TABLE 2
CATALYTIC CONVERSION TO CARBON DIOXIDE

	Reactant	Gaseous contact time, τ (sec)	Catalyst	Conversion at °C						μ
				149°	204°	260°	315°	371°	426°	482°
A	10% CO	0.1	Nod A	15	84	~100	—	—	—	—
			Pt/Al_2O_3	—	7	~97	—	—	—	—
B	6.7% n-C_4H_{10}	12.0	Nod A	—	20	80	~100	—	—	—
			Nod B	—	65	85	~100	—	—	—
			Nod C	—	84	100	~100	—	—	—
			CuO	—	0	2	10	52	78	—
C	2.0% n-C_4H_{10}	0.4	Nod B	—	—	—	10	50	60	80
D	3.0% CH_4	0.1	Nod A	—	—	—	—	—	13	~100
			Nod C	—	—	—	—	—	33	~100
			Pt/Al_2O_3	—	—	—	—	—	—	64

cases the nodule materials, in their natural state, exhibited activities greater than those of the commercial oxidation catalysts.

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Appearance of N_2O in the Catalytic Reduction of NO by CO

Nitrous oxide was reported recently as a product of the catalytic reduction of nitric oxide by hydrogen on supported Pt (*1*) and by carbon monoxide on supported copper chromite (*2*). In both cases the N_2O has been predominant at temperatures close to the reaction threshold which in turn depended on the reaction conditions. With the increase of the catalyst temperature, the N_2O concentration passed through a peak until at sufficiently high temperatures only the products of complete reduction [NH_3 in the case of ref. (*1*), N_2 in the case of ref. (*2*)] appeared in the outlet stream. Both studies were performed with a large excess of the reducing agent and the N_2O peak was observed at relatively low temperatures. In the present work, associated with the catalytic removal of air pollutants from automobile exhaust and carried out with a stoichiometric excess of NO over the reducing agent CO, it was observed that the appearance of N_2O in the outlet is quite a common phenomenon which persisted in some cases at relatively high temperatures.

The reaction between CO and NO in an integral flow reactor was studied on a series of supported catalysts, consisting of transition metal oxides or platinum on a 95% alumina–5% silica base supplied by the American Cyanamid Co. The catalysts were prepared by impregnation of the support with the corresponding nitrate solution, solutions of ammonium dichromate and copper nitrate in the case of $CuCrO_4$ catalysts, and with a chloroplatinate solution in the case of platinum. The vanadia catalyst was supplied by the American

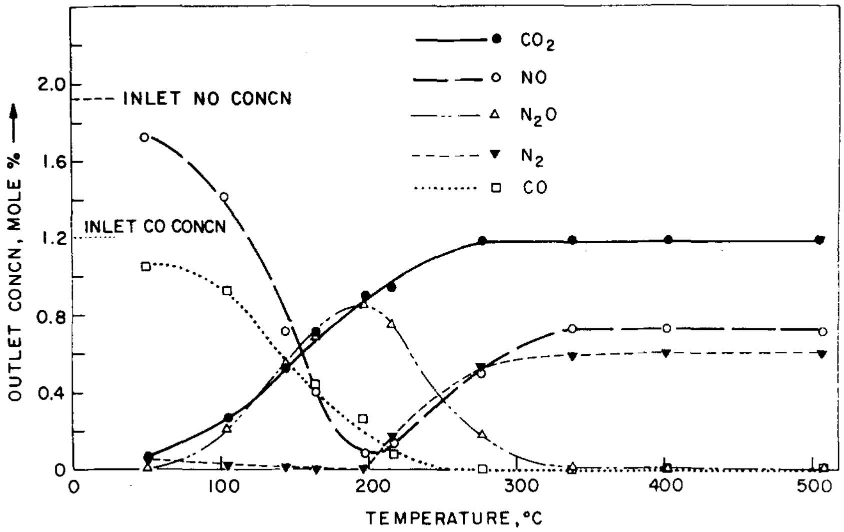

FIG. 1. Change of the outlet composition with temperature in the CO + NO reaction on supported Fe_2O_3.

Cyanamid Co. The catalysts were dried and calcined at 600°C for 8 hr, with the exception of the Pt catalyst which was dried and reduced in a hydrogen stream at 400°C. The support pellets were cylinders 25–30 mm long with an average diameter of 1.5 mm. The pore volume was 0.70–0.75 cc/g. The transition metal content was ~10% by weight (3.7% in the case of Pt). The total surface area of the supported catalyst was 210–230 m^2/g. In a typical run 80 cc of the catalyst weighing about 45 g was used and a mixture containing ~1.2 mole % CO, ~2.0 mole % NO, and the balance He carrier gas was passed over this catalyst at atmospheric pressure at a flow rate of 1400 cc/min. The gas mixture was analyzed by a CEC 21-614 mass spectrometer calibrated for pure gases. The concentrations of the gas constituents He, H_2O, CO, N_2, NO, CO_2, and N_2O were calculated from a set of simultaneous equations, using the peak intensities at $m/e = 4, 14, 18, 22, 28, 30$, and 44. The water content due partly to traces in feed gases and partly to the incomplete dehydration of the catalysts was always less than 0.5% and mostly below 0.1%. The continuous monitoring of the product stream by the mass spectrometer allowed the determination of the onset of steady state conditions at a given temperature of operation. Measurements at a given temperature were taken only after the surface of the catalyst had been equilibrated with the gas phase.

