The Effect of a TiO_2 Support on the Oxidation of Carbon Monoxide over a Vanadium Oxide Catalyst

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The catalytic activity of V_2O_5 for the oxidation of CO was significantly lowered by supporting on TiO_2; this is in contrast to the known promoting effect of TiO_2 for the oxidation of hydrocarbons.

The use of a TiO_2 support promotes the oxidation of hydrocarbons over vanadium oxide catalysts,[1-3] and this effect has been quantitated for the oxidation of benzene in terms of the turnover frequency.[4] It was then interesting to investigate the effect of a TiO_2 support on the activity of V_2O_5 for the oxidation of CO.

Two kinds of TiO_2, denoted by TiO_2(a) and TiO_2(r), were used as supports (anatase and rutile, respectively). TiO_2(a) and TiO_2(r) were prepared by the hydrolyses of $Ti(SO_4)_2$ and $TiCl_4$, respectively, followed by calcination in air at 873 K for TiO_2(a) and in O_2 at 773 K for TiO_2(r). The respective BET (Brunauer–Emmett–Teller) surface areas of TiO_2(a) and TiO_2(r) were 48.2 and 16.8 $m^2\ g^{-1}$. The supported vanadium oxide catalysts were prepared by impregnation of the support with an oxalic acid solution of ammonium metavanadate followed by calcination at 773 K in a stream of O_2. Unsupported V_2O_5 was prepared by the thermal decomposition of ammonium metavanadate at 773 K in an O_2 stream.[5] The V_2O_5–TiO_2(a) (2 mol % V_2O_5)–REDOX catalyst was prepared from V_2O_5–TiO_2(a) (2 mol % V_2O_5) by a reduction–oxidation treatment, *i.e.* reduction in a stream of H_2 at 673 K for 1 h followed by reoxidation using O_2(20%) at 673 K for 1 h (this redox cycle was repeated 5 times).[5] Kinetic studies were carried out using the flow reaction technique under the following conditions: 613—743 K, 4.5 % CO, and 75.2 % O_2. The number of surface V=O species on the catalyst was determined using the rectangular pulse technique.[6,7]

Table 1 shows the rate and turnover frequency for the oxidation of CO when an excess of oxygen was present, where the reaction rate was zero order with respect to the concentration of O_2, and where the catalyst was confirmed to be in the V^{5+} state. Here, the turnover frequency is defined as the rate of CO_2 formation divided by the number of surface V=O species. This was done in order to eliminate a trivial effect of the TiO_2 support on the activity, *i.e.* the increase in the surface area of V_2O_5 caused by spreading the V_2O_5 on the support. As is evident from Table 1, when the content of V_2O_5 in V_2O_5–TiO_2(a) was low (*e.g.* 2 or 5 mol % V_2O_5), the turnover frequency was 5—7 times smaller than that of the unsupported V_2O_5. This means that TiO_2(a) retards the activity of V_2O_5 as catalyst for the oxidation of CO. A significant retardation was also found for the reaction using V_2O_5–TiO_2(r) (Table 1).

Table 1. Rate and turnover frequency for the oxidation of CO on V_2O_5–TiO_2 catalysts.[a]

Catalyst	Content of V_2O_5/mol %	Number of surface V=O species/μmol g(catalyst)$^{-1}$	Rate/μmol g(catalyst)$^{-1}$ s^{-1}	Turnover frequency/ ks^{-1}
V_2O_5–TiO_2(a)	2	120	9.9	82
	5	184	9.7	53
	10	135	22.8	169
	25	60	28.4	473
	50	31	15.8	510
V_2O_5–TiO_2 (r)	1	77	2.4	31
	2	109	10.2	94
	5	118	14.8	126
	10	105	23.2	221
	25	91	18.9	208
	50	60	16.7	279
Unsupported V_2O_5	100	22	9.7	439
V_2O_5–TiO_2(a)-REDOX	2	134	42.1	314

[a] Reaction conditions: 673 K, 4.5 mol % CO and 75.2 mol % O_2.

Although Table 1 gives data for reactions at 673 K, similar results were also found when the reactions occurred at temperatures between 673 and 743 K. Such a retarding effect by the TiO_2 support on the activity of V_2O_5 is in contrast to the known promoting effect of TiO_2 for the oxidation of hydrocarbons.[1–4]

At low contents of V_2O_5, the catalyst grows epitaxially on the TiO_2 support to expose its (010) crystal face,[1–3,7] whereas various faces are exposed on unsupported V_2O_5. It is therefore considered that a smooth V_2O_5 surface with few defects is formed for the V_2O_5–TiO_2 catalysts having a low concentration of V_2O_5, and that the number of defects increases with increasing content of V_2O_5. This suggests that the smooth V_2O_5 surface with few surface defects formed when V_2O_5 is supported on TiO_2 is responsible for the significant reduction in activity for the oxidation of CO compared with that of unsupported V_2O_5. The marked increase in the turnover frequency for the V_2O_5–TiO_2(a) (2 mol % V_2O_5) system after redox treatment (Table 1) supports the validity of this conclusion, because the severe redox treatment of V_2O_5 increases the number of surface defects.[5] This conclusion is also compatible with those of previous studies that the surface V=O species located in the (010) face of V_2O_5 are the active sites for the oxidation of hydrocarbons,[1–4,8] whereas the active sites for the oxidation of CO are located at the surface defects (*e.g.* steps, kinks, or vacancies).[5]

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