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Reactions of Pentane and 2-Methylbutane over Solid Super Acids Prepared by Different Conditions

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The reaction of pentane to 2-methylbutane was carried out at 0 °C over solid super acid catalysts which were prepared by treatment of various metal oxides with SbF_5 under different conditions, and the preparation conditions that affect the catalytic behavior of the catalyst were examined. Among the different base metal oxides, TiO_2–ZrO_2 became the most active catalyst when treated with SbF_5. The maximum conversion to 2-methylbutane which appeared in the reaction of pentane was high when a base metal oxide was treated with SbF_5 at a low temperature, and also when the reaction temperature was low. At the maximum conversion, the selectivity of the catalysts for the skeletal isomerization was almost 100%. As the reaction of pentane proceeded, the catalytic activity for the skeletal isomerization to 2-methylbutane was decreased but that for the formation of 2-methylpropane from 2-methylbutane was increased. The reaction mechanism is briefly discussed.

Recently, many attempts have been made to prepare solid super acids which show catalytic activity for skeletal isomerization of alkanes at low temperature, and most of them are patented. Other than the patents, Magnotta *et al.* reported that a complex of $AlCl_3$ with polystyrene sulfonic acid is active for the cracking and isomerization of hexane at 85 °C.[1,2] Olah *et al.* presented Nafion-H as a solid super acid.[3–5] Ono *et al.* reported that mixtures of aluminum halides with metal sulfates or with metal chloride showed high activities for the isomerization of pentane at room temperature.[6–8]

In our previous paper, we reported the preparation of solid super acids which exhibited catalytic activity for the skeletal isomerizations of butane and 2-methylpropane at room temperature.[9] The solid super acids were prepared by treatment of various types of metal oxides with SbF_5. Over these catalysts, pentane underwent skeletal isomerization to 2-methylbutane.[10] The selectivity to 2-methylbutane was 100% in the initial stage of the reaction, but lowered in the final stage of the reaction, which was caused by successive production of 2-methylpropane. As a result, there appeared a maximum conversion to 2-methylbutane in the course of the reaction. In this paper, several factors which might affect the maximum value of the conversion to 2-methylbutane are examined, and the reasons for appearance of the maximum are discussed. The variable factors examined are the type of base metal oxide, the temperature of treatment of base metal oxide with SbF_5, the number of treatment with SbF_5, the pretreatment temperature of base metal oxide, the reaction phase, and the presence of H_2.

Experimental

Preparation of Catalyst. Solid super acids were prepared by exposure of various metal oxides to SbF_5 vapor followed by evacuation of excess SbF_5. The base metal oxides used in this study were SiO_2, TiO_2, ZrO_2, Al_2O_3, SiO_2–Al_2O_3, and TiO_2–ZrO_2. Silica, TiO_2, and ZrO_2 were prepared by hydrolysis of aqueous solutions of ethyl orthosilicate, titanium tetrachloride, and zirconium dichloride oxide, respectively, with aqueous ammonia, followed by washing with deionized water and calcination at 500 °C in air. Alumina was AE-11 γ-Al_2O_3 purchased from Nishio Ind. Co. Ltd. Silica–alumina was N 631L obtained from Nikki Chemicals Co. Ltd. Titanium dioxide–zirconium dioxide was prepared by hydrolysis of aqueous solution of a mixture of $TiCl_4$ and $ZrOCl_2$ with aqueous ammonia, followed by washing and calcination at 500 °C in air. The composition was 63% TiO_2 and 37% ZrO_2 by mole.

Prior to exposure to the vapor of SbF_5, all base metal oxides were outgassed at 500 °C for 2 h. Procedures of exposure to SbF_5 for 10 min and following evacuation for 10 min were carried out at different temperatures in the range of 0—100 °C, and were repeated different times.