Figures 1 and 2 show the complete distribution of reactants and products in the reactor outlet with the change of temperature on supported α-Fe_2O_3 and NiO catalysts, respectively. At low temperatures, close to the reaction threshhold N_2O is the only reaction product, similar to the situation in the above-cited examples (*1*, *2*). The reduction in this range follows closely the reaction

$$2NO + CO = CO_2 + N_2O \qquad (1)$$

and hence the lines of CO_2 and N_2O concentrations coincide within the limits of experimental error. On the other hand at the high-temperature end, the formation of N_2 accounts for all the CO_2 by the overall reaction

$$NO + CO = CO_2 + \tfrac{1}{2}N_2 \qquad (2)$$

and the observed ratio of CO_2 to N_2 equals 2. In the region where the N_2O formation predominates, the concentration of NO drops below the values which are obtained at higher temperatures. This minimum reflects the stoichiometry of (1) and is the outcome of deficiency of CO in the temperature range where (2) represents the overall stoichiometry.

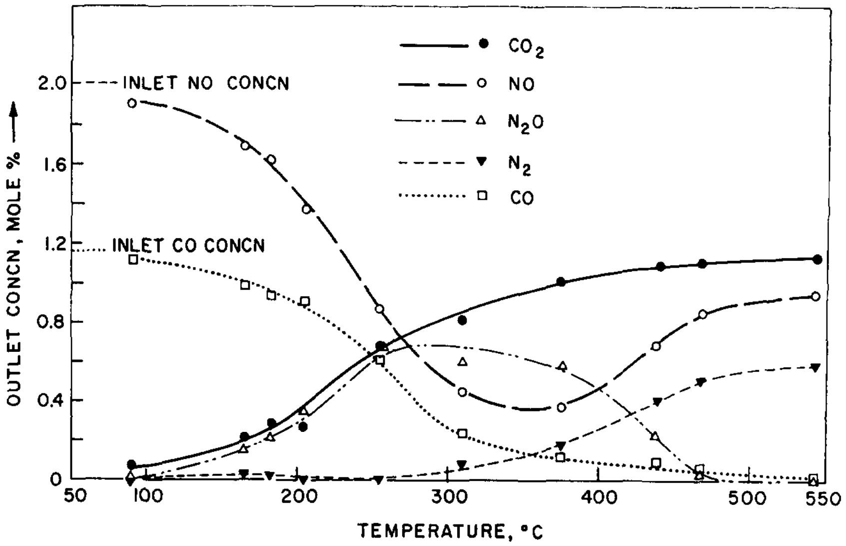

FIG. 2. Change of the outlet composition with temperature in the CO + NO reaction on supported NiO.

Comparing the N_2O peak in the reaction on Fe_2O_3 and NiO catalysts one notices that in the latter instance it is flatter, broader, and shifted to higher temperatures. In general, this flattening and shifting of the peak is the more pronounced the less effective the catalyst is in the formation of CO_2 under the described reaction conditions The reaction thresholds and the temperatures at which 50% of the CO is converted to CO_2 (which serve as a measure of the catalyst effectiveness) are similarly shifted. Table 1 gives the maxima of the N_2O concentration for the series of catalysts examined and the temperatures of their occurrence along with the temperatures at which 50% of the CO is converted.

The following considerations can account for the appearance of an N_2O peak with increasing temperature. Firstly, there is a possibility that the mechanism of the NO reduction changes with temperature. This may or may not involve a common surface precursor as postulated by Kokes (*1*) in the $NO + H_2$ reaction on Pt. Alternately, an unchanged mechanism may obtain in

TABLE 1

RELATIVE EFFECTIVENESS OF SUPPORTED CATALYSTS IN THE CO–NO REACTION AND THE CHARACTERISTICS OF THE N_2O PEAKS[a]

Catalyst (supported)	Temperature of 50% CO removal (°C)	Temperature of N_2O maximum (°C)	Maximum N_2O concentration in outlet (%)
Fe_2O_3	145°	200°	0.84
$CuCr_2O_4$	155°	180°	0.36
Cu_2O	175°	220°	0.28
Cr_2O_3	220°	240°	0.62
NiO	250°	300°	0.68
Pt	285°	300°	0.61
Co_3O_4	350°	350°	0.12
Bare support	425°	460°	0.34
MnO	435°	None present	None present
V_2O_5	560°	None present	None present

[a] Flow rate 1400 cc/min; inlet gas composition ~1.2% Co, ~2% NO; catalyst volume 80 cc.

the whole temperature range with the reaction proceeding in two consecutive processes (1) and

$$N_2O + CO \rightarrow N_2 + CO_2 \quad (3)$$

If the second step has a higher potential energy barrier it may be rate-limiting at lower temperatures. In this instance the product of the first step, N_2O, is a true gas-phase intermediate. The presence of the N_2O peak when using a wide variety of catalysts and in a wide range of temperatures suggests that this possibility cannot be excluded. It appears that the N_2O peak was accentuated in our case by the scarcity of the reducing agent and the resulting slowing down of step (3). Other experimental data not given here indicate that under overall reducing conditions, at a reversed ratio of reactants, the N_2O peak is shifted towards lower temperatures and is less prominent.

