Oxidation of Carbon Monoxide over Palladium–Tin(IV) Oxide Catalysts: An Example of Spillover Catalysis

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Summary Pd–SnO_2 catalysts are more active for CO oxidation than either Pd–SiO_2 or SnO_2, but are relatively inactive for C_2H_4 hydrogenation; grinding of Pd–SiO_2 and SnO_2 mixtures enhances CO oxidation activity, indicating that Pd induces activity on the SnO_2 surface.

Although the migration of hydrogen atoms from metal to oxide in supported metal catalysts is now well established,[1] there are no unequivocal examples of a metal inducing, on a supporting oxide, catalysis of a reaction which the metal itself catalyses. The experiments of Gardes *et al.*[2] merely show that spiltover hydrogen on Al_2O_3 is capable of reacting with C_2H_4. We now show that Pd on or in admixture with SnO_2 induces additional catalytic activity on the oxide.

Pd–SnO_2 catalysts were prepared (i) by impregnating SnO_2 gel[3] with H_2PdCl_4 solution, or (ii) by cation-exchanging it with $Pd(NH_3)_4(OH)_2$, or (iii) by co-precipitating $Pd(OH)_2$ and hydrated SnO_2 from chloride solution with KOH, followed by washing, drying, and rewashing. 4·8% Pd–Al_2O_3 was prepared by an analogous co-precipitation method; various Pd–SiO_2 catalysts were made by impregnation using H_2PdCl_4 solution. Dried materials were reduced either in H_2 or in CO, usually at 150—160 °C. Rate measurements were performed in a flow reactor using total $CO + O_2 + N_2$ flow rates of 100 cm^3 min^{-1}; for kinetic measurements, conversions were kept below 10%.

For CO oxidation, catalysts were pretreated first in air at 230 °C for 2 h, then in 6% CO–air at 100 °C for 16 h. Temperatures for 5% conversion and activities at 120 °C are given in Table 1: the synergistic effect of combining Pd with SnO_2 is clearly demonstrated. For Pd–SnO_2 catalysts (ii), conversions at 100 °C were proportional to Pd content between 0·2 and 2%. Orders in O_2 were zero above a critical concentration which increased with increasing Pd concentration and with increasing temperature. Orders in CO were zero for 1·5—6% CO. These orders are quite different from those normally found for Pd (+1 in O_2, −1 in CO)[4] and for SnO_2 (0 in O_2, *ca.* 0·5 in CO).[3]

Table 1. Activities of various supported Pd catalysts for CO oxidation and for C_2H_4 hydrogenation.

	CO oxidation			C_2H_4 hydrogenation[a]	
Catalyst	Wt./mg	$T_{5\%}$ °C[b]	$C_{120°}$ %[c]	Wt./mg	$T_{5\%}$ °C[b]
1% Pd–SnO_2 (i)	200	109	8·4	300	*ca.* 65
1% Pd–SnO_2 (ii)	200	82	24	300	97
2% Pd–SnO_2 (iii)	500	120	5	500	212
SnO_2	200	190	<1	—	—
2% Pd–SiO_2 (i)	100	180	<1	150	<−55
5% Pd–SiO_2 (i)[d]	200	200	⩽1	—	—
4·8% Pd–Al_2O_3 (iii)	250	170	<1	250	<20

[a] Determined using 10% C_2H_4 + 90% H_2 at 100 cm^3 min^{-1} after reduction at 150 °C for 1 h and 1 h stabilisation at room temperature. [b] Temperature for 5% conversion. [c] Conversion at 120 °C. [d] Prereduced in H_2 at 480 °C.

The rate of reduction of the SnO_2 support by CO at 120 °C, followed gravimetrically, increased in proportion to Pd concentration for type (ii) catalysts: the rate of reoxidation of partially reduced SnO_2 was likewise catalysed by Pd.

Additional evidence for spillover-induced catalysis has come from examining various mixtures of 5% Pd–SiO_2 and SnO_2 (Table 2). Thorough grinding increased the activity more than 10-fold, but most significantly the kinetics then resembled those shown by Pd–SnO_2 catalysts, while for the unground mixture they indicated that both components were reacting separately. However the activity of the ground mixture was still inferior to that shown by 0·5% Pd–SnO_2 (ii) (20—30% conversion at 150 °C).

Attempts to apply standard characterisation procedures to Pd–SnO_2 catalysts encountered difficulties. Transmission electron microscopy was uninformative owing to the opacity of the SnO_2, and *X*-ray diffraction gave no clear evidence for Pd particles, which if present must therefore have been smaller than 5 nm. C_2H_4 hydrogenation has been employed in an attempt to see whether the high activity for CO oxidation is merely due to a very high Pd dispersion; temperatures for 5% conversion into C_2H_6 are given in Table 1. All Pd–SnO_2 catalysts were relatively inactive compared with Pd–SiO_2 (i), demonstrating that this explanation is probably not valid.

Table 2. Activities of 20 mg 5% Pd–SiO_2[a], of 180 mg SnO_2, and of mixtures thereof for CO oxidation at 150 °C.

Catalyst	Conversion %
5% Pd–SiO_2 (20 mg)	0·03
SnO_2 (180 mg)	0·23
Simple mechanical mixture	0·33
Ground mixture	3·75
Components ground individually and separated in reactor by SiO_2	0·48

[a] See footnote to Table 1.

We believe we have shown that Pd can induce catalysis of CO oxidation on SnO_2 by a mechanism which differs from that normally observed.[3]

(*Received*, 21*st July* 1975; *Com.* 829.)

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