Specific surface area was determined by applying the adsorption isotherm of N_2 at the boiling point to BET equation. The amount of SbF_5 remained in the resulting catalyst was determined by measuring the weight change of the sample on exposure to SbF_5.

The reaction was carried out primarily at 0 °C in a closed recirculation reactor having a volume of *ca.* 325 ml. The initial pressure of a reactant was about 50 Torr (1 Torr= 133 Pa), and the amount of catalyst was 0.1 g before exposure to SbF_5. The reaction was also carried out in liquid phase under the atmospheric pressure of N_2 or the 13.5 kg/cm^2 of H_2. The reaction products were analyzed by gas chromatography. A 6-m column packed with VZ-7 was operated at room temperature.

Results

As shown in Table 1, the amount of SbF_5 remained in the catalysts after treatmetn with SbF_5 at different temperatures decreased with increase in the pretreatment temperature. Generally, the amount of SbF_5 was smaller for single component metal oxides than for binary ones. The specific surface areas of the catalysts decreased to a considerable extent on treatment with SbF_5. The areas became smaller as the treatment temperature was lower. For example, the area (445 m^2/g) of SiO_2–Al_2O_3 became 205 when SbF_5 was adsorbed at 30 °C and evacuated at 50 °C and 86 when SbF_5 was adsorbed at 0 °C and evacuated at 0 °C.

The product distributions in the reaction of pentane in 60 min (or 70 min) over the different types of base metal oxides treated with SbF_5 are summarized in

Table 1. Amount of SbF_5 remained in catalyst, wt %

Catalyst[a]	SbF_5 ads. temp/°C	Evacuation temp 0 °C	30 °C	50 °C	100 °C
SbF_5-SiO_2-Al_2O_3	0	49.7	37.6	27.7	
	10	53.2	40.9	34.5	30.7
	30		34.1	32.2	
	100				17.2
SbF_5-TiO_2-ZrO_2	0	49.9	30.0	32.8	
	10		33.5	27.2	
	30			29.8	
	100				30.9
SbF_5-SiO_2	0	33.1	18.8	12.8	
	10			18.2	
	30			17.2	
SbF_5-Al_2O_3	0	37.1			
SbF_5-TiO_2	0	23.1			
SbF_5-ZrO_2	0	24.8			

a) Adsorption-desorption cycle in SbF_5 treatment was repeated four times.

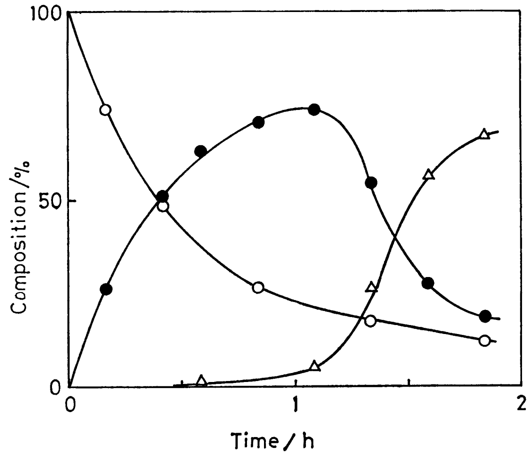


Fig. 1. Time course of reaction of pentane over SbF_5–SiO_2–Al_2O_3(10-30) IV catalyst at 0 °C.
○: Pentane, ●: 2-methylbutane, △: 2-methylpropane.

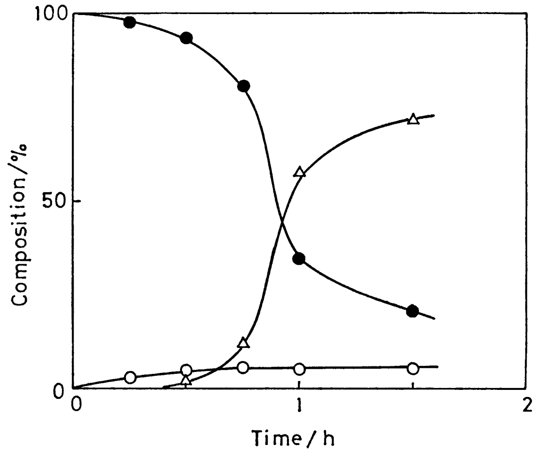


Fig. 2. Time course of reaction of 2-methylbutane over SbF_5–SiO_2–Al_2O_3(10-30) IV catalyst at 0 °C.
○: Pentane, ●: 2-methylbutane,' △: 2-methylpropane.

