Effect of Potassium Promoter on Sintering of Iron Oxide in Catalyst Preparation

Potassium-promoted iron oxide catalyst is one of the best available for dehydrogenation of ethylbenzene to styrene and is used in many commercial plants. The method of preparation of this catalyst is characterized by drastic heat treatment. The patent (*1*) emphasizes that by subjecting the catalyst to a suitable heat treatment, usually between 900° and 950°C for 3 hr, the oxidizing activity of the catalyst can be substantially reduced with only a minor depreciation of the dehydrogenation activity.

We have studied the effect of a potassium promoter on sintering of the iron oxide in the process of catalyst preparation, particularly the change of apparent bulk density and shrinkage of the catalyst.

The catalyst was prepared as follows: Ferric hydroxide prepared by addition of an aqueous solution of ammonia to a solution of ferric nitrate was decomposed to ferric oxide at 500°C in air. The ferric oxide powder and a suitable amount of potassium carbonate were mixed by hand grinding in an agate mortar, and compressed into tablets under a pressure of 100 kg/cm^2. The tablets were calcined at 930°C in an electric furnace for 2 hr in the presence of air, and crushed into granules. The fraction of the catalyst granules passing through a sieve of 1.5 mm size but not of 1.0 mm size was chosen for apparent bulk density measurement. Apparent bulk density was measured as follows: A weighed amount of the granules was placed in an ordinary glass cylinder and the cylinder vibrated till the granules showed a constant volume. Shrinkage of the catalyst tablet, 0.5 cm long and 1.00 cm in diameter before calcination, was measured by an ordinary micrometer after cooling the tablet to room temperature. The maximum variation between samples heated in the same way was less than 2%. Specific surface area was obtained by applying the BET method to the adsorption isotherm of nitrogen at −196°C. Total pore volume was obtained from the amount of nitrogen adsorbed at the relative pressure of 0.984 in the adsorption of nitrogen at −196°C.

TABLE 1
APPARENT BULK DENSITY OF THE FINISHED CATALYST WITH VARIOUS POTASSIUM PROMOTER CONTENTS

K_2O (wt %)	0	0.5	3.0	10.0
Apparent bulk density (g/cc)	1.86	1.69	1.43	1.30

The apparent bulk density of the finished catalyst with various concentrations of potassium promoter is shown in Table 1. The concentration of potassium promoter is indicated as weight percent of potassium oxide. Apparent bulk density of these catalysts before calcination was 1.40

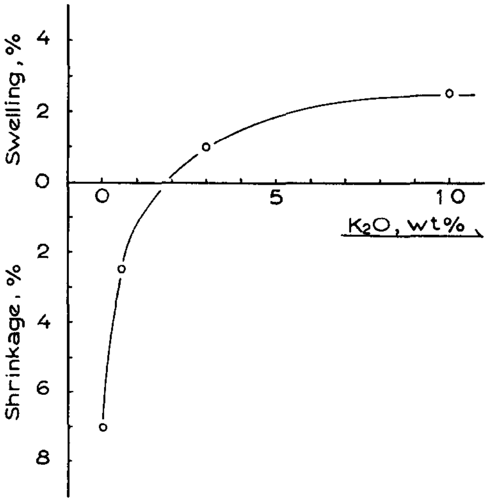


FIG. 1. Shrinkage or swelling of the catalyst by calcination in the process of preparation.

to 1.45 g/cc, and in the absence of potassium promoter its value increased to 1.86 after calcination. The increase in apparent bulk density by calcination is diminished progressively with increasing concentration of potassium oxide. As the concentration of potassium oxide reaches about 3%, the apparent bulk density of the finished catalyst becomes lower than that of uncalcined catalyst. Figure 1 shows the effect of the concentration of potassium oxide on shrinkage or swelling of the catalyst tablet. Shrinkage or swelling of the tablet is indicated as a change of the diameter. Shrinkage of the tablet without potassium oxide is 7%, whereas swelling was observed when the concentration of potassium oxide was above 3%. As shown in Fig. 2, the relation of shrinkage or swelling to apparent bulk density is linear except when the concentration of potassium oxide was above 3%. Table 2 illustrates the specific surface area and the total pore volume of the catalyst with and without potassium promoter. The differences between the values of the specific surface area and the total pore volume for iron oxide catalysts with and without potassium promoter are slight.

