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Acidity and Catalytic Activity of Iron(II) Sulfate Heat-treated at High Temperature

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Synopsis. Acidity and catalytic activity of $FeSO_4$ calcined at 500—900 °C were studied. The product obtained by calcination at 700 °C showed maximum acidity at $H_0 \leqq 1.5$ and activity for isomerization of *d*-limonene oxide, polymerization of isobutyl vinyl ether and dehydration of 2-propanol. When calcined at 750 °C the product showed no acidity or activity.

Studies were carried out on the Friedel-Crafts benzylation,[1] benzoylation[2] and isopropylation[3] of toluene with their corresponding halides and polycondensation of benzyl chloride[4] catalyzed by iron sulfates heat-treated in the air at 200—900 °C. Maximum activity was found for the catalyst calcined at 700 °C. The specific surface area of the calcined sulfates indicated no relationship with their catalytic activities. The acidic property of calcined iron sulfates has not been investigated as regards relationship with catalytic activity, though several workers observed the maximum acidity of iron sulfates calcined at 120—200 °C.[5,6] In this paper we report the acidity of $FeSO_4$ calcined over 500 °C and its correlation with catalytic activities for isomerization of *d*-limonene oxide, polymerization of isobutyl vinyl ether and dehydration of 2-propanol.

Experimental

Catalysts were prepared by heating $FeSO_4 \cdot 7H_2O$ at 200—300 °C for 1—1.5 h followed by powdering below 100 mesh. Calcination was then carried out in the air in Pyrex glass tubes (quartz tubes for temperatures over 600 °C) for 3 h. The catalysts were stored in sealed ampoules.

The acidic property of the catalysts was determined by titration with butylamine using 4-phenylazodiphenylamine as a Hammett indicator: 0.05—0.2 ml of 0.1 M butylamine benzene solution was added to 0.5 g of the powder (below 100 mesh) suspended in 30 ml of benzene at intervals of 5—6 h. Since the catalyst is colored, the end point of titration was taken when a color change was observed on SiO_2–Al_2O_3 plastered on a small slip of filter paper, acidic coloration being seen with an indicator. The slip consumed 0.02—0.03 ml of 0.1 M butylamine. As the amount of consumed amine, 0.03 ml was subtracted from the titre per slip after slips were added until the acidic color of the indicator on SiO_2–Al_2O_3 remained unchanged. It took 4—5 d for titration.

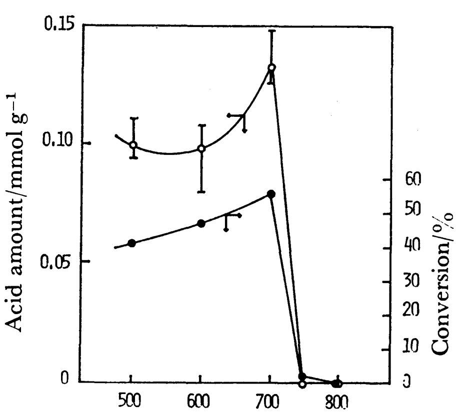
Isomerization of *d*-limonene oxide was carried out with a mixture of 0.5 ml of the epoxide, 2.5 ml of toluene and 0.3 g of the catalyst with stirring at 90 °C for 15 min.[7]

Polymerization of isobutyl vinyl ether was performed with a mixture of 5 ml of the ether, 45 ml of toluene and 80 mg of the catalyst with stirring at room temperature for 30 min. Conversion (%) on the polymerization reaction was obtained on the basis of the unreacted monomer by gas chromatography using a 1-m column of tricresyl phosphate on Celite 545 (95 °C, He: 1.0 kg/cm²) with benzene as an internal standard.

Dehydration of 2-propanol was carried out at 170 °C by using a microcatalytic pulse reactor (catalyst amount: 30 mg, carrier gas: He, flow rate: 30 ml/min, pulse size: 0.4 μl). The catalyst was heat-treated in a reactor at 500 °C for 1.5 h before the reaction. Effluent products were directly introduced into a gas chromatographic column for analysis (Porapak R-2 m, 128 °C). The percentage conversion is given as the average value from the 5 to 10 th pulse reaction.

Results and Discussion

Figure 1 shows the acid amount ($pK_a \leqq 1.5$) of $FeSO_4$ calcined at 500—800 °C. The substance obtained by calcination at 700 °C was found to be the most acidic. It is of interest that the acid amount was zero when calcined at 750 °C. The substance obtained by treatment at 900 °C also showed no acidity. The acidic amount of $FeSO_4$ treated at 700 °C was 0.052 mmol/g at $pK_a \leqq -3.0$.



