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The Catalytic Activity and Selectivity of Metal Sulfates for the Isomerization of *n*-Butenes

MAKOTO MISONO, YASUKAZU SAITO, AND YUKIO YONEDA

From the Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo, Japan

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The selectivity and activity of *n*-butene isomerization have been investigated over a series of metal sulfates on silica gel, mainly sulfates of the first long period of metals, at the reaction temperature of 61.5°C after various pretreatments. Both selectivity and activity varied markedly among catalysts. For instance, the reaction rate and the selectivity of *trans–cis* isomerization from 2-butenes were very high for strongly acidic sulfates, such as ferric or aluminum sulfate, while they were low for weakly acidic sulfates, such as magnesium or manganese sulfate.

Both the selectivity (*trans*-2-butene/1-butene ratio from *cis*-2-butene) and activity of metal sulfates on silica gel with the same pretreatment give a linear correlation with the acid strength of metal sulfates, which is assumed to be represented quantitatively by the electronegativity of the metal ion, derived from $x_i = x_0 + (\Sigma I_n)^{1/2}$, where x_0 and I_n are the electronegativity of the neutral atom and the *n*th ionization potential of the atom, respectively. The acid strength of the catalysts measured by the Hammett indicators was verified to be consistent in order with the prediction according to x_i values. Both high activity and high *trans*-/1-butene ratio were observed for sulfuric acid mounted on silica gel.

For all catalysts studied, the following relationships are deduced generally among three selectivities: *trans*/1 from *cis*-2-butene, *cis*/*trans* from 1-butene, and *cis*/1 from *trans*-2-butene: $(trans/1) \sim (cis/1)$ and $(cis/1) \sim 1$.

INTRODUCTION

For the basis of the prediction of effective catalysts, it is significant to study the activities or selectivities of a series of catalysts in terms of their chemical or electronic properties. The measured acidity of heterogeneous catalysts has successfully been correlated with their activities [For example, see ref. (*1*).] The thermodynamic or electronic properties of the catalysts, which are independent of the catalyst preparation, have also been studied in correlation with the catalytic activity: the decompositions of formic acid (*2*) and nitrous oxide (*3*), the H_2–O_2 reaction (*5*, *6*), the H_2–D_2 exchange reaction (*7*), the heat of adsorption on metals (*4*), the oxidation of hydrocarbons (*8*), and other reactions reviewed by Boreskov (*9*).

As regards the relationships between the selectivity and the properties of catalysts, little work has been done. The selectivity between dehydration and dehydrogenation of ethanol or formic acid has been reported on (*10*, *11*). Schwab *et al.* (*10*b) suggested that the surface structure determined the selectivity. According to Mars (*11*) the electrostatic force represented by the cation charge and its radius is the controlling factor. It was attempted to correlate the selectivity in the oxidation of propylene with the reducibility of catalysts (*12*).

In this paper the selectivity and the activity of the *n*-butene isomerization over metal sulfates mounted on silica gel are investigated. This reaction was chosen because the selectivity between *cis–trans* rotation and double-bond migration is sensitive to the catalyst properties. Foster and Cvetanovic (*13*) discussed generally the relationship between the selectivity of this reaction and the acidity or basicity for a number of catalysts. They suggested that the selective double-bond shift over basic catalysts resulted from a butenyl carbanion and the high selectivity of *cis–trans* rotation over acidic catalysts from a butyl carbonium ion.

As far as the mechanism of *n*-butene isomerization on acidic catalysts is concerned, many studies have been reported. Proposed intermediates or mechanisms are a *sec*-butyl carbonium ion (*14*), a pi complex (*15*), a butenyl carbonium ion (*16*), and a hydrogen switch mechanism (*17*). Brouwer (*18*) claimed the coexistence of two mechanisms on silica-alumina and alumina. One is a concerted mechanism, or a hydrogen switch mechanism, for the double-bond shift and the other is a butyl carbonium ion mechanism for *cis–trans* isomerization. The role of a proton in *n*-butene isomerization over acidic catalysts was pointed out to be important by Ozaki *et al.* (*19*) and Hall *et al.* (*20*).

The correlation of the catalytic activity of metal sulfates with their acidic nature has already been reported (*21–23*). In this paper, not only the catalytic activity but also the selectivity are investigated in terms of the acidic nature of metal sulfates. The acid strength of metal sulfates is determined by the properties of constituent ions, which is affirmed by the indicator measurements.

EXPERIMENTAL

Materials

a. **Catalysts.** Metal sulfates mounted on silica gel were prepared by impregnating calcined silica gel (Wako Chemicals Co. Ltd.; surface area, 830 m^2/g) with 5% aqueous solutions of metal sulfates for several hours. The amount of impregnated metal sulfates was nominally 0.4 mg-atom (metal ion)/g catalyst, which is slightly in excess of the capacity of the silica gel carrier. Increasing the impregnation level to 0.8 mg-atom/g catalyst hardly increased the activity of $Al_2(SO_4)_3$-SiO_2. Almost all catalysts were used after drying at 110°C. A few catalysts were calcined additionally at 550°C for 7 hr prior to a run, as described in the text.

b. Reagents. Commercial butenes were obtained from Matheson Co., Inc. Their impurities were less than 0.1% according to the gas-chromatographic analysis.

