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Reactivity of Solid Acids with Methylene Chloride

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In order to discriminate the natures of solid acids, the reactivity of methylene chloride with solid acids like alumina, silica-alumina and alumina-boria to give carbon monoxide and methyl chloride was studied with a pulse technique. The reactivities varied about ten thousandfold among these solid acids. The methyl chloride formation was predominant on alumina particularly at low reaction temperatures, with a distinctly small activation energy in comparison with that on silica-alumina or alumina-boria. The nature of the active sites for this reaction was discussed in connection with the effect of the calcination temperature as well as of the sodium ion-poisoning on activity. Furthermore, it was found that the feature of this reaction was in marked contrast with the typical solid acid catalysis such as the dealkylation reaction of alkylbenzenes. The reaction of methylene chloride with a set of the surface hydroxyl group and the oxidizing site is assumed to give methyl chloride through a radical mechanism.

It is well known that alumina and silica-alumina are in remarkable contrast with each other as solid acid catalysts. Silica-alumina has about one thousand times or even more higher catalytic activity than alumina has in such typical catalytic reactions as dealkylation of alkylbenzenes,(1) isomerization of xylene or cyclohexene(1) and oligomerization of propylene.(2) It is also to be noted that the ethylene/ether selectivities in dehydration of ethanol at 325°C on alumina and silica-alumina are quite different, although both give nearly the same activity.(3)

Alumina is known to exhibit exceedingly higher catalytic activities than silica-alumina does for the H-D exchange reaction between hydrogen and deuterium or between the surface hydroxyl groups and either deuterium or deuterated methane.(4) For example, the activation energy of the exchange reaction of the hydroxyl groups with deuterated methane was 5.7 kcal/mol for alumina, but 33.4 for silica-alumina.(4)

Many works have already been published concerning the triphenylcarbonium ion formation from triphenyl methane on solid acids.(5) Lately, Arai *et al.*(6) reported an interesting contrast between alumina and silica-alumina for the triphenyl methane chemisorption; a considerable amount of triphenyl methyl radical alone was formed on alumina, whereas both triphenylcarbonium ion and triphenyl methyl radical were formed on silica-alumina.

As well as silica-alumina, all of alumina-boria-(10% B_2O_3)(1) and aluminas treated with boron trifluoride, hydrogen fluoride or ammonium fluoride(1,7) gave higher catalytic activities for the dealkylation and other acid-catalyzed reactions.

The present authors have found that methylene chloride reacts with solid acids to give methyl chloride and carbon monoxide as the gaseous products and that the rate and the selectivity of methyl chloride/carbon monoxide varied extermely with the kind of the solid acid.(8) In other words, this reaction can characterize the specific nature of alumina as the solid acid in comparison with silica-alumina. The specific nature of alumina may be due to the cooperation of both the surface hydroxyl group and the oxidizing site for the radical reaction, as is previously concluded by the LFER (Linear Free Energy Relationships) approach with the aid of the simple molecular orbital theory.(8)

Experimental

Reagents. Methylene chloride and *n*-butylamine of G. R. grade (Tokyo Kasei Co.) were used without any purification. No impurities were detected by gas chromatography.

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1) I. Mochida and Y. Yoneda, *J. Catalysis,* **7**, 386, 393 (1967).

2) M. Misono and Y. Yoneda, This Bulletin, **40**, 42 (1967).

3) J. Take and Y. Yoneda, to be published.

4) J. G. Larson and W. K. Hall, *J. Phys. Chem.,* **69**, 3080 (1965).

5) W. K. Hall and R. P. Porter, *J. Catalysis,* **5**, 366 (1966); A. E. Hirshler and J. O. Hudson, *ibid.,* **3**, 239 (1964).

6) H. Arai, Y. Saito and Y. Yoneda, This Bulletin, **40**, 312 (1967).

7) E. V. Ballor, R. T. Barth and R. A. Flinn, *J. Phys. Chem.,* **65**, 1639 (1961); H. R. Gerberich, F. E. Vutinsky and W. K. Hall, *J. Catalysis,* **6**, 209 (1966).

8) I. Mochida and Y. Yoneda, *ibid.,* **9**, 57 (1967).

