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HCl-Vapour-Etching for the Preparation of Monolayer V_2O_5/TiO_2 Catalysts with High Exposure of Active Sites

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A novel method was proposed for the preparation of monolayer V_2O_5/TiO_2 catalysts with very high exposure of active sites. In the method, extra vanadium species in highly loaded V_2O_5/TiO_2 catalysts are selectively etched by HCl vapour.

Much attention has been paid to the supported V_2O_5 catalyst near monolayer-region because of its superior catalytic properties.[1] In the monolayer catalyst, all the vanadium ions are to be exposed on the surface, which is expected to be one of the factors leading to the superior catalytic properties. However, all the vanadium ions do not form surface V=O species which are the active sites for $NO-NH_3$ reaction and oxidations of some hydrocarbons because of the presence of inactive isolated vanadium species.[2] That is, the dispersion of V_2O_5, defined as the ratio of the number of surface V=O species to that of V_2O_5, is less than 60%.

In the present letter, we describe that a monolayer V_2O_5/TiO_2 catalyst with high exposure of active sites can be obtained by a novel method, selective etching of extra vanadium species by HCl vapour from highly loaded V_2O_5/TiO_2 catalyst.

Impregnated V_2O_5/TiO_2 catalysts were prepared by impregnating TiO_2 (Nippon Aerosil, P25) with oxalic acid solution of ammonium vanadate followed by drying and subsequent calcination in flowing O_2 at 773 K for 3 h.[2] A monolayer catalyst was prepared by exposing the 20 mol% V_2O_5/TiO_2 catalyst thus prepared to a flow of a mixture of 5.4% HCl vapour and He ($60 cm^3$/min) for 14 h at 573 K. The other types of monolayer catalysts were prepared, for the comparison, by immersing the 20 mol% V_2O_5/TiO_2 catalyst in 0.3 mol dm^{-3} ammoniacal solution for 48 h at room temperature followed by washing with water,[3,4] and by exposing the TiO_2 support to a flow of $VOCl_3$-He mixture for 3 days at 473 K followed by the hydrolysis with H_2O vapour at the same temperature.[5] The catalysts thus obtained were dried and calcined in the same way as above.

The content of supported vanadium was determined by an inductively coupled plasma instrument (ICP, Shimadzu ICPQ-1000). The NARP ($NO-NH_3$ rectangular pulse) technique was used to measure the number of surface V=O species and to confirm the monolayer structure in the same way as described previously.[4]

When HCl vapour was fed over a highly loaded V_2O_5/TiO_2 catalyst, orange-colored solid products were precipitated in a water-trap settled immediately after the catalyst bed, indicating that V_2O_5 on the catalyst was removed. Actually, the V_2O_5 content was decreased to 1.08 mol% by the treatment for 14 h at 573 K.

Table 1. The number and the dispersion of surface V=O species of various V_2O_5/TiO_2 catalysts

	Impregnation	CVD of $VOCl_3$	Etching by NH_4OH	Etching by HCl
V_2O_5 (μmol g^{-1})	124	148	159	134
$V{=}O_S$ (μmol g^{-1})	30	64	84	119
Dispersion (%)	24	43	53	89

Probably the following reaction, ΔG° of which is -94 kJ/mol at 573 K, would occur:

$$V_2O_5(s) + 6HCl(g) \longrightarrow 2VOCl_3(g) + 3H_2O(g).$$

As shown in Table 1, the impregnation method gave only a poor dispersion, which agrees well with the reported results that considerable amount of inactive vanadium species are formed at low V_2O_5 content.[2] The CVD of $VOCl_3$ and the NH_4OH-etching resulted in higher dispersion than the impregnation, but the dispersion was still less than 55%. In contrast to these results, the HCl-vapour-etching method gave a very high dispersion, i.e., ca. 90%, indicating that the monolayer catalyst is composed of 90% active phase and only 10% inactive vanadium species. HCl vapour may react selectively with inactive surface vanadium species as well as extra V_2O_5 lamellae deposited on the first layer to remove these species, leading to high exposure of active sites.

One may suspect that chlorine possibly remains on the catalyst and is hardly removed. It should be noted, however, that the residual chlorine can be easily removed by gas-phase NH_3 treatment.[6]

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