$\text{Si}(\text{OC}_2\text{H}_5)_4$	Hydrolysis	
TiO_2	TiCl_4	Hydrolysis	
SnO_2	SnCl_4	Hydrolysis	
TiO_2 - SiO_2	$\text{TiCl}_4 + \text{Si}(\text{OC}_2\text{H}_5)_4$	Coprecipitation	$[\text{Ti}]/[\text{Si}] = 9/1$
TiO_2 - ZrO_2	$\text{TiCl}_4 + \text{ZrOCl}_2$	Coprecipitation	$[\text{Ti}]/[\text{Zr}] = 63/37$
SiO_2 - ZrO_2	$\text{Si}(\text{OC}_2\text{H}_5)_4 + \text{ZrOCl}_2$	Coprecipitation	$[\text{Si}]/[\text{Zr}] = 95/5$
MoO_3	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$	Pyrolysis	
MgO	$\text{Mg}(\text{OH})_2$	Pyrolysis	
H, Ca, La, Ce-Y 13X 5A 4A	13Y(SK-40)	Ion-exchange	Union Carbide Co. Union Carbide Co. Union Carbide Co. Union Carbide Co.
SiO_2 - Al_2O_3 (I)	SL		Shokubai Kasei Co.
SiO_2 - Al_2O_3 (II)	N631L		Nikki Kagaku Co.
Al_2O_3 (I)	Albes-FE		Showa Tansan Co.
Al_2O_3 (II)	$\text{Al}(\text{O}i\text{-C}_3\text{H}_7)_3$	Hydrolysis	

TABLE 2

Activities of NH_4F -Treated $\text{SiO}_2\text{-Al}_2\text{O}_3$ and Al_2O_3 (I) for Cracking of 2-Methylpropane and for Isomerization of 1-Butene

Catalyst	Conversion of 2-MP ^{a,c} (% hr ⁻¹ g ⁻¹)	Conversion of 1-butene ^b (% min ⁻¹ g ⁻¹)
$\text{SiO}_2\text{-Al}_2\text{O}_3$ (I)	1.4	52
$\text{NH}_4\text{F-SiO}_2\text{-Al}_2\text{O}_3$ (I)	2.1	105
Al_2O_3 (I)	0	3.0
$\text{NH}_4\text{F-Al}_2\text{O}_3$ (I)	4.6	14

^a Reaction temperature, 350°C.

^b Reaction temperature, 25°C.

^c 2-Methylpropane.

Reactant. Alkanes used as reactants were methane, ethane, propane, butane, 2-methylpropane, pentane, 2-methylbutane, 2,2-dimethylpropane, hexane, cyclohexane, and methylcyclopentane. 1-Butene was also used. They were purified by repeated freeze and thaw cycles and finally by passage through 4A or 5A molecular sieves at appropriate temperatures.

Reaction procedure. Two types of reactors were employed. One was an all-glass static reactor, and the other was a closed recirculation reactor. In the former, a reactant was admitted to the catalyst through a breakable seal, a total volume of the reactor being ~30 ml. The reaction products were analyzed at the end of the reaction. In the latter, the reactor had a volume of ~340 ml, and the reaction products were periodically analyzed by gas chromatography. A 6-m column packed with VZ-7(Gas Chro Kogyo Co. Ltd.) was operated at room temperature.

In some experiments, $\text{SiO}_2\text{-Al}_2\text{O}_3$ (II) was pretreated with D_2O at 500°C to exchange surface OH groups with OD groups before treatment with SbF_5 .

RESULTS

1. Catalytic Activities of Solid Super Acids for Reactions of Butane and of 2-Methylpropane

NH_4F -treated $\text{SiO}_2\text{-Al}_2\text{O}_3$ and Al_2O_3 .

The activities of the catalysts for the cracking of 2-methylpropane became appreciable above reaction temperatures of 300°C. Products consisted mostly of methane and C_5 -alkanes. The activities were compared by the conversion of 2-methylpropane in 1 hr per 1 g catalyst. Increases in the activity by NH_4F treatment were observed to some extent for both catalysts as shown in Table 2, though the activities were not high. The activities for the double-bond migration of 1-butene are also given in Table 2. Marked increase was observed by NH_4F treatment.

Infrared study of pyridine adsorbed on the NH_4F -treated catalysts showed that only Lewis acid sites were present on these surfaces.

FSO_3H -treated catalysts. No catalysts treated with FSO_3H showed appreciable activities for reactions of alkanes at room temperature. For the double-bond migration of 1-butene, treatment with FSO_3H brought about an increase in the activity except for MgO, as given in Table 3. The high activity of MgO is ascribed to its basic sites (15-17). By treatment of MgO with FSO_3H , the reaction became an acid-catalyzed type, which was suggested by a decrease in the *cis/trans* ratio of 2-butenes.