9) R. J. Kokes, H. Tobin and P. H. Emmett, *J. Am. Chem. Soc.,* **77**, 5860 (1955); D. W. Bassett and H. W. Habgood, *J. Phys. Chem.,* **64**, 769 (1960).

TABLE 1. CATALYSTS

No.	Catalyst Symbol	Catalyst Name	Surface area m^2/g	Composition	Remarks
1	A-3-550[1]	alumina	170		(a)
2	A-3-700[1]	alumina	110		(a)
3	A-3-900[1]	alumina	45		(a)
4	A-3-Na[2]	alumina-NaOH	150		(b)
5	A-B[2]	alumina-boria	290	10% B_2O_3	(c)
6	Al-S[2]	aluminum sulfate		0.4 mmol/g-SiO_2	
7	SA-1[2]	silica-alumina	540	13% Al_2O_3	(d)
8	SA-2[2]	silica-alumina	310	27% Al_2O_3	(d)
9	SA-1-Na-1[2]	silica-alumina-NaOH	450	0.048 meq Na/g	(e)
10	SA-1-Na-2[2]	silica-alumina-NaOH	480	0.087 meq Na/g	(e)
11	SA-1-Na-3[2]	silica-alumina-NaOH	480	0.168 meq Na/g	(e)
12	SM-1[2]	silica-magnesia	560	16% MgO	(f)
13	S-1[2]	silica	600		(g)
14	S-F[2]	silica-NH_4F			(h)
15	H-10X[3]	H-Molecular Sieve 10X			(i)

1) The tail numerals designate the calcination temperature.
2) Calcined at 550°C.
3) Calcined at 450°C.
a) F-110, active alumina of Alcoa.
b) By impregnation of A-3 with aq. NaOH.
c) By coprecipitation of $Al(NO_3)_3$ and H_3BO_3 with NH_4OH.
d) Nippon Cat, a cracking catalyst of Shokubi Kasei Co.
e) By impregnation of SA-1 with aq. NaOH.
f) TY-13, a cracking catalyst of Nikki Kagaku Co.
g) Q-12, active silica gel for chromatograph of Wako Co.
h) By treatment of S-1 with aq. NH_4F.
i) By protonation of Molecular Sieve 10X with the NH_4Cl exchange method.

Solid Acids. Solid acids are listed in Table 1. They were calcined for 8 hr in air. All acids in Table 1 except for 13, 14, and 15 were used also in the previous work[1] as catalysts.

Apparatus and Procedure. An ordinary pulse technique was adopted.[9] Hydrogen as the carrier gas was purified by removing water and oxygen with a dry ice - ethanol cold trap and activated copper on kieselguhr, respectively. No difference in the reactivity or the selectivity was observed even if helium was used as the carrier gas. Tricresyl phosphate (Japan Chromato Co.) was used in the analytical column (4 m) at the room temperature. The identification of the products, *i. e.* carbon monoxide and methyl chloride was made by gas chromatography with an analytical column of silica gel and Molecular sieve 5A at the room temperature for the former and by mass spectrometry for the latter. By-products such as chloroform or formaldehyde were not detected at all by gas chromatography.

The reaction temperature was set between 250 and 420°C. After the solid acid was pretreated for 1 hr in a hydrogen gas flow at 450°C, 2 μl of methylene chloride was injected into the gas flow at the top of the reactor through a silicon serum cap with a micro-syringe. The reaction was nearly first order under experimental conditions and the conversion was proportional to the reciprocal space velocity under low conversions, so that the initial rate constant, k ($ml/g\cdot min$), was obtained directly from the slope.[9] This unit of the rate constant is converted into the usual one, mol/min·atm·g-cat, by the multiplication of a factor, 4.16×10^{-5}. The reactivity decreased remarkably pulse by pulse. Owing to the prevailing poisoning for the carbon monoxide formation, the ratio of CH_3Cl/CO increased pulse by pulse. Therefore, the rate constant was obtained from the conversion of the first pulse for a fresh catalyst. The rate and the selectivity of the first pulse were satisfactorily reproducible. The initial selectivities were constant under 30% conversion.

Results and Discussion

The reactivities of the fifteen solid acids were summerized in Fig. 1. The maximum reactivity was 8.2×10^2 $ml/g\cdot min$ for H-10X and the minimum, 9.9×10^{-2} for S-1. All the solid acids have nearly equal surface areas (170—600 m^2/g) with a few exceptions. Therefore, the difference in the reactivity should be attributed to their surface nature.