Calcination temp/°C

Fig. 1. Acidity of calcined $FeSO_4$ and its catalytic activity for isomerization of *d*-limonene oxide.
(○): Acid amount at $pK_a \leqq 1.5$,
(●): isomerization of *d*-limonene oxide.
Selectivity was 20% 1-methyl-3-isopropenylcyclopentyl-1-carboxaldehyde (I), 66% dihydrocarvone (II), 7% *exo*-carveol (III) and 7% *endo*-carveol (IV) in all runs.

Since the acidity could not be determined accurately because of the coloration of the substance, catalytic activities by several acid-catalyzed reactions were examined. The activity for isomerization of *d*-limonene oxide is shown in Fig. 1. We see that the activity is in line with acidity, the catalyst calcined at 750 °C being quite inactive in spite of the remarkable activity attained by heat treatment at 700 °C.[8]

The following two reactions were carried out (Fig. 2): (1) polymerization of isobutyl vinyl ether, which is known to be catalyzed by Lewis catalysts such as BF_3-

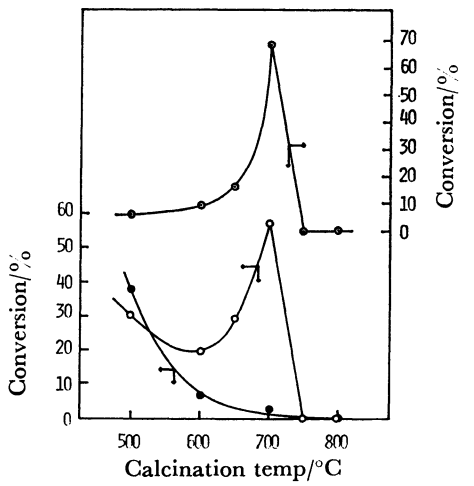


Fig. 2. Catalytic activities for polymerization of isobutyl vinyl ether (⊙) and for dehydration of 2-propanol (○). (●): dehydration of 2-propanol over $NiSO_4$ at 190 °C.

etherate and $TiCl_4$,9) and (2) the dehydration of 2-propanol to propylene, which is generally catalyzed by acidic sites at $-3<H_0\leqq+1.5$.10) Both reactions give maximum activity by calcination at 700 °C. Both activities are in line with the acidity (Fig. 1), the catalyst calcined at 750 °C being inactive.

In order to examine such a rapid decrease in catalytic activity for other metal sulfate, $NiSO_4$ was subjected to reaction with 2-propanol. The activity decreased rapidly by calcination above 500 °C. The catalysts calcined above 700 °C were almost inactive. The acidity of $NiSO_4$ increases initially with rise in temperature of heat-treatment, reaching a maximum at *ca.* 350 °C, and decreasing subsequently.11) It seems that activity is related with acidity. The amount of diisopropyl ether formed by the dehydration of 2-propanol was almost negligible for all the catalysts of $FeSO_4$ and $NiSO_4$.

In the polymerization of isobutyl vinyl ether, $FeSO_4$ (700 °C) gave 91% conversion for 2 h. The yield insoluble in an excess amount of methanol was 74% with 0.96 dl/g of the reduced viscosity.12)

ESCA studies of $FeSO_4$ showed that the sulfate completely decomposes to form α-Fe_2O_3 at 675—700 °C, recrystallization proceeding rapidly.13) A small amount of sulfur (0.12—0.15 wt %), which remains in the catalyst after decomposition, exists as SO_4^{2-} on the surface treated at 700 and 750 °C.14) $NiSO_4$ reveals its acidity on the sulfate configuration between the monohydrate and anhydrous forms.15) Other metal sulfates, $Al_2(SO_4)_3$, $ZnSO_4$, $MgSO_4$, and $CdSO_4$, also show surface acidity on the sulfate salts, the maxima appearing at 180—400 °C.11) The creation of acid sites on the Fe_2O_3 catalyst by decomposition of the sulfate at 700 °C is specific, and the inactivity caused by calcination at a slightly higher temperature, 750 °C, is noteworthy.

As regards the polymerization of isobutyl vinyl ether, solid acid catalysts such as $NiSO_4$ (calcined at 350 °C), SiO_2-Al_2O_3 (500 °C, Al_2O_3: 15 wt %, Nikki Chemical Co.), Al_2O_3 (500 °C, KAT6, Nishio Chemical Co.) and TiO_2 (hydrogel) were found to be almost inactive under the present reaction conditions.

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8) High activity of $FeSO_4$ (700 °C) was also observed in the isomerization of carvomenthene oxide. The catalyst (0.27 g) in a mixture of 0.5 ml epoxide and 2.5 ml toluene gave 82% total conversion in 10 min at 80 °C, the selectivity being 30 and 55% for the products corresponding to I and II, respectively, in the case of *d*-limonene oxide.

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12) The viscosity was determined by 0.5 g of polymer in 100 ml of benzene at 25 °C. The catalysts calcined at 500, 600, and 650 °C gave 43, 59, and 61% conversions with the methanol-insoluble yields of 12, 32, and 46%, respectively, for 24 h.

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