the metal–oxygen bond with double-bond character is that of molybdenum.

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

The rates and the selectivities of *n*-butene isomerization over a series of silica-gel-supported metal sulfates were discussed in correlation with the acid strength in a previous paper (*1*). In the present work unsupported metal sulfates have been investigated in comparison with silica-gel-supported metal sulfates.

Commercial metal sulfates of G. R. grade [$Al_2(SO_4)_3\cdot18H_2O$, $NiSO_4\cdot7H_2O$, $MgSO_4\cdot7H_2O$, $ZnSO_4\cdot7H_2O$, and $CuSO_4\cdot5H_2O$] were calcined at various temperatures for 4 hr after the precalcination at 100°C overnight and were kept in vacuum desiccators. The same apparatus for the reaction was used as in the previous paper (*1*). The calcined metal sulfates were evacuated for 1 hr at the reaction temperature of 61.5°C just before the reaction. The acid strength of the calcined metal sulfates was measured after evacuation for 1 hr at about 60°C.

The effects of the calcination temperature on the catalytic activities and the selectivities of *cis*-2-butene isomerization over aluminum sulfate, nickel sulfate, and magnesium sulfate were obtained as shown in Fig. 1. The activities are given by the initial rate constants calculated by assuming first order reactions and the selectivities by the initial ratios of two isomerized butenes. It is of interest to note that the catalytic activity changed markedly with the calcination temperature for all catalysts, whereas the selectivity scarcely changed. The activity changes are not due merely to the surface area changes, because the surface areas (N_2 adsorption) of nickel sulfates were obtained as 16.8 m^2/g (calcined at 200°C), 9.9 (300°), and 7.8 (500°), whereas the rate constants of these catalysts were 2.3×10^{-4}, 1.7×10^{-3}, and 1.8×10^{-5} g^{-1} min^{-1}, respectively. The highest activity was displayed for each catalyst when its water content was intermediate between the monohydrated structure and the anhydrous one, as shown in Fig. 1. Takeshita *et al.* (*2*) proposed from the study of X-ray, ESR, acidity measurements, etc., that the acidity of nickel sulfate is associated with its metastable structure produced by the transition from the monohydrated structure to the anhydrous one. Their interpretation for nickel sulfate may be applicable to aluminum sulfate and magnesium sulfate as well.

The highest acid strength of metal sulfates calcined at several temperatures was measured by the use of the Hammett indi-

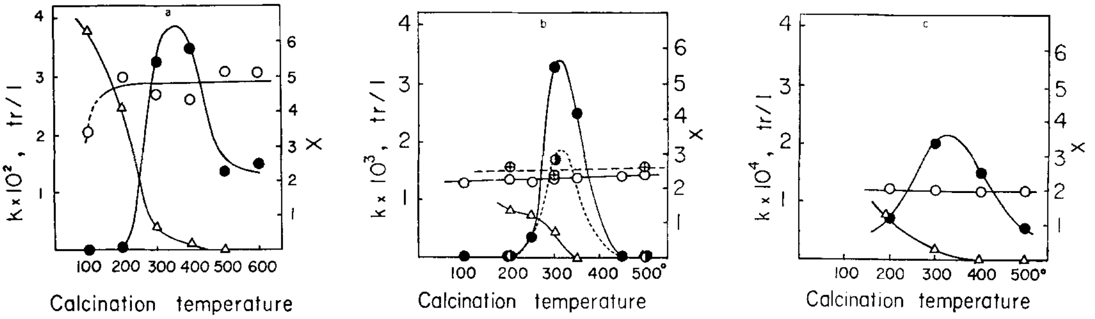

FIG. 1. The effects of the calcination temperature on the catalytic activities and the selectivities of metal sulfates for *cis*-2-butene isomerization and the water content of metal sulfates: (a) $Al_2(SO_4)_3$, (b) $NiSO_4$, (c) $MgSO_4$; k, rate constant ($g^{-1}min^{-1}$) (●, ◑); *tr*/1, the initial *trans*-2-butene/1-butene ratio (○, ⊕); x, moles of water in metal sulfate (△). Broken and solid lines for nickel sulfate correspond to (A) and (B) in Table 3, respectively.

cators and the results are summarized in Table 1. The extent of the color change from basic to acidic is represented in the increasing order as $- < \pm < + < ++$. The intrinsic color of nickel sulfate made the decision of color, basic or acidic, of two indicators ($pK_A = -5.6$ and -8.2) uncertain. However, its acid strength may be similar to zinc sulfate since the electronegativity of Ni^{2+} and Zn^{2+} are almost the same (*3*). It is to be noted in Table 1 that the highest acid strength for each catalyst is nearly independent of the calcination temperature and that silica gel as the supporting material causes an increase in the acid strength of sulfates. The acid strength of aluminum sulfate corresponded to benzalacetophenone ($pK_A = -5.6$). When sup-

TABLE 1

THE COLOR CHANGES OF THE INDICATORS ON METAL SULFATES CALCINED AT VARIOUS TEMPERATURES

Catalyst	Calcination temperature (°C)	pK_A of indicators[a]				
		+3.3	+1.5	−3.0	−5.6	−8.2
$Al_2(SO_4)_3$	200°	++	++	+	−	−
	300°	++	++	++	+	−
	400°	++	++	++	+	−
	500°	++	++	+	±	−
$ZnSO_4$	200°	++	+	+	−	−
	300°	++	++	+	−	−
	400°	++	++	+	−	−
	500°	++	++	−	−	−
$NiSO_4$	300°	++	++	+	−?	−?
$MgSO_4$	200°	++	++	−	−	−
	300°	++	++	−	−	−
	400°	++	++	−	−	−
	500°	++	++	−	−	−
$Al_2(SO_4)_3$-SiO_2[b]	100°	++	++	++	++	++
$ZnSO_4$-SiO_2[b]	100°	++	++	+	±	−
$MgSO_4$-SiO_2[b]	100°	++	++	−	−	−

[a] Indicators are the same as in the previous work (*1*).