Procedure

a. Reaction procedure. A circulation system with total volume of 175 ml consisted of a 15-ml diameter cylindrical Pyrex reactor and a magnetic circulation pump. The amount of catalyst was changed, depending on its activity, to get an appropriate reaction rate. In usual experiments about 100 mg was used after the pretreatments described below. Butenes were introduced into the system as gases mixed with dry nitrogen. Initial partial pressure of the butene was 135 ± 5 mm Hg.

b. Pretreatments of catalysts. Standard pretreatment was as follows: Catalysts were equilibrated in the reactor with about 10 mm Hg of water vapor at 100°C for 1 hr and then evacuated for 2 hr at the same temperature. The gas mixture was introduced after the temperature had been lowered to the reaction temperature of 61.5°C. In the experiments with *trans*-2-butene or 1-butene the equilibration with water vapor was omitted.

In the case of wet pretreatment, catalysts were equilibrated with about 10 mm Hg of water vapor for 1 hr at 61.5°C and then evacuated for 5 min just before the introduction of the gas mixture. Some experiments were carried out in the presence of water vapor without evacuation. The treatment with water vapor was undertaken with the intention that the extent of hydration of metal sulfates before evacuation should be similar for all catalysts. Practically, however, the effects on activity were not pronounced and were less so for selectivity.

c. Analysis. Gas mixtures, sampled by a syringe from the reaction system at various reaction times, were analyzed by a gas chromatograph employing a hydrogen flame type detector and a 4-m dioctylsebacate and dimethylsulfolane column. When *trans*-2-butene was the starting butene, a 9-m dioctylsebacate analyzing column was used.

Measurements of Acid Strength

The acid strength of the catalysts was measured qualitatively after the pretreatments using a series of the Hammett indicators. The catalysts were pretreated in glass tubes by the same procedure as for the reactions. They were cooled to room temperature and filled with dry nitrogen. The color changes of a series of indicators were observed for each catalyst by the spot test, immediately after the catalysts were exposed to air to prevent the strong acid sites from being poisoned by the moisture in air.

RESULTS

1. Isomerization of cis-2-Butene over Metal Sulfates on Silica Gel

Variation of the composition of three butenes during the reaction time is shown in Fig. 1 for three typical catalysts. The equilibrium compositions determined from two experiments with *cis*- and *trans*-2-butene agreed to be 4.8% ± 0.5% 1-butene, 69.1% ± 2% *trans*-2-butene and 26.1% ± 1% *cis*-2-butene, at 61.5°C.

In Fig. 2 the *trans*/1 ratio of the isomerized butenes is plotted against the conversion (the mole fraction of the isomerized butenes). The *trans*/1 ratio was extrapolated to zero conversion to get the ratio of rate constants of the two reactions of *n*-butene isomerization: the *cis–trans* rotation and the double-bond migration to 1-butene. The extrapolated *trans*/1 ratios are given in Table 1. To represent the activities of catalysts, the reciprocals of the reaction time in minutes required to obtain 10% conversion on 1 g of catalyst were used. The activities for wet pretreatment were estimated using the data of 3% conversion due to their low activities. These values are also given in Table 1.

The *trans*/1 ratio ranged from 0.85 for $MgSO_4$-SiO_2 with wet pretreatment to 10.1 for H_2SO_4-SiO_2 with standard pretreatment. For catalyst with wet pretreatment, the following trend was found:

$$H^+ > Fe^{3+} > Al^{3+} > Sc^{3+} > Cu^{2+} > Zn^{2+} > Cd^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Mg^{2+}$$

This order held approximately for catalysts with other pretreatments, as well.

Effects of dehydration, produced by different pretreatments, on the activity and selectivity were also examined. Generally speaking, higher activity and a little larger value in the *trans*/1 ratio were obtained by the standard pretreatment than by the wet pretreatment, probably owing to an increase in both acid strength and content. $Fe_2(SO_4)_3$-SiO_2 showed a monotonic decrease of activity and the *trans*/1 ratio above 100°C of pretreatment, presumably as the result of the decomposition of ferric sulfate at high temperatures, since the *trans*/1 ratio or the activity was not recov-