SbCl_5 -treated $\text{SiO}_2\text{-Al}_2\text{O}_3$. The SbCl_5 -

TABLE 3

Activity of FSO_3H -Treated Catalyst for Isomerization of 1-Butene at 0°C^a

Catalyst	Activity (% g ⁻¹ min ⁻¹)	<i>cis/trans</i>
MgO	108.2	5.9
$\text{SiO}_2\text{-Al}_2\text{O}_3$ (II)	11.5	1.3
$\text{TiO}_2\text{-ZrO}_2$	0.2	4.6
$\text{FSO}_3\text{H-MgO}$	1.6	1.0
$\text{FSO}_3\text{H-ZrO}_2$	43.5	1.4
$\text{FSO}_3\text{H-SiO}_2\text{-Al}_2\text{O}_3$ (II)	82.7	0.8
$\text{FSO}_3\text{H-TiO}_2\text{-ZrO}_2$	97.0	1.0
$\text{FSO}_3\text{H-SiO}_2\text{-ZrO}_2$	2.6	2.4

^a Catalyst, 0.1 g (MgO; 0.05 g); initial pressure, 50 Torr.

TABLE 4
Reaction of Butane over SbF₅-Treated Catalyst at Room Temperature^a

Catalyst	Time (hr)	Product distribution (%)							
		C ₁	C ₃	C ₄	2-MP ^c	C ₅	2-MB ^d	2,2-DMB ^e	Other hexanes
SiO ₂ -Al ₂ O ₃ (I)	720			100					
SbF ₅ -TiO ₂	280		6.4	17.1	59.1	1.1	13.4	2.0	1.0
SbF ₅ -SiO ₂	280		6.9	25.2	54.8	1.0	6.8	2.9	2.1
SbF ₅ -SnO ₂	24	15.0	1.1	52.8	29.3	0.2	1.3	0.1	0.1
SbF ₅ -MgO	24	0.3	1.3	73.2	24.2	0.1	0.8	0.1	
SbF ₅ -Al ₂ O ₃ (I)	280		0.1	77.2	21.1	0.1	1.3	0.1	
SbF ₅ -TiO ₂ -SiO ₂	280		21.9	13.1	58.1	0.6	4.8	1.0	0.5
SbF ₅ -SiO ₂ -Al ₂ O ₃ (I)	280		4.4	32.7	47.7	1.1	8.1	3.7	2.6
SbF ₅ -SiO ₂ -Al ₂ O ₃ (II)	20		1.8	49.7	41.0	0.6	4.8	1.4	0.7
SbF ₅ -TiO ₂ -ZrO ₂	20		0.7	67.1	30.3	0.2	1.3	0.3	0.1
SbF ₅ -SiO ₂ -ZrO ₂	20	0.1	0.4	84.4	14.2	0.1	0.7	0.2	0.1
SbF ₅ -HY	20	0.1	0.1	99.2	0.7				
SbF ₅ -CaY	20	0.1	0.1	99.2	0.6				
SbF ₅ -CeY	20	0.2	0.1	99.4	0.4				
SbF ₅ -LaY	20	4.5	0.2	94.6	0.7				
SbF ₅ -4A	23			98.5	1.3		0.2		
SbF ₅ -5A	23			98.2	1.7				
SbF ₅ -13X	23		0.1	66.1	27.8	0.1	1.0		
M. A.-SiO ₂ -Al ₂ O ₃ ^b	24		0.4	80.5	18.5	0.1	0.5		0.1

^a Catalyst, 0.15 g; reactant ca. 5 ml (NTP) in static reactor.

^b FSO₃H-SbF₅-SiO₂-Al₂O₃ (II).

^c 2-Methylpropane.

^d 2-Methylbutane.

^e 2,2-Mimethylbutane.

TABLE 5
Reaction of 2-Methylpropane over SbF₅-Treated Catalyst at Room Temperature^a

Catalyst	Time (hr)	Product distribution (%)								
		C ₁	C ₃	C ₄	2-MP	C ₅	2-MB	2,2-DMB	Other hexanes	C ₇
SiO ₂ -Al ₂ O ₃ (I)	600				100					
TiO ₂ -SiO ₂	720				100					
SbF ₅	280		2.9	0.2	96.4		0.5			
SbF ₅ -SiO ₂	280		7.0	11.8	66.8	1.6	5.6	4.4	2.7	0.3
SbF ₅ -Al ₂ O ₃ (II)	280		0.2	0.9	97.9	0.1	0.9			
SbF ₅ -SiO ₂ -Al ₂ -Al ₂ O ₃ (I)	280		6.8	11.0	65.0	1.2	9.6	3.7	2.2	0.4
SbF ₅ -TiO ₂ -ZrO ₂	20	0.1	0.6	1.7	95.7	0.2	1.4	0.1		
SbF ₅ -LaY	72	4.3	1.1	0.6	93.8	0.1	0.4			

^a Catalyst, 0.15 g; reactant ~5 ml (NTP) in static reactor.