Further experiments using the supported Fe_2O_3 catalyst were performed to test the plausibility of the two-step reduction of NO by CO. Figure 3 shows the distribution of gas constituents in the outlet in a similar experiment when 0.7% N_2O were added to the inlet stream. The peak in the N_2O concentration and the dip in the NO concentration are again noted in the same temperature range, but the decay of the N_2O peak includes also the originally added amount and the N_2O concentration drops to zero at about the same temperature as is the case in the absence of N_2O in the inlet stream. This preferential removal of N_2O at the higher temperatures is compatible with the two-step mechanism referred to above.

In the temperature range which corresponds to the ascent side of the N_2O peak, reaction (3) is slower than (1). This was established experimentally by reducing N_2O with CO using the same catalyst and space velocity. As seen from Table 1 and Fig. 1 the temperature at which 50% of the CO is removed by reaction (1) on the supported Fe_2O_3 catalyst is 145°. The corresponding temperature in reaction (3) has been found to be 175° notwithstanding a somewhat larger excess of the oxidizing component (1.05% CO and 2.71% N_2O).

The decomposition of N_2O to N_2 and O_2 does not contribute to the decay of the N_2O peak in the case of the Fe_2O_3 catalyst. Significant N_2O decomposition was observed only above 350°C, which is consistent with the previously established fact that Fe_2O_3 is a poor catalyst for this reaction (*3*). The N_2O decomposition may be important in N_2O peak decay on other

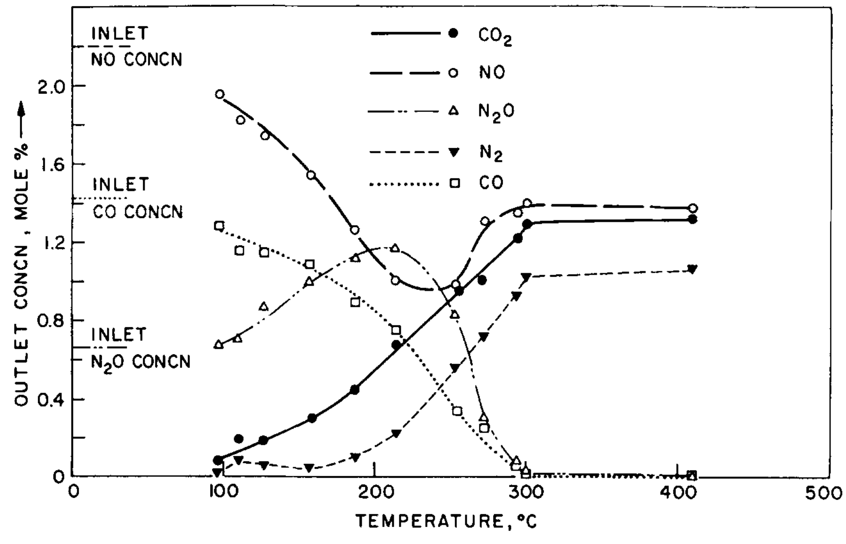

FIG. 3. Change of the outlet composition with temperature in the CO + NO reaction on supported Fe_2O_3 in the presence of added N_2O.

catalysts such as Cu_2O and Co_3O_4 which are very good catalysts for this reaction in the temperature range used.

Additional corroborative evidence for the N_2O as a gas-phase intermediate was obtained by changing the flow rate over the supported Fe_2O_3 catalyst. Increasing the gas flow rate over the catalyst at constant temperature, in the region of the decay of the N_2O peak, should increase the N_2O/N_2 ratio in the outlet gas if the N_2O is a gas-phase intermediate. Table 2 emphasizes this. Examination of Fig. 5 in the paper of Baker and Doerr (*2*) indicates a similar behavior of the N_2O concentration with increasing space velocity at constant temperature in the range of the N_2O peak decay.

TABLE 2

CHANGE OF N_2O/N_2 RATIO WITH FLOW RATE ON SUPPORTED Fe_2O_3 AT 273°C DURING CO–NO REACTION[a]

Flow rate (cc/min)	% CO conversion	N_2 concn. in outlet (%)	N_2O concn. in outlet (%)	N_2O/N_2 mole ratio in outlet
1400	65.6	0.442	0.122	0.276
2800	39.5	0.229	0.158	0.690
7600	16.2	0.035	0.137	3.910

[a] Inlet gas composition CO 1.50%, NO 2.27%, balance He.

More detailed studies of the catalytic reduction of NO are in progress.

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