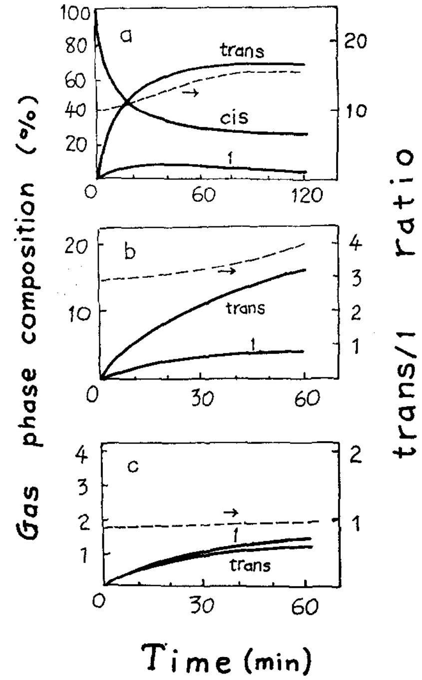

FIG. 1. Variation of the gas-phase composition of *n*-butenes in reaction of *cis*-2-butene at 61.5°C: (a) H_2SO_4-SiO_2, 98 mg with standard pretreatment; (b) $CuSO_4$-SiO_2, 108 mg with standard pretreatment; (c) $MgSO_4$-SiO_2, 115 mg with wet pretreatment.

TABLE 1

THE CATALYTIC ACTIVITY AND SELECTIVITY OF METAL SULFATES ON SILICA GEL FOR THE ISOMERIZATION OF *cis*-2-BUTENE AT 61.5°C

Catalyst[a]		Pretreatment[a]	Activity[b]	Selectivity[c] (*trans*/1)
H_2SO_4-SiO_2		st	1.1×10^3	10.1
		wt	8.4×10^2	9.2
$Fe_2(SO_4)_3$-SiO_2		st (1st run)	6.3×10^2	6.4
		(2nd run)	1.8×10^2	5.4
		wt	6.0×10^2	7.4
		200	1.3×10^2	5.1
		360	7.9	1.6
$Al_2(SO_4)_3$-SiO_2	(I)*	st (1st run)	7.9×10^2	6.9
		(2nd run)	5.3×10^2	6.2
	(II)	st	6.6×10^2	6.5
		wt	2.7×10^2	5.1
		wt	2.6×10^2	5.7
		400	1.6×10^2	4.5
		H_2O	(0.7)	3.3
$Sc_2(SO_4)_3$-SiO_2		wt	2.1×10	3.5
$CuSO_4$-SiO_2	(I)	st	6.5×10	2.9
		wt	1.5×10	2.2
		400	7.8	3.1
$ZnSO_4$-SiO_2*		st	1.3×10^2	3.0
		wt	9.4	2.1
$NiSO_4$-SiO_2	(II)	st	1.3×10^2	2.3
		wt	7.4	1.4
		200	1.2×10^2	1.8
		300	7.8	1.9
		400	4.8	2.1
		H_2O	(0.08)	1.2
	(III)*	st	6.4×10	1.7
		400	1.4×10^2	2.8
$CdSO_4$-SiO_2	(I)	st	7.6×10	1.7
		wt	1.7×10	2.0
$CoSO_4$-SiO_2	(I)	wt	7.2	1.2
	(II)*	st	6.1×10	1.3
		wt	1.0×10	1.2(1.6)[d]
$MnSO_4SiO_2$		st	1.9×10	0.85
		wt	5.3	1.3
$MgSO_4$-SiO_2	(I)*	st (1st run)	3.7×10	1.1
		(2nd run)	3.6×10	1.1
		wt	4.1	0.85
		400	5.9×10	2.1
	(II)	wt	3.0	0.85
		H_2O	(0.05)	0.90
SiO_2		wt	(0.005)	0.70
		st	0.15	0.80
		400	(0.035)	0.70

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[a] st and wt mean the standard and wet pretreatments, respectively. The figures indicate the temperatures of evacuation before run. The catalysts precalcined at 450°C for 7 hr are shown by asterisks. H_2O means that the reaction was done in the presence of water vapor. (I), (II), or (III) designates the preparation number of catalyst.

[b] Activity is calculated as 10^2/(time in min required to get 10% conversion on 1 g of catalyst). The inaccurate data are given in parentheses.

[c] Selectivity is the ratio of *trans*-2-butene/1-butene, extrapolated to conversion zero.

[d] See Fig. 2 (7).

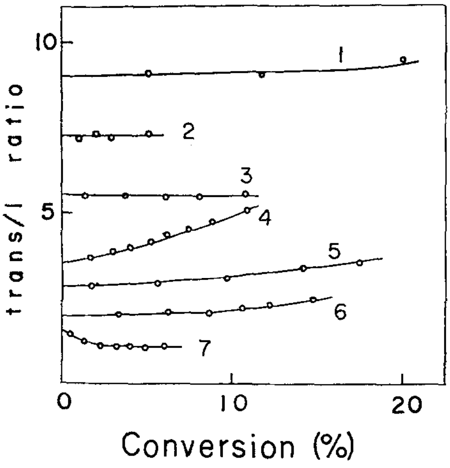

FIG. 2. The *trans*/1 ratio as a function of the conversion: 1, H_2SO_4-SiO_2; 2, $Fe_2(SO_4)_3$-SiO_2; 3, $Al_2(SO_4)_3$-SiO_2; 4, $Sc_2(SO_4)_3$-SiO_2; 5, $CuSO_4$-SiO_2; 6, $NiSO_4$-SiO_2; 7, $CoSO_4$-SiO_2.

