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MoO$_3$ and GeO$_2$ Doping Effect on Pd–V$_2$O$_5$ Vapor-Phase Ethylene to Acetaldehyde Oxidation Catalyst

In a recent paper (*1*) Evnin and coworkers reported an interesting study concerning the heterogenization of the Wacker reaction by employing a Pd–V$_2$O$_5$-based catalyst, supported on α-alumina. They found that the best productivities and catalyst lifetimes were obtained by adding to the Pd–V$_2$O$_5$ a third component, typically a transition metal, e.g., Ti, Ru, Ir, Rh, Pt. By monitoring the V^{4+} concentration in the catalyst by ESR measurements, they showed that the catalytic activity could be related to the redox capability of the catalyst.

If this is in fact the case, the catalyst action should be governable and predictable by calculated additions of the correct dopent to the V$_2$O$_5$ matrix. The present note concerns an attempt to affect the action of the Pd–V$_2$O$_5$ catalyst by doping the V$_2$O$_5$ matrix with transition metal ions in various concentrations.

Due to the *n*-type semiconducting nature of V$_2$O$_5$, the quasi-free electron concentration can be increased by the addition of stable group 6 hexavalent ions and decreased by the addition of stable group 4 tetravalent ions. Among the possible ions, Mo^{6+} and Ge^{4+} were chosen, since: (i) they form solid solutions with V$_2$O$_5$, at least up to 25 mol% MoO$_3$ (*2*) and 15.9 mol% GeO$_2$ (*3*), without separation of crystal phases other than V$_2$O$_5$, due to the comparable values of the ionic radii (V^{5+} 0.59, Mo^{6+} 0.62, Ge^{4+} 0.53 Å); (ii) the coprecipitation of the mixture of matrix (V^{5+}) and host (Mo^{6+} or Ge^{4+}) ion oxides can be done from solutions containing only NH$_4^+$ as a foreign ion, so avoiding the introduction of ions which are difficult to remove.

Nine different catalysts were prepared by pouring the α-alumina support into solutions of ammonium metavanadate in which ammonium molybdate or GeO$_2$ were dissolved in calculated amounts. The excess water was evaporated *in vacuo* in a rotating device at about 50°C until a dry uniformly covered powder was obtained. The solid was then calcined in air at 400°C for 4 hr before impregnation with a PdCl$_2$ solution. The final activation was also done at 400°C in a slow air flow for 4 hr. The physicochemical characteristics of the support (Atomergic Chemetals G/S 40, 99.98 wt% pure α-alumina) were: particle size, 8 μm; surface area (BET method, krypton gas), 1.3 ± 0.3 m^2 g^{-1}, bulk density, 0.6 g cm^{-3}; crystal shape, hexagonal. Ultraviolet-visible

TABLE 1

Catalyst Composition

Type	V$_2$O$_5$ (wt%)	Pd (wt%)	GeO$_2$ (mol%)[a]	MoO$_3$ (mol%)[a]
A	10.2	0.77	—	—
B	9.4	0.84	0.41	—
C	10.3	0.87	1.01	—
D	10.2	0.93	4.24	—
E	10.5	0.78	9.30	—
F	9.7	0.82	—	0.49
G	10.2	0.78	—	0.80
H	9.8	0.78	—	3.80
I	10.6	0.83	—	7.50

[a] GeO$_2$ and MoO$_3$ content is expressed as mol% with respect to the sum of V$_2$O$_5$ + dopent oxide moles. This sum corresponds to about 10 wt% of the final catalyst.

