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The Acid Strength and the Catalytic Activity of Solid Catalysts in the Oligomerization of Propylene

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The reaction activities and the reaction products of the oligomerization of propylene on several acidic solid catalysts, *e. g.*, silica-alumina, sodium-exchanged silica-alumina and some other acidic catalysts, have been investigated in a circulation system in the range of 130—300°C and 100—600 mmHg. The acid strength and the acid contents of catalysts were qualitatively measured by amine titration, using several indicators, over the range from 1.5 to -12.8 in H_0 function. Correlations between the reaction activity of the oligomerization of propylene and the acid strength as well as the acid content of the catalysts were demonstrated. The activation energies, the pressure dependency of the rate, and the reaction products were correlated with the acid strength as well. The high activity of some catalysts due to very strong acid sites was deactivated by coke formation in the initial stage of the reaction process. On the basis of an analysis of the reaction products, the major reaction at the stationary stage was ascertained to be the trimerization of propylene, which seemed to occur on moderately strong acid sites. The acid types responsible for the activity were discussed by the aid of "added back water."

It is generally believed that the activity of acidic solid catalysts is closely related to their acid contents and acid strength, as well as to their acid types (protonic or non-protonic). The oligomerization of propylene on acidic solid catalysts has been studied as one of the testing reactions useful in estimating their catalytic activities. Some relationships between the acid content and activity have been reported.[1-4] The dependency of the catalytic activity on the acid strength were reported by Johnson[2] and by Holm, Bailey and Clark;[3] however, their results were opposite to one onother. Tanabe[5] claimed that acid sites with strength in the range of $H_0 \leqq +1.5$ are active in the polymerization of propylene in the case of nickel and cupric sulfate catalysts.

Also, a reaction scheme including side reactions was reported by Shephard, Rooney and Kemball,[6] who reported that the main reaction products were iso-paraffins not higher than C_6. Some investigators suggested that the acid type responsible for the activity is protonic.[3-7]

The distribution of the acid strentgh of a silica-alumina catalyst has not been clarified in the range of acid strength stronger than -8.2 in H_0 function, because this value, corresponding to that of anthraquinone, is the strongest limit of indicators in the usual amine-titration method.[8] With the aid of ultraviolet spectroscopy in our laboratory, however, several new indicators were introduced for the measurement of the acid strength up to -12.8 in H_0 function, and the distribution of the acid strength of silica-alumina and some other acidic catalysts were determined.[9] They discovered that the silica-alumina catalyst changed in the distributions of its acid strength under sodium-exchange treatment in the range stronger than -8.2 in H_0 function.

Experimental

Apparatus and Procedure. The reaction process of propylene oligomerization was followed by observing the pressure decrease with a mercury manometer. The reaction system, 170 m*l* in volume, consisted of a cyrindrical pyrex reactor 15 mm in diameter and a magnetic circulation pump. In usual experiments 30—500 mg portions of catalysts diluted by 1 g of α-alumina were heated up to 450°C under a vacuum and then kept in a stream of dry, deoxygenated nitrogen for 2—3 hr at this temperature.

The reaction temperature in the range of 130—300°C was controlled within ± 1°C in an electric furnace. After an evacuation period of 30 min, propylene was expanded into the system to a certain predetermined initial pressure (100—600 mmHg).

A sample (0.3 m*l*) of substances in the gas phase was taken out with a syringe from the reaction system through

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[1] M. W. Tamele, *Discussions Faraday Soc.*, **8**, 270 (1950).

[2] O. Johnson, *J. Phys. Chem.*, **59**, 827 (1955).

[3] V. C. F. Holm, G. C. Bailey and A. Clark, *ibid.*, **63**, 129 (1959).

[4] M. Sato, T. Aonuma and T. Shiba, Proc. Third Int. Congr. on Catalysis, North Holland, Amsterdam (1965), p. 396.

[5] Y. Watanabe and K. Tanabe, *J. Res. Inst. Catalysis, Hokkaido Univ.*, **12**, 56 (1964).

[6] F. E. Shephard, J. J. Rooney and K. Kemball, *J. Catalysis*, **1**, 379 (1962).

[7] R. L. Hodgson and J. H. Raley, *ibid.*, **4**, 6 (1965).

[8] H. Benesi, *J. Phys. Chem.*, **61**, 970 (1957).