ered by rehydration. In general, different pretreatments caused smaller changes in the *trans*/1 ratios than in the activities for all catalysts. The *trans*/1 ratio of $NiSO_4$-SiO_2(II), for example, extended from 1.2 to 2.3, but its activity varied 0.08 to 130. However, the changes in the selectivity caused by different pretreatments were less pronounced than those observed with different catalysts. For example, the *trans*/1 ratio changed only from 1.2 to 2.3 for $NiSO_4$-SiO_2(II) with different pretreatments, while it changed from 0.8 to 9.2 for the same pretreatment for different catalysts. The small effect of the water content on the selectivity for these catalysts is quite different from its effect for γ-alumina found by Brouwer (*18*).

The selectivity (*trans*/1 ratio) and the activity are plotted in Figs. 3 and 4 for various catalysts with wet pretreatment against the electronegativity of metal ions, x_i, which is assumed to represent the acid strength of metal sulfates, as discussed in a later section. This electronegativity of metal ion (*24*) is defined as

$$x_i = x_0 + (\Sigma I_n)^{1/2} \qquad (1)$$

where x_0 is the electronegativity of a neutral atom (*25*) and ΣI_n the sum of ionization potentials in electron volts from an atom to an ion. Figures 3 and 4 clearly show that both the selectivity of *cis–trans* isomerization and the total reaction rate increased for strongly acidic catalysts.

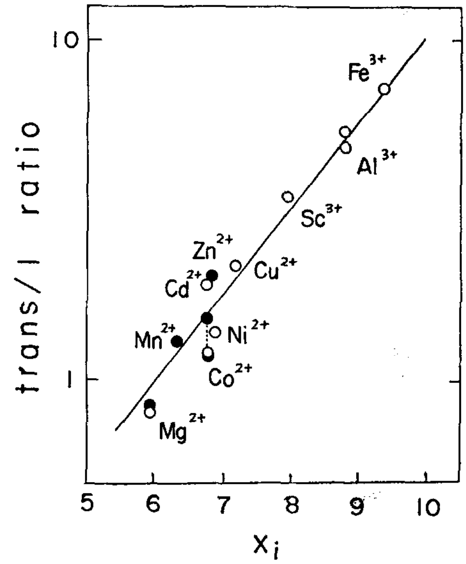

FIG. 3. Selectivity in the isomerization of *cis*-2-butene on metal sulfates on silica gel with the wet pretreatment as a function of the electronegativity of metal ion, x_i.

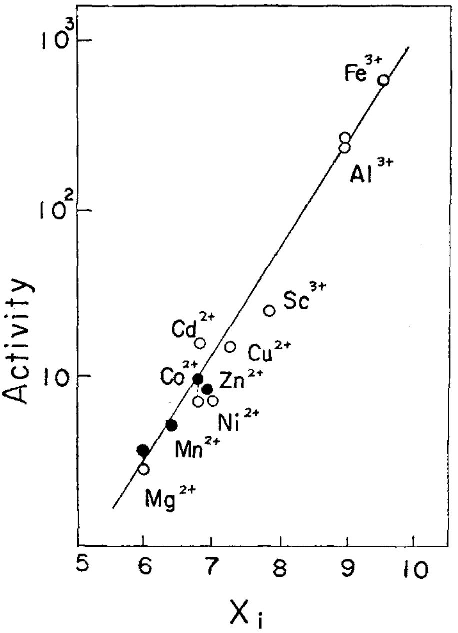

FIG. 4. Activity as a function of the electronegativity of metal ion, x_i.

2. Isomerization of trans-2-Butene and 1-Butene

The activity of metal sulfates mounted on silica gel for the isomerization of *trans*-2-butene or 1-butene was in the following order: $H^+ > Al^{3+} > Ni^{2+} > Cu^{2+} \sim Mg^{2+}$.

The ratio of the isomerized butenes extrapolated to zero conversion is given in Table 2, together with the *trans*/1 ratio from *cis*-2-butene on the same catalyst with the standard pretreatment. Both the *cis*/1 ratio and *trans*/1 ratio changed in a similar way from one catalyst to another. The ratio of *cis*/1 ranged from 1.8 for $MgSO_4$-SiO_2 to 10.1 for H_2SO_4-SiO_2, while the *trans*/1 ratio varied from 1.2 to 10.1. The ratio of *cis*/1 beyond the equilibrium was obtained from *trans*-2-butene on $Al_2(SO_4)_3$-SiO_2 and H_2SO_4-SiO_2. On these catalysts, the *cis*/1 ratio decreased gradually to its equilibrium ratio of 5.4 during the course of reaction, while it increased from the lower side up to the equilibrium value on other catalysts. These results eliminate the possibility that the secondary reactions of 1-butene to *cis*- or to *trans*-2-butene in micropores or on the catalyst surface might give the high *cis*/1 or *trans*/1 ratio on active catalysts. It should be noted that the velocity of circulation in the reaction system was sufficiently high compared with the reaction rate, for the changes of the amount of catalyst to result in no change in selectivity.