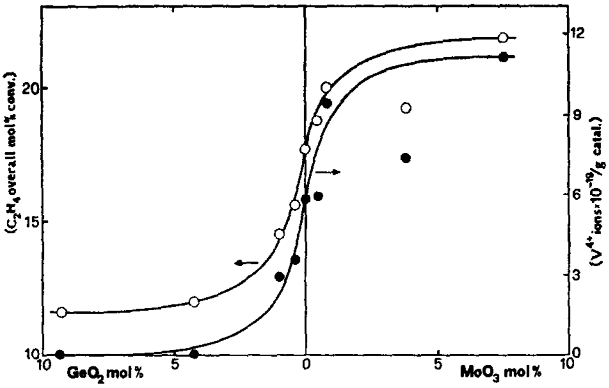

FIG. 1. Overall C_2H_4 conversion (○) and V^{4+} concentration (●) vs catalyst composition. Reaction parameters: 140°C, catalyst weight 4.04 g, reactant flow rates (mol hr^{-1}): C_2H_4, 0.011; O_2, 0.039; H_2O, 0.073; N_2, 0.136.

spectrophotometric titration was employed for the determination of vanadium (*4*), germanium (*5*), and molybdenum (*6*) in the catalysts; palladium was determined by atomic absorption spectrophotometry (*7*). X-Ray analyses (Debye method) did not show any appreciable difference among the various doped and undoped catalysts. Moreover, no signals attributable either to metallic Pd or to Pd salts were detected. In Table 1 the main analytical data for the catalysts are reported.

Ethylene was a pure-grade reagent, >99.9 mol% pure (GC), the main impurities being 0.05 mol% ethane, <300 ppm carbon dioxide, <50 ppm methane, and <1 ppm acetylene. Oxygen and nitrogen were cylinder gases, >99.9 mol% pure. A conventional pyrex glass microreactor–gas chromatograph assembly, previously described (*8*), was employed. The gas chromatograph (TC detector) was equipped with two 6 m long, 2 mm i.d. columns, packed with 80–100 mesh Porapak P, and as carrier gas $\geqslant 99.99$ mol% pure hydrogen, 25 ml/min in each column, was employed. The column temperature was programmed as follows: 4 min 40°C isotherm, 16°C/min up to 130°C and final 130°C isotherm. Qualitative and quantitative preformed standards allowed an accurate determination of the analytical correction factors to be made. Since the scope of the work was the study of the influence of the physicochemical nature of the catalysts on the activity, all the reaction tests were made in the same conditions, namely: 140°C, atmospheric pressure, catalyst weight 4.04 g (4.4 ml), reactant flow rates (mol hr^{-1}): ethylene 0.011, oxygen 0.039, water 0.073, nitrogen 0.136. The trend of the ethylene overall mol% conversion as a function of catalyst composition is given in Fig. 1. In every case the selectivity toward acetaldehyde was very high (from 96.1 to about 100 mol% of the converted olefin, the remaining part being CO_2 and acetic acid) at conversion levels up to 25 mol% of the fed ethylene.

EPR spectra of the catalysts were recorded by means of a V-4502 Varian spectrometer. The spectra were recorded at room temperature on fresh, reduced, and reoxidized catalysts. Reduction and reoxidation were conducted by treating the samples with a small flow of either ethylene + water (50 + 50 mol%), or oxygen, for 0.5 hr at 140°C. Outgassing at room temperature was performed on all samples before sealing the EPR capillary containers. A 2 wt% $VOSO_4$ in $(NH_4)_2SO_4$ finely ground dry solid mixture was employed as the comparative standard for V^{4+} concentration determinations. At the highest