[9] J. Take and Y. Yoneda, to be published.

a silicone cerum cap and analyzed by a gas chromatograph employing a column of dioctylsebacate on celite (2.5 m) plus dimethylsulfolane on celite (2 m), and a hydrogen flame ionization detector. Hydrocarbons of C_4, C_5 and C_6 (except hexenes) were separated well. All peaks could be identified by comparing their retention volumes with those of known substances. The identification of products as olefins or paraffins was independently checked by the removal of olefins from a sample by means of treatment with sulfuric acid. For the purpose of a quantitative analysis, *n*-butane was used as the inner standard substance, as it was not present among the products. The oily products collected by an ice-trap were analyzed by another column of Apiezon L grease on Diasolid (4 m) at 150°C.

In order to determine the amount as well as the hydrogen/carbon ratio of the products retained on the surface of the catalysts, dry oxygen was introduced at a 1 atm to the reaction system at 450°C overnight under circulation in order to burn the products out into carbon dioxide and water. The color of the catalysts became nearly white under this treatment.

Anthracene (a 0.1 wt% benzene solution) and tetraline were injected onto the catalysts in a stream of nitrogen about 15—120 min before the introduction of propylene in some experiments.

Materials. The catalysts used are summarized in Table 1. Their strengths, although only qualitatively, and sodium contents are shown in the same table. The strength of the acid sites on SA-1, SA-1-Na-1 and Al-S was higher than that of the indicator, −12.8 in pK_a (2, 4-dinitrotoluene), and the acid contents decreased in the order: SA-1>Al-S>SA-1-Na-1. SA-Na-HAcO and SA-1-Na-3 were the weakest acid catalysts among the measured catalysts.

Propylene (99.9% purity, Matheson Co.) was used after it had been dehydrated by passing it through a calcium chloride column.

The tetraline was a GR grade reagent. The anthracene was purified by recrystallization.

Results

The Measurement of the Pressure Decrease. The pressure decrease of propylene was quite different from catalyst to catalyst, as Fig. 1 shows. The initial rate of pressure decrease in the catalysts with very strong acid sites (SA-1, SA-1-Na-1 and Al-S) was high, but it quickly diminished (initial process, type I) and approached

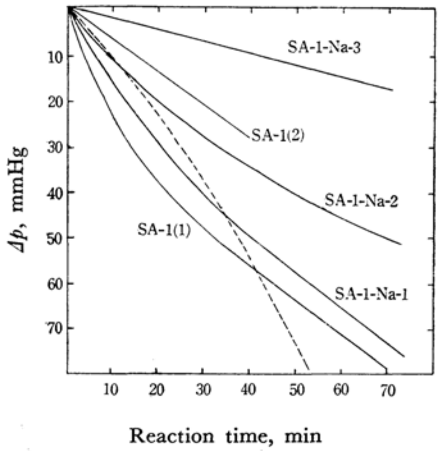

Fig. 1. Pressure decrease curve on various catalysts. Amount of catalyst: 52±2 mg, Reaction temperature: 200°C, Initial pressure: 400 mmHg. Broken line shows the initial process, type III: SA-1-Na-3, 139 mg, 250°C. SA-1 (1) and (2) correspond to the first and second run (after an interval of 30 min of evacuation) on SA-1, respectively.

TABLE 1. CATALYSTS

Catalysts		BET Surface area m²/g	Na Content meq./g	Acid strength[a]	Remarks
Symbol	Constituent				
SA-1	Silica-alumina	540	0.003	Very strong	b
SA-1-Na-1		450	0.048	Very strong	c
SA-1-Na-2		480	0.087	Strong	c
SA-1-Na-3		480	0.168	Relatively weak	c
SA-Na-HCl		—	0.119	Strong	d
SA-Na-HAcO		—	0.200	Relatively weak	e
Al-S	Aluminum sulfate on silica	—	—	Very strong	f
A-3	γ-Alumina	—	—	—	g
A-4	γ-Alamina	—	—	—	h

a) Measured by amine titration (see text)

b) Silica-alumina cracking catalyst (Al_2O_3 13wt%). Supplied from Shokubai-Kasei Co. Ltd.

c) SA-1 was exchanged with a sodium hydroxide aqueous solution.

d), e) Sodium-exchanged silica-alumina was partially reactivated by aqueous HCl and HAcO, respectively.