TABLE 2

THE SELECTIVITIES OF ISOMERIZATION OF *n*-BUTENES ON METAL SULFATES ON SILICA GEL AT 61.5°C

Catalyst	*cis*/1 ratio from *trans*-2-butene[a]	*trans*/1 ratio from *cis*-2-butene[b]	*cis*/*trans* ratio from 1-butene[a]
H_2SO_4-SiO_2	10.1	10.1	1.1
$Al_2(SO_4)_3$-SiO_2(II)	6.3	6.5	1.2
$CuSO_4$-SiO_2(I)	3.5	2.8	1.1
$NiSO_4$-SiO_2(II)	2.9	2.3	1.25
$MgSO_4$-SiO_2(II)	1.7	1.2	1.25

[a] Catalysts were evacuated for 2 hr at 100°C before run.

[b] Standard pretreatment.

The *cis*/*trans* ratio from 1-butene, on the other hand, was relatively insensitive to the catalyst composition, as the values between 1.1 and 1.25 were observed for all catalysts. Among the three selectivity ratios for every catalyst investigated, the following relationship was found to hold generally, as Haag and Pines (*15*a) obtained on alumina:

$$(cis/trans)(trans/1)(1/cis) = 1 \qquad (2)$$

When the *trans*/1 ratio, calculated from the other two ratios by Eq. (2), is plotted against the value obtained experimentally, an excellent correlation is found, as shown in Fig. 5. In this figure, some data from the literature measured at similar conditions are included.

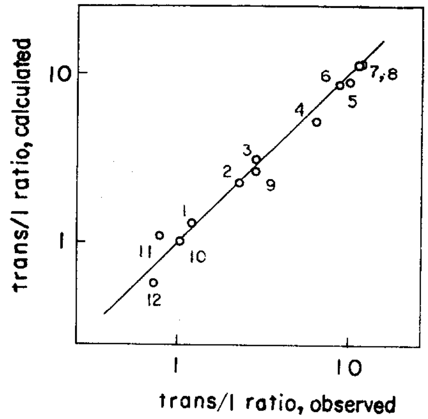

FIG. 5. The relationship between the *trans*/1 ratio calculated from Eq. (2) and that observed in the isomerization of *cis*-2-butene: 1, $MgSO_4$-SiO_2; 2, $NiSO_4$-SiO_2; 3, $CuSO_4$-SiO_2; 4, $Al_2(SO_4)_3$-SiO_2; 5, H_2SO_4-SiO_2; 6, ion exchange resin (Dowex 50W); 7, H_2SO_4 (aqueous); 8, H_3PO_4 (aqueous); 9, silicotungstic acid on Aerosol; 10, silica-alumina; 11, clay; 12, Vycor glass. 7, 8 are from ref. (*27*), 9, 10 are from (*18*) and 11, 12 from (*13*).

In Fig. 6 the *cis*/1 and *cis*/*trans* ratios are plotted against the *trans*/1 ratio. A good correlation in this figure would lead to the following equations:

$$(cis/1) \sim (trans/1) \qquad (3)$$

and

$$(cis/trans) \sim 1 \qquad (4)$$

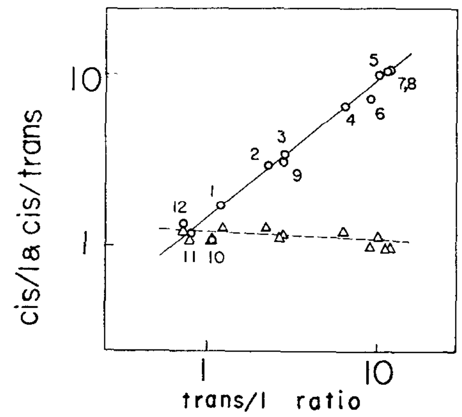

FIG. 6. The relationships between three observed selectivity ratios: ○, the *cis*/1 ratio from *trans*-2-butene; △, the *cis*/*trans* ratio from 1-butene; 1, 2, 3, ... are the same as those in Fig. 5.

although there was a tendency to deviate from these equations for catalysts with low x_i values.

3. Measurement of Acid Strength

The observed color of the indicators on catalysts is given in Tables 3 and 4. In these tables, the extent of color changes to acidic colors are qualitatively indicated in the decreasing order as follows: ++, +, ±, −, − −. The borderline of the color changes in the series of indicators for each catalyst is shown by broken lines in these tables. These lines give approximately the acid strength of the catalysts.

