Effect of Water on Ethylation of Benzene Catalyzed by Silica-Alumina

Toshiro TAKAHASHI, Jukichi ISHII and Kenji HIRAI

Daikyowa Petrochemical Co., Yokkaichi Laboratory, Daikyocho, Yokkaichi, Mie

(Received June 1, 1967)

It has been known that the re-hydration of silica-alumina catalyst increases the activity in cracking,[1] isomerization,[2] and dealkylation[3] of hydrocarbons. We found the same phenomena in vapor-phase ethylation of benzene.

Experimental

Materials. The silica-alumina catalyst (commercial name N 631 H) was obtained from Japan Gasoline Co. The physical properties of the catalyst were as follows: composition SiO_2 74 wt%-Al_2O_3 26 wt%, surface area (m^2/g) 230, apparent sp. gr. (g/ml) 0.544, acidity (meq/g) 0.42.

The acidity of the catalyst was measured in benzene by Benesi's method using *p*-dimethylaminoazobenzene as indicator and *n*-butylamine as base. The silica-alumina catalyst was sized to 14/20 mesh and activated at 530°C for 4 hr in dry nitrogen before use in every experiment, but the water-content of the catalyst was not measured.

Apparatus and Procedure. The reactor was an integral flow type. Fifty milliters of a catalyst were packed in the stainless steel tube of 20 mm in inside diameter and 700 mm in length. The products were collected for every thirty minutes and analyzed by gas chromatography. The selectivities to ethylbenzene and diethylbenzene were over 90—95 mol%.

1) R. C. Hansford, *Ind. Eng. Chem.*, **39**, 849 (1947)
2) S. G. Hinden, A. G. Oblad and G. A. Mills, *J. Am. Chem. Soc.*, **77**, 535 (1955).
3) K. V. Topchieva *et al.*, Preprint of the 5th World Petroleum Congress, Sec-III, Paper-10, 133 (1959).

Results and Discussion

The conversion activity of ethylene under a fixed reaction condition was taken as a measure of the reaction activity. The condition was as follows: reaction temperature 300°C, reaction pressure 20 kg/cm², benzene/ethylene molar ratio 5.47, time factor *W/F* (cat·g/mol) 30.35. Water content in feed benzene was measured by Karl-Fischer titration. The effect of water on conversion of ethylene is shown in Fig. 1. In order to determine the effect of water which may be produced in the course of reaction, alcohols and diethyl ether were added in feed benzene. The results are shown in Table 1. An example using methyl alcohol is shown in Fig. 1. Diethyl ether and alcohols except isopropyl alcohol increased the conversion of ethylene. The relation between

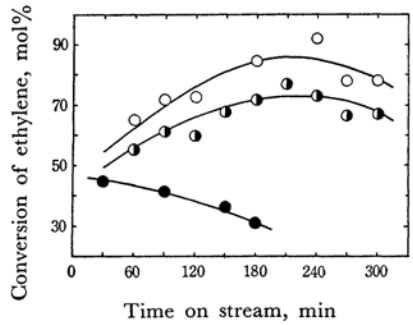

Fig. 1. Effect of water on conversion of ethylene.

Water cont. in feed-benzene
● 0.0158
◑ 0.0836
○ 0.2813*

* (Water contained in feed-benzene) + (Water produced stoichiometrically during the reaction)

Table 1. The increase of the activity by adding alcohols or diethyl ether in feed-benzene

Additive	Wt % of additive	Wt % of water*	Conversion of ethylene (mol%) *vs.* time on stream (min)			
			30	60	90	180
Methyl alcohol	0.4	0.28	—	65.0	72.2	84.5
Methyl alcohol	1.0	0.65	—	62.3	62.8	60.3
Methyl alcohol	1.5	0.88	—	40.5	41.8	42.2
Ethyl alcohol	0.4	0.22	50.8	—	54.6	63.3
Isopropyl alcohol	0.4	0.18	39.2	36.6	38.5	41.0
n-Butyl alcohol	0.4	0.16	72.6	—	68.2	80.8
Diethyl ether	0.4	0.16	54.6	56.4	63.6	78.5

* (Water in benzene)+(Water produced stoichiometrically during the reaction)

Table 2. Change of activity by adding water

Catalyst	N 631 L*1		SiO_2-MgO*1	Chrombead*2	
Composition, wt %					
SiO_2	87		80	90	
Al_2O_3	13		—	9.7	
MgO	—		20	—	
Cr_2O_3	—		—	0.15	
Surface area, m²/g	400		243	350	
Acidity, meq/g	0.40		0.90	0.23	
Reaction condition					
Temp., °C	300	300	350	300	300
Press., kg/cm²	20	20	20	20	20
W/F, cat. g/mol·hr	30.0	30.0	30.0	30.0	30.0
Water added in feed-benzene, wt %	0.0677	0.0195	0.28*3	0.28*3	0.0677
Conversion of ethylene mol %*4	82.1	52.5	5.5	30.9	19.2

*1 Obtained from Japan Gasoline Co., Ltd.
*2 Obtained from Kali—Chemie A. G., Germany.
*3 0.4 wt % addition of methyl alcohol in feed-benzene.
*4 The maximum value obtained in the overall time on stream.

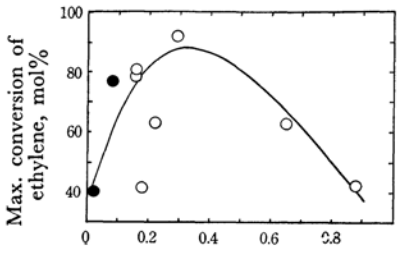

Fig. 2. Effect of water on activity.

● Water contained in feed benzene
○ (Water contained in feed-benzene) + (Water produced stoichiometrically during the reaction)

the quantities of water and the maximum conversion of ethylene in the overall time on stream is shown in Fig. 2. It may be concluded that 0.1—0.7 wt% water in feed-benzene activate the silica-alumina catalyst.

Using other acid catalysts, the same experiments were repeated. The results are shown in Table 2. It may be concluded that silica-alumina catalyst shows the increase of activity by the addition of water in ethylation of benzene except few cases. It is supposed that the increase of activity by adding water may be related to the strength of acid site on the catalyst.