The activation energies for methyl chloride and carbon monoxide formation were different from each others. On alumina, the former was smaller than the latter, with the reverse trend on alumina-boria, as shown in Table 2, It is unlikely that the trend in the adsorption strengths of the two

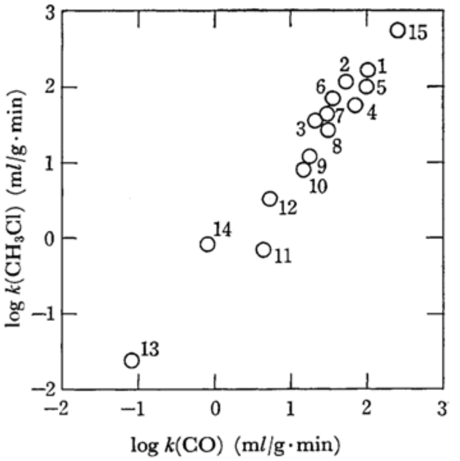

Fig. 1. Reactivities of various solid acids. (400°C) Numbers refer to Table 1.

TABLE 2. ACTIVATION ENERGY OF THE CARBON MONOXIDE AND METHYL CHLORIDE FORMATION

Solid acid	Carbon monoxide kcal/mol	Methyl chloride kcal/mol
A-3-550	21	6.1
A-3-700	21	6.5
A-3-900	23	21
A-3-Na-550	24	23
A-B	21	27
SA-1	24	40
SA-2	(24)*	(40)*
SA-1-Na-3	(24)*	(70)*
H-10X	21	26

* Calculated from the rates at two reaction temperatures.

products on alumina is opposite to that on alumina-boria. The addition of *n*-butylamine before the reaction caused a severe posioning for both formations, especially for methyl chloride, as will be discussed later. Hence, different routes for each product should be postulated.

By the titration with silver nitrate in aqueous solution, nearly all chlorine atoms lost during the reaction were found to remain on alumina. This reaction may be analogous to that of alumina with carbon tetrachloride to synthesize anhydrous aluminum chloride.[10]

The Carbon Monoxide Formation. The temperature dependence of the rate constant of the carbon monoxide formation, together with the values of activation energies is shown in Fig. 2 and Table 2. The activation energy was nearly the same for all solid acids that contained alumina, although the rate constants themselves varied greatly among them. The rate constant per unit surface area was large for the solid acid of high alumina content. At 400°C alumina had larger reactivity per unit surface area by five thousands times than silica had, as shown in Fig. 1. The correlation between the reactivity per unit weight of the component alumina and the surface area is

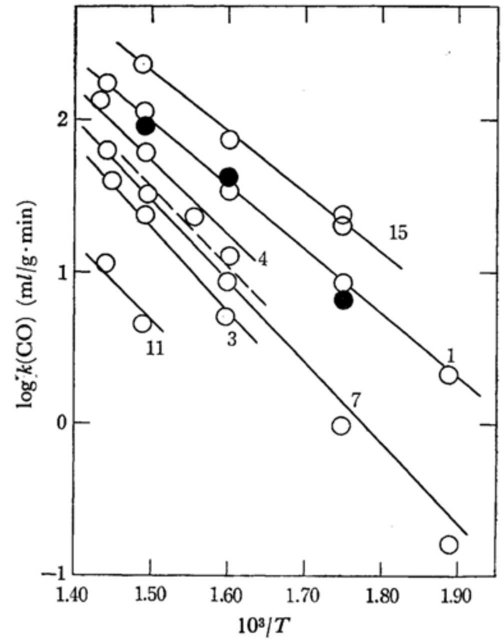

Fig. 2. Arrhenius plots of carbon monoxide formation on various solid acids containing alumina as a component.
Numbers refer to Table 1. The closed circles are for A-B and the dotted line is for SA-2.

