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Fine Particles Produced from Automotive Emissions-Control Catalysts

Abstract. *High concentrations of metal-containing condensation nuclei have been thermally induced from stabilized catalysts containing chromium, copper, and nickel under conditions closely resembling those found in automobile exhaust. Commercial and developmental catalyst formulations have been found to emit fine particles under a broad range of controlled conditions at temperatures ranging from 185° to 800°C, in filtered air, in a mixture of 3 percent carbon monoxide in molecular nitrogen, and in the product stream of a pulsed flame combustor.*

The intention of the automobile manufacturers to install oxidative catalytic emissions-control systems on passenger vehicles beginning with the 1975 model year, in response to federal emission standards, raises key questions regarding the use of catalysts for these purposes. Certain catalyst compositions typical of those now being developed for the control of automotive exhaust pollutants in 1976 (particularly nitrogen oxides, NO_x) are reported to contain, in addition to Pt, Cr, Ni, and other elements of known toxicity. In studies published by the industry the claim has been made that there is no hazard from nickel carbonyl $[\text{Ni}(\text{CO})_4]$ derived from exhaust CO in contact with a Ni-containing catalyst (Monel Metal) (1). However, in view

of the fact that particulate Ni is not detected by colorimetric tests for the carbonyl group, the possibility of the thermal decomposition of $\text{Ni}(\text{CO})_4$ (if formed) to free Ni in passage through the exhaust system cannot be discounted. This would result in the emission of fine particles of Ni in the respirable size ranges (that is, less than 1 μm in diameter).

The effect of certain gaseous constituents (namely, the halogens), even in trace concentrations, on the rates of emission of particles from heated Pt wire has been reported by Vonnegut (2). Chaston attributed the apparent volatility of Pt in air or O_2 at temperatures above 500°C to the formation of PtO_2 vapor (3). Since oxidative-type Pt catalytic converters operate in the

temperature range from 500° to 1000°C (mid-bed temperature), it is not unreasonable to expect some loss of Pt as PtO_2 vapor. The PtO_2 vapor emerging from the converter would undergo decomposition and subsequent condensation into a finely dispersed Pt aerosol as the exhaust cools.

An extremely sensitive instrument for detecting fine particles in the mid-to lower-respirable size ranges, without regard for chemical composition, is the condensation nuclei counter (CNC). This instrument detects submicroscopic airborne particles in the approximate range from 0.001 to 0.1 μm in diameter and is sensitive to concentrations as low as 10^{-14} g/cm³. In this study a thermoparticulate analysis (TPA) system was used similar to one described by Murphy *et al.* (4). The carrier gas (room air or 3 percent CO in N_2) passed through an absolute filter producing an aerosol with less than 1000 condensation nuclei (CN) per cubic centimeter, the approximate threshold of the instrument. The filtered carrier gas then passed over the sample which was contained in a heated Vycor tube placed centrally with respect to the horizontal electric furnace. The sample temperature was regulated to $\pm 10^\circ\text{C}$ and recorded. The resulting aerosol was cooled before entry into the CNC. Temperature and CNC output were recorded on the same chart.

A pulsed flame combustor (PFC), described by Meguerian (5), was used to produce a gas stream quite similar in composition to the exhaust gas from an internal-combustion engine. The aerosol sample resulting from contact of the PFC exhaust with the catalyst was diluted by a factor of 8 with filtered air to prevent condensation of H_2O vapor in the cooling system.

On the basis of currently available information pertaining to NO_x reduction catalysts for use in two-stage catalytic emissions-control systems (6), two representative compositions were selected for study: copper chromite (the composition of this material is variable; in this report copper chromite will be represented by the formula CuCr) and Monel Metal (70 percent Ni, 30 percent Cu). The four samples chosen include the following: (i) sintered Monel 400; (ii) Girdler G-22, Ba-promoted CuCr; (iii) CuCr supported on Kaiser KA-201 gamma alumina beads; and (iv) KA-201 beads (specific surface, 340 m²/g) as received without catalyst impregnate. The

Table 1. Onset of thermal CN evolution from catalytic materials.

Material	Atmosphere	Temperature (°C)
Monel 400, sintered	3% CO in N_2	185
Monel 400, sintered	Air	630
Girdler G-22	3% CO in N_2	240
Girdler G-22	Air	615
CuCr on Kaiser KA-201	3% CO in N_2	240
CuCr on Kaiser KA-201	Air	610
Kaiser KA-201 without catalyst	3% CO in N_2	> 810
Kaiser KA-201 without catalyst	Air	> 810