Table 2. Treatment with SbF_5 was done at 0 °C both for adsorption and for desorption, and repeated four times. Among the catalysts examined, the SbF_5–TiO_2–ZrO_2 catalyst showed the highest activity. The SbF_5–SiO_2–Al_2O_3 catalyst and the SbF_5–SiO_2 also exhibited high activity.

The time courses of the reactions of pentane and 2-methylbutane over the SbF_5–SiO_2–Al_2O_3 catalyst which was prepared by exposure of SiO_2–Al_2O_3 to SbF_5 at 10 °C followed by evacuation at 30 °C and repeating four times (hereafter represented by SbF_5–SiO_2–Al_2O_3 (10-30) IV) are shown in Figs. 1 and 2. Pressure changes during the reactions were negligible. In the reaction of pentane, only 2-methylbutane was produced in the initial stage of the reaction. In 30 min, 2-methylpropane began to be produced and became a predominant product in 90 min. The maximum conversion to 2-methylbutane was observed in about 60 min. The formation of hexanes was very small compared with that of 2-methylpropane. In the reaction of 2-methylbutane, pentane was produced in the initial period of the reaction in a small amount, and 2-methylpropane began to be formed in 30 min and became the main product.

The features of the time courses in these reactions were commonly observed for all catalysts prepared from different base metal oxides. However, the maximum conversion to 2-methylbutane from pentane varied with the treatment temperature with SbF_5. The maximum conversions to 2-methylbutane are given in Table 3, and the reaction times to give the maximum conversion are also included in Table 3 in parentheses. As the treatment temperature, especially the evacuation temperature, became higher, the value of the maximum conversion was decreased, and

Table 2. Reaction of pentane over solid super acid at 0 °C

Catalyst	Time / min	Product distribution/% 2-MP[a]	Pentane	2-MB[b]	2,2-DMB	Other hexanes
SbF_5-SiO_2-Al_2O_3	60	0.2	48.0	51.6		
SbF_5-TiO_2-ZrO_2	60	0.2	37.4	62.0	0.3	0.1
SbF_5-SiO_2	60	0.2	42.2	57.3		
SbF_5-Al_2O_3	70		71.1	28.5		
SbF_5-TiO_2	60	0.1	89.8	9.5		
SbF_5-ZrO_2	60	12.6	76.5	10.1	0.1	0.7

a) 2-Methylpropane. b) 2-Methylbutane. c) 2,2-Dimethylbutane.

Table 3. Maximum conversion to 2-methylbutane in reaction of pentane, %

Catalyst	SbF_5 ads. temp/°C	Evacuation temp 0 °C	30 °C	50 °C	100 °C
SbF_5-SiO_2-Al_2O_3	0	80(210)[a]	73(60)	34(15)	
	10	78(180)	73(65)	60(35)	10(25)
	30		58(30)	24(20)	
	100				5(10)
SbF_5-TiO_2-ZrO_2	0	87(210)	32(15)	15(15)	
	10		43(30)	14(15)	
	30			20(20)	
	100				20(20)
SbF_5-SiO_2	0	83(210)	43(60)	20(30)	
	10			53(60)	
	30			39(60)	

a) Numbers in parentheses denote reaction time in minute.