Table 3 shows that the acid strength decreases from H_2SO_4-SiO_2 to $MgSO_4$-SiO_2 in parallel with the *trans*/1 ratio. The acid strengths of H_2SO_4-SiO_2, $Fe_2(SO_4)_3$-SiO_2, $Sc_2(SO_4)_3$-SiO_2, and $Al_2(SO_4)_3$-SiO_2 were strong enough to exhibit the acidic color of anthraquinone ($pK_A = -8.2$), while $CuSO_4$-SiO_2, $NiSO_4$-SiO_2, $ZnSO_4$-SiO_2, $CdSO_4$-SiO_2, or $CoSO_4$-SiO_2 gave the acidic color of indicators in the range of −3.0 to −5.6 in pK_A. The acid strength of $MgSO_4$-SiO_2 or $MnSO_4$-SiO_2 was about +1.5 to −3.0 in pK_A.

It is found in Table 4 that the changes in acid strength caused by different pretreatments were less pronounced than those among catalysts, although there was a

TABLE 3
THE COLOR CHANGES OF THE INDICATORS ON METAL SULFATES ON SILICA GEL WITH THE STANDARD PRETREATMENT[a]

	pK_A values of Indicators					
Metal sulfates on silica gel	+3.3 (a)	+1.5 (b)	−3.0 (c)	−5.6 (d)	−8.2 (e)	x_i
H^+	++	++	++	++	++	−
Fe^{3+} (*)	++	++	++	+(?)	+(?)	9.4
Al^{3+}	++	++	++	++	++	8.8
Sc^{3+}	++	++	++	++	+	7.9
Cu^{2+} (*)	++	++	+	+	±	7.2
Zn^{2+}	++	++	+	±	−	6.8
Cd^{2+}	++	++	+	±	−	6.8
Ni^{2+} (*)	++	++	+	−(?)	−(?)	6.9
Co^{2+} (*)	++	++	+	−(?)	−(?)	6.8
Mn^{2+}	++	++	−	−	−	6.4
Mg^{2+}	++	++	−	− −	±(?)	6.0
SiO_2	+	+	− −	− −	− −	−

[a] Indicators: (a) Butter yellow. (b) Benzeneazodiphenylamine. (c) Dicinnamal acetone. (d) Benzalacetophenone. (e) Anthraquinone. The color changes which were less clear are shown by (?). The colored catalysts are shown by (*).

TABLE 4
THE COLOR CHANGES OF THE INDICATORS ON METAL SULFATES ON SILICA GEL WITH DIFFERENT PRETREATMENTS

Catalyst	Pretreatment[a]	pK_A values of indicators[b]					*trans*/1 ratio
		+3.3	+1.5	−3.0	−5.6	−8.2	
Al^{3+}	wt	++	++	+	+	±	5.0–5.6
	st	++	++	++	++	+	6.5
	400	++	++	++	++	+	4.5
Cu^{2+}	wt	++	++	+	−(?)	−(?)	2.2
	st	++	++	+	+	±	2.9
	400	++	++	+	+	±	3.1
Zn^{2+}	wt	++	++	+	−	−−	2.1
	st	++	++	+	±	−	3.0
	400	++	++	+	±	±(?)	—
Mg^{2+}	wt	++	+	−	−−	−	0.8
	st	++	++	−	−	−	1.1
	400	++	++	±	−	−	2.1
SiO_2	wt	+	+	−−	−−	−−	0.7
	st	+	+	−−	−−	−−	0.8
	400	+	+	−−	−−	−−	0.7

[a] wt, st, and 400 are the same as those in Table 1.
[b] The indicators are the same as those in Table 3.

small increase in the acid strength or content from the wet to the standard pretreatment. This suggests that the acid strength of these catalysts is determined primarily by the constituent metal ion and sulfate ion, and it is modified by the dehydration. The difference of the acid strength among catalysts seemed to be decreased by 400°C evacuation due to the increase of the acid strength of $MgSO_4$-SiO_2 by 400°C evacuation.

DISCUSSION

The electronegativity of an atom in a molecule represents the power of the atom to attract electrons (*26*). The electronegativity of an ion will be given by adding the ionization potentials, or the energy to remove electrons, to the electronegativity of the corresponding atom. In fact, x_i values of metal ions, thus obtained, had good correlations with their affinity to the base, since the equilibrium constants of $Me^{n+}(aq) + OH^-(aq) \rightleftarrows MeOH^{(n-1)} + (aq)$ and the solubility products of metal hydroxides were well explained by the x_i values. So the relative acid strength of metal ions as Lewis acids may be determined by x_i (*24*). Subsequently, the acid strength of a metal ion in metal sulfate may also be determined by x_i.

However, this does not necessarily mean that the acidic site of metal sulfate is a nonprotonic one. Takeshita *et al.* (*22*) have proposed possible origins of protonic sites on nickel sulfate. Ozaki *et al.* (*19*) have found that proton transfer between a catalyst and a substrate was involved in the *n*-

butene isomerization on nickel sulfate mounted on silica gel. The acid strength of protonic sites remaining after dehydration may also be given by the x_i value of the metal ion, as the pH of the aqueous solution of metal sulfate is determined by the basic strength of the corresponding metal hydroxide, which is in good correlation with x_i.

The order in the acid strength of metal sulfates measured by the Hammett indicators was in reasonable accordance with that of x_i.

