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NOTES

Deep Sea Manganese Nodules as Oxidation Catalysts

Oxidation of combustible materials is known to be catalyzed by compositions involving transition metals. Such catalysis is presently of more than academic interest due to efforts to reduce combustible trace materials in automotive emissions. Effective elimination by catalytic oxidation is quite feasible, but cost of catalyst is one factor in the development of low-cost converters.

Manganese nodules are found at great depth on the sea floor of the oceans (*1*). They are said to have been formed by the agglomeration of colloidal precipitates of manganese and iron oxides (*2*, *3*). In view of this mode of formation relatively high specific surface areas can be expected; this fact, and the composition—being rich in transition metal oxides—suggested the possibility that manganese nodules may be effective oxidation catalysts.

Three Pacific Ocean nodule materials, made available by John L. Mero of the Institute of Marine Resources of the University of California, were subjected to tests. The material denoted as Nod A was dredged from a depth of 9840 ft off California (22-18 N lat., 107-48 W long.), Nod B originated from 4150 ft depth off Tahiti (16-29 S lat., 145-33 W long.), and Nod C from 17670 ft depth off Hawaii (23-17 N lat., 141-13 W long.). Compositions for these materials have been reported (*3*). Typically, they contain 20 to 30 wt % of Mn, 3 to 20% of Fe, and small amounts of Co, Ni, Cu.

Surface areas were determined by the standard nitrogen BET method after heat treatment to various severities (temperatures). In all cases the material was heated to the indicated temperature for 1.5 hr in air, and subsequently held in (forepump) vacuo for an additional 1.0 hr. Results are summarized in Table 1. For catalysis, substantial surface areas are available; they are seen to be thermally sufficiently stable for meaningful experimentation.

TABLE 1
SURFACE AREAS OF NODULES

	Surface area (m^2/g) after heat treatment at—		
	250°C	450°C	550°C
Nod A	54	45	28
Nod B	101	—	—
Nod C	185	131	—

Catalytic observations were made in a microreactor, using a stream of dilute hydrocarbon or of carbon monoxide, in air. Nodule material was crushed and a 16–20 mesh size fraction used. The conversion to carbon dioxide was measured by gas chromatographic sampling of the effluent. Table 2 summarizes results. The gaseous contact time, τ, is the superficial gaseous reactor residence time calculated from $\tau =$ catalyst volume/gaseous volumetric flow rate. Conversion data represent the percentage of the maximum stoichiometrically possible conversion figures for each case.

Experiments B and D show that the relative activity among nodule materials follows their surface area (compare Table 1 and 2). For comparison, tests were carried out with two commercial oxidation catalysts. The CuO composition was Type K catalyst from Houdry Process Corp.; the Pt/Al_2O_3 catalyst was one purchased from Oxy-Catalyst, Inc. and contained 0.1 wt % of platinum. In all

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.

References

1. Menard, H. W., and Shipek, C. J., *Nature* **182,** 1156 (1958).
2. Dietz, R. S., *Calif. J. Minerol. Geol.* **51,** No. 3 (1955).
3. Mero, J. L., *Mining Congr. J.,* October 1960.

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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