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Effect of Sulfate Ion on Catalytic Activity of AlPO$_4$ in the Skeletal Isomerization of Cyclohexene

Several oxides such as TiO_2 (*1, 2*), ZrO_2 (*3–5*), Fe_2O_3 (*6*), and SnO_2 (*7, 8*), or mixed oxides like ZrO_2–SnO_2 (*8*) show a surprisingly high acidity and hence high catalytic activity for the isomerization of cyclopropane and the dehydration of 2-butanol when they are promoted by the addition of sulfate ion from an aqueous solution of ammonium sulfate. These facts are considered to be due to the generation of strong acid sites on the addition of SO_4^{2-}. The sulfate impregnation of $AlPO_4$ (*9*) produced, at a lower concentration of SO_4^{2-}, an enhanced conversion in the 1-butanol dehydration, but a poisoning effect and a selectivity shift to ca. 100% 1-butene is observed for large amounts of SO_4^{2-}. However, the catalytic activities of other oxides such as MgO, CaO, CuO, ZnO, CdO, Al_2O_3, La_2O_3, ThO_2, Bi_2O_5, CrO_3 and NiO are reported to be unaffected by the addition of sulfate ion (*10*).

In a previous paper (*11*) we have shown that $AlPO_4$ (Al/P = 1) catalyzes the cyclohexene skeletal isomerization which is known to be promoted by acid sites of high strength. Besides, the apparent rate constants and the selectivity factors to 1-methylcyclopentene formation increase linearly with increased number of acid sites of high strength, measured by a spectrophotometric method using aniline as the titrant ($pK_a = 4.6$).

On the other hand, the impregnation of $AlPO_4$ with alkali or fluoride ions leads to a change in the acidity–basicity balance (*12–14*). Thus, the acidity properties can be decreased by alkali treatment (*12, 14*) or increased by fluoride loading (*13*). The $AlPO_4$ surface only exhibits acid and electron acceptor properties when the fluoride content is higher than 3 wt%.

The present communication deals with the effect of SO_4^{2-} on the catalytic activity of $AlPO_4$ (Al/P = 1) in the skeletal isomerization of cyclohexene carried out in a microcatalytic pulse reactor. The Bassett–Habgood kinetic model, that is applied in first-order processes in which the surface reaction is the controlling step and the partial pressure of the reactant is low, was used. Thus, $AlPO_4$ has been found to be a solid whose activity and hence surface acidity is greatly enhanced by the addition of a small amount of sulfate ion (1–3 wt%).

$AlPO_4$ (Al/P = 1) was prepared from aqueous solutions of $AlCl_3 \cdot 6H_2O$ and H_3PO_4 (85 wt%) by precipitation with propylene oxide and stirring at 273 K. The precipitate was allowed to stand at room temperature for 18 h. After filtration it was washed several times with 2-propanol, dried at 393 K for 24 h and then calcined at 923 K for 3 h (*11*).

$AlPO_4$ samples including SO_4^{2-} were prepared by impregnation with aqueous solutions of $(NH_4)_2SO_4$ until incipient wetness was attained, followed by drying at 393 K for 24 h and calcining at 573 K for 3 h. The content of SO_4^{2-} was in the range 1–5 wt% ($AlPO_4$–1S to $AlPO_4$–5S). Surface areas and pore size distributions were determined for each of the $AlPO_4$–SO_4^{2-} samples using BET nitrogen adsorption at 77 K. X-Ray diffractions were measured using Fe-filtered Co$K\alpha$ radiation and the scans were taken between 15 and 80° 2θ to check for crystallinity of the sulfate-treated samples.

The skeletal isomerization of cyclohexene (CH) was carried out at 523–673 K in a

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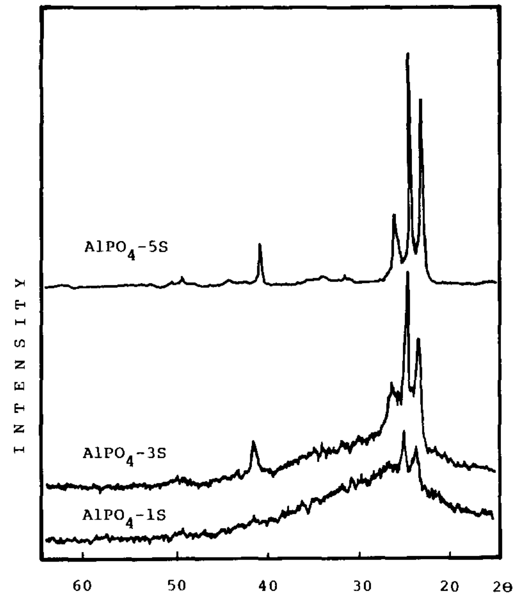


