

## Low-temperature Catalytic Reduction of Nitric Oxide by Carbon Monoxide on SnO<sub>2</sub>-CuO Gels

By MARTIN J. FULLER\* and MALCOLM E. WARWICK

(Tin Research Institute, Fraser Road, Greenford, Middlesex UB6 7AQ)

**Summary** After thermal activation at 450°, coprecipitated SnO<sub>2</sub>-CuO gels, particularly those having a Cu:Sn atomic ratio of between 0.5:1 and 0.6:1, show high activity and high selectivity for N<sub>2</sub> formation at low temperature (150°) in the catalytic reduction of NO with CO compared with a commercial barium-promoted copper chromite catalyst (Girdler G-22).

THE low-temperature catalytic reduction of NO to N<sub>2</sub>O and, more importantly, N<sub>2</sub> has been extensively studied with a view to automobile exhaust purification. Comparative studies<sup>1,2</sup> of laboratory-prepared and commercial catalysts, including promoted and supported oxides and supported metals (*e.g.* Ni, Pt, Ru, Rh) have shown commercial barium-promoted copper chromite (Girdler Catalyst G-22, Chemetron Corp.) to be the most active catalyst at low temperatures (100–200°). Coprecipitated SnO<sub>2</sub>-CuO gels, which we have previously shown to be active low-temperature CO-oxidation catalysts,<sup>3</sup> are now shown to be very active catalysts at 150° for the NO-CO reaction, and to exhibit high N<sub>2</sub> selectivity at this temperature.

The Table shows a comparison of the catalytic activities of various batches of SnO<sub>2</sub>-CuO gels,<sup>3</sup> similarly prepared Al<sub>2</sub>O<sub>3</sub>-CuO gels, SnO<sub>2</sub> gel,<sup>4</sup> and commercial barium-promoted copper chromite (granulated Girdler G-22 pellets, nominal composition 23.3% Cr, 32.6% Cu, 9.6% Ba) for the CO-NO reaction at 150°. Each catalyst was pre-activated at 450°, first in air for 3 h, then in argon for 16 h. The product gases were separated and analysed on a Molecular Sieve type 5A column (Perkin-Elmer F 11 gas chromatograph, hot wire detectors, and He carrier gas) at 100° (N<sub>2</sub>, NO, and CO) and 350° (N<sub>2</sub>O and CO<sub>2</sub>). NO conversion data quoted in the Table refer to the reaction after 6 h (essentially steady state), and the quoted specific surface areas refer to the used catalysts.

TABLE. Reduction, at 150°, of 12–14% NO in CO at flow rate of 30 cm<sup>3</sup> min<sup>-1</sup> through 36–72 B.S.S. mesh catalysts activated at 450°.

Catalyst	Weight (g)	S <sub>N</sub> <sup>BET</sup> (m <sup>2</sup> g <sup>-1</sup> )	% NO conversion		
			to N <sub>2</sub>	to N <sub>2</sub> O	Total
SnO <sub>2</sub> ,0.51-CuO	0.5	109	39	32	71
SnO <sub>2</sub> ,0.52-CuO	1.0	90	68	24	92
SnO <sub>2</sub> ,0.55-CuO	0.5	112	42	30	72
Girdler G-22	1.0	40	<1	17	17
Girdler G-22 <sup>a</sup>	1.0	65	14	22	36
SnO <sub>2</sub>	1.0	30	0	0	0
Al <sub>2</sub> O <sub>3</sub> ,0.20-CuO	1.0	250	0	0	0
Al <sub>2</sub> O <sub>3</sub> ,0.73-CuO	1.0	104	0	0	0

<sup>a</sup> Pre-reduced in CO at 450° for 16 h.

The inactivity of the SnO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>-CuO gels at 150° illustrates the synergistic effect on catalytic activity of coprecipitating Sn<sup>IV</sup> and Cu<sup>II</sup> oxides, previously observed for CO oxidation on SnO<sub>2</sub>-CuO gels<sup>3</sup> and subsequently to be described in more detail.<sup>5</sup> As has been previously reported<sup>1</sup> pre-reduction of Girdler Catalyst G-22 was found to enhance its activity, particularly for N<sub>2</sub> selectivity, but this is at least partly accounted for by an increase in specific surface area on reduction. It is apparent from the Table that, on both a unit surface area and a unit weight basis, the SnO<sub>2</sub>-CuO catalysts have superior activity for the NO-CO reaction and, in particular, a much higher selectivity for reduction to N<sub>2</sub> compared with the Girdler G-22 catalyst.

We thank the International Tin Research Council for permission to publish this work, and Dr. J. W. Price for helpful discussions.

(Received, 9th November 1973; Com. 1545.)

<sup>1</sup> R. J. Ayen and Yu-Sim Ng, *Air & Wat. Pollut. Internat. J.*, 1966, **10**, 1.

<sup>2</sup> G. L. Bauerle, G. R. Service, and K. Nobe, *Ind. and Eng. Chem. (Product Res. and Development)*, 1972, **11**, 54.

<sup>3</sup> M. J. Fuller and M. E. Warwick, *J.C.S. Chem. Comm.*, 1973, 210.

<sup>4</sup> M. J. Fuller and M. E. Warwick, *J. Catalysis*, 1973, **29**, 441.

<sup>5</sup> M. J. Fuller and M. E. Warwick, to be published.