f) Aluminum sulfate was impregnated on silica gel from an aqueous solution.

g) Hydrated and calcined from aluminum isopropoxide.

a stationary value after about 30 min. The rate of the initial process (type I) was approximately represented by the following equation;[1,2]

$$v = -\mathrm{d}p/\mathrm{d}t = k_0 p/\{1+b(p_0-p)\}, \qquad (1)$$

where p is the total pressure (mmHg), p_0 is the initial pressure of propylene (mmHg), b is a constant of the retardation term (mmHg^{-1}), and k_0 is the rate constant of the first order (min^{-1} g^{-1}). The dependency of the initial rate on the initial pressure of propylene, however, was found to deviate from the first order; *e. g.*, $v_0=k'p_0^{1.18}$ on SA-1-Na-1 at 200°C for the pressure range of 100—600 mmHg. However, the first-order approximation of Eq. (1) held well at the low conversion level of this work. Some values of k_0 were obtained from Eq. (1), and some others were obtained directly from the slope of the log p *vs.* the time plot at $t=0$. These results are given in Table 2. As will be discussed below, k_0 may be regarded as a criterion of the activity of a fresh catalyst; b is the rate of deactivation per 1 mmHg of pressure decrease. The stationary rate constant of the first order, k_{st}, which was calculated from the log p *vs.* the time plots at $t=50$ min, and the apparent activation energies are shown in the same table.

After the stationary rate was obtained, the reaction system was evacuated for 5—10 min; then another run was repeated on the same catalyst under the same conditions. The rate of the second run was nearly constant from the beginning, without having the initial process (type I); moreover, it was identical with the stationary rate of the former run, as is shown in Fig. 1 for SA-1,

TABLE 2. RATE OF PRESSURE DECREASE AND ACTIVATION ENERGY

Catalyst	Reaction temp. °C	Amount of catalyst mg	First order rate const. min^{-1}g^{-1}		b mmHg^{-1}	Apparent activation energy E_A (kcal/mol)		Initial process[a]
			k_0	k_{st}		Initial	Stationary	
SA-1	300	29.7	0.586	0.262	0.015	6.9	8.4	I
	255	30.4	0.272	0.112	0.024			
	200	54.8	0.168	0.044	0.044			
	200	49.0	0.160	—	0.071			
	200	51.8	0.162	—	0.040			
	200	116.0	0.165	—	0.045			
	130	108.8	0.035	—	>0.3			
SA-1+ Anthracene[b]	200	56.0	0.094	0.032	0.038	—	—	I—II
SA-1+ Tetraline[c]	200	61.0	0.120	0.032	0.049	—	—	I
SA-1-Na-1	200	51.1	0.120	0.046	0.036	5.8	7.1	I
	200	70.3	0.124	—	0.052			
SA-1-Na-2	300	56.6	0.100	0.085	0.0024	3.7	6.0	II
	250	54.9	0.090	0.067	0.0064			I—II
	200	59.3	0.055	0.030	0.020			I—II
	161	69.9	0.037	0.017	0.051			I
SA-1-Na-3	300	210.4	0.018	0.018	0	2.7	5.3	III
	250	139.4	0.015	0.015				III
	205	50.0	0.013	0.013				II
	200	248.2	0.012	0.012				II
	200	500.7	0.011	0.007	0.005			II
SA-Na-HCl	200	169.7	0.039	—	0.011	—	—	I—II
SA-Na-HAcO	300	220.7	0.037	0.033	0.001	3.6	4.6	III
	250	223.7	0.028	0.021	0.004			II
	200	285.7	0.019	0.014	0.010			I—II
Al-S	200	61.7	0.104	—	0.032	—	—	I
A-3	200	438.0	6×10^{-5}	—	—	—	—	—
A-4	200	214.7	8×10^{-4}	—	—	—	—	—

Initial pressure: 400 mmHg

a) See text.

b) SA-1 preadsorbed with anthracene.

c) SA-1 preadsorbed with tetraline.

