Promoting Effect of TiO_2 and Al_2O_3 Supports on the Activity of Vanadium Oxide Catalyst for the Oxidation of Benzene Measured in Terms of the Turnover Frequency

By MAKOTO INOMATA, AKIRA MIYAMOTO,* and YUICHI MURAKAMI
(*Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Nagoya* 464, *Japan*)

Summary. The following relationship, V_2O_5–TiO_2 > unsupported V_2O_5 > V_2O_5–Al_2O_3, was found to hold for the turnover frequency for the oxidation of benzene, which indicates the promoting effect of the TiO_2 support on the reaction with vanadium oxide catalyst.

TiO_2 supports promote the oxidation of hydrocarbons on vanadium oxide catalysts,[1–3] and this promotion has been suggested to be due to two effects: increase in the effective surface area of V_2O_5 and enhanced activity of the V=O bond in V_2O_5–TiO_2.[1] The former effect has already been proven from the measured number of surface V=O species on V_2O_5–TiO_2 and V_2O_5–Al_2O_3 catalysts.[4] In this study, the turnover frequency for the oxidation of benzene on V_2O_5–TiO_2 and V_2O_5–Al_2O_3 was determined in order to establish the latter effect.

TiO_2 composed of anatase, was prepared by hydrolysis of $Ti(SO_4)_2$ followed by calcination in air at 873 K, while Al_2O_3 was commercially available (Sumitomo γ-Al_2O_3). Vanadium oxide supported on the carriers was prepared by impregnation of the carrier with an oxalic acid solution of ammonium metavanadate followed by calcination at 773 K in a stream of O_2. The number of surface V=O species on the catalysts was measured by the rectangular pulse technique described previously.[4,5] V_2O_5–TiO_2 (10 mol %) and V_2O_5–Al_2O_3 (25 mol %), treated with an ammoniacal solution, were prepared in a similar manner to that of Yoshida *et al.*[6] These catalysts were confirmed by the rectangular pulse technique to be monolayer catalysts.[5] Kinetic studies were carried out with the conventional flow method. In the oxidation of benzene, maleic anhydride, benzoquinone, CO, and CO_2 were produced, although the selectivity to benzoquinone was low.

TABLE. Rate and turnover frequency for the oxidation of benzene on V_2O_5–TiO_2 and V_2O_5–Al_2O_3[a]

Catalyst	Content of V_2O_5 /% mol	Rate /μmol g^{-1} s^{-1}	Turnover frequency /ks^{-1}
V_2O_5–TiO_2	1	10.2	181
	2	15.3	128
	5	18.6	101
	10	16.8	124
	25	6.1	101
	50	4.2	65
	100[b]	1.3	58
V_2O_5–Al_2O_3	1	0.0	—[c]
	2	0.2	(50)[d]
	5	1.6	20
	10	10.6	30
	25	17.4	43
	35	15.7	43
	50	10.2	41
	100[b]	1.3	58
V_2O_5–TiO_2 (monolayer)[e]		9.8	78
V_2O_5–Al_2O_3 (monolayer)[e]		0.8	42

[a] Reaction conditions: temp. 662 K; concentration of benzene, 1.43 mol %; concentration of O_2, 20 mol %. [b] Unsupported V_2O_5. [c] The rate of the reaction and the number of surface V=O species were both negligibly small. [d] Errors may have been caused by the slow rate of the reaction and the small number of surface V=O species. [e] The fraction of the (010) face of V_2O_5 on the surface of the catalyst, *i.e.*, $S_{(010)}/S_{BET}$ defined in Ref. 4 was 35% for V_2O_5–TiO_2 (monolayer) and 2% for V_2O_5–Al_2O_3 (monolayer).

The Table shows the results for the rate and turnover frequency for the oxidation of benzene under excess oxygen conditions where the rate of the reaction was zeroth order and first order with respect to the concentrations of O_2 and benzene, respectively. Here, the turnover frequency is defined as the rate of benzene disappearance divided by the number of surface V=O species. As shown in the Table, at any content of V_2O_5, the turnover frequency for V_2O_5–TiO_2 was larger than that for the unsupported V_2O_5, although the difference in the turnover frequency between V_2O_5–TiO_2 and the unsupported V_2O_5 became smaller with greater content of V_2O_5. It should also be noted that the turnover frequency for the V_2O_5–TiO_2 mono-layer catalyst is larger than that for the unsupported V_2O_5 catalyst. However, the turnover frequency for V_2O_5–Al_2O_3 was smaller than that for the unsupported V_2O_5. Correspondingly, the activation energy of the reaction on V_2O_5–TiO_2 (*ca.* 84 kJ mol^{-1}) was smaller than that on the unsupported V_2O_5 (92 kJ mol^{-1}), which was, in turn, smaller than that on V_2O_5–Al_2O_3 (*ca.* 120 kJ mol^{-1}). These data clearly indicate the enhanced activity of the surface V=O species on V_2O_5–TiO_2 for the oxidation of benzene.

(*Received*, 22*nd November* 1979; *Com.* 1219.)

[1] D. J. Cole, C. F. Cullis, and D. J. Hucknall, *J. Chem. Soc., Faraday Trans.* 1, 1976, **72**, 2185.
[2] G. C. Bond, A. J. Sárkány, and G. D. Parfitt, *J. Catal.*, 1979, **57**, 176.
[3] A. Vejux and P. Courtine, *J. Solid State Chem.*, 1978, **23**, 93.
[4] M. Inomata, A. Miyamoto, and Y. Marukami, *J. Chem. Soc., Chem. Commun.*, 1979, 1009.
[5] A. Miyamoto, Y. Yamazaki, M. Inomata, and Y. Murakami, *Chem. Lett.*, 1978, 1355.
[6] S. Yoshida, T. Iguchi, S. Ishida, and K. Tarama, *Bull. Chem. Soc. Jpn*, 1972, **45**, 376.