

SnO₂-CuO Gels: Novel Catalysts for the Low-temperature Oxidation of Carbon Monoxide

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Summary Coprecipitated SnO₂-CuO gels, particularly those having a Cu: Sn atomic ratio of between 0.5:1 and 0.6:1, are very active catalysts for the low-temperature (<100°) oxidation of CO, and after thermal activation at 450° in a 5–6% CO in air mixture the low-temperature, steady-state CO-oxidation activity of a catalyst of composition SnO₂·0.53CuO is superior, on a unit-volume catalyst bed basis, to a similarly treated commercial hopcalite (a mixed Mn-Cu oxide).

THE low-temperature oxidation of CO on thermally-stable metal and metal oxide catalysts has been studied with a view to automobile exhaust purification. Granular hydrous SnO₂ gel, after thermal activation at 200–500°, is an active CO-oxidation catalyst at temperatures below 200°.^{1,2} We now report that coprecipitated SnO₂-CuO gels are very active catalysts for this reaction, and even show a room-temperature effect.

TABLE Oxidation of 5–6% CO in air at flow rate of 100 cm³ min⁻¹ through 3.0 cm³ beds of 36–72 B.S.S. mesh catalysts activated at 450° in 5–6% CO in air

Catalyst	Weight (g)	Temperature required for given oxidation (°)			
		Initial 50%	Steady state 25%	50%	75%
SnO ₂	7.4	88	160	179	186
SnO ₂ ·0.53CuO ..	6.0	<0	45	65	80
Hopcalite	2.4	58	97	113	116

SnO₂-CuO catalysts were prepared by the dropwise addition of concentrated aqueous ammonia to well-stirred solutions of 0.1M [SnCl₄ + Cu(NO₃)₂] to a pH of 7.0 ± 0.1. The precipitates were washed to imminent peptization and air dried at room temperature to give granular translucent dried gel products (for Cu:Sn atomic ratios ≤ 0.7:1).

Catalysis studies were carried out using the previously described apparatus,² and the Table shows a comparison of the activity of a catalyst of composition SnO₂·0.53CuO (S_{BET}^N 141 m² g⁻¹ after activation at 450°) with that of

SnO₂ gel (36 m² g⁻¹ at 450°). The values for initial activities were obtained exactly 30 min after thermal activation. The steady-state data were obtained for increasing-temperature steps after allowing the catalysts to equilibrate for ca. 40 h at temperatures which gave steady-state oxidations of between 5 and 20%. It is apparent that the freshly activated SnO₂-CuO catalyst is very active at temperatures below ambient and even after equilibration to steady-state conditions it still shows some room-temperature activity.

It has been confirmed that the activity of SnO₂-CuO catalysts cannot be ascribed to the presence of active CuO on an inactive SnO₂ support since, upon increasing the Cu:Sn atomic ratio of the gels (from 0:1 to 1:1), a maximum CO-oxidation activity (expressed as rate per unit weight, per unit surface area or per unit-volume catalyst bed) is observed at a Cu:Sn atomic ratio of between 0.5:1 and 0.6:1. Further confirmation of the active participation of tin in the SnO₂-CuO gels was obtained by assessing the catalytic activities for CO oxidation of similarly prepared Al₂O₃-CuO gels. These had specific surface areas (100–200 m² g⁻¹) comparable with those of the SnO₂-CuO gels, but were found to have negligible CO-oxidation activity for temperatures up to at least 100°.

The Table also contains data for steady-state CO oxidation on a similarly treated hopcalite (mixed Mn-Cu oxide) supplied by Hopkin and Williams. Although the hopcalites are very effective low-temperature CO-oxidation catalysts after activation at moderate temperatures (200–300°), they are known to lose much of their activity when subjected to higher temperatures.³ After heating in CO-air at 450°, the low-temperature activity of the hopcalite is inferior (see Table), on a unit-volume catalyst bed basis, to that of the SnO₂-CuO catalyst.

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¹ M. J. Fuller, *Chem. and Ind.*, 1972, 96.

² M. J. Fuller and M. E. Warwick, *J. Catalysis*, in the press.

³ E. Cheylon, *Mém. Services chim. Etat*, 1944, 31, 304.