FIG. 1. X-Ray diffraction profiles for $AlPO_4$-1S, $AlPO_4$-3S, and $AlPO_4$-5S samples.

microcatalytic pulse reactor as has been reported elsewhere (*11*). A pulse of 1 μl of CH was introduced over 20–100 mg of catalyst pretreated in a nitrogen stream (40 ml/min) at 573 K for 1 h. The reaction products 1-, 3-, and 4-methylcyclopentenes (1-, 3-, and 4-MCP) were analyzed using two columns in series packed with Chromosorb GAW-DMCS (80/100) treated with 5 wt% of polyphenylether and 5 wt% of squalane, respectively. The oven temperature was 323 K. Response factors were equal for all alkenes (CH, 1-, 3-, and 4-MCP) and the elution order was 3-MCP, 4-MCP, 1-MCP, and CH.

The impregnation of $AlPO_4$ with $(NH_4)_2SO_4$ up to 2.5 wt% leads simultaneously to a slight decrease in surface area and pore volume and an increase in the most frequently occurring pore radius. An increase in the sulfate content above 3 wt% results in a considerable decrease in the textural properties due to the crystallization of $AlPO_4$, as can be seen by X-ray diffraction in Fig. 1.

The overall effect is a moderate variation in textural properties of $AlPO_4$ catalysts for sulfate loading in the range 1–3 wt%, with a large increase in surface acid properties demonstrated through its activity for the CH skeletal isomerization, as is indicated below. This fact is very important since the catalytic properties of $AlPO_4$ are strongly dependent on their textural and surface acid properties and thus sulfate impregnation is able to modify the latter while retaining the textural properties of the parent structure.

The isomerization activity, expressed by the total conversion to 1-, 3-, and 4-MCP, is fitted to the Bassett–Habgood equation

$$\ln(1/1 - X) = RTkK(W/Q)$$

where X is the molar fractionary conversion, R the gas constant, T the reaction temperature, k the rate constant of the surface process, K the adsorption constant of the cyclohexene on the catalyst, W the catalyst weight, and Q the flow rate of the carrier gas.

The operating variables, spatial time and particle size, were so chosen as to eliminate transport influences on the reaction rate. Besides, the thermal process without a catalyst is negligible and the concentration of 1-MCP was always higher than that of 3-MCP for all catalysts studied. Apparent rate constants, kK, at 673 K of reaction temperature, from the linear plots $\ln(1/1 - X)$ vs Q^{-1}, apparent activation energies, E_a, and Arrhenius parameters, $\ln A$, and from $\ln X$ vs T^{-1} and selectivity factors to 1-MCP formation, α, were obtained for $AlPO_4$ with and without the addition of 1–5 wt% SO_4^{2-} and are collected in Table 1, together with the surface area, S_{BET}, and the main pore radius, r_p, of these samples.

The most striking feature of the results shown in Table 1 is that the catalytic activity and hence the strong acid sites number depend upon the sulfate content of the catalyst. Thus, the catalytic activity increases sharply to a maximum at 2.5–3 wt% SO_4^{2-}, above which a rapid decline occurs up to 5 wt%. The activities per unit mass of $AlPO_4$

TABLE 1

Effect of SO_4^{2-} on Catalytic Activity of $AlPO_4$ in the Skeletal Isomerization of Cyclohexene at 673 K

Catalyst	S_{BET} ($m^2\ g^{-1}$)	r_p (nm)	$Kk \times 10^6$ (mol atm^{-1} g^{-1} s^{-1})	E_a (KJ mol^{-1})	ln A[a]	σ
$AlPO_4$	79	6.7	3.2	59.1	6.8	1.5
$AlPO_4$-1S	60	8.9	14.3	60.9	8.3	2.5
$AlPO_4$-2S	46	8.9	75.0	59.9	9.3	3.6
$AlPO_4$-2.5S	45	8.9	123.8	61.7	10.2	3.8
$AlPO_4$-3S	40	8.9	125.0	59.8	9.7	4.1
$AlPO_4$-4S	18	—[b]	1.6	61.7	7.4	2.0
$AlPO_4$-5S	16	—	1.5	61.0	7.3	1.7

[a] A is expressed in mol atm^{-1} g^{-1} s^{-1}.

[b] The adsorption isotherm is reversible exhibiting no hysteresis, a behavior which is expected for nonporous adsorbents.

at 673 K of reaction temperature are 4, 25, 38, and 39 times higher than those of the catalyst without SO_4^{2-} at the same reaction temperature for 1, 2, 2.5, and 3 wt%, respectively. Also, the activity is dropped again by a factor of 2 when the sulfate content is 4–5 wt%.