Over a series of metal sulfates, the selectivity between the *cis–trans* isomerization and the double-bond migration from 2-butenes was found to change by tenfold among catalysts, while the *cis–trans* ratios from 1-butene were between 1.1 and 1.25. The properties of catalysts that control the selectivity from 2-butene must change continuously from H_2SO_4-SiO_2 to $MgSO_4$-SiO_2 as the *trans*/1 and *cis*/1 ratios do. Among the properties of catalysts which may determine the selectivity, the acid strength of metal sulfates explains the results most satisfactorily for the following reasons: (1) A close relationship between the acidity and the catalytic activity of metal sulfates has been reported (*21–23*). (2) *n*-Butenes are well isomerized in the presence of acidic catalysts (*14–20*). (3) The acid strength of metal sulfates represented by x_i changes continuously from H_2SO_4-SiO_2 to $MgSO_4$-SiO_2 in the same order with the selectivity ratio. (4) The measured acid strengths of the catalysts used are generally in good correspondence with the x_i values.[*]

If the acid strength is the determining factor of the selectivity, the observed minor effects of pretreatments both on the selectivity and on the acid strength can be well understood. This is also verified by the facts that both the *trans*/1 ratio and the acid strength increased a little for most catalysts after a standard pretreatment instead of the wet one.

Different pretreatments caused a larger effect on the activity than on selectivity. Since the selectivity of this reaction may reflect the acid strength of active sites and the activity may be determined by both the acid strength and the content, it may be reasonably concluded that the acid strength of active sites changes less pronouncedly than the acid content does by the different pretreatments. The *trans*/1 ratios are plotted against the activity in Fig. 7 for catalysts with the standard pretreatment. This figure suggests that both of them were determined by the acid strength of the catalyst, and further that the acid content with this pretreatment changed ordinarily from catalyst to catalyst.

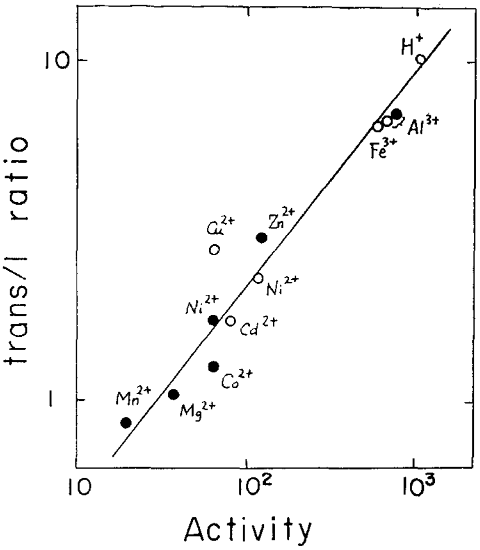

FIG. 7. The relationship between the selectivity and the activity for the standard pretreatment.

It seems very difficult to find a mechanism which can explain satisfactorily the obtained results. However from Eq. (2), as pointed out by Pines and Haag (*15*a), it may be certain that either the reactions of the three isomers proceed in the same reaction order concerning the pressure of the

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[*] The *trans*/1 ratios of $Al_2(SO_4)_3$-SiO_2 (wet pretreatment), $CuSO_4$-SiO_2 (standard pretreatment), and $CuSO_4$-SiO_2 (400°C evacuated) were considerably different from each other, whereas the color changes of indicators were very similar. A possible explanation is that stronger acid sites exist to a smaller extent on $Al_2(SO_4)_3$-SiO_2 (wet) than the other, but a quantitative measurement of acid strength and of content is necessary to affirm the validity of the explanation.

starting butene or via a common intermediate on every catalyst, or that they follow both ways.

A pi-complex intermediate (*15*) had been postulated from the high *cis/trans* ratio, but the *cis/trans* ratios of the present work were not so high and were independent of the acid strength. Both the hydrogen switch mechanism (*17*) and the butenyl carbonium ion mechanism (*16*) should cause selective double-bond migration, which is in disagreement with the present results. Among the previously proposed mechanisms, the coexistence of two mechanisms on a certain catalyst suggested by Brouwer (*18*) seems to be reasonable: the *cis-trans* isomerization by a *sec*-butyl carbonium ion mechanism. Equation (2) also holds even if two intermediates are present on a catalyst, as far as the ratio of the concentrations of two intermediates through which all three isomers react does not depend on the starting butenes, or as far as the reaction orders concerning the starting butenes are identical for three isomers. It is interesting to note that the observed ratio of *trans*/1 or *cis*/1 on H_2SO_4-SiO_2 is almost identical with that reported for the homogeneous isomerization by sulfuric acid (*27*) and with the ratios of the olefinic products resulting from the hydrogen bromide elimination from *sec*-butyl bromide via a *sec*-butyl carbonium ion (*27*).

It may be concluded that the carbonium ion mechanism prevails on strongly acidic catalysts, resulting in high *trans*/1 or *cis*/1 ratios, and that the concerted mechanism gives a predominately low value of the ratios.