$\text{SiO}_2\text{-Al}_2\text{O}_3$ (II) catalyst was inactive for the reactions of butane, pentane, and hexane at room temperature, but exhibited activities for the reactions of 2-methylpropane and of 2-methylbutane. Over 0.15 g of the catalyst in the static reactor, 3.2% 2-methylpropane and 8.8% 2-methylbutane were converted in 20 hr at room temperature.

SbF₅-treated catalysts. All catalysts treated with SbF_5 exhibited activities for the reactions of butane and of 2-methylpropane at room temperature. The product distributions obtained in the static reactor over 0.15 g catalyst are summarized in Table 4 for the reaction of butane and in Table 5 for the reaction of 2-methylpropane. The activity of catalyst varied with the kinds of metal oxides which were treated with SbF_5 . On treatment with SbF_5 , TiO_2 , SiO_2 , SnO_2 , MgO , $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{TiO}_2\text{-SiO}_2$, $\text{TiO}_2\text{-ZrO}_2$, and 13X molecular sieves became highly active catalysts, while Al_2O_3 (II), MoO_3 , ion-exchanged Y-type molecular sieves, and A-type molecular sieves showed rather low activities.

FSO₃H-SbF₅ (magic acid)-treated $\text{SiO}_2\text{-Al}_2\text{O}_3$. The $\text{FSO}_3\text{H-SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ catalyst showed considerable activity for the reaction of butane at room tempera-

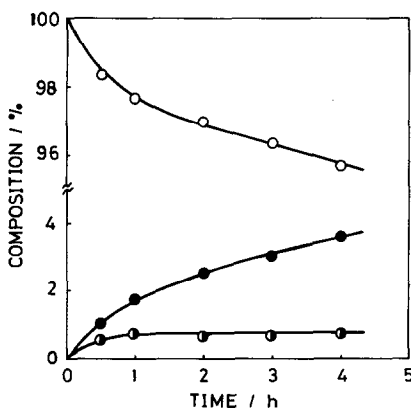


FIG. 1. Time dependence of composition in the reaction of propane at 20°C. Catalyst, 0.5 g, initial pressure, 58.5 Torr; ○, propane; ●, ethane, ●, methane.

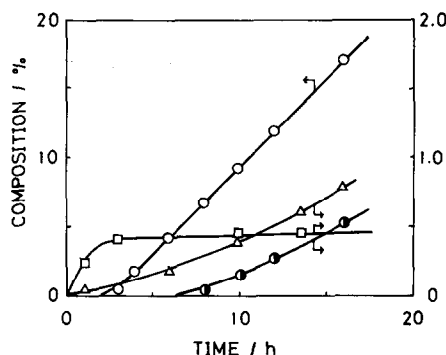


FIG. 2. Time dependence of composition in the reaction of butane at 18°C. Catalyst, 0.51 g; initial pressure, 96 Torr; ○, 2-methylpropane; □, methane; △, propane; ●, 2-methylbutane.

ture. The product distribution is given in the last line in Table 4. The activity was not as high as that of the $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ (II) catalyst.

2. Conversions of Alkenes over the $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ Catalyst

Since the metal oxides treated with SbF_5 were the most effective for the reaction of butane, the reactions of a series of alkanes over the $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ (II) catalyst were undertaken to characterize the catalytic features of the solid super acid catalyst in comparison with those of liquid super acids.

Methane, ethane, and 2,2-dimethylpropane did not undergo any reactions at room temperature. On the other hand, the other alkanes reacted at room temperature or below. The time courses of the reactions are shown in Fig. 1 for propane, Fig. 2 for butane, Fig. 3 for 2-methylpropane, Fig. 4 for pentane, Fig. 5 for 2-methylbutane, Fig. 6 for hexane, Fig. 7 for cyclohexane, and Fig. 8 for methylcyclopentane.

In the reaction of propane, products consisted mostly of methane and ethane; the latter was produced only in the initial period of the reaction.