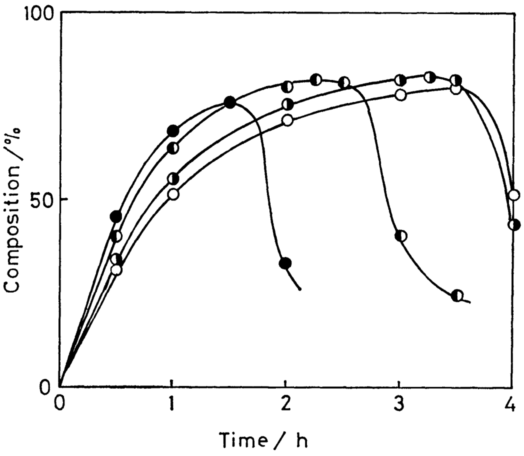


Fig. 3. Time courses of formation of 2-methylbutane from pentane over SbF_5-SiO_2-Al_2O_3(0-0) I—IV catalysts at 0 °C.
●: SbF_5-SiO_2-Al_2O_3 (0-0) I, ◐: II, ◑: III, ○: IV.

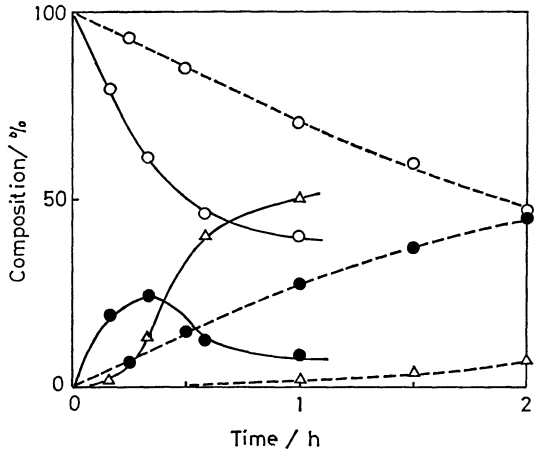


Fig. 4. Effect of reaction temperature in reaction of pentane over SbF_5–SiO_2–Al_2O_3(30-50) IV catalyst.
——: At 0 °C, ----: at −20 °C, ○: pentane, ●: 2-methylbutane, △: 2-methylpropane.

the reaction time to give the maximum was shortened. Among three different types of catalysts, the SbF_5–SiO_2–Al_2O_3 catalyst exhibited a high maximum conversion over a wide range of the pretreatment temperature, while the SbF_5–TiO_2–ZrO_2 was most easily affected by the treatment temperature, the maximum conversion being lowered from 87% to *ca.* 15% by raising the temperature of evacuation from 0 °C to 50 °C.

The number of repetition of adsorption-desorption cycle in treatment of base metal oxide with SbF_5 also affected the reaction time to reach the maximum conversion to 2-methylbutane. The time courses of the formation of 2-methylbutane from pentane over the SbF_5–SiO_2–Al_2O_3 catalysts which were prepared with different number of repetition of adsorption-desorption cycle at 0 °C are shown in Fig. 3. Although the maximum conversions to 2-methylbutane were almost the same, the initial conversion rates decreased and the reaction times to reach the manixmum conversion was prolonged as the number of repetition increased. The SbF_5–SiO_2–Al_2O_3(0-0) I catalyst and the SbF_5–SiO_2–Al_2O_3(0-0) IV catalyst had the surface areas of 120 and 86 m^2/g, respectively, and contained 49.3 and 49.7 wt % of SbF_5, respectively.

In Fig. 4, the time courses of the reaction of pentane over the SbF_5–SiO_2–Al_2O_3(30-50) IV catalyst at 0 °C and at −20 °C are shown. The maximum conversion to 2-methylbutane was higher when the reaction was carried out at lower temperature, though the initial conversion rate was lower.