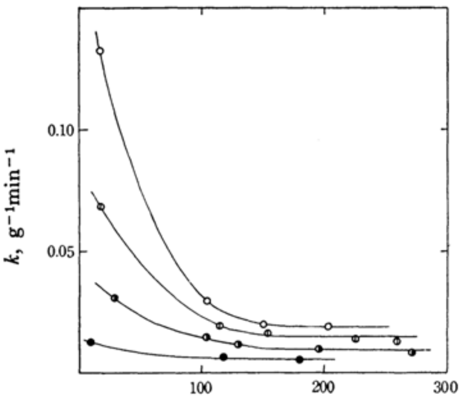

Fig. 2. Changes of Activities by repeated runs at 200°C, 400 mmHg
○ SA-1, 143 mg ; ⦶ SA-1-Na-1, 322 mg;
◑ SA-1-Na-2, 411 mg; ● SA-1-Na-3, 501 mg

as an example. By the repeated runs the activity of the catalysts slowly diminished as is shown in Fig. 2. The pressure dependencies of the initial rate at the stationarily-deactivated stages were:

$$v_0 = k'p_0^{1.50} \text{ on the deactivated SA–1} \quad (200°\text{C, } 100\text{—}600 \text{ mmHg}) \qquad (2)$$

and

$$v_0 = k'p_0^{1.68} \text{ on the deactivated SA-Na-HCl} \quad (200°\text{C, } 100-600 \text{ mmHg}) \qquad (3)$$

The catalysts with relatively weak acid sites (SA-1-Na-3, SA-Na-HAcO) behaved in the same way as those with stationarily-deactivated strong acid catalysts. This group of catalysts showed nearly constant activity from the beginning of the reaction (initial process, type II) and $v_0 = k'p_0^{1.50}$ for SA-1-Na-3 in the range of 100—600 mmHg at 200°C.

In a few experiments with low-activity catalysts (fresh as well as deactivated by reactions) at low propylene pressures and high temperatures, a short induction period was observed, as is shown in Fig. 3 (initial process, type III). In Fig. 3 it is shown clearly that the catalysts began to exhibit an induction period when the activity decreased after repeated runs or when the initial pressure was reduced. In the last column of Table 2, the types of initial process on the fresh catalysts at 400 mmHg are given.

As the conversions were limited at a low level, the deviation from linearity in the log p *vs.* the time plot was considered to be mainly due to the deactivation of the catalyst during the course of the reaction. Therefore, values of k were obtained as the slope of the log p *vs.* t plots, while those of b were obtained from the equation: $b = (k_0/k_{st})/(p_0 - p\,(50))$. They may represent, relatively, the activities and the rates of deactivation of catalysts with an initial process, types II and III.

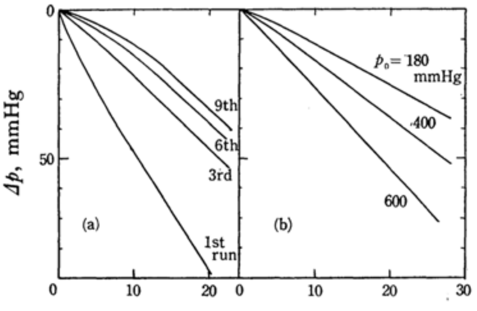

Fig. 3. Initial procees, type III.
(a) SA-Na-HCl, 170 mg, 200°C, Initial pressure: 400 mmHg.
(b) Deactivated SA-1, 118 mg, 200°C

k_0, k_{st} and b were sensitively affected by the velocity of circulation, as is shown in Fig. 4, in the case of very strong acid catalysts, especially when a large quantity of catalysts was used. The data summarized in Table 2 are collected when the velocity of circulation was sufficiently high compared with the rate of reaction. These conditions were obtained by reducing the amount of catalysts; the k_0 values are almost constant, *e. g.*, 0.168, 0.160, 0.162 and 0.165, with various amounts of catalyst at 200°C and 400 mmHg for SA-1.

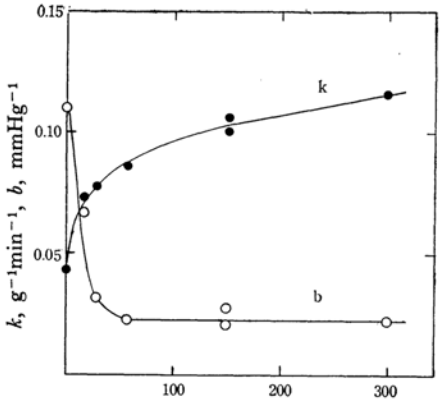

Fig. 4. Effect of circulation velocity on k and b. 200°C, 400 mmHg, SA-1-Na-1, 150 mg; circulation velocity was measured at 1 atm.