In the reaction of butane, the main product was 2-methylpropane which was pro-

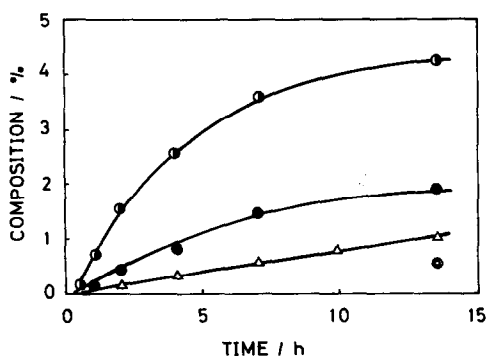


FIG. 3. Time dependence of composition in the reaction of 2-methylpropane at 20°C. Catalyst, 0.5 g; initial pressure, 105 Torr; ●, 2-methylbutane; ●, butane; △, propane, ⊙, hexanes.

duced with an induction period of more than 2 hr. The induction period was shortened by an increase in the initial pressure of butane. The induction period disappeared in the subsequent runs, which were performed after brief evacuation of the system. A small amount of methane was produced only in the initial stage of the reaction. Hydrogen was not detected in the products. The detection limit was less than 1%. In the reaction of 2-methylpropane, the main products were 2-methylbutane, butane, and propane. In contrast to the reaction of butane, an induction period was not ob-

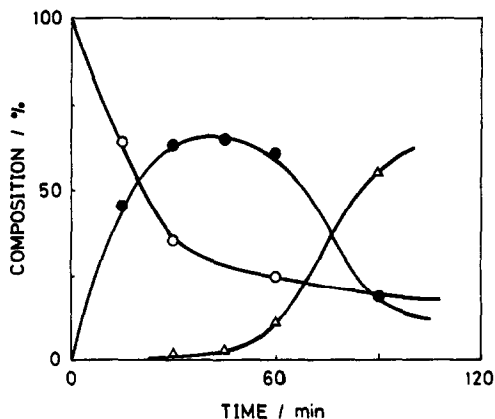


FIG. 4. Time dependence of composition in the reaction of pentane at 0°C. Catalyst, 0.1 g; initial pressure, 43 Torr; ○, pentane; ●, 2-methylbutane; △, 2-methylpropane.

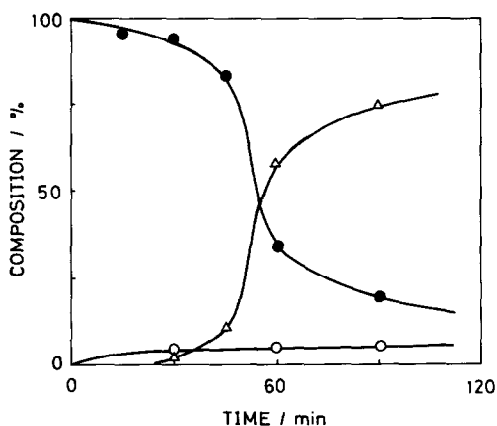


FIG. 5. Time dependence of composition in the reaction of 2-methylbutane at 0°C. Catalyst, 0.1 g, initial pressure, 45 Torr; ●, 2-methylbutane; ○, pentane; △, 2-methylpropane.

served. Over the $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ catalyst that had been treated with D_2O before treatment with SbF_5 , no D atoms could be detected in any products.

Pentane underwent rapid isomerization to give 2-methylbutane in the initial stage of the reaction. In 30 min, 2-methylpropane began to form, and its rate of formation quickly increased. Pressure change during the reaction was negligible, and the formation of hexanes was very small compared

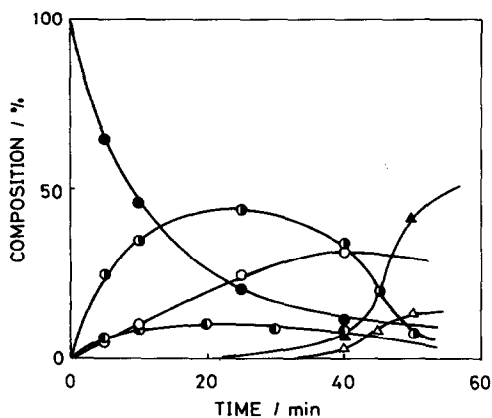


FIG. 6. Time dependence of composition in the reaction of hexane at 0°C. Catalyst, 0.1 g; initial pressure, 46 Torr; ●, hexane; ○, 2,2-dimethylbutane; ●, 3-methylpentane; ●, 2,3-dimethylbutane + 2-methylpentane; △, 2-methylbutane; ▲, 2-methylpropane.