When the reaction mixture was briefly evacuated at a certain reaction time and the fresh reactant was introduced, both the conversion rate of pentane and that of 2-methylbutane in the subsequent runs were quite dependent on the reaction time in the previous runs. The time courses of the previous reaction of pentane and the subsequent reaction are shown in Figs. 5 and 6 in which the subsequent reactant was pentane and 2-methylbutane, respectively. When the previous reaction was stopped before the conversion to 2-methylbutane reached the maximum, the isomerization of pentane to 2-methylbutane was faster than the formation of 2-methylpropane from 2-methylbutane in the subsequent runs. On the contrary, when the previous reaction was run to such an extent that the conversion to 2-methylbutane had passed the maximum and the formation of 2-methylpropane had

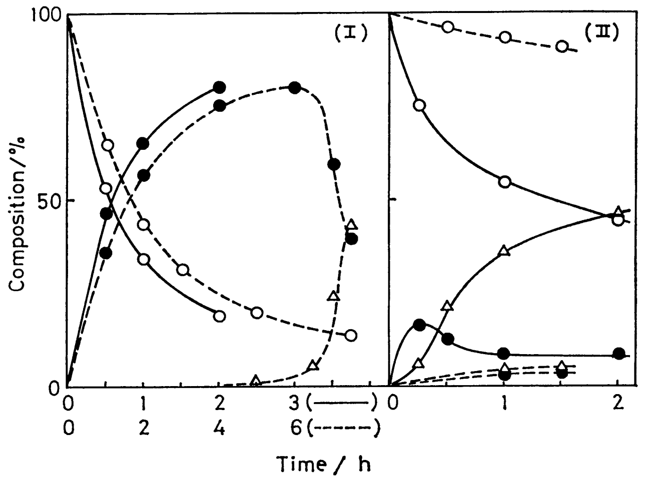


Fig. 5. Time courses of reaction of pentane in the first run (I) and in the second run (II) over SbF_5–SiO_2–Al_2O_3(0-0) IV catalyst at 0 °C.
○: Pentane, ●: 2-methylbutane, △: 2-methylpropane.

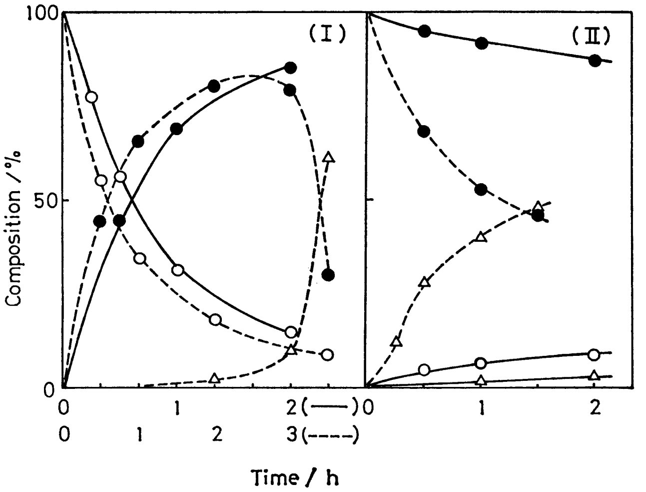


Fig. 6. Time courses of reaction of pentane in the first run (I) and of 2-methylbutane in the second run (II) over SbF_5–SiO_2–Al_2O_3(0-0) IV catalyst at 0 °C.
○: Pentane, ●: 2-methylbutane, △: 2-methylpropane.

been considerable, the formation of 2-methylpropane from 2-methylbutane became much faster than the isomerization of pentane to 2-methylbutane in the subsequent runs. If the nature of active sites were unchanged throughout the reaction, the reaction features in the subsequent runs would be independent of the reaction time in the previous runs. Therefore, the nature of active sites should gradually change as the reaction proceeds.

