BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 446—451 (1967)

Alkylation of Benzene with Ethylene by the Metal Sulfate Supported on the Silica-Alumina Catalyst

Yukimasa FUKUI, Hideo TAKAOKA, Jukichi ISHII, Kenji HIRAI
and Toshiro TAKAHASHI

Daikyowa Petrochemical Co., Ltd., Yokkaichi Laboratory, Daikyocho 2-3, Yokkaichi, Mie

(Received June 30, 1966)

The vapor-phase alkylation of benzene with ethylene over the various metal sulfates supported on the silica-alumina (SA) catalysts has been studied by a flow method under a pressure of 30 kg/cm^2 and within the temperature range of 230—450°C. The metal sulfate supported on the SA catalyst showed a relatively higher activity than the SA used as a carrier, and the activity of the metal sulfate as the modifier of SA is in the order of; manganous sulfate$>$zinc sulfate$>$chromic sulfate$>$cupric sulfate. Under the optimum conditions, in which benzene and ethylene were brought to reaction at the molar ratio of 2.5, a LHSV of benzene of 1.2 hr^{-1}, under a pressure of 30 kg/cm^2 and a reaction temperature of 300°C over the manganous sulfate supported on a SA catalyst (the weight ratio of manganese to SA is 1/10), the conversion of ethylene was 56.7% and the selectivity to ethylbenzene and diethylbenzene was 94.0%.

Aromatic hydrocarbons have been alkylated with olefins in the presence of various catalysts by many investigators, and much work has been reported. It is well known that aluminum chloride, aluminum bromide, and boron fluoride, as Friedel-Crafts-type catalyst, and sulfuric acid, phosphoric acid and fluoric acid, as protonic-acid catalysts, are often used industrially for the alkylation of benzene with olefin in the liquid phase reaction. These catalysts are considered to be proton donors which form carbonium ions. For the vapor-phase alkylation, solid phosphoric acid and silica-alumina catalyst have been used. Recently, alkar process has been developed by the Universal Oil Products Company for the economical manufacture of a wide variety of alkylated aromatics. This process is operated in the vapor phase with the boron fluoride - alumina catalyst.

We have found that silica-alumina catalysts supported with various metal sulfates showed higher activities than the SA in the ethylation of benzene at a relatively low temperature. Among various metal sulfates, manganous sulfate, zinc sulfate, chromic sulfate and cupric sulfate gave considerably good selectivities and ethylene conversions.

Experimental

Materials. Ethylene was obtained from a cylinder supplied by the Takachiho Chemical Industrial Corporation. Its purity was above 99.9%. Benzene was purified by distillation in the presence of sodium metal after treatment with concentrated sulfuric acid and a sodium hydroxide aqueous solution. A series composed of silica-alumina, alumina-boria and silica-magnesia, which were used as carriers, was obtained from the Japan Gasoline Co., Ltd. The physical properties of these carriers are shown in Table 1. All the catalysts were prepared by the impregnation method, in which these carriers were dipped into a metal sulfate solution for 24 hr, after which water was vaporized on a water bath. The catalysts were calcined at 270°C for 4 hr after they had been dried at 120°C for 2 hr. The catalysts were used in experiments without any treatment.

TABLE 1. PHYSICAL PROPERTIES OF VARIOUS CARRIERS

Carrier	Composition wt, %	Surface area m^2/g	Apparent SG g/ml
SA-1	SiO_2(90) Al_2O_3(10)	344	0.798
SA-2	SiO_2(87) Al_2O_3(13)	400	0.562
SA-3	SiO_2(74) Al_2O_3(26)	230	0.544
SA-4	SiO_2(55) Al_2O_3(45)	263	0.525
SA-5	SiO_2(30) Al_2O_3(70)	202	0.524
AB-20	Al_2O_3(80) B_2O_3(20)	300	0.729
SM-20	SiO_2(80) MgO(20)	243	0.701
Alumina	Al_2O_3(100)	294	0.700
Silicagel	SiO_2(100)	542	0.764