An analysis of the Reaction Products. *The Reaction Products in the Gas Phase.* The amounts of gas-phase products, except for the remaining propylene, together with their compositions, are summarized in Table 3. Hydrocarbons not lower than C_7 were neglected, because only trace amounts of them were found by gas chromatographic analysis.

Table 3. Composition of gas phase products

Catalyst	Reaction temp. °C	Amount of catalyst mg	Reaction time min	Pressure decrease mmHg	Composition, mmHg						$\Delta p^{*a)}$ mmHg
					i-C_4	C_4'	i-C_5	C_5'	i-C_6	C_6'	
SA-1	200	52.4	5	16.7	0.2	1.0	0.1	0.9	0.9	3.5	5.4
		54.8	20	40.3	0.3	1.5	0.2	1.4	1.7	4.3	7.7
		54.8	60	75.2	0.9	1.9	0.7	2.1	2.3	6.4	11.7
	300	29.7	8	49.4	0.7	7.5	0.6	6.1	3.1	11.7	22.3
		29.7	45	145.0	3.5	14.3	2.1	9.7	4.1	12.3	31.2
SA-1+ Anthracene	200	54.3	8	14.6	0	0.6	0.1	0.8	0.8	3.5	5.1
		54.3	60	56.0	0.4	1.2	0.2	0.9	1.5	9.0	11.9
SA-1+ Tetraline	200	61.2	10	21.9	0.2	0.6	0.2	1.1	1.3	3.3	5.7
SA-1-Na-1	200	76.5	7	15.0	0.2	1.1	0.2	1.3	1.3	3.9	6.6
		51.1	60	66.0	0.6	1.4	0.3	1.5	2.0	4.7	8.6
SA-1-Na-3	200	248.2	15	17.2	0	0.4	0.1	0.8	0.9	4.5	6.1
		248.2	45	45.4	0.5	1.7	0.3	2.5	2.0	4.5	9.0

Initial pressure: 400 mmHg

a) Δp^* is the contribution of gas phase products to the total pressure decrease calculated as described in text.

The paraffin/olefin ratio was larger for strong acid catalysts, such as SA–1 and SA-1-Na-1, than for such weak acid catalysts as SA-1-Na-3; this suggests that the hydrogen transfer reaction by which paraffins are produced occurs more readily on the stronger acid sites. However, there were no further remarkable differences in composition among catalysts when they were compared with each other at the same conversion level. This is in accord with the findings of Shephard, Rooney and Kemball[6] that the paraffins in products are only those with side chains, the amounts of which increase during the course of reaction. Although we obtained much more olefins, especially C_6', than they did, this difference may be due to the experimental conditions.

The contribution to the total pressure decrease by the gas-phase products, Δp^*, shown in the last column of Table 3, was calculated as follows;

$$\Delta p^* = p(C_6+C_6')+\frac{1}{2}\{p(i\text{-}C_4+C_4')+p(i\text{-}C_5+C_5')\}, \qquad (4)$$

on the assumption that products in the gas phase cause a pressure decrease in the following way:

$$2C_3' \rightarrow C_6 \text{ or } C_6' \text{ and } 3C_6' \rightarrow C_9' \rightarrow i\text{-}C_4 \text{ or } C_4' \text{ plus } i\text{-}C_5 \text{ or } C_5'.$$

This assumption seems reasonable because the amounts of C_4 hydrocarbons and of C_5 hydrocarbons were almost equal, as is shown in Table 3.

Catalysts treated with perylene or with tetraline exhibited the same behavior in the pressure-decreasing process and gave products in the gas phase similar to those of SA-1-Na-1. This was not in accord with the findings of Shephard, Rooney and Kemball[6] at 100°C. A prolonged treatment with tetraline resulted in a decrease in catalytic activity.