The pretreatment temperature of the base metal oxide also affected the catalytic activity. The SbF_5–SiO_2–Al_2O_3(0-0) IV catalyst whose SiO_2–Al_2O_3 had been outgassed at 100 °C prior to treatment with SbF_5 exhibited twice as high conversion rate of pentane as the standard catalyst. The catalytic activity of the SbF_5–SiO_2–Al_2O_3(0-0) IV catalyst whose SiO_2–Al_2O_3 had been outgassed at 1000 °C was negligibly small.

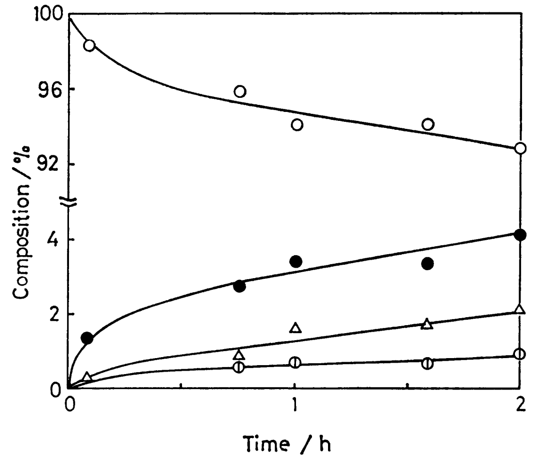


Fig. 7. Liquid phase reaction of pentane over SbF_5–TiO_2–ZrO_2(30-50) IV catalyst at 0 °C under atmolspheric pressure of N_2. Amount of catalyst: 0.269 g, amount of pentane: 10 ml.
○: Pentane, ●: 2-methylbutane, ⦶: hexanes, △: butane.

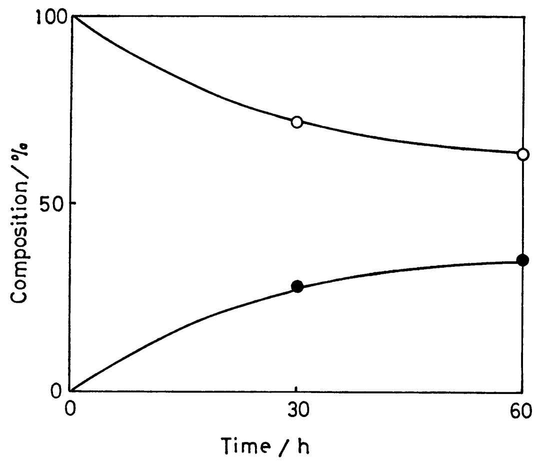


Fig. 8. Liquid phase reaction of pentane over SbF_5–TiO_2–ZrO_2(0-0) IV catalyst at 15 °C under 13.5 kg/cm^2 of H_2. Amount of catalyst: 0.200 g, amount of pentane: 2 ml.
○: Pentane, ●: 2-methylbutane.

The liquid phase reaction of pentane was carried out over the SbF_5–TiO_2–ZrO_2(30-50) IV catalyst under the atmosphere of N_2. The main product was 2-methylbutane as shown in Fig. 7. 2-Methylpropane was produced from the initial period of the reaction, but not increased to be a main product even in 120 min. Presence of H_2 (13.5 kg/cm^2) greatly enhanced the catalytic activity of the SbF_5–TiO_2–ZrO_2(0-0) IV catalyst and the products consisted primarily of 2-methylbutane as shown in Fig. 8. In Fig. 9, the time course of the reaction of 2-methylbutane over the SbF_5–SiO_2–Al_2O_3(30-50) IV catalyst is shown. The conversion rate of 2-methylbutane remained constant until the conversion level of 50%. The main products were hexanes; mostly 2,3-dimethylbutane and 2-methylpentane. To check the elusion of Sb into liquid phase, the liquid products after the reaction