On the other hand, apparent activation energies are practically constant for all samples studied. This, together with the first-order kinetics obtained, indicates that the transition state is of the same type for all catalysts. Thus, differences in catalytic activities can be attributed to the more or less developed carbocationic character of the reaction intermediates which is a function of the acid strength of the catalyst. Besides, the application of the Wheeler criterion (*15*) on the selectivity factor σ ($\sigma = X_1/X_3$, where X_1 and X_3 are, respectively, the molar fractionary conversion to 1- and 3-MCP) allows us to conclude that these isomerization products are competitors. Thus, as in previous studies (*11, 14*), the different σ values for each catalyst are due to the different A_1/A_3 ratios, since for each catalyst the 1- and 3-MCP formation has the identical apparent activation energies

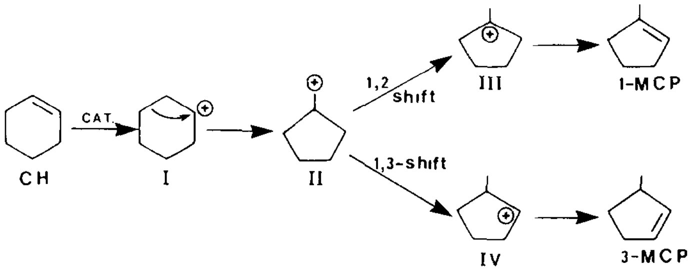
$$\sigma = X_1/X_3 = [A_1 \exp(E_{a_1}/RT)]/[A_3 \exp(E_{a_3}/RT)] = A_1/A_3$$

Besides, the selectivity to 1-MCP as a function of the sulfate loading follows the same behavior as the catalytic activity, i.e., they increase with increased sulfate loading up to 3 wt%, although the increase is only three times higher than those of pure $AlPO_4$.

From the optimum performance envelope (OPE) curves (*16*) obtained by plotting product yields vs conversion it is possible to infer that, in the range of conversions studied, the two main reaction products, 1- and 3-MCP, seem to be primary stable products, while 4-MCP should be a secondary product. In this sense, a previous study of the CH isomerization on $AlPO_4$ and $AlPO_4$–Al_2O_3 catalysts (*17*) carried out in a continuous flow fixed-bed reactor shows that 1- and 3-MCP are the primary products of reaction and that later they are isomerized to 4-MCP. The positive slope at the origin of the plot conversion vs residence times for 1- and 3-MCP demonstrates that these are primary reaction products.

Thus, the previously proposed mechanism, through intermediates with a more or less developed carbocationic character (*11*) accounts for the experimental results.

Thus, an increase in the surface acidity of $AlPO_4$ produces intermediates III and IV with a more developed carbocationic char-



acter and hence it increases the conversion to 1- and 3-MCP, the former being larger than the latter due to the greater stability of tertiary carbonium ion III in relation to secondary carbonium ion IV. So, we have to expect an increase in selectivity factors and thus, an increase in the sulfate content up to 3 wt% leads to $AlPO_4$ catalysts with higher surface acidity and hence higher activity and selectivity to 1-MCP in relation to pure $AlPO_4$.

The origin of the added strong acidity of $AlPO_4–SO_4^{2-}$ can be attributed to the inductive effects of the sulfate groups on neighboring hydroxyls enhancing their protonic mobility through the weakening of the O–H group. So the introduction of sulfate anion reduces the absolute number of OH groups but increases the acid strength of those remaining. A further increase of sulfate content results in a decline of activity because of the decrease in the concentration of Brønsted acid sites as well as in a rise in the degree of crystallinity. The ir spectra also show the substitution of hydroxyl groups in the samples with higher sulfate loading. An equivalent view has been expressed for the increased Brønsted acidity in fluorinated Al_2O_3 (*18*).

The present results are in accord with those reported by Tada *et al.* (*9*, *19*) on the dehydration of 1-butanol on $AlPO_4$, both unpromoted and promoted with sulfate ions. These authors find that SO_4^{2-} ions produced an enhanced conversion at lower concentrations, but a poisoning effect in larger amounts, and that the selectivity is shifted from ether to 1-butene.

Thus, the present study provides direct evidence that the treatment of $AlPO_4$ with aqueous ammonium sulfate, followed by drying and calcination, leads to the generation of strong acid sites as measured by cyclohexene skeletal isomerization activity. Thus, the solids $AlPO_4–SO_4^{2-}$ are expected to act as efficient catalysts in several acid catalyzed reactions where the pure $AlPO_4$ is active and even in other processes where pure $AlPO_4$ is not able to act as a catalyst. Experiments to check this hypothesis are in progress.

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