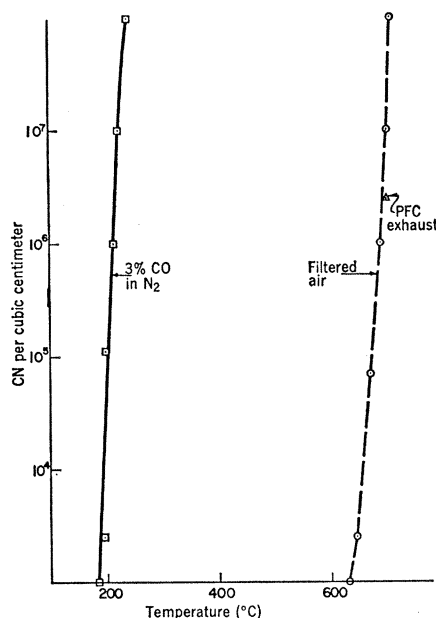
Fig. 1. Curve derived from a thermoparticulate analysis in which carrier gas (room air or 3 percent CO in N₂) was allowed to pass over a sample of sintered Monel 400 that had earlier been subjected to 300 hours of exposure to automobile engine exhaust.

samples of Monel and the CuCr on KA-201 had been subjected to 300 hours of exposure to automobile engine exhaust (unleaded fuel); the Girdler G-22 was a fresh sample. Quantities of the respective catalysts (10 to 30 mg) were proportioned to gas flow rates in order to approximate the space velocities expected in an actual emissions-control system. The catalyst sample was swept with a flow of 1.2 liter min⁻¹ (at standard temperature and pressure) of the respective carrier gases corresponding to bed space velocities of 100,000 to 300,000 volume/volume-hour. The initial heating rates under oxidizing conditions (filtered air) were of the order of 30° to 40°C min⁻¹. After the heated samples had been allowed to cool to room temperature, the heating schedule was repeated under reducing conditions (3 percent CO in N₂).

The onset temperatures of sustained particle emissions from the catalysts are shown in Table 1. The onset temperatures depend very markedly on the composition of the carrier gas. The presence of CO lowers the onset temperature, relative to that of an air atmosphere, by approximately 400°C in each case.

It has been postulated that metal carbonyls may form in the lower temperature ranges (7) and, being unstable at moderately elevated temperatures, may decompose leaving finely divided particles of either metal or metal oxide depending upon the prevailing partial pressure of oxygen. When the empty Vycor tube or a bare catalyst support was heated to 810°C in contact with a flow of filtered air or 3 percent CO in N₂, there was no sustained evolution of particles.

The TPA curve shown in Fig. 1 reveals the abruptness with which high CN concentrations (> 10⁶ CN per cubic centimeter) are reached above the onset temperatures. In Fig. 1, the point labeled PFC exhaust (700°C, 2.5 × 10⁶ CN per cubic centimeter) corresponds to the maximum particle concentration measured in aerosols derived by contact of PFC exhaust with Monel catalyst. The combustor had



been adjusted to a lean ratio of air to fuel providing approximately 2 to 3 percent residual oxygen to eliminate high CN concentrations which were observed under a rich ratio of air to fuel in the absence of Monel. This single point falls very close to the curve obtained for filtered air. This observation is taken to suggest that similar particle emissivity might be anticipated in exhaust systems equipped with catalytic converters under similar conditions. The TPA curves for the other catalysts mentioned exhibit similar characteristics. Experiments with supported CuCr conducted under cycling oxidation-reduction conditions (atmospheres alternating between filtered air and 3 percent CO in N₂) showed that particle evolution could be prolonged indefinitely in the temperature range from 200° to 350°C, although no significant particle emission was seen to occur under oxidizing conditions alone.

From the foregoing it can be inferred that the vehicle operations most conducive to CN emission from catalytic material would be start-up and idle modes which provide relatively high concentrations of CO (2 to 8 percent) and moderately low exhaust temperatures (less than 300°C). However, nucleogenesis may also be expected during acceleration modes following periods at idle and under high-speed cruise modes effecting high temperatures (1000°C) in the second-stage converter operating with the addition of excess air.

Diffusion loss measurements of the

particles on aerosols derived from the Monel and the CuCr catalysts indicate size distributions having a geometric median between 100 and 200 Å.

Since CN detectors provide no direct information on the chemical composition of the particles detected, a series of experiments was conducted jointly with the General Electric Research and Development Center in Schenectady, New York, to determine the composition of the aerosol generated from CuCr with the use of a surface ionization chamber interfaced with a magnetic sector mass spectrometer. Fine Cr-containing particles were detected in a stream of filtered air which had passed over the Girdler G-22 CuCr at 700° to 750°C. The analytical system of the mass spectrometer is particularly sensitive to Cr, which has a low work function. Unfortunately the system lacked adequate sensitivity to detect Ni aerosols that may have been derived from Monel.

In summary, high concentrations (> 10⁶ CN per cubic centimeter) of metal-containing CN have been thermally induced from several stabilized catalysts containing Cr, Ni, and Cu under conditions of temperature and gas composition similar to those of catalytic automotive emissions-control systems. In view of the high particle emissivity rate projected for a large number of vehicles equipped with catalytic emissions controls, it would seem prudent to anticipate the impact which such a pollution control strategy might itself pose to the future health of the population.

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References and Notes

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