[b] From ref. (*1*).

ported on silica gel, the acidity became stronger than −8.2 in pK_A. The acid strength of nickel sulfate or zinc sulfate was comparable to benzeneazodiphenylamine ($pK_A = -3.0$) and increased to −5.6 by being supported on silica gel. Magnesium sulfate exhibited the acid strength of 1.5 in pK_A with or without carrier. Three metal sulfates appearing in Fig. 1 were thus chosen as typical examples which differ considerably in acid strength.

The three selectivity ratios for the three isomers of *n*-butene are given in Table 2, including the previous results for the silica-gel-supported catalysts. The relationship of Haag and Pines (*4*), i.e., (*trans*/1) (1/*cis*) (*cis*/*trans*) = 1, is verified to hold approximately for all catalysts. The selectivity of the *cis–trans* isomerization over the double-bond migration starting from 2-butenes, which is reflected in the *trans*/1 and the *cis*/1 ratios, increases along with the acid strength given in Table 1, from magnesium sulfate to aluminum sulfate. This trend agrees with the one observed for the silica-gel-supported catalysts, although the differences in both the selectivity and the acid strength are larger for the supported metal sulfates. The *cis*/*trans* ratio is dependent slightly on the catalysts whether supported or not. But the values are higher for the unsupported catalysts.

TABLE 2

The Three Selectivity Ratios of *n*-Butene Isomerization over Metal Sulfate Catalysts at 61.5°C

Metal sulfate	Unsupported (calcined at 300°C)			Silica-gel-supported (evacuated at 100°C)[a]		
	trans/1	*cis*/1	*cis*/*trans*	*trans*/1	*cis*/1	*cis*/*trans*
H_2SO_4	(11.0)[b]	(11.0)[b]	(1.0)[b]	10.1	10.1	1.1
$Al_2(SO_4)_3$	2.7	5.9	2.4	6.5	6.3	1.2
$CuSO_4$	1.6	5.5	2.5	2.8	3.5	1.1
$NiSO_4$	1.4	4.9	2.9	2.3	2.9	1.25
$MgSO_4$	1.2	4.4	2.8	1.2	1.7	1.25

[a] From ref. (*1*).

[b] For aqueous sulfuric acid (*6*).

It was proposed in the previous paper (*1*) that the selectivities of the isomerization of 2-butene over silica-gel-supported metal sulfates are determined by the highest acid strengths which are dependent primarily on the catalyst substance through the electronegativity, x_i, of the constituent metal ion (*3*). The catalytic activity, on the other, depends on the highest acid strength of the catalyst concerned and the number of acid sites having this strength. The same interpretation seems to be applicable to the present results for the unsupported metal sulfates, since the following results are essentially the same as those of the supported metal sulfates.

(1) Both the selectivity represented as the *trans*/1 ratio and the highest acid strength of the unsupported metal sulfates are almost independent of the calcination temperature (Table 1 and Fig. 1).

(2) The order of the *trans*/1 ratios among the catalysts was in agreement with that of the highest acid strength. This trend also agrees with the electronegativities of the constituent metal ions.

(3) The catalytic activity, in contrast to the selectivity, changed markedly with the calcination temperature (Fig. 1).

(4) When metal sulfates are calcined at 300°C, the order of the catalytic activities agrees with the orders of the electronegativities of metal ions and of the acid strength. The rate constants per unit surface area are Al^{3+} ($\sim 10^{-3}$ m^{-2}min^{-1}) > Cu^{2+}, Ni^{2+}, Zn^{2+} ($\sim 10^{-4}$) > Mg^{2+} ($\sim 10^{-5}$), as shown in Table 3.

(5) The activity decreased from aluminum sulfate to magnesium sulfate by a factor of 10^2 with a decrease in the acid strength from −5.6 to +1.5 in pK_A (Tables 2 and 3), indicating that the activity de-

TABLE 3
THE FIRST ORDER RATE CONSTANTS OF *cis*-2-BUTENE ISOMERIZATION OVER UNSUPPORTED METAL SULFATE CATALYSTS CALCINED AT 300°C

Metal sulfate	Surface area (m^2/g)	Rate constant per unit surface area ($m^{-2}min^{-1}$)	Electronegativity of metal ion, x_i[a]
$Al_2(SO_4)_3$	18.2	1.8×10^{-3}	8.8
$CuSO_4$	2.9	2.9×10^{-4}	7.2
$NiSO_4$ (A)[b]	9.9	1.7×10^{-4}	6.9
(B)[b]	12.4	2.6×10^{-4}	6.9
$ZnSO_4$	3.0	1.1×10^{-4}	6.8
$MgSO_4$	10.8	2.0×10^{-5}	5.9

[a] From ref. (*3*).
[b] (A) and (B) are taken from the different lots.

creases sharply with decrease of the acid strength.

It may be seen from (5) that the reaction proceeds mainly on the stronger acid sites of the given catalysts, since the weak acid sites, if present, may contribute much less to the total activity than the stronger acid sites. A more quantitative analysis of this point would be possible if the distribution of the acid strengths was known (*5*). It is derived from (1) and (2) that the selectivity is determined by the highest acid strength. The results of (3) and (4) are well understood if the activity is determined not only by the acid strength but also by the number of acid sites. Among catalysts with similar acid contents the catalytic activity increases with the electronegativity of the metal ion, but the number of acid sites of the given metal sulfate changes with the extent of dehydration.

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