Apparatus and Procedure. The apparatus is shown in Fig. 1. Fifty cc of a catalyst were packed in the stainless steel tube 20 mm in inside diameter and 700 mm long. The reactant ethylene was admitted into the reactor from the gas reservoir through the flow-controlling needle valve at the flow rate of 100 ml/min NTP. The pressure in the reactor was always kept constant at 30 kg/cm^2 by an automatic pressure controlling valve. Then, benzene was introduced at a determined feed rate with the Bosch-type high-pressure pump. The molar ratio of benzene to ethylene was 2.5. The temperature was measured by a chromel-alumel thermocouple which was immersed into the catalyst bed. The exhausted gas was rapidly cooled with running water at the exit of the tube, and then passed through the flask, which was immersed in ice-water to condence all the liquid products. The outlet gas was caught in the gas holder. The product was analyzed at 30 min intervals after an induction period of 30 min. As no fouling of the catalyst was observed during 180 min of reaction, the conversion of ethylene was calculated by means of the average value of all the samples. All liquid and gaseous products were analyzed by the gas chromatographic method. A PEG-6000 column, 3 m long, was used at 120°C for the analysis of C_6–C_{12} hydrocarbons. An acetonylacetone column, 10 m long, was used for C_2–C_5 hydrocarbon analysis at 0°C. Methane was analyzed by a molecular sieve column, 3 m long, at 0°C. Hydrogen was used as the carrier gas for the analysis of all the products described above. An active charcoal column, 2 m long, was used for the analysis of hydrogen in the gaseous products, using nitrogen as the carrier gas. The acidities and acid strengths of all the catalysts were determined by Benesi's method[1] in a benzene solution, using n-butylamine as the base and a set of Hammett indicators. The total acidity was measured using p-dimethylaminoazobenzene, (pK_a + 3.3) as an indicator.

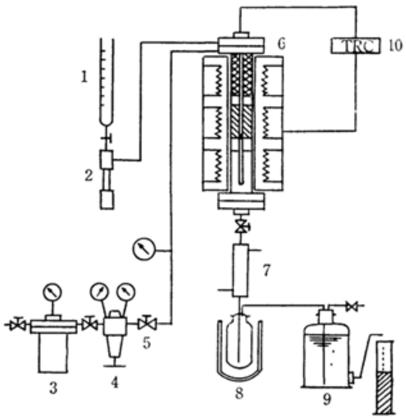

Fig. 1. Reaction apparatus.

(1) Charge cylinder
(2) Charge pump
(3) Ethylene reservoir
(4) Automatic pressure controlling valve
(5) Flow controlling valve
(6) Reactor
(7) Cooler
(8) Condenser
(9) Exhaust gas holder
(10) Temperature recorder controller (TRC)

Results and Discussion

Material Balance. An example of the material balance of both ethylene and benzene is

---

[1] H. A. Benesi, *J. Phys. Chem.*, **61**, 970 (1957); *J. Am. Chem. Soc.*, **78**, 5490 (1956).

TABLE 2. AN EXAMPLE OF MATERIAL BALANCE
Temperature: 300°C Catalyst: 50 *ml*
Pressure: 30 kg/cm² LHSV: 1.2

Catalyst	SA-3	$MnSO_4$-SA-3
Feed ethylene (mol)	0.1740	0.1297
Unreacted ethylene (mol)	0.1173	0.0555
Reacted ethylene (mol)	0.0567	0.0742
Ethylbenzene	0.0410	0.0537
Diethylbenzene	0.0050	0.0079
Isopropylbenzene	0.0002	0.0003
sec-Butylbenzene	0.0008	0.0013
Ethylene dimers in off gas	0.0009	0.0002
Loss	0.0019	0.0011
[(Feed ethylene−Loss)/ (Feed ethylene)]×100 (%)	98.9	99.2
Ethylene conversion (%)	32.6	57.2
Feed benzene (mol)	0.3380	0.3380
Unreacted benzene (mol)	0.2888	0.2683
Reacted benzene (mol)	0.0470	0.0632
Loss (mol)	0.0022	0.0065
[(Reacted benzene+Unreacted benzene)/Feed benzene] ×100 (%)	99.3	98.0