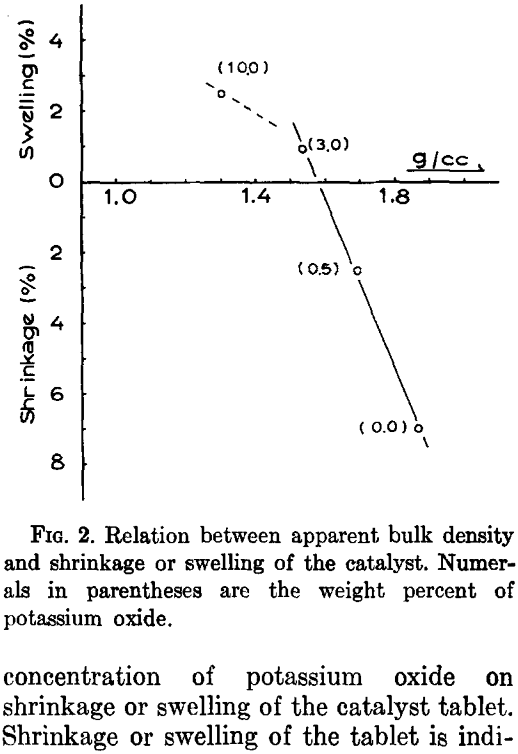


FIG. 2. Relation between apparent bulk density and shrinkage or swelling of the catalyst. Numerals in parentheses are the weight percent of potassium oxide.

TABLE 2

SURFACE AREA AND PORE VOLUME OF THE CATALYST

	Surface area (m^2/g)	Pore volume (cc/g)
Fe_2O_3 uncalcined	28	0.33
Fe_2O_3 calcined	2.5	0.20
Fe_2O_3-K_2O (3 wt %) uncalcined	29	0.33
Fe_2O_3-K_2O (3 wt %) calcined	3.0	0.18

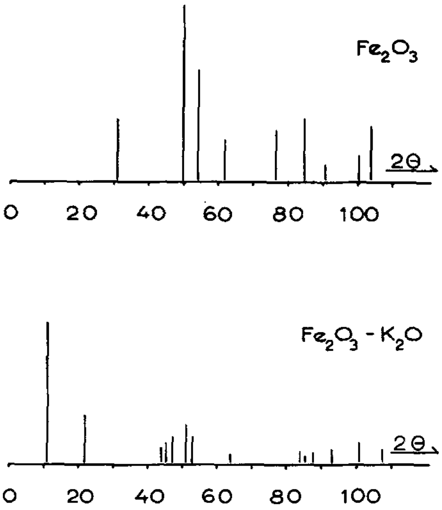


FIG. 3. X-Ray powder diffraction diagrams of iron oxide catalyst with and without potassium promoter. Radiation, Cr — $K\alpha$; K_2O, 10 wt %.

The effect of potassium promoter on prevention of sintering of the catalyst appears to be caused largely by the formation of $K_2Fe_{22}O_{34}$. The specific gravity of $K_2Fe_{22}O_{34}$ is 4.24 (*2*), whereas that of ferric oxide is 5.13. X-Ray powder diffraction diagrams of the iron oxide catalyst with and without potassium promoter are given in Fig. 3. The diagram of the iron oxide catalyst with potassium oxide is essentially similar to that of $K_2Fe_{22}O_{34}$ (*3, 4*). The weight percent of K_2O in $K_2Fe_{22}O_{34}$ is 5.06, and this value is near to the composition where the deviation from the linear relation was observed, as shown in Fig. 2.