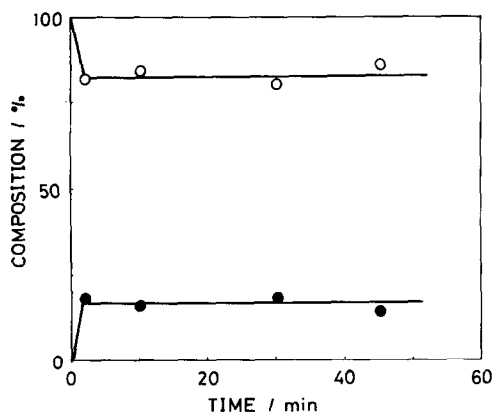


FIG. 7. Time dependence of composition in the reaction of cyclohexane at room temperature. Catalyst, 0.2 g; initial pressure, 44 Torr; ○, cyclohexane; ●, methylcyclopentane.

with that of 2-methylpropane. In the reaction of 2-methylbutane, a small amount of pentane was produced in the initial stage of the reaction and 2-methylpropane began to form in 30 min and became the main product.

The reaction of hexane proceeded faster than that of pentane and only the skeletal isomers were produced in the initial stage of the reaction. In 30 min, 2-methylpropane began to form and became the dominant product in 60 min. The feature of the forma-

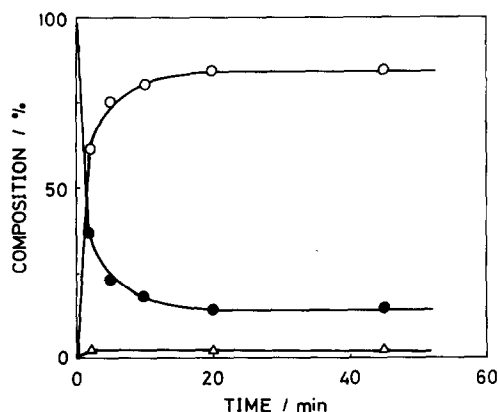


FIG. 8. Time dependence of composition in the reaction of methylcyclopentane at room temperature. Catalyst, 0.2 g; initial pressure, 48 Torr; ●, methylcyclopentane; ○, cyclohexane; △, 2-methylpropane.

tion of 2-methylpropane that began in about 30 min was commonly observed in the reactions of butane, pentane, 2-methylbutane, and hexane.

The isomerization between cyclohexane and methylcyclopentane occurred very rapidly over the catalyst at 20°C. In the reaction of cyclohexane, equilibrium was reached in 4 min, and no other products were detected. In the reaction of methylcyclopentane, equilibrium was reached in 20 min, and a small amount of 2-methylpropane (2%) was produced in the initial stage of the reaction.

3. Effect of the Treatment Temperature with SbF_5 on the Surface Properties and Catalytic Activity of $SbF_5-SiO_2-Al_2O_3$ Catalyst

The amounts of SbF_5 in the $SbF_5-SiO_2-Al_2O_3$ (II) catalysts that were treated with SbF_5 at different temperatures are plotted against the adsorption–evacuation temperature in Fig. 9. The amount of SbF_5 was as large as 50 wt% at an adsorption–evacuation temperature of 0°C. The amount of SbF_5 that is necessary to make monolayer corresponds to about 50 wt%; the amount sharply decreased up to 100°C, and then gradually decreased up to 300°C. Changes in specific surface area with treatment are also given in Fig. 9. The surface area of $SiO_2-Al_2O_3$ (II) before treatment with SbF_5

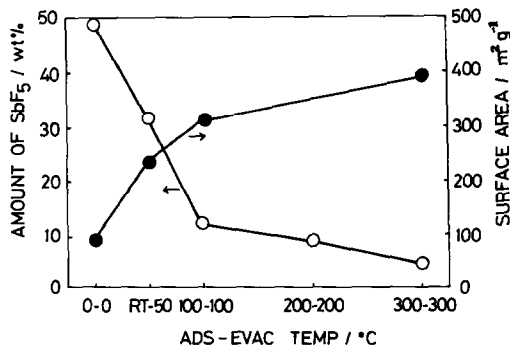


FIG. 9. Amount of SbF_5 and surface areas of $SbF_5-SiO_2-Al_2O_3$ (II) catalysts treated with SbF_5 at different temperatures.