shown in Table 2. More than 90% of the reacted ethylene was present in the form of ethylbenzene homologues. The side reactions, such as the polymerization and cracking of ethylene, were found to involve under 2% based on the reacted ethylene. More than 98% of the benzene was recovered in the liquid product. The carbon deposit on the surface of the catalyst was calculated to be 2—3%.

Catalytic Activity of Metal Sulfate. The catalytic activities of various metal sulfates supported on the silica-alumina were examined. SA-3 was used as the silica-alumina carrier. The weight ratio of the metal in the sulfate to SA-3 was 1/10. The catalytic activities were measured by the conversion of ethylene under a constant temperature, a constant pressure, and a constant feed rate. The conversion of ethylene and the selectivity to ethylbenzene homologues were calculated by the following formula:

$$\text{Ethylene Conversion} = \frac{(\text{fed ethylene} - \text{unreacted ethylene})\ (\text{mol})}{(\text{feed ethylene})\ (\text{mol})} \times 100\ (\%)$$

$$\text{Selectivity} = \frac{(\text{ethylbenzene} + \text{diethylbenzene} \times 2)\ (\text{mol})}{(\text{reacted ethylene})\ (\text{mol})} \times 100\ (\%)$$

Manganous sulfate, zinc sulfate, chromic sulfate, and cupric sulfate increased the activity of the SA-3 catalyst, while cobalt sulfate, nickel sulfate, aluminum sulfate, and cadmium sulfate decreased it. The acidities of these catalysts were then measured, and it was found that the metal sulfate supported on the SA-3 catalysts always showed a lower acidity than SA-3. At the same time, the acidities and activities of several silica-alumina catalysts which were different in composition were measured. The results are shown in Table 3 and in Fig. 2. No direct correlation was observed between the acidities and the activities of the catalysts, but a rough correlation was found in a

TABLE 3. ACIDITIES AND ACTIVITIES OF THE VARIOUS ACID CATALYSTS

Catalyst	Acidity meq/g	Acidity (meq/m²) ×10³	Ethylene conversion %*
SA-1	0.35	1.02	21.8
SA-2	0.40	1.00	32.0
SA-3	0.42	1.82	32.6
SA-4	0.37	1.40	26.9
SA-5	0.36	1.78	23.5
AB-(20)	0.15	0.50	9.5
SM-(20)	0.90	3.66	2.5
$MnSO_4$-SA-3	0.38	1.68	56.7
$ZnSO_4$-SA-3	0.37	1.46	47.5
$Cr_2(SO_4)_3$-SA-3	0.28	2.80	42.5
$CuSO_4$-SA-3	0.34	1.54	40.2
$FeSO_4$-SA-3	—	—	32.1
$NiSO_4$-SA-3	0.27	1.42	15.3
$CdSO_4$-SA-3	0.33	1.15	34.5
$CoSO_4$-SA-3	0.23	1.27	25.5

* Reaction condition: Temperature 300°C
Pressure 30 kg/cm², LHSV (benzene) 1.2 hr⁻¹
Benzene/ethylene 2.5 (mol/mol)

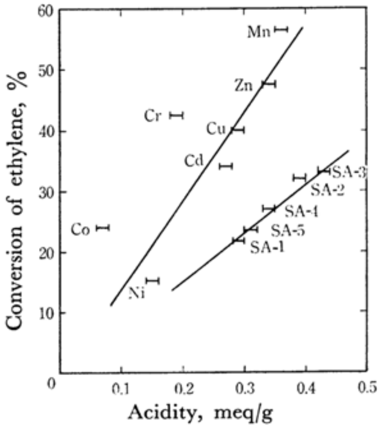

Fig. 2. Relation between the acidity and the conversion of ethylene by various catalysts.
Temperature: 300°C
Benzene/ethylene: 2.5 (mol/mol)
Pressure: 30 (kg/cm²)
LHSV (benzene): 1.2 (hr⁻¹)
* All of the metal sulfates were supported on SA-3 carrier.

series of metal sulfates supported on the SA-3 catalysts, and also within a series of various SA-catalysts of different compositions.