Products Retained on the Catalyst Surface. In order to examine the initial process in detail, the amounts of the reaction products retained on the catalyst surface and their hydrogen/carbon ratios were analyzed by burning them out into carbon dioxide and water in the reaction system. They were calculated as $p_{CO_2}/3$ and $2p_{H_2O}/p_{CO_2}$ respectively. The results are given in Fig. 5 for SA-1 with a fast deactivation and for SA-1-Na-3 without it. The mass balance of the system made it clear that all the initial products except for a small amount of C_4-to-C_6 hydrocarbons were retained on the surface of the catalysts, and that the oligomerization products, mainly C_9 hydrocarbons, as will be described below, began to condense when the activity of the catalysts approached a stationary state. In the stationary state, most of the products condensed, although some increase in the gas-phase substances was observed.

The hydrogen/carbon ratio fell rapidly at the initial stage for both SA-1 and SA-1-Na-3 catalysts, but it approached quite different values, 0.55 for the former and 1.3 for the latter. The hydrogen/carbon ratio may be connected with the degree of dehydrogenation or aromatization of surface products, or coke formation, so these results may suggest that coke formation proceeds faster and to a greater extent on stronger acid sites.

Oily Products. The chromatograms obtained for oily products consisted of two main peaks, assigned to a mixture of C_9 hydrocarbons, and many small peaks. The compositions of oily products are shown in Table 4, with SA-1 at 200°C as an example. The amount of oily products can be estimated from the difference between curve 1 (or 1′) and curve 2 (or 2′) in Fig. 5.

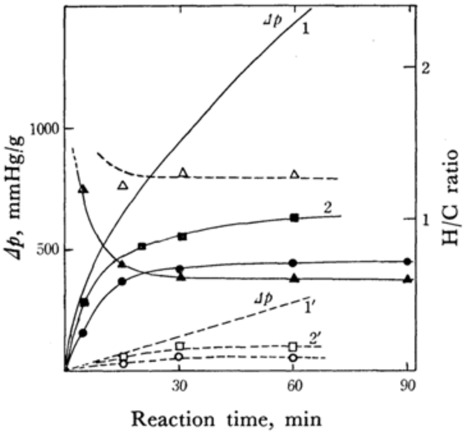

Fig. 5. Correlations of pressure decrease, gas phase products, surface products and their hydrogen/carbon ratio to the reaction time.
Solid line: SA-1, 52 mg, 200°C, 400 mmHg
Broken line: SA-1-Na-3, 250mg, 200°C, 400mmHg
● or ○: Amount of surface products ($P_{CO_2}/3$)
■ or □: Gas-phase products (Δp^*) + amount of surface products
▲ or △: Hydrogen/carbon ratio ($2p_{H_2O}/p_{CO_2}$)
Δp: Total pressure decrease

TABLE 4. COMPOSITION OF OILY PRODUCTS

Number of carbons	6	7	8	9	>9
mol%	1.3	3.4	19.8	57.0	19.5

Reaction temperature: 200°C, Initial pressure: 400 mmHg, Reaction time: 40 min, Catalyst: SA-1 204 mg

Effect of "Added Back Water." According to the standard procedure of Haldeman *et al.*,[10] about 20 mmHg of water was introduced into the reaction system after it had been evacuated for 2 hr at 450°C; then the temperature was lowered to the reaction temperature of 200°C. The amount of added back water was controlled by the evacuation time before the reaction at 200°C.

TABLE 5. EFFECT OF " ADDED BACK WATER "

Evacuation period at 200°C, hr	Rate constant, min^{-1}g^{-1} k_0	k_{st}	b, mmHg^{-1}
0.5	0.053	0.030	0.020
1	0.186	0.056	0.027
2	0.158	0.050	0.034
a	0.165	0.045	0.045
b	0.162	0.044	0.045

Reaction temperature: 200°C, Initial pressure: 400 mmHg, Catalyst: SA-1 55±2 mg
a) Preheated in vacuum for 3 hr at 450°C and without " added back water."
b) Standard pretreatment without " added back water.'

The results are summarized in Table 5. An adequate amount of added back water raised activities a little and reduced the deactivation ability during the reaction. In experiments without added back water, catalysts with high activities always showed a high rate of deactivation. Therefore, this small but definite effect of added back water would suggest that the small amount of water converts inactive non-protonic acid sites to active protonic sites, which are then less active in coke formation.

These observations of the effect of "added back water" on the activity are essentially in accord with the results of Hindin *et al.*,[11] Haldeman *et al.*[10] and Ozaki *et al.*[12]

An excess amount of water, which was realized by a short time of evacuation, reduces both k and b, probably because of the conversion of strong acid sites to weaker ones.