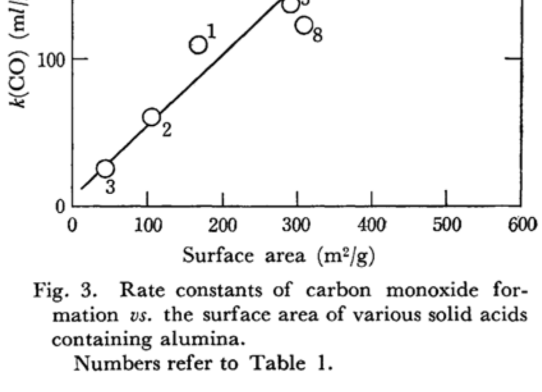

Fig. 3. Rate constants of carbon monoxide formation *vs.* the surface area of various solid acids containing alumina.
Numbers refer to Table 1.

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[10] K. Knox, R. D. Srivanstava, V. Norman, J. Y. Basserr and J. H. Hollowing, *J. Am. Chem. Soc.*, **79**, 3358 (1957).

shown in Fig. 3. Several solid acids, appearing in Fig. 3, were prepared by coprecipitation so that the aluminum atoms may be distributed throughout the surface and the bulk. The average rate constant of the carbon monoxide formation per unit surface area of the component alumina was 0.5 m*l*/min. From this close correlation, the "surface aluminate group," a group of a surface aluminum ion and its surrounding oxygen ions, which disperses on the surface as mentioned above, is proposed to participate in the carbon monoxide formation on these solid acids.

A series of the sodium ion-poisoned silica-alumina catalysts (SA-1, SA-1-Na-1, SA-1-Na-2, and SA-1-Na-3) gave the declining reactivities linearly with the increasing extent of sodium ion-poisoning, as shown in Fig. 4, with the activation energy uninfluenced (Table 2). These facts suggest the decrease in the amount of the active sites. Because the surface hydroxyl groups existing on silica-alumina are only silanols that are reportedly not influenced by this poisoning,[11] sodium ions impregnated to SA-1 are possibly coordinated to the surface aluminate groups.

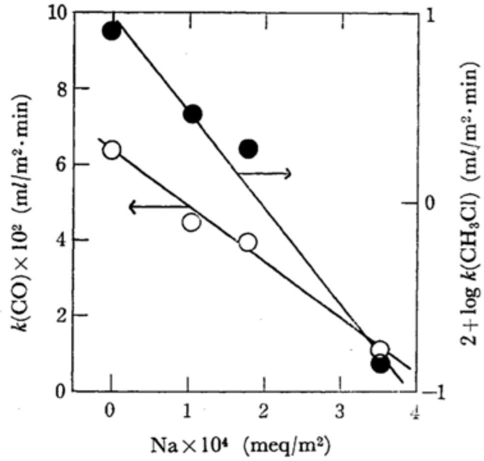

Fig. 4. Rate constants of carbon monoxide and methyl chloride formation *vs.* the amount of sodium ion. Catalyst, SA-1.

The Methyl Chloride Formation. The activation energy for the methyl chloride formation depends largely on the kind of the solid acids, which is in remarkable contrast to the case of the carbon monoxide formation. The temperature dependence and the activation energy are shown in Fig. 5 and Table 2, respectively. The alumina catalyst, A-3-550, had a markedly large activity of 1. 2 m*l*/m²·min at 400°C and a small activation energy of 6.1 kcal/mol whereas the silica-alumina catalyst, SA-1, had 7.8×10^{-2} m*l*/m²·min and 40 kcal/mol, respectively. The difference of the activation energies for the methyl chloride formation between alumina and silica-alumina thus resembles the case of the H-D exchange reaction between deuterated methane and the surface hydroxyl groups on these solid acids.[4]

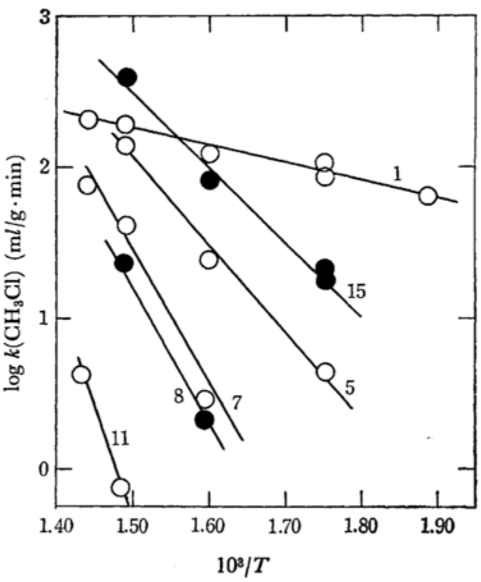

Fig. 5. Arrhenius plots of methyl chloride formation on various solid acids.
Numbers refer to Table 1.