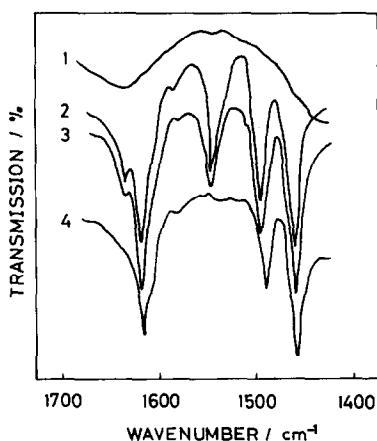


FIG. 10. Infrared spectra of pyridine adsorbed on $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ (II) catalysts treated with SbF_5 at different temperatures. (1) Background; adsorption-
evacuation temperatures: (2) 20–20°C; (3) 100–100°C; (4) 300–300°C.

was 445 m^2/g . As the amount of SbF_5 increased, the surface area decreased.

In Fig. 10 are shown the ir spectra of pyridine adsorbed on the $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ (II) catalysts that were treated with SbF_5 at different temperatures. Pyridine adsorbed on the catalyst that had been treated below 100°C showed the adsorption bands at 1540 and 1460 cm^{-1} , indicating that both

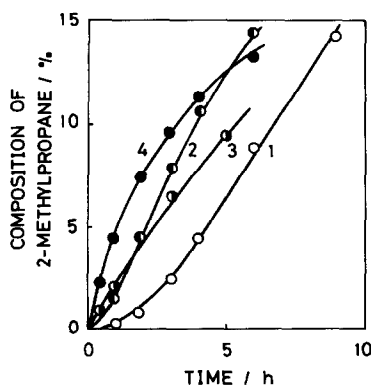


FIG. 11. Time dependence of composition in the reaction of butane over $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ (II) catalysts treated with SbF_5 at different temperatures. Reaction temperature, 20°C; catalyst, 0.5 g; initial pressure, 90 Torr; adsorption-
evacuation temperatures in treatment with SbF_5 : (1) room temperature-50°C; (2) 100–100°C; (3) 200–200°C; (4) 300–300°C.

Brönsted and Lewis acid sites exist on the surface. However, pyridine on the sample that had been treated with SbF_5 at 300°C, for both adsorption and evacuation, did not show the band at 1540 cm^{-1} , but at 1460 cm^{-1} . This indicates that only Lewis acid sites are present on this catalyst. It was also observed that the treatment with SbF_5 decreased in the band intensity of OH groups at about 3700 cm^{-1} on $\text{SiO}_2\text{-Al}_2\text{O}_3$.

The time dependences of 2-methylpropane composition produced in the reaction of butane over the $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ (II) catalysts that were treated with SbF_5 at different temperatures are shown in Fig. 11. When both adsorption and evacuation of SbF_5 were performed at a high temperature, the induction period became short. However, the activities did not greatly differ from each other.

The acid strengths of the catalysts that were treated with SbF_5 at room temperature for adsorption and at 50°C for evacuation are given in Table 6. The strongest acid sites of $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ (II) were in the H_0 range $-13.75 \sim -14.52$, while those of $\text{SbF}_5\text{-TiO}_2\text{-SiO}_2$ and of $\text{SbF}_5\text{-Al}_2\text{O}_3$ (II) were in the H_0 range $-13.6 \sim -13.75$. Compared with the acid strengths of $\text{SiO}_2\text{-Al}_2\text{O}_3$ (II), $\text{TiO}_2\text{-SiO}_2$, and Al_2O_3 (II), the acid strengths of the SbF_5 -treated samples became enhanced.

DISCUSSION

Treatments with NH_4F , FSO_3H , SbCl_5 , and $\text{FSO}_3\text{H-SbF}_5$ enhanced the activities of

TABLE 6

Acid Strength of SbF_5 -Treated Catalyst^a

Catalyst	H_0			
	-12.70	-13.16	-13.75	-14.52
$\text{SiO}_2\text{-Al}_2\text{O}_3$ (I)	+	+	-	-
$\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ (I)	+	+	+	-
$\text{TiO}_2\text{-SiO}_2$	-	-	-	-
$\text{SbF}_5\text{-TiO}_2\text{-SiO}_2$	+	+	-	-
$\text{SbF}_5\text{-Al}_2\text{O}_3$ (II)	+	+	-	-

^a +, present; -, absent.

metal oxides for acid-catalyzed reactions. The $\text{FSO}_3\text{H-SbF}_5$ -treated catalyst catalyzed the reaction of butane, although its activity was not as high as those of the SbF_5 -treated catalysts. The SbCl_5 -treated catalyst catalyzed the reactions of 2-methylpropane and 2-methylbutane, but it could not catalyze the reactions of butane and pentane. Neither FSO_3H -treated catalyst nor NH_4F -treated catalyst could catalyze the reactions of alkanes at room temperature, but their activities for 1-butene isomerization were much higher than those before treatment. Therefore, it is evident that SbF_5 was the most effective among the reagents with which metal oxides were treated. On treatment with SbF_5 , many metal oxides became active for the reactions of alkanes that possess secondary or tertiary C-H bonds at room temperature. The effectiveness of the reagents decreases in the order $\text{SbF}_5 > \text{FSO}_3\text{-SbF}_5 > \text{SbCl}_5 \gg \text{FSO}_3\text{H} > \text{NH}_4\text{F}$. The catalytic activities of these catalysts for reactions of different kinds of hydrocarbons are qualitatively classified and given in Table 7. The catalytic activities of liquid super acids and conc. H_2SO_4 are also included.