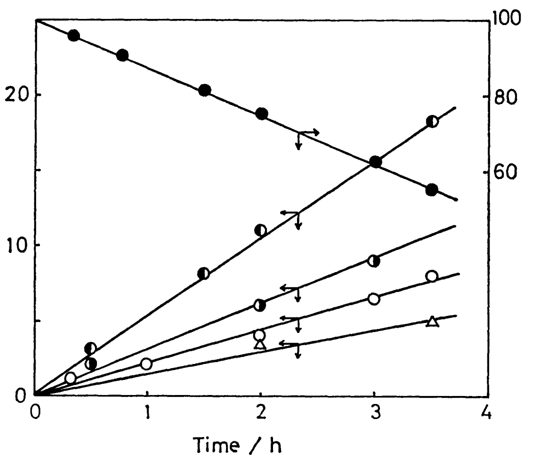


Fig. 9. Liquid phase reaction of 2-methylbutane over SbF_5–SiO_2–Al_2O_3(30-50) IV catalyst at 20 °C under atmospheric pressure of N_2. Amount of catalyst: 0.269 g, amount of pentane: 10 ml.
○: Pentane, ●: 2-methylbutane, △: 2-methylpropane, ◐: 2,3-dimethylbutane+2-methylpentane, ◑: 2,2-dimethylbutane+3-methylpentane.

were subjected to atomic absorption spectroscopic analysis. No Sb could be detected.

In order to check whether SbF_3 which may be formed by reduction of SbF_5 is active or not, the reaction of pentane over SbF_3–SiO_2–Al_2O_3 was carried out at 0 °C in a gas phase. The catalyst was found to be completely inactive.

Discussion

The skeletal isomerization of pentane to 2-methylbutane is important, since 2-methylbutane is known to be a harmless sbustance which raises the octane value of gasoline. In the present work, the maximum conversion of pentane to 2-methylbutane was found to be affected by various factors which appeared in preparation of the SbF_5–oxide catalysts. Out of the factors examined in this study, the temperature at which the base metal oxide was treated with SbF_5 exhibited the greatest effect. To obtain a high maximum conversion to 2-methylbutane, the treatment temperature is desirable to be low. Comparison of Table 3 with Table 1 reveals that the maximum conversion increases with the increase of the amount of SbF_5 remained in the catalysts, though the surface areas of the catalysts decreases with the increase of the amount of SbF_5.

The decrease in the conversion to 2-methylbutane as the reaction proceeds is caused by the formation of 2-methylpropane from 2-methylbutane.

Since the catalyst that had been used for the reaction to a considerable extent became not so active for the skeletal isomerization of pentane but active for the formation of 2-methylpropane from 2-methylbutane, the nature of active sites on the catalyst should gradually change as the reaction proceeds.

On the freshly prepared catalyst, only the active sites for the skeletal isomerization of pentane, I-sites, may exist, and I-sites are gradually transformed to the sites which are active for the formation of 2-methylpropane from 2-methylbutane, C-sites, during the skeletal isomerization. An alternative explanation could be this. Both I-sites and C-sites exist on the fresh catalyst, and only I-sites are gradually poisoned as the reaction proceeds. The I-sites are considered to act as Lewis acid sites which abstract hydride ions from pentane to form the carbenium ions, since the existence of Lewis acid sites on SbF_5–SiO_2–Al_2O_3 has been evidenced by infrared spectra of adsorbed pyridine.[11)]

According to the deuterium tracer study,[12)] 2-methylpropane is not produced by a simple cracking of 2-methylbutane. Two different mechanisms can be proposed for the formation of 2-methylpropane from 2-methylbutane. One of them is the recombination of four methyl and/or methylene groups on the catalyst surface (Eq. 1),[12)] and the other is the disproportionation of 2-methylbutane, that is, the dimerization-decomposition mechanism (Eq. 2).[13,14)]