The surface hydroxyl groups, throughout these solid acids including alumina, should be concluded to participate in the methyl chloride formation from the following experimental results.

(1) This reaction resembles the H-D exchange reaction between deutereated methane and the surface hydroxyl groups of alumina or silica-alumina, as mentioned above.

(2) Each pulse of the reactant decreased largely and irreversively the reactivity of the solid acid.

(3) Any product of the disproportionation reaction, *e. g.* chloroform, was not detected.

(4) The reaction rate was not changed by the carrier gas of hydrogen or helium.

(5) The active hydroxyl groups on alumina surface with the highest wave number in the infrared spectroscopy were found to react with carbon tetrachloride at 200°C by Peri and Hannan.[12]

The reactivities of alumina calcined at various temperatures, as well as the sodium ion-poisoned alumina, are shown in Fig. 6 and Table 3. The impregnation of sodium ion and the calcination at high temperatures decreased the reactivity of alumina to a great extent. Analogus poisoning effects of sodium ion to alumina were reported for

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[11] M. R. Basila, *J. Phys. Chem.*, **66**, 2223 (1962) (IR); W. K. Hall, H. P. Leftin, F. J. Chersleke and D. E. O'Relly, *J. Catalysis*, **2**, 506 (1963) (NMR).

[12] J. B. Peri and H. B. Hannan, *J. Phys. Chem.*, **64**, 1526 (1960); J. B. Peri, *ibid.*, **70**, 2937 (1966) (silica gel).

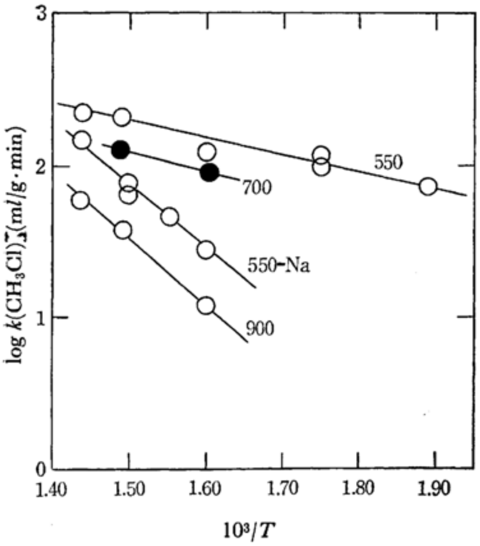

Fig. 6. Arrhenius plots of methyl chloride formation on alumina calcined at various temperatures.
Numerals represent the calcination temperatures.

TABLE 3. THE CALCINATION TEMPERATURE EFFECT ON THE METHYL CHLORIDE FORMATION ACTIVITY OF ALUMINA

Alumina	Calcination temp. °C	Activity of the unit surface area at 400°C ml/m^2·min
A-3-550	550	1.2
A-3-700	700	1.2
A-3-900	900	0.85
A-3-Na-550	550	0.48

the H_2-D_2 exchange reaction.[13] These deactivation may be due to the decrease in both the reactivity and the amounts of the hydroxyl groups and the oxidizing sites. Peri[14] reported by infrared spectroscopy the decrease of the surface hydroxyl groups of alumina by the calcination.

A linear relationship between the logarithms of the reaction rate constants and the amounts of sodium ion added was observed in the series of the sodium ion-posioned silica-alumina catalysts, as shown in Fig. 4. The activation energy also increased with sodium ion-poisoning, as shown in Table 2. These facts resemble the case of the typical solid acid catalysis. Sodium ion is coordinated to the surface aluminate group, as was discussed for the carbon monoxide formation. The hydroxyl groups on silica-alumina have been identified as the silanol groups and no Al-OH has been detected by either IR or NMR.[11] Silica-alumina had larger activity by about three thousands times than silica gel for the methyl chloride formation at 400°C, as shown in Fig. 1, in spite of the fact that the same amount of the hydroxyl groups was present on silica-alumina and silica gel both calcined at 550°C.[11] With sodium ions coordinated to the surface aluminate groups, the cooperation of the exposed aluminum ion with the neighboring silanol groups will be lost according to the decrease in the reactivity of the both sites. Therefore, the methyl chloride formation may be largely retarded by the sodium ion-poisoning, as is the case for the typical solid acid catalysis. It is also reasonable that the two silica-alumina catalysts of different alumina content (SA-1 and SA-2) exhibited nearly the same activation energy for the methyl chloride formation.