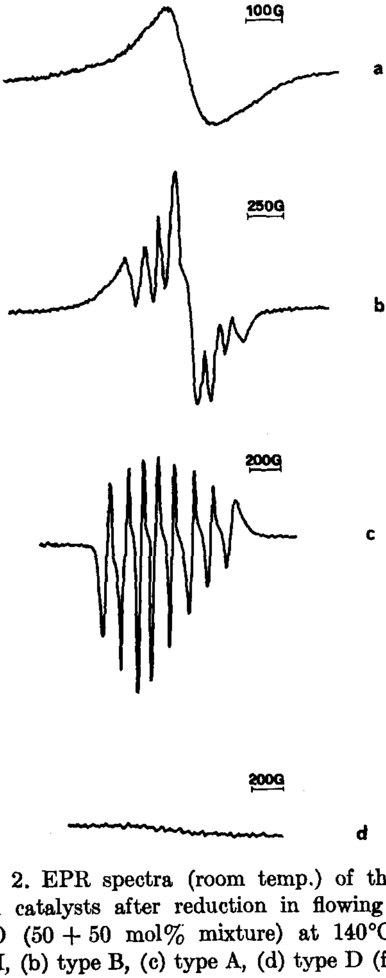

FIG. 2. EPR spectra (room temp.) of the employed catalysts after reduction in flowing $C_2H_4 + H_2O$ (50 + 50 mol% mixture) at 140°C; (a) type H, (b) type B, (c) type A, (d) type D (for the catalyst composition see Table 1).

MoO_3 concentrations in the catalyst, the obtained EPR spectra did not differ from those reported in (*1*); i.e., they presented only broad resonance signals in the $g = 1.980 \pm 0.005$ region and with $\Delta H_{\text{peak to peak}} = 100 \sim 200$ G (Fig. 2a). But when very small percentages of either MoO_3 or GeO_2 were present, or in the absence of any dopent, the spectra generally presented a more or less resolved hyperfine structure due to the ^{51}V nuclei ($I = \frac{7}{2}$) (Figs. 2b, and 2c). Finally, very low or no signals were detected for high GeO_2 percentages in the solid (Fig. 2d). In every case the signals recorded for the fresh catalyst samples were about as intense (within ±5%) as those for the corresponding reoxidized ones. Moreover, not only was the depth of the "redox well," calculated as the difference between V^{4+} concentrations in the reduced and reoxidized state, quite constant (within ±5%) for each catalyst, even after many redox cycles, but also when the V^{4+} concentration, as determined for the reduced state of the various catalysts, was plotted as a function of the catalyst composition, a good correlation was found between that parameter and catalyst activity (Fig. 1). On the other hand, the V^{4+} concentration can be assumed as an index of the mobility of electrons in the solid, i.e., of the ability of the catalyst to favor electron transfer to and from the surface Pd centers and, from these, in and out of the system, so favoring the Pd center redox mechanism. Then the higher the specific (i.e., referred to each Pd ion) V^{4+} concentration, the higher should be the specific (i.e., referred to each Pd ion) catalyst activity. In fact, the plot of the latter of these two parameters vs the former shows a quite linear increase in specific activity with V^{4+} specific concentration (Fig. 3). In such a plot the "deviation" relative to the type H catalyst (3.8 MoO_3 mol%), appearing in Fig. 1, no longer appears.

Thus, by the addition of relatively small quantities of the proper dopent to the V_2O_5

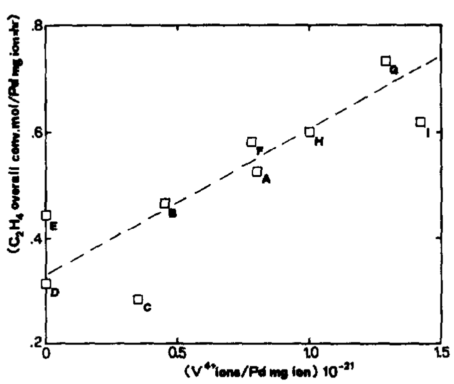

FIG. 3. Specific activity vs V^{4+} specific concentration. Letters refer to catalyst composition (see Table 1).

matrix, it is possible to affect the activity, apparently by acting only on the electron mobility of the solid support, without affecting the nature of the Pd surface centers. The relative insensivitity of the reaction selectivity to the change in catalyst composition seems to confirm this hypothesis.

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Lucio Forni
Giuseppe Gilardi
Instituto di Chimica Fisica e Centro C.N.R.
Università di Milano, Milano, Italy
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