The acidities of these catalysts were measured at different acid strengths with Hammett indicators for both SA and manganous sulfate supported on the SA catalyst. The results are shown in Fig. 3. Some metal sulfate-supported catalysts showed higher conversions than SA in spite of their lower acidities. This may be supposed to illustrate how the surface of SA has been modified by metal sulfates and how the modified acid sites thus produced are responsible for the higher activities.

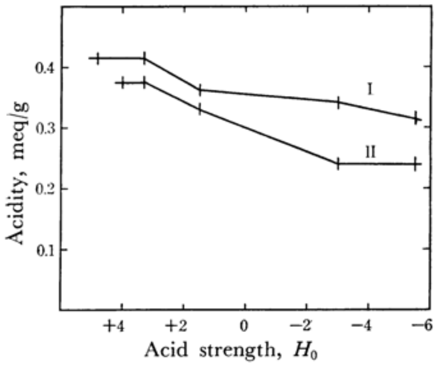

Fig. 3. Distribution of acid strength.
I: SA-3 catalyst
II: $MnSO_4$-SA-3 catalyst

The Effect of the Calcination Temperature on the Catalysts. The metal sulfate-supported catalysts, at various degrees of hydration, exhibited different activities. When the manganous sulfate-supported catalyst was treated before reaction at temperatures of 220—400°C, it was found that the conversion of ethylene increased as the calcination temperature was raised to at least 280°C, but that thereafter it gradually decreased with the increase in the temperature. The effect of the calcination temperature on the activity of the catalyst is shown in Fig. 4.

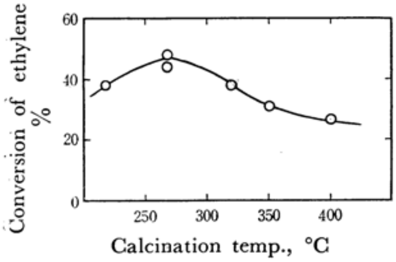

Fig. 4. Effect of calcination temperature.
Temperature: 270°C
LHSV: 1.2 (hr^{-1})
Pressure: 30 (kg/cm^2)
Benzene/ethylene: 2.5 (mol/mol)

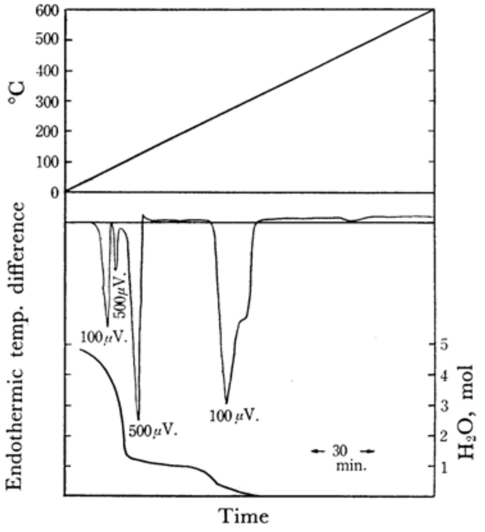

Fig. 5. Normal curves of differential thermal analysis and thermo balance of the hydrate of manganous sulfate.
Sample: $MnSO_4 \cdot 5H_2O$
Sample weight: 500 mg
Referential material: α-Al_2O_3
Atmosphere: Nitrogen
Heating rate: 3.3°C/min

A differential thermal analysis and thermobalance examination of the hydrate of manganous sulfate were then made, as Fig. 5 shows. From the differential thermal analysis the endothermic peaks were found at temperatures of about 70°C, 80°C, 110°C, 260°C and 285°C, These peaks were due to the dehydration of manganous sulfate. From the result of the thermobalance examination, it was also shown that manganous sulfate was changed from monohydrate to nonhydrate at 230—500°C by releasing water.