REFERENCES

1. TAMELE, M. W., *Discussions Faraday Soc.* **8,** 270 (1950); Johnson, O., *J. Phys. Chem.* **59,** 827 (1955); Misono, M., and Yoneda, Y., *Bull. Chem. Soc. Japan* **40,** 42 (1967).

2. FAHRENFORT, J., VAN REIJEN, L. L., AND SACHTLER, W. M. H., *Proc. Symp. Mech. Heterogeneous Catalysis Amsterdam, 1959,* p. 23 (Elsevier, Amsterdam, 1960).

3. MAKISHIMA, S., YONEDA, Y., AND SAITO, Y., *Actes Congr. Intern. Catalyse, Paris, 1960,* p. 67 (Technip, Paris, 1961).

4. TANAKA, K., AND TAMARU, K., *J. Catalysis* **2,** 366 (1963).

5. POPOVSKY, V. V., AND BORESKOV, G. K., *Probl. Kinetika i Kataliza Akad. Nauk SSSR* **10,** 67 (1960).

6. KOMURO, I., YAMAMOTO, H., AND KWAN, T., *Bull. Chem. Soc. Japan* **36,** 1532 (1963).

7. DOWDEN, D. A., MACKENZIE, N., AND TRAPNELL, B. M. W., *Proc. Roy. Soc. (London)* **A237,** 245 (1956); Dowden, D. A., *Actes Congr. Intern. Catalyse, Paris 1960,* p. 1499 (Technip, Paris, 1961).

8. MORO-OKA, Y., AND OZAKI, A., *J. Catalysis* **5,** 116 (1966); MORO-OKA, Y., AND MORIKAWA, Y., AND OZAKI, A., *ibid.* **7,** 23 (1967).

9. BORESKOV, G. K., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* p. 163 (North-Holland Publ. Co., Amsterdam 1965).

10. (a) SABATIER, P., AND MAILHE, A., *Ann. Chim. Phys.* **20,** 289 (1910); (b) SCHWAB, G., AND SCHWAB-AGALLIDIS, E., *J. Am. Chem. Soc.* **71,** 1806 (1949).

11. MARS, P., *Proc. Symp. Mech. Heterogeneous Catalysis, Amsterdam, 1959,* p. 49 (Elsevier, Amsterdam, 1960).

12. SACHTLER, W. M. H., AND DE BOER, N. H., *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964,* p. 252 (North-Holland Publ. Co., 1965).

13. FOSTER, N. F., AND CVETANOVIC, R. J., *J. Am. Chem. Soc.* **82,** 4274 (1960).

14. (a) THOMAS, C. L., *Ind. Eng. Chem.* **41,** 2564 (1949); (b) OBLAD, A. G., MESSENGER, J. U., AND BROWN, H. T., *ibid.* **39,** 1462 (1947).

15. (a) HAAG, W. O., AND PINES, H., *J. Am. Chem. Soc.* **82,** 2488 (1960); (b) LUCCHESI, P. J., BAEDER, D. L., AND LONGWELL, J. P., *ibid.* **81,** 3235 (1959).

16. LEFTIN, H. P., AND HERMANA, E., *Intern. Congr. Catalysis, 3rd, Amsterdam, 1964* (North-Holland Publ. Co., Amsterdam 1965).

17. TURKEVICH, J., AND SMITH, R. K., *J. Chem. Phys.* **16,** 466 (1948).

18. BROUWER, D. M., *J. Catalysis* **1,** 22 (1962).

19. OZAKI, A., AND KIMURA, K., *J. Catalysis* **3,** 395 (1964).

20. HIGHTOWER, J. W., AND HALL, W. K., *J. Am. Chem. Soc.* **89,** 778 (1967); GERBERICH, H. R., AND HALL, W. K., *J. Catalysis* **5,** 99 (1966); GERBERICH, H. R., LARSON, J. G., AND HALL, W. K., *ibid.* **4,** 526 (1965).

21. WATANABE, Y., AND TANABE, K., *J. Res. Inst. Catalysis, Hokkaido Univ.* **12,** 56 (1964).

22. TAKESHITA, T., OHNISHI, R., MATSUI, T., AND TANABE, K., *J. Phys. Chem.* **69,** 4077 (1965).

23. TARAMA, K., TERANISHI, S., HATTORI, K., AND

ISHIBASHI. T., *Shokubai* (*Tokyo*) **4**, 69 (1962); Ogino, Y., *ibid.* **4**, 73 (1962).

24. MISONO, M., OCHIAI, E., SAITO, Y., AND YONEDA, Y., *J. Inorg. Nucl. Chem.*, in press.
25. GORDY, W., AND THOMAS, J. O., *J. Chem. Phys.* **24**, 439 (1956).
26. PAULING, L., "The Nature of the Chemical Bond," p. 16. Cornell Univ. Press, New York, 1939.
27. SMITH, W. B., AND WATSON, JR., W. H., *J. Am. Chem. Soc.* **84**, 3174 (1962).