Catalysis by Adsorbed Hydrogen Sulphide of the Dealkylation of Cumene at High Temperature

By MASATOSHI SUGIOKA,* TOMIJI HOSOTSUBO, and KAZUO AOMURA
(*Department of Chemistry, Faculty of Engineering, Hokkaido University, Sapporo* 060, *Japan*)

Summary Hydrogen sulphide adsorbed on metal Y zeolites (MZeY, M = Cd, Ni, Cu, Ag, or Co) enhances its catalytic activity for the dealkylation of cumene at high temperature.

THE catalytic activity of metal Y zeolites, MZeY, (M = Cd, Ni, Cu, Ag, or Co) for the dealkylation of cumene at 300 °C was enhanced by pretreatment with H_2S at this temperature. The increased catalytic activity of these metal zeolites by pretreatment with H_2S was sustained in a series of experiments; carbonaceous deposits accumulated on the catalyst surface. In contrast, the catalytic activity of MZeY zeolites (Me = Na, Mg, Ca, or Zn), and SiO_2, Al_2O_3, and SiO_2–Al_2O_3 was enhanced very little by this treatment, or by pretreatment with H_2O at 300 °C. The initial activities of these solid acid catalysts at 300 °C with and without H_2S pretreatment are shown in the Table.

The increased catalytic activity of the MZeY zeolites with H_2S pretreatment was poisoned by pyridine injection, implying that the increased catalytic activity is due to increase in the acidity of the zeolite. I.r. spectra of H_2S adsorbed on MZeY indicated that there was interaction between the OH groups on the surface and chemically adsorbed H_2S.[1]

As the dealkylation of cumene has been reported to proceed on the Brönsted acid site of the solid acid catalysts[2] the increase in the catalytic activity of MZeY (M = Cd, Ni, Cu, Ag, or Co) upon H_2S pretreatment for this reaction may be attributed to the formation of new Brönsted acid sites by the interaction of OH groups and H_2S on the MZeY surface.

Table. Initial activities of various solid acid catalysts at 300 °C.

Catalyst[a]	%-Ion exchanged	$k \times 10^{-2}$/[b] (ml g^{-1} min^{-1}) Without H_2S (k_o)[c]	With H_2S (k_t)[d]	k_t/k_o[e]
SiO_2	—	0	0	—
Al_2O_3	—	0	0	—
SiO_2–Al_2O_3	—	1·0	1·1	1·1
NaY zeolite	—	0	0	—
MgY „	69·2	4·6	4·5	1·0
CaY „	73·8	5·1	5·1	1·0
CdY „	75·2	2·9	15·9	5·5
NiY „	68·8	3·1	15·7	5·1
CuY „	77·3	3·1	16·5	5·3
AgY „	93·9	2·0	9·2	4·6
CoY „	71·4	5·2	12·8	2·5
ZnY „	78·6	12·9	17·1	1·3

[a] 5—10 mg; heated at 500 °C in air and 450 °C in a helium stream. MZeY zeolites were prepared by Na exchange from NaY zeolite (SK-40). [b] First-order rate constant in the initial reaction. [c] $1{\cdot}4 \times 10^{-5}$ mol of pure cumene was injected into the reaction vessel at 300 °C. [d] $0{\cdot}9 \times 10^{-4}$ mol of H_2S was added to the catalysts at 300 °C and after 10 min dealkylation was carried out in a stream of helium. The amount of adsorbed H_2S on MZeY (M = Cd, Ni, Cu, Ag, Co, or Zn) was *ca.* 10^{-6} mol/10 mg-MZeY. [e] Activity ratio.

(*Received*, 10*th October* 1975; *Com.* 1157.)

[1] M. Sugioka, T. Hosotsubo, and K. Aomura, unpublished data.
[2] M. F. L. Johnson and J. S. Melik, *J. Phys. Chem.*, 1961, **65**, 1146; M. Okuda and T. Tachibana, *Bull. Chem. Soc. Japan*, 1963, **36**, 462; I. Mochida and Y. Yoneda, *J. Catalysis*, 1967, **7**, 386.