Tarama *et al.*[2] reported that the acidity of the solid metal sulfate was of the Brönsted type, and that it was due to the residual water of the hydrate. Tanabe *et al.*[3] also reported from an examination of the thermobalance, the X-ray diffraction, and ESR spectra, that the hydrate of nickel sulfate, which showed a maximum acidity, was in the intermediate state between monohydrate and nonhydrate upon calcination at 350°C. In our case of manganous sulfate, the same phenomenon was observed, and the relation between the calcination temperature and the catalytic activity corresponded with the degree of hydration of the catalyst.

Activity Change by Different Carriers. The activities of manganous sulfate-supported catalysts were examined with various carriers,

---

[2] K. Tarama, S. Teranishi, K. Hattori, T. Ishibashi, *Shokubai*, **4**, No. 1, 69 (1962).

[3] T. Takeshita, R. Ohnishi, T. Matsui and K. Tanabe, *ibid*, **6**, No. 4, 270 (1964).

Table 4. Activities of the manganous sulfate supported catalysts with various kind of carriers

Catalyst		Ethylene conversion*
Carrier	Metal sulfate	%
SA-1	$MnSO_4$	34.7
SA-2	$MnSO_4$	57.5
SA-3	$MnSO_4$	56.7
SA-4	$MnSO_4$	42.4
SA-5	$MnSO_4$	25.1
SM-2	$MnSO_4$	3.0
AB-2	$MnSO_4$	10.5
Al_2O_3	$MnSO_4$	4.0
SiO_2	$MnSO_4$	7.8

* Reaction condition: Temperature 300°C; Pressure 30 kg/cm^2; LHSV (benzene) 1.2, Benzene/ethylene 2.5 (mol/mol)

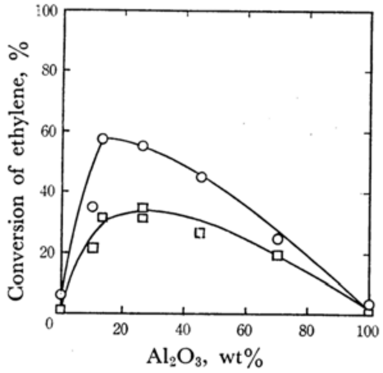

Fig. 6. Comparison of the activities of both catalysts, SA and $MnSO_4$-SA.
—○— $MnSO_4$-SA catalyst
—□— SA catalyst
Temperature: 300°C
Benzene/ethylene: 2.5 (mol/mol)
Pressure: 30 (kg/cm^2)
W/F: 53 (cc-cat/g-mol·hr^{-1})

such as silica-gel, alumina, silica-alumina, silica-magnesia, and alumina-boria, as is shown in Table 4.

Only small increases in activity were found for silica-gel, alumina, alumina-boria, and silica-magnesia carriers. The silica-magnesia carrier did not show any higher activity in spite of its high acidity. This indicates that the catalytic activities were due to their intrinsic properties and not to the number of acid sites. The effect of manganous sulfate addition to silica-alumina on the catalytic activity was also examined, as is shown in Fig. 6. A series of manganous sulfates supported on the SA-3 catalysts always showed higher activities than SA-3 carrier, and the activities varied with the alumina contents in SA. The catalytic activity showed a maximum at 13 wt% of alumina.

As has been mentioned above, it can be said that the increase in activity upon the addition of metal sulfate depends largely upon the activity of the carrier, although it could not be completely explained why some metal sulfates supported on the silica-alumina catalysts showed higher activities than silica-alumina carriers in spite of their lower acidities.