Discussion

Initial Process and Coke Formation. From a comparison of the values in Table 2 with the acid strength of the catalysts it is obvious that the initial process, characterized by k_0 and b, is closely related to the acid strength. The stronger the acid strength of the catalyst, the larger the values of k_0 and b. At the same acid strength, k_0 was larger with the catalyst with greater acid content.

The results shown in Fig. 5 provide a good suggestion for the elucidation of the initial process. The feature of the pressure decrease was shown again for SA-1 and SA-1-Na-3. SA-1 showed the high initial rate of pressure decrease and fast deactivation which is characteristic of the initial process of type I. On the other hand, SA-1-Na-3 was much less active, showing little deactivation. The amounts retained on the surface of the catalyst increased at first; then for both catalysts they gradually became saturated. The saturated values were quite different, *e. g.*, about 450 mmHg of propylene for SA-1 and about 60 mmHg for SA-1-Na-3. The hydrogen/carbon ratios, which decreased initially, reached different constant values, 0.55 for SA-1 and 1.3 for SA-1-Na-3. All of these observations can be reasonably explained if

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[10] R. G. Haldeman and P. H. Emmett, *J. Am. Chem. Soc.*, **78**, 2922 (1956).

[11] S. G. Hindin, A. G. Oblad and G. A. Mills, *J. Am. Chem. Soc.*, **77**, 535, 538 (1955).

[12] A. Ozaki and K. Kimura, *J. Catalysis*, **3**, 395 (1964).

one considers that the coke formation proceeded in this initial process to degrees depending on the acid strength of the catalysts. Considering the smaller hydrogen/carbon ratio and the larger aount of surface products for SA-1 compared with those for SA-1-Na-3, it may naturally be concluded that an extreme and rapid coke formation took place with SA-1, thus causing a fast deactivation in the initial process (type I), and that the rate of coke formation diminished to zero during this initial process, after which the stationary state was obtained.

In conclusion, in the initial process of type I, fast polymerization, or oligomerization, takes place on the very strong acid sites, followed by an extreme and rapid coke formation which causes the deactivation of the very strong acid sites.

In the case of SA-1-NA-3, the acid sites of which are not so strong as those of SA-1, the coke formation proceeds slowly and not so extremely as to cause the deactivation of the catalyst. This interpretation may be related to the fact that b is very small for less active catalysts, as is shown in Table 2.

The color change in the SA–1 catalyst from white to yellow in the first 5—10 min of reaction, and then to dark brown after 30 min, may support the fast and extreme coke formation on it, while the color of the SA-1-Na-3 catalyst changed only to pale yellow after a prolonged reaction period, indicating little coke formation.

The small values of b and the greater amounts of gas-phase products shown in Tables 2 and 3 at an elevated reaction temperature are reasonable, because the cracking of polymerized surface products, precursors of coke, might be easier.

The high initial activity and the high apparent activation energy on strong acid sites may be explained qualitatively as follows: the concentration of carbonium ions is supposed to be higher on the stronger acid sites than on the weaker ones, while the true activation energy of the reaction between carbonium ions and propylene is assumed to be independent of the acid strength. The lower reaction order on stronger acid catalysts supports this reasoning.

Stationary State. In the stationary state, the activities of all the catalysts are similar as a result of the deactivation of very strong acidic and very active catalysts during the initial process. It seems most reasonable to surmise that the very strong acid sites are deactivated and that the moderately strong acid sites are responsible for the activity at the stationary state. However, it can not be discerned whether very strong acid sites are deactivated completely or they are converted to moderately strong acid sites by interaction with the olefin in the stationary state.

The stationary activity was not altered by the evacuation at the reaction temperature. However, it could be lowered to a less active one by stopping the circulation, either from the beginning of the reaction or after the stationary activity had once been established.

The stationary activity, corresponding to the extent of deactivation by coke formation, may be determined by the magnitude of two rates, the rate of the cracking or desorption of surface products and that of the coke formation. The latter might be promoted by the high concentration of oligomerized products near the surface of the catalyst, so that their removal by the rapid circulation resulted in a higher activity in the stationary state. The evacuation at 450°C for 3 hr completely recovered the initial process of SA-1-Na-1 at 200°C, probably because of the recovery of very strong acid sites by the cracking of surface products, namely coke on them, though the catalysts became black in color after evacuation.

