Influence of Coprecipitated Cobalt on the Reducibility of Vanadium Phosphate

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The reducibility of β-vanadium phosphate doped with cobalt has been measured and correlated with changes in the textural properties brought about by this dopant.

In recent years numerous patents have been issued for processes which attempt to increase the activity, selectivity, and lifetime of vanadium phosphate based catalysts used in the selective oxidation of n-butane or butenes to maleic anhydride by the addition of small quantities of a third metal.[1–6] The exclusive role of some additives is probably to increase the catalyst lifetime by supressing sublimation of phosphorus at the high temperatures at which these catalysts work and thus retaining an optimum P : V ratio.[7,8] This is the case with alkaline earth metals. Other metals have been reported to increase the selectivity. Among the metals which have been reported in the patent literature as dopants for this purpose Zn,[4,9–11] Ti,[10] U,[12] Cu,[3,5] Si,[6] and Ca[2] have figured prominently. However no explanation of their mode of action has been reported. In particular it is known that additives may drastically change the textural properties of catalysts,[13] but there have been no reports of this aspect for vanadium phosphate based catalysts.

We report herein an attempt to determine the influence of coprecipitated cobalt on the textural properties and reactivity towards hydrogen of well crystallised β-VPO_5. Indeed it is generally recognised that the catalytic properties of oxidation catalysts are related to their reducibility and oxidisability.[14] We have shown that this is true for undoped VPO catalysts.[15–17] It was thus logical to investigate together the influence of cobalt on the textural properties and reducibility of doped catalysts.

In order to demonstrate as clearly as possible the influence of added cobalt it was necessary to begin with a well defined system. Therefore we could not choose a catalyst which would give an optimum selectivity as this would contain several phases.[16] Instead, the P : V ratio (= 1) and calcination conditions were chosen so as to give an undoped material consisting almost entirely of β-VPO_5 whose structure is well known.[18]

The catalysts used in this study were prepared by adding 9.1 g V_2O_5 and the appropriate amount of $Co(NO_3)_2.6H_2O$, to give Co : V atomic ratios in the range 0—0.05, to 150 g 85% lactic acid in water and refluxing for 16 h. This was followed by the addition of 11.42 g 85% H_3PO_4 in water and the resulting solution was refluxed for a further 4 h. The excess lactic acid was evaporated off and the solid obtained was calcined at 773 K in air for 16 h. This material was made into pellets, broken up, and sieved. The particles of size 0.315—0.5 mm were retained. The average oxidation states of vanadium were measured by dissolution of the catalysts in 2 M H_2SO_4 followed by double titration using $KMnO_4$ and $Fe(NH_4)_2(SO_4)_2$.[15,16] Values close to +4.9 were obtained over the whole range of cobalt contents. Specific surface areas were measured by the Brunauer–Emmett–Teller (B.E.T.) method using nitrogen as the adsorbate at 77 K. Reductions by hydrogen gas were carried out on a McBain spiral spring balance at 573 K. The full details of this procedure are given elsewhere.[17]

Table 1 summarises the reduction behaviour of the various cobalt containing catalysts in the form of the percentage weight losses measured after their exposure to hydrogen for the periods indicated. A 5% weight loss corresponds to the total transformation of β-VPO_5 into $(VO_2)_2P_2O_7$, *i.e.* the

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Table 1. Influence of added cobalt on the reducibility and surface area of β-VPO_5.

Co : V	Weight loss, %[a]				B.E.T. surface area/ $m^2\ g^{-1}$
	2 h	4 h	8 h	15 h	
0.0	1.78	2.38	2.96	3.41	9.7
0.01	0.99	1.57	2.20	2.85	6.8
0.025	0.61	1.00	1.55	2.24	6.1
0.05	0.30	0.45	0.80	1.27	3.3

[a] Percentage weight losses after exposure of the catalyst to hydrogen at 573 K for the periods indicated.

reduction of vanadium from the v to the iv oxidation state. These data indicate that coprecipitated cobalt strongly inhibits the reduction process.

The B.E.T. surface areas of the catalysts are reported in Table 1. A good correlation was observed between reducibility and surface area indicating that the primary influence of cobalt was to modify the textural properties of β-VPO_5 thereby reducing its surface area and thus its reactivity towards hydrogen.

We thank the Service de Programmation de la Politique Scientifique, (Belgium), for financial support, Dr P. Grange for his advice, and F. Blondeau for help with some of the measurements.

Received, 8th November 1982; Com. 1267

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