A Comparison of the Reactivity between the Manganous Sulfates Supported on the Silica-alumina Catalyst and the Silica-alumina Catalyst. The effect of the contact time and temperature on the activities of the manganous sulfates supported on the SA-3 and SA-3 catalyst were examined. The relation between the conversion of ethylene and W/F is shown in Fig. 7, while the effect of the temperature on the activity of the catalysts is shown in Fig. 8. Calculating the initial rate of reaction

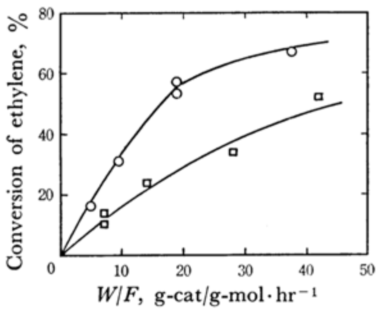

Fig. 7. W/F vs. Conversion of ethylene.
Temperature: 300°C LHSV: 1.2 (hr^{-1})
Pressure: 30 (kg/cm^2)
Benzene/ethylene: 2.5 (mol/mol)
—○— $MnSO_4$-SA-3 —□— SA-3
$r_{(Mn\text{-}SA)_0}=3.6\times10^{-2}$ (g-mol/g-cat·hr)
$r_{(SA)_0}=1.8\times10^{-2}$ (g-mol/g-cat·hr)

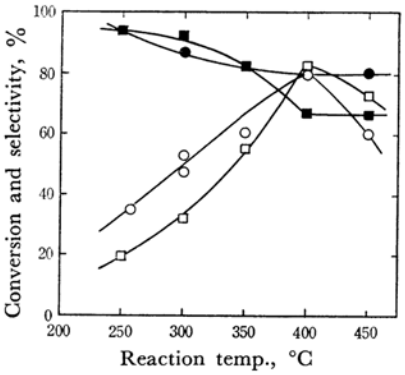

Fig. 8. Effect of reaction temperature.
—○— Conversion } $MnSO_4$-SA-3
—●— Selectivity
—□— Conversion } SA-3
—■— Selectivity
Pressure: 30 (kg/cm^2)
Benzene/etylene: 2.5 (mol/mol)
LHSV: 1.2 (hr^{-1})

from the conversion *vs.* W/F curves in Fig. 7, the initial rate for the manganous sulfate supported on the SA-3 catalyst was twice as fast as the one for the SA-3 catalyst. As Fig. 8 shows, the manganous sulfate-supported catalyst showed a higher conversion of ethylene than the SA-3 catalyst in the temperature range of 250—400°C, but the results were reversed above 400°C. The decrease in the conversion of ethylene was due to the fouling of the catalyst. Selectivity was higher at a low temperature, and the side reaction was negligible for both catalysts. At temperatures above 400°C, the selectivity for the SA-3 catalyst was remarkably reduced.

Summary

The vapor-phase alkylation of benzene with ethylene was carried out over a metal sulfate supported on the SA-catalyst. It was found that some metal sulfates, such as manganous sulfate, zinc sulfate, chromic sulfate, and cupric sulfate, increased the activity of the silica-alumina catalyst, and that these metal sulfates supported on the SA catalysts always showed higher activities than the SA used as a carrier, although the acidities of these catalysts were lower than that of the SA-carrier. Therefore, a direct correlation between the acidity and the activity of the catalyst was not always observed, though one was found within the series of metal sulfates supported on the SA-3 catalyst, and also within the series of various compositions of SA catalysts. It has been suggested that the sites of the metal sulfate-supported catalyst are characteristic and are active in the ethylation of benzene, but the characteristic properties of these catalysts have not been explained.

The authors wish to thank Dr. Hiroshi Watanabe, President of Daikyowa Petrochemical Co., and Dr. Kiyoshi Ikebe, Director of the research and investigation section of that company for permission to publish this work. The authors also wish thank Mr. Shigeyoshi Yoshioka and Mr. Kenji Sakai for their analytical assistance.