REFERENCES

1. EGGERTSEN, F. T., AND VOGE, H. H., U. S. Patent 2,414,585.

2. OTSUBO, Y., AND YAMAGUCHI, K., *J. Chem. Soc. Japan* **82,** 676 (1961).

3. ADELSKOLD, V., *Arkiv. Kemi. Min. Geol.* **12A** (No. 29), 1 (1938).

4. GORTER, E. W., *Philips Res. Rept.* **9,** 259 (1954).

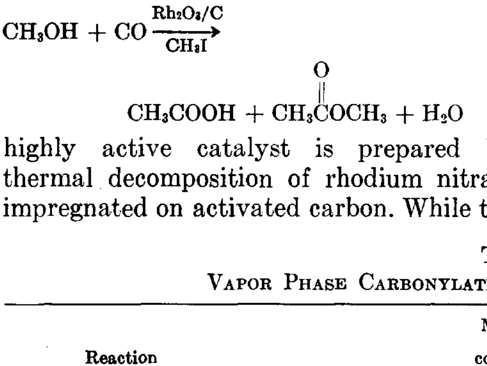
K. SHIBATA
T. KIYOURA

Central Research Laboratory
Toyo Koatsu Industries, Inc.
Kuden, Totsukaku
Yokohama, Japan

Received October 1, 1968

Vapor Phase Carbonylation of Methanol to Acetic Acid

Low pressure carbonylation of methanol using a soluble rhodium catalyst in the liquid phase has recently been reported (*1*). We wish to report that the vapor phase carbonylation of methanol to acetic acid using a supported rhodium catalyst and a methyl iodide promoter has now been effected at atmospheric pressure Eq. (1). A highly active catalyst is prepared by thermal decomposition of rhodium nitrate impregnated on activated carbon. While the active catalytic species has not been fully defined, the results obtained with this system are similar to those found in liquid phase studies (*1, 2*). This catalyst (3% rhodium content) is effective at low temperatures (175–250°C) and low pressures (15–300 psia) with very high selectivity (>99%).



$$CH_3OH + CO \xrightarrow[CH_3I]{Rh_2O_3/C} CH_3COOH + CH_3\overset{\overset{O}{\|}}{C}OCH_3 + H_2O \quad (1)$$

Some typical results obtained with a 10 cc catalyst charge (4.5–5.0 g) in fixed bed flow reactor system are presented in Table 1. It may be seen that even at atmospheric pressure (runs 1–3) reasonable conversions of methanol are obtained. (At these conversions methyl acetate is the major product obtained due to esterification of the

TABLE 1
VAPOR PHASE CARBONYLATION OF METHANOL TO ACETIC ACID[a]

Run no.	Reaction: Pressure (psia)	Reaction: Temp. (°C)	Feed rate (moles/hr): CH_3OH	Feed rate (moles/hr): CH_3I	Feed rate (moles/hr): CO	Methanol conversion[b] (mole %)	Product analysis (weight %): $[CH_3]_2O$	CH_3OH	CH_3I	CH_3OAc	HOAc	H_2O
1	15	175	0.25	0.02	0.50	9.5	0.5	59.1	20.3	15.3	0.7	4.1
2	15	210	0.25	0.02	0.50	14.8	0.5	50.9	19.1	21.4	2.4	5.7
3	15	245	0.25	0.02	0.50	21.5	0.5	42.0	17.3	26.6	6.4	7.2
4	215	200	0.25	0.006	0.50	92.6	0	0.2	1.0	9.0	87.6	2.2
5	215	200	0.25	0.002	0.50	88.3	0	0.4	1.1	14.2	80.7	3.6
6	135	205	1.18	0.035	1.98[c]	15.4	0.3	53.9	9.1	27.9	1.4	7.4
7	175	205	1.18	0.035	1.98[c]	20.8	0.4	45.6	8.7	33.7	2.4	9.2
8	215	205	1.18	0.035	1.98[c]	22.2	0.4	42.9	8.7	35.8	2.4	9.8

[a] 10 cc catalyst (4.5–5.0 g) used in a fixed bed flow reactor system.

[b] Calculated as moles $\left[\frac{CH_3OAc + HOAc}{2[CH_3]_2O + CH_3OH + 2CH_3OAc + HOAc}\right] \times 100.$

[c] Feed diluted with 1.52 moles/hr of hydrogen.