Alumina-boria (10% B_2O_3) has higher activity for the typical solid acid catalysis such as dealkylation,[1] but it was less reactive than alumina for the methyl chloride formation. The activation energy of alumina-boria for this reaction was about 20 kcal/mole larger than alumina (Table 2) and the reactivity per unit surface area at 400°C was 4.6×10^{-1} ml/m^2·min for alumina-boria, whereas 1.2 for alumina. These results are understandable, if the hydroxyl groups are assumed not preferably to be bound to aluminum but rather to boron on the alumina-boria surface.

The Effect of the *n*-Butylamine Addition before the Reaction. The effect of the *n*-butylamine addition before the reaction is shown in Table 4. Both the reaction temperature and the addition temperature were 350°C. The addition of *n*-butylamine hindered strikingly both the methyl chloride and the carbon monoxide formations with alumina as well as alumina-boria, probably because of its strong coordination to the active sites. By exposing the amine-poisoned solid acids in the hydrogen gas flow at the reaction temperature for a certain period, the reactivity was gradually recovered presumably in accordance with the desorption of *n*-butylamine. The recovery from the *n*-butylamine poisoning of alumina was much faster than that of alumina-boria for the methyl chloride formation, as shown in Table 4. The reactivity was recovered up to 79% of the fresh alumina after 60 min, but only up to 11% for alumina-boria after 75 min. This slow recovery may be due to the stronger acidity of alumina-boria than alumina. The fresh alumina, however, was more active than alumina-boria for the methyl chloride formation, as described previously.

For the recovery of the reactivity for the carbon monoxide formation, it was also slower for alumina-boria than for alumina; the recovery of 71% for alumina after 60 min and of 13% for alumina-boria after 75 min. The active sites for the carbon monoxide formation on alumina-boria should be

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[13] H. Pines and J. Ravoire, *ibid.*, **65**, 1859 (1961).
[14] J. B. Peri, *ibid.*, **69**, 211 (1965).

TABLE 4. THE EFFECT OF *n*-BUTYLAMINE ADDITION BEFORE THE REACTION

	Alumina (A-3-550)			Alumina-boria (A-B)		
Catalyst amount (mg)	40.5	40.8	38.7	90.8	79.6	86.0
n-Butylamine amount (μl)	0	0.4	0.4	0	0.4	0.4
Time of elution* (min)	—	3	60	—	2	75
CH_3Cl formation rate ($ml/g\cdot min$)	3.76×10^2	9.58	2.98×10^2	3.80×10	3.28	4.16
CO formation rate ($ml/g\cdot min$)	1.05×10^2	1.78×10	7.46×10	4.54×10	3.89	5.77
CH_3Cl/CO	3.46	0.54	4.0	0.84	0.84	0.72

* The period of keeping the solid acids in the hydrogen gas flow at 350°C between the *n*-butylamine addition and the reaction.

more acidic than on alumina, since *n*-butylamine interacts more strongly with the former than the latter. But the difference in their acidities may be unrelated to their oxidizing abilities.

Proposed Reaction Mechanism. In aspect to the reactivities of alumina, silica-alumina or alumina-boria, the methyl chloride formation is similar to the H-D exchange reaction between their surface hydroxyl groups and deuterated methane, that may proceed through the radical mechanism, but is different from the typical solid acid catalysts that have been confirmed to be caused by the Bronsted acid sites. This reaction was unrelated to the strength of *n*-butylamine adsorption on these solid acids. Furthermore, alumina was found to have a lot of triphenyl methyl radical-forming sites.⁶⁾ These facts strongly suggest a radical mechanism to form methyl chloride from methylene chloride with these solid acids, and also that alumina is more reactive in some radical reactions than silica-alumina or alumina-boria, which is more acidic. The radical mechanism of the methyl chloride formation is consistent with the previous conclusion deduced from the reactant effects with the utilization of the simple LCAO-MO reactivity indexes.⁸⁾

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