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DETERMINATION OF EXPOSED SURFACE AREA OF V_2O_5 ON V_2O_5/Al_2O_3 CATALYSTS BY TPD OF NH_3

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Exposed surface area of V_2O_5 on V_2O_5/Al_2O_3 catalysts was determined by temperature programmed desorption of NH_3. The exposed surface was mostly composed of (010) face of V_2O_5 at low V_2O_5 content, but the exposed surface areas of other faces were comparable to that of (010) face at high V_2O_5 content.

The determination of exposed surface area of active component can lead to better understanding of catalytic activity of supported catalysts. But no general methods have been developed for supported oxide catalysts. We have successfully measured the number of surface V=O species of supported V_2O_5 catalysts by rectangular pulse technique in which the reaction of NO with NH_3 on surface V=O was utilized.$^{1)}$ In the present letter, we describe the determination of exposed surface area of V_2O_5, $S_{V_2O_5}$, on V_2O_5/Al_2O_3 catalysts by temperature programmed desorption (TPD) of NH_3.

The catalysts used were V_2O_5/Al_2O_3(VPS) described elsewhere.$^{2)}$ TPD of NH_3 was conducted with a conventional TPD apparatus$^{3)}$ with a heating rate of 5 K/min, after the catalyst was calcined at 773 K for 0.5 h, exposed to NH_3 at room temperature for 0.5 h, and evacuated at room temperature for 0.5 h.

TPD spectra on the catalysts were essentially identical to each other. It had a single peak with a peak maximum around 350 K and a long tailing. Figure 1A shows the surface concentration of adsorbed NH_3, that is, the ratio of the amount of desorbed NH_3 in TPD run to the BET surface area of catalyst. The concentration was the lowest on Al_2O_3, and increased with an increase in V_2O_5 content. The difference in the concentration between V_2O_5 and Al_2O_3 was enough large to evaluate $S_{V_2O_5}$ on the assumption that the concentrations of adsorbed NH_3 on exposed surfaces of V_2O_5 and Al_2O_3 are identical to those on unsupported V_2O_5 and Al_2O_3 alone, respectively. Since the amount of desorbed NH_3, $[NH_3]$, consists of those desorbed from the exposed surfaces of V_2O_5 and Al_2O_3, it can be expressed as follows:

$$[NH_3] = C_V \cdot S_{V_2O_5} + C_{Al} \cdot (S_{BET} - S_{V_2O_5}) \qquad (1)$$

where S_{BET} and $S_{BET}-S_{V_2O_5}$ are the BET surface area of catalyst and the exposed surface area of Al_2O_3, respectively, and C_V and C_{Al} are the surface concentrations of NH_3 on unsupported V_2O_5 and Al_2O_3 alone, respectively. Since C_V, C_{Al}, S_{BET}, and $[NH_3]$ can be measured, one can calculate $S_{V_2O_5}$ from the equation.

Figure 1B shows $S_{V_2O_5}$ thus calculated per unit weight of support, Al_2O_3. It increased with V_2O_5 content; especially it increased steeply around 10 mol% of V_2O_5. Figure 1B includes the exposed surface area of (010) face of V_2O_5, S_{010},$^{2)}$ calculated from the number of surface V=O species. The trend of S_{010} is similar to that of

$S_{V_2O_5}$, which supports the calculated results of the latter. The difference between $S_{V_2O_5}$ and S_{010} corresponds to exposed surface areas of the other faces of V_2O_5. Figure 1B indicates that the exposed surface of V_2O_5 consists mostly of (010) face at V_2O_5 content below 10 mol%, while, at high V_2O_5 content, the exposed surface areas of the other faces are comparable to S_{010} and the ratio of S_{010} to $S_{V_2O_5}$ is close to S_{010}/S_{BET} of V_2O_5, *ca.* 0.5.[1)]

The present method is based on the above-mentioned assumption which is similar to that in the determination of metal surface area that chemisorption stoichiometry is independent of surface structure.[4)] The assumption may be valid as a working basis, unless a new compound is formed by the reaction between active component and support. IR spectra of adsorbed NH_3 seemed to support the assumption. On Al_2O_3, two bands ascribable to coordinately adsorbed NH_3[5)] were observed at 1610 and 1260 cm^{-1}, and, on V_2O_5, a band ascribable to ammonium ion was observed at 1420 cm^{-1}. IR spectra on V_2O_5/Al_2O_3 catalysts had only these three bands, indicating that the adsorbed NH_3 on the catalysts was the superposition of these on unsupported V_2O_5 and Al_2O_3 alone.

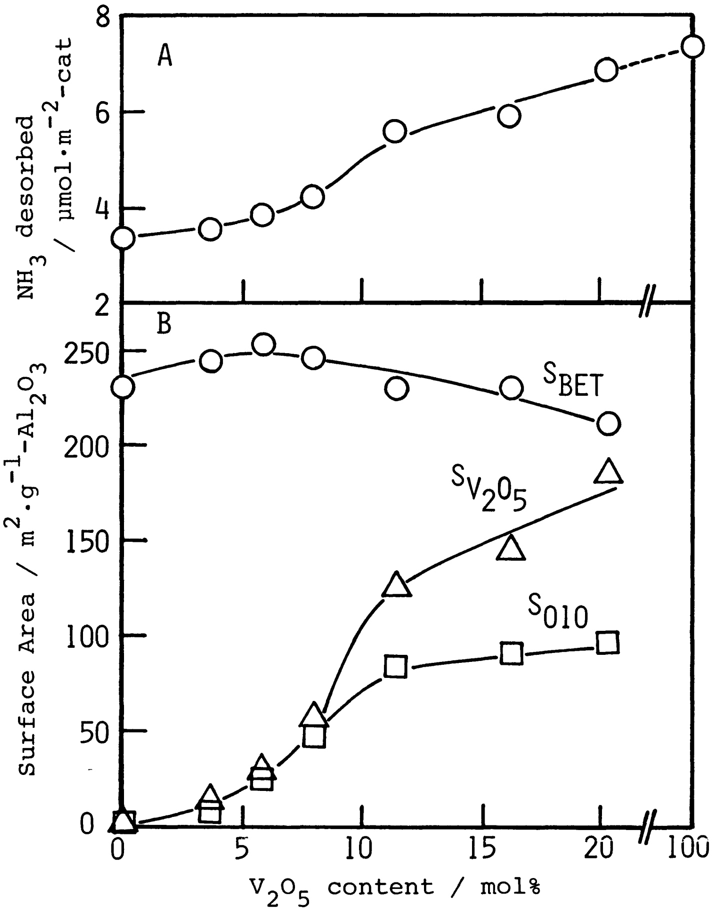

Fig. 1. Surface concentration of NH_3 and exposed surface area of V_2O_5.

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