Structure Sensitivity of Carbon Monoxide Oxidation on Vanadium Pentoxide

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Well developed thin plates of V_2O_5 with a large contribution of the (010) face to the surface area were found to be about 30 times more active for CO-oxidation than agglomerates of needle type V_2O_5 without predominant exposure of this face.

Although the surface V=O species located on the (010) face of V_2O_5 have been considered to be active sites in several oxidation reactions,[1] their role in CO-oxidation is still a subject of controversy. Kera[2] pointed out the high activity of the (010) face for CO-oxidation. In contrast, Mori et al.[3] suggested that surface defects such as steps, kinks, or vacancies exhibit a much higher activity for CO-oxidation than the surface V=O species located on the (010) face. Their conclusion was based on the results of a comparative kinetic study which involved the determination of the surface V=O species by using the rectangular pulse technique.[4] Here, we report another kinetic approach to assign the role of the sites located on the (010) face for CO-oxidation.

Our study was based on the investigation of the CO-oxidation rates on two vanadium pentoxide samples of different grain morphology, *i.e.* with different contributions of the (010) planes to the surface area. Sample A consisted of thin well developed plates of V_2O_5 with the large faces corresponding to (010) planes; sample B contained poorly defined agglomerates of needle type grains. Scanning electron micrographs and X-ray diffraction results showing the morphology of similarly prepared samples have been reported elsewhere.[5] Sample A was obtained from pure ammonia metavanadate which was heated for 2 h at 700 °C and subsequently allowed to cool in the oven. Sample B was commercially available V_2O_5 supplied by Fluka AG, Switzerland. The Brunauer–Emmett–Teller (B.E.T.) surface areas of the fresh samples as measured by krypton adsorption at 77 K were: sample A, 0.37 ± 0.02 m^2 g^{-1}; sample B, 1.54 ± 0.05 m^2 g^{-1}. Calculations were based on a cross-sectional area of 19.5 Å^2 for a krypton atom. The surface area of sample B was practically constant throughout the measurements. In contrast, the surface area of sample A decreased to 0.068 m^2 g^{-1} during the first hour on stream accompanied by a decrease in activity. Kinetic measurements were started after steady-state activity was attained, *i.e.* after the surface area was practically constant.
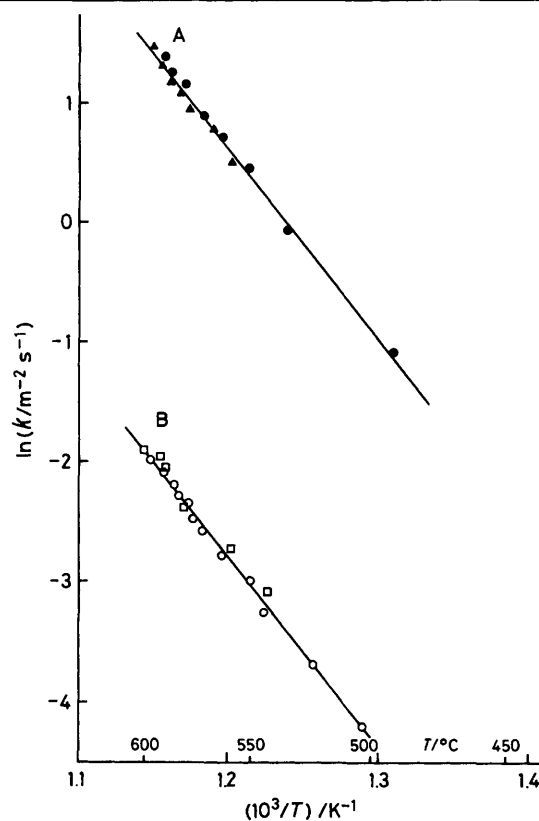
Figure 1. Arrhenius plots of kinetic data measured with thin plates (sample A) and needle type agglomerates (sample B) of V_2O_5. Different symbols in each line represent data collected in two repetitive runs. Using $r = k_0.e^{-E/RT}[CO]$, for sample A: $E = 133 \pm 6$ kJ mol^{-1}, ln $k_0 = 19.8 \pm 0.9$; for sample B: $E = 132.5 \pm 5.5$ kJ mol^{-1}, ln $k_0 = 16.3 \pm 0.75$.

Assuming no surface roughness, we estimated for the fresh sample A an average V_2O_5 plate thickness of about 2 μm from the measured B.E.T. surface area; this plate thickness agreed fairly well with the plate thickness observed by electron microscopy.

Kinetic measurements were performed in a differential flow reactor under the following conditions: 500—600 °C; partial pressures: CO, 1 kPa; O_2, 1.2 kPa; diluent gas N_2; total pressure, 100 kPa; total flow rate, 110 cm³ min⁻¹ (s.t.p.), catalyst load, 1 g; particle size, 120—250 μm. Under these conditions, conversion never exceeded 5%. The concentrations of CO and CO_2 were measured by i.r. analysers at the reactor inlet and outlet, respectively. Catalyst samples were heated in air to 600 °C before kinetic measurements were started. Reported reaction rates are steady-state values.

The reaction was found to be first order with respect to CO and zero order with respect to O_2 for both samples in the given temperature range. A similar behaviour has been observed by Roozeboom et al.[6] for supported monolayer and bulk V_2O_5-catalysts. Reaction rate constants were calculated using the rate equation: $r = k$ [CO], which after integration over the fixed bed yields the relation: $\ln (c/c_0) = -kS\tau$. Here, r is the reaction rate referred to the surface area; c_0 and c are the CO concentrations at the reactor inlet and outlet, respectively; S is the specific surface area; and τ the mean residence time in the catalyst bed.

Figure 1 presents the Arrhenius plots of the measurements performed with sample A and B. Note that both samples exhibited the same activation energies; however, the pre-exponential factor k_0 was about 30 times larger for the well developed plates (sample A) than for the needle type agglomerates (sample B). This indicates that the number of active sites per unit surface area was about 30 times lower on

sample B. Finally, it should be emphasized that well developed plates prepared by melting and subsequent controlled cooling of sample B exhibited about the same B.E.T. surface area and specific activity as the plates prepared from ammonia metavanadate (sample A). This confirmed that the observed difference in the activity of samples A and B should be attributed exclusively to their different morphology.

In conclusion, our kinetic measurements indicate that the active sites (probably V=O species) located on the (010) face of V_2O_5 play an important role for CO-oxidation. Thin plates of V_2O_5 exposing predominantly the (010) face were found to be about 30 times more active than needle type agglomerates without preferential exposure of this plane. The higher activity of the V_2O_5 plates is attributed to their larger number of active sites (V=O) per unit surface area.

References

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