Type of Acid Site. Acidic solid catalysts have been believed to have protonic acid sites and non-protonic acid sites, or oxidation sites. The active sites for the polymerization or oligomerization of propylene have been suggested by several investigators to be protonic. Holm, Bailey and Clark(3) showed that the polymerization activity of silica-aluminas paralleled the Brönsted acidity as measured by the sodium-ion exchange method in an aqueous solution, but not the total acidity as obtained from the amine titration. Shiba *et al.*(4) demonstrated a good relationship between the polymerization activity of silica-aluminas and the Brönsted acidity, which was obtained as the difference between the total acidity and the Lewis acidity. Shephard, Rooney and Kemball(6) reported that the absence of any reaction of propylene and the formation of perylene radical ions on the sodium-exchanged silica-alumina supported the ideas that Brönsted sites are required for this reaction and that Lewis sites are inactive, but responsible for the coke formation. They also concluded that perylene is adsorbed only on the Lewis acid sites.

The conclusion that the protonic acid sites are responsible for the polymerization or oligomerization of propylene and not the non-protonic sites, does not seem strange, but re-examinations are necessary for the following reasons. First, in the present work it has been demonstrated that the sodium-exchanged silica-alumina changes its distribution of acid strength depending on the extent of exchange, as does the catalytic activity. The anthracene-treated catalyst, which was green in color, indicating the presence of a σ-complex,(13) had a smaller activity than did an untreated one.

Secondly, the radical-forming sites of silica-alumina in the absence of oxygen gas, which were

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13) A. N. Terenin, V. A. Barachevsky, V. E. Kolmogorov and A. N. Terenin, *Doklady Akad. Nauk, USSR*, **152**, 1143 (1963).

reasonably ascribed to the strong non-protonic site,[14] have been considered to be insensitive to the sodium-ion exchange treatment.[14c] However, their amounts were only 10^{10}—10^{12} sites/cm^2.[14] These values are much smaller than that of the total acidic sites, about 10^{13} sites/cm^2, so that the invariableness of the amount of the radical-forming sites under the sodium-ion exchange treatment does not seem to eliminate the possibility that the non-protonic sites with moderate acid strengths are active.

Thirdly, it may need further examination to conclude which of the following three reactions is the most reliable method to measure non-protonic acid sites: (1) polyacene→the cation radical, (2) ϕ_3CH or $\phi_3CCl \rightarrow \phi_3C^+$, (3) $\phi_3CH \rightarrow \phi_3C\cdot$, the relative amounts of radicals formed from triphenyl methane on the catalysts used in this experiment were found to be 1.0 (SA-1), 0.7 (SA-1-Na-1) and 0.4 (SA-1-Na-3);[15] the radical-forming sites clearly decrease upon sodium-ion exchange.

The activities of catalysts in the present work were explained well in terms of their acid contents and strengths without considering the type of acid, except for the small effect of the "added back water." A more quantitative discussion will be presented in the near future. Although the distribution of the acid strength of γ-alumina could not be determined quantitatively, its acid strength seems rather weak; the small observed activity and the small deactivation of γ-alumina in this work can be explained in a way similar to that used for other catalysts without considering the acid type.

Most of the remarks made by Shephard, Rooney and Kemball[6] hold in the present work as well, if their Lewis site and Brönsted site are replaced by a very strong acid site and a moderately strong acid site respectively.

It is rather natural that the protonic acid sites are active for the polymerization of propylene on acidic solid catalysts, because such Lewis acids as $AlCl_3$, $SnCl_4$ and $SbCl_5$ always require co-catalysts for the polymerization, the isomerization of paraffins, or the Friedel-Craft reaction because of their insufficient ability to produce carbonium ions from hydrocarbons.

A further investigation including the quantitative measurement of the activity, the acid content and strength, seems necessary to determine the active type of acid.

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[14] a) W. K. Hall, *J. Catalysis,* **1**, 53 (1962); b) D. M. Brouwer, *ibid.*, **1**, 372 (1962); c) J. J. Rooney and R. C. Pink, *Trans. Faraday Soc.*, **58**, 1632 (1962); d) H. Imai, Y. Ono and T. Keii, *J. Phys. Chem.*, **69**, 1082 (1965).

[15] H. Arai and Y. Yoneda, This Bulletin, in press.