In liquid super acids (e.g., 1:1 mixture of $\text{FSO}_3\text{H-SbF}_5$), methane undergoes protolytic condensation to give higher alkanes

and molecular hydrogen at about 60°C . Ethane and 2,2-dimethylpropane can undergo similar reactions (4). On the other hand, over the $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ catalyst, no reactions of methane, ethane, and 2,2-dimethylpropane occurred, and no evolution of molecular hydrogen molecule was observed. Since the $\text{FSO}_3\text{H-SbF}_5$ (1:1) solution exhibits an acid strength of $H_0 < -20$, it can protonate the primary, secondary, and tertiary C-H bonds as well as the C-C bonds of alkanes to yield carbonium ions. However, the acid strength of the Brønsted acid sites on the $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ catalyst is at most in the H_0 range $-13.75 \sim -14.52$. The difference in the acid strength seems to result in different catalytic behavior. The acid sites on the $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ are not strong enough to cleave the primary C-H bonds. The initiation of the reaction of alkanes that possess secondary or tertiary C-H bonds will be discussed later.

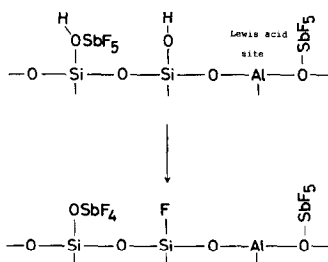
Antimony pentafluoride alone did not show considerable activity and became active when adsorbed on metal oxides. The activity depended upon the kinds of metal oxides and upon the method of treatment. These indicate that SbF_5 is not merely mounted on the surface but reacts with the surface. The ir spectrum of pyridine ad-

TABLE 7
Classification of Catalytic Activities of Various Catalysts

Catalyst	Reaction of alkane with			Reaction alkene
	Primary C-H	Secondary C-H	Tertiary C-H	
$\text{FSO}_3\text{H-SbF}_5$ HF-SbF_5 (liquid super acid)	+	+	+	+
SbF_5 -metal oxide $\text{FSO}_3\text{H-SbF}_5$ - metal oxide	-	+	+	+
SbCl_5 -metal oxide conc. H_2SO_4	-	-	+	+
FSO_3H -metal oxide NH_4F -metal oxide	-	-	-	+

^a +, active; -, inactive at room temperature.

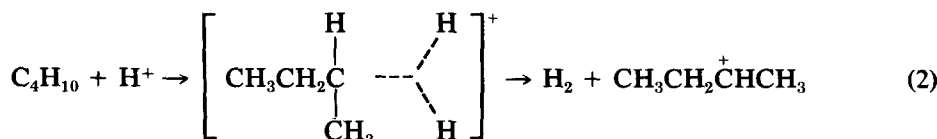
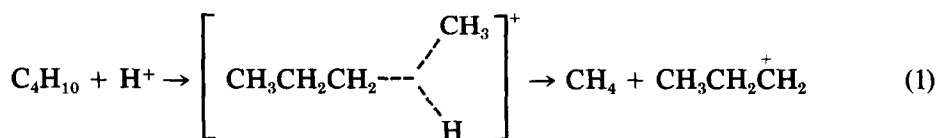
sorbed on the $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ (II) catalyst that had been treated with SbF_5 at a low temperature showed an intense band at 1540 cm^{-1} . It has been reported that the ir spectrum of pyridine adsorbed on $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalyst that had been outgassed at about 500°C showed only a weak band at 1540 cm^{-1} (18, 19). Appearance of the intense band at 1540 cm^{-1} for the $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ (II) catalyst suggests that the OH groups of the original $\text{SiO}_2\text{-Al}_2\text{O}_3$ (II) became strong Brönsted acid sites that can produce pyridinium ion on adsorption of pyridine. Disappearance of the Brönsted acid sites on treatment with SbF_5 at 300°C suggests that SbF_5 reacted with the surface OH groups. Although the formation of HF molecules could not be detected, the reaction of SbF_5 with $\text{SiO}_2\text{-Al}_2\text{O}_3$ is considered as follows.