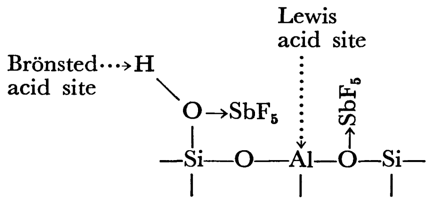
$$\text{2-methylbutane} \xrightarrow{\text{cracking}} \begin{array}{l}\text{methyl and/or}\\ \text{methylene groups}\end{array} \xrightarrow{\text{recombination}} \text{2-methylpropane} \qquad (1)$$

$$\text{2-methylbutane} \xrightarrow{\text{dimerization}} C_{10}\text{ species} \xrightarrow{\text{decomp.}} \text{2-methylpropane} + \text{a hexane} \qquad (2)$$

In the Eq. 1, 2-methylbutane was formed from pentane over the I-sites at first and it cracked to the methyl and/or methylene groups over the C-sites. The methyl and/or methylene groups accumulate on the surface as the reaction proceeds. When the accumulation becomes saturated, four methyl and/or methylene groups recombine to produce 2-methylpropane and it desorbs into the gas phase. Since the formation of hexanes are very small compared with that of 2-methylpropane in the gas phase reactions, 2-methylpropane may be produced mainly by the Eq. 1.

In the liquid phase reactions, however, not so large difference exists between the formation of 2-methylpropane and that of hexanes. Therefore, in the liquid phase reactions, the contribution of the Eq. 2 may be much larger than that of the Eq. 1 to the formation of 2-methylpropane. The effect of hydrogen is considered to prevent the carbonization of hydrocarbons or to retard the reduction of SbF_5.

Since the catalytic activity became smaller when the base metal oxide had been previously outgassed at higher temperature, the presence of OH groups on the base metal oxide seems to be necessary to form the active sites by treatment with SbF_5. In the catalyst, SbF_5 may not be simply adsorbed on the surface but may be reacted with surface, propably with surface OH groups. The existence of Brönsted acid sites, besides Lewis acid sites, is also evidenced by infrared study on adsorbed pyridine.[11)] The speculative structure of acid sites on SbF_5–SiO_2–Al_2O_3 may be drawn as follows.



SbF_5 adsorbs on oxygen atoms of Al–O–Si and O–H to attract the electron pairs of the oxygen atoms and by the inductive effects, both Lewis and Brönsted acid sites are considered to increase their acid strengths. A small amount of SbF_5 may be reduced to SbF_3 which is inactive for the reaction of pentane.

References

1) V. L. Magnotta, B. C. Gates, and G. C. A. Schuit, *J. Chem. Soc., Chem. Comm.*, **1976**, 342.

2) V. L. Magnotta and B. C. Gates, *J. Catal.*, **46**, 266 (1977).

3) G. A. Olah, J. Kaspi, and J. Bukala, *J. Org. Chem.*, **42**, 4187 (1977).

4) J. Kaspi and G. A. Olah, *J. Org. Chem.*, **43**, 3142 (1978).

5) J. Kaspi, D. D. Montgomery, and G. A. Olah, *J. Org. Chem.*, **43**, 3147 (1978).

6) Y. Ono, T. Tanabe, and N. Kitajima, *Chem. Lett.*, **1978**, 625.

7) Y. Ono, S. Sakuma, T. Tanabe, and N. Kitajima, *Chem. Lett.*, **1978**, 1061.

8) Y. Ono, T. Tanabe, and N. Kitajima, *J. Catal.*, **56**, 47 (1979).

9) K. Tanabe, and H. Hattori, *Chem. Lett.*, **1976**, 625.

10) O. Takahashi, H. Hattori, and K. Tanabe, submitted for publication in *J. Catal.*

11) O. Takahashi, H. Hattori, and K. Tanabe, *Shokubai*, **20**, 28 (1978).

12) O. Takahashi and H. Hattori, submitted for publication in *J. Catal.*

13) A. Schneider and R. M. Kennedy, *J. Am. Chem. Soc.*, **73**, 5017 (1951).

14) D. A. McCaulay, *J. Am. Chem. Soc.*, **81**, 6437 (1959).