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Remarkable Effects of Supporting Oxides for Complete Oxidation of Styrene

It is well known that catalyst supports act not only as supports but also as a kind of promotor for catalytic reactions (*1*, *2*). In this brief paper, a series of 66 catalysts were prepared by combining six supports, Al_2O_3, Al_2O_3/SiO_2, SiO_2, TiO_2, ZrO_2, MgO, with 12 oxides of following metals, K, Ca, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Zr, and Mg. The former three supports were Neobead-C, Neobead-D, and Silbead-N obtained from Mizusawa Ind. Chem. Ltd. and the rests were first-grade reagents from Kanto Chem. Co. The surface area of these supports was 139 (Neobead-C), 125 (Neobead-D), 394 (Silbead-N), 4.6 (TiO_2), 8.6 (ZrO_2), 6.1 m^2/g (MgO), respectively. The amount of promotor material impregnated on each support was 5 wt% as metal. Their catalytic activity was tested for the complete oxidation of styrene which is one of the malodorous hydrocarbons.

All materials were made by the same method; the catalyst supports were impregnated in an aqueous solution of metal nitrates, however, K_2CO_3, NH_4VO_3, and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were used in case of potassium, vanadium, and molybdenum,

TABLE 1

Catalytic Conversion to CO_2[a]

Promotor metal oxides	Catalyst supports					
	Al_2O_3	Al_2O_3/SiO_2	SiO_2	TiO_2	ZrO_2	MgO
Potassium oxide	2	0	0	0	2	0
Calcium oxide	2	0	0	4	0	0
Chromium oxide	6	8	2	4	13	2
Manganese oxide	3	0	0	0	2	2
Cobalt oxide	3	2	0	2	100	0
Vanadium oxide	16	20	2	49	34	—
Copper oxide	21	31	4	100	100	34
Nickel oxide	3	0	0	2	3	0
Molybdenum oxide	2	4	6	18	23	5
Iron oxide	5	12	0	2	9	2
Zirconium oxide	11	4	0	—	—	0
Magnesium oxide	2	4	3	—	—	—

[a] The conversion is expressed as percentage of styrene converted to CO_2. The materials supported on Al_2O_3 and Al_2O_3/SiO_2 are spherical beads of 3 to 4 mm diameter. The materials supported on SiO_2 are crushed beads of 10 to 14 mesh which were crushed by heat treatment. The particle size of materials supported on TiO_2, ZrO_2, and MgO is 5 to 14 mesh.

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then each was dried at 200°C in air overnight, and subsequently heated at 500–600°C in air overnight. The shape or particle size of each catalyst is indicated in Table 1.

Catalytic activity measurement was made in a microreactor, using a stream of diluent styrene, 200 ppm, in air. Space velocity was 10,000/hr. The catalyst was mounted in an 8-cm-long glass reactor of 1.0-cm diameter, and the temperature was maintained at 300°C. The stoichiometry of the reaction is described by the equation shown below and the conversion (%) to carbon dioxide was estimated according to it.

$$C_8H_8 + 10\,O_2 = 8\,CO_2 + 4\,H_2O.$$

The concentration of styrene and carbon dioxide in effluent gas was measured by gas chromatography and infrared spectra.

Catalytic activities of 66 catalysts are summarized in Table 1. From this table, one may find conspicuous effects of supporting materials, which greatly depend on the combination of supports and promotor metals. It is worthy of emphasis that copper oxide–TiO_2, copper oxide–ZrO_2, and cobalt oxide–ZrO_2 gave prominent activity for complete oxidation of styrene. Among these three catalysts, cobalt oxide–ZrO_2 is quite unique, because cobalt oxide supported on other materials gives no activity for this oxidation reaction. As the catalytic activity of ZrO_2 itself is rather low except for a few examples such as isomerization of olefins and dehydration of alcohols, observed unique high catalytic activity is caused by a combination of cobalt oxide and ZrO_2. Though these findings are neither per unit area nor general, the present experiment indicates the possibility of a more effective catalyst of binary oxides for oxidation reaction.

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REFERENCES

1. Boudart, M., *Adv. Catal.* **20**, 153 (1969).
2. Krylov, O. V., "Catalysis by Non-Metals." Academic Press, New York and London, 1970.

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