At a low temperature, SbF_5 coordinates to the OH group on the Si atom and to the O atom adjacent to the Al atom of Lewis acid site. Coordination to the OH group increases the acid strength of the OH group, and coordination to the O atom increased the acid strength of the Lewis acid site. At a high temperature, SbF_5 reacts with the OH group to give -OSbF_4 and HF. The HF produced may react with an other OH group to form H_2O and the F bound to Si or Al.

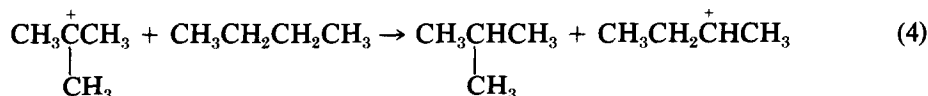
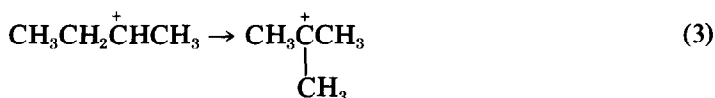
Formation of a carbenium ion from an alkane in an acidic medium results from the following two mechanisms. (I): Hydride ion abstraction from the alkane by a Lewis acid. (II): Protonation of the alkane by a Brönsted acid via the carbonium ion route.

In the reaction with $\text{FSO}_3\text{H-SbF}_5$ (magic acid) solution, the carbenium ion is formed by the mechanism (II) (4). Butane gives products in the order $\text{CH}_4 > \text{C}_2\text{H}_6 \gg \text{H}_2$, and 2-methylpropane gives $\text{H}_2 > \text{CH}_4 \geq \text{C}_3\text{H}_8$ at room temperature. A part of the hydrogen formed is used for reduction of SbF_5 to SbF_3 . The proposed mechanisms of the formation of CH_4 or H_2 from butane are;



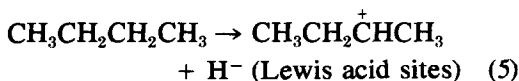
Once the *s*-butyl cation is formed (Eq. (2)), it undergoes skeletal rearrangement to give the *t*-butyl cation (Eq. (3)). The *t*-butyl

cation abstracts a hydride ion from the butane molecule to yield 2-methylpropane and *s*-butyl cation (Eq. (4)).

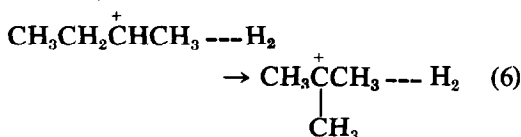


In this way, butane isomerization can proceed by a chain reaction.

In the reaction of butane over the $\text{SbF}_5\text{-SiO}_2\text{-Al}_2\text{O}_3$ catalyst, no hydrogen molecules were detected in the products, and the amount of methane evolved in the initial stage of the reaction was small. If methane were produced by the protonation of the C-C bonds of butane (Eq. (1)), a D atom would be incorporated into the methane molecule when the surface OH groups of the catalyst had been replaced by OD groups. This was not observed. When the treatment of $\text{SiO}_2\text{-Al}_2\text{O}_3$ with SbF_5 was carried out at 300°C , only Lewis acid sites were present. Over this catalyst, the butane isomerization proceeded. These suggest that the surface hydrogen atoms on the fresh catalyst do not participate in the reaction. Therefore, it is suggested that the reaction is initiated by abstraction of a hydride ion from butane by Lewis acid sites as follows (mechanism I).



An alternative mechanism might be considered as follows. Butane is protonated by the Brønsted acid sites to give a carbonium ion intermediate. The absence of hydrogen evolution might be explained by the concept that the hydrogen formed by Eq. (2) is used up for reduction of SbF_5 or that the hydrogen is loosely bound to the carbenium ion and does not leave during the skeletal rearrangement (Eq. (6)).



Once the *s*-butyl cation is formed, it undergoes skeletal rearrangement or cracking as summarized in the literature (20-22). Further details of the mechanisms of skeletal rearrangement and cracking will be discussed in the subsequent paper in which D atoms are used as tracers. The mechanism of carbenium ion formation is considered to be common for other alkanes.

An induction period for the formation of 2-methylpropane was observed in the reactions of butane, pentane, 2-methylbutane, and hexane. The interpretation of the similarity might be as follows. A precursor of 2-methylpropane, probably *t*-butyl cation, which is formed by methyl shift of *s*-butyl cation, by β -scission reaction, or by combination of methylene and methyl groups, is strongly adsorbed on the surface and accumulated in the initial stage of the reactions. 2-Methylpropane begins to be desorbed from the surface into the gas phase as the accumulation becomes saturated.

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