Enhanced Activity of Promoted $(VO)_2P_2O_7$ by Preferential Exposure of the (020) Plane

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The loading of various promoters on $(VO)_2P_2O_7$ enhances its activity in the selective oxidation of n-butane to maleic anhydride by inducing the preferential exposure of the (020) plane.

It is widely accepted that $(VO)_2P_2O_7$ is the active phase for the selective oxidation of n-butane to maleic anhydride[1] and that the activity and selectivity depend on the crystallographic plane exposed on the surface.[2] The (020) plane of $(VO)_2P_2O_7$, characterized by the presence of paired vanadium pseudo-octahedra orientated *trans* to one another, has been claimed to be the catalytically selective plane.[3] The loading of appropriate promoters is expected to improve the catalytic performance, and many attempts have been made to synthesize improved VPO catalysts by adding various elements.[4] However, the mechanism of promotion effects has not yet been well investigated. The present communication reports that the loading of promoters induces the preferential exposure of the (020) plane leading to high activity and selectivity.

$(VO)_2P_2O_7$ was prepared in an organic medium by the reported method.[5] Ti, W, Zr, Mo, Fe, Co, Ni, Cu, Ca, K, Si, Ge, and La were chosen as promoter elements. All the promoted catalysts were prepared by impregnation of the precursor ($VOHPO_4 \cdot 0 \cdot 5H_2O$) with a solution containing the required amount of promoter element. The atomic content of the promoter was 5%. The solid product thus obtained was activated in a flow of 2% n-butane in air at 673 K. *X*-Ray powder diffraction patterns were obtained with Cu-K_α radiation. The Brunauer–Emmett–Teller (B.E.T.) surface area was determined by using a conventional flow-type apparatus with N_2 as an adsorbate. The oxidation of n-butane was carried out using a continuous flow reactor. The space velocity was 5660 ml g^{-1} h^{-1}; the reactant gas contained 2.0% of n-butane, 18.8% of oxygen and 79.2% of nitrogen. The products were analysed by on-line gas chromatography.

The *X*-ray diffraction patterns of the promoted and unpromoted catalysts agreed well with that of β-$(VO)_2P_2O_7$ prepared in an organic medium as reported in the literature.[6]

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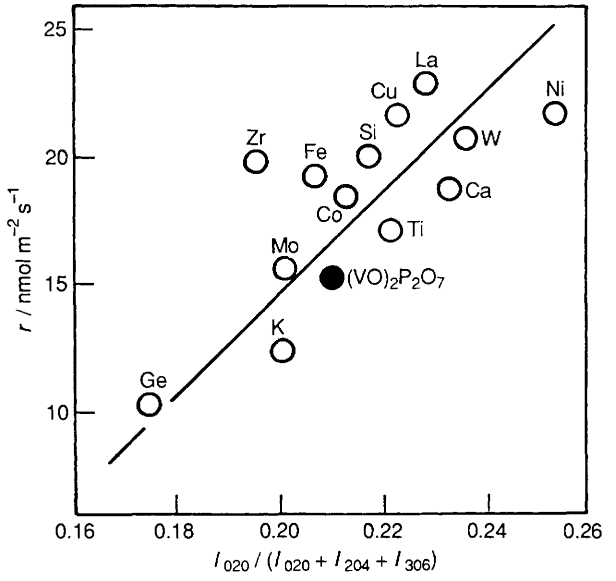

Figure 1. Specific reaction rate (r) of n-butane oxidation at 663 K as a function of exposure of the (020) plane of promoted $(VO)_2P_2O_7$ catalysts.

However, the relative intensity of the (020) plane differed from catalyst to catalyst, indicating that the morphology of the $(VO)_2P_2O_7$ crystal is modified by the loading of promoters.

The loading of promoters improved the activity in the oxidation of n-butane to maleic anhydride. Although the B.E.T. surface areas of all promoted catalysts are higher than that of the umpromoted one, the improvement of activity is, in most cases, due to the increase in specific reaction rate defined as the reaction rate per surface area, as shown in Figure 1. The selectivity to maleic anhydride is also improved significantly in most cases. The highest selectivity (*ca.* 80%) is obtained on Co-promoted $(VO)_2P_2O_7$, while the selectivity of the unpromoted catalyst is only 51% under the same conditions.

The specific reaction rate may be directly correlated with the preferential exposure of the (020) planes, defined as $I_{020}/(I_{020} + I_{204} + I_{306})$. I_{020}, I_{204}, and I_{306} are the intensities of the strongest three lines in the X-ray diffraction patterns. Figure 1 indicates that the specific reaction rate increases almost linearly with exposure of the (020) plane. The oxidation of n-butane to maleic anhydride is a 14-electron oxidation involving the abstraction of eight hydrogen atoms and insertion of three oxygen atoms. Such a complex catalytic oxidation needs the co-operative action of two strong functions: *i.e.* an oxidizing function and an acidic function.[1] Lewis and Brønsted acid sites and active lattice oxygen (V=O species) have been confirmed to exist on the (020) plane, and the (020) plane has been suggested as the active plane for the selective oxidation of n-butane.[7] Thus, the correlation shown in Figure 1 strongly suggests that the loading of promoters enhances the activity of the $(VO)_2P_2O_7$ catalyst by inducing the preferential exposure of the (020) plane. Although in most cases the selectivities improved significantly, a direct relationship between the selectivity and the exposure of the (020) plane has not been found. This suggests a modification of the local surface structure and/or the property of individual active sites by the loading of the promoters.

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