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Possible Formation of Highly Stable Manganese Carbonyls on Ceria Supported MnO_x

Both manganese and cerium oxides are excellent catalysts for total oxidations (*1*, *2*). They are promising candidates for the burn-off of light alcohols present in exhaust gases of novel gasoline blends (*3–5*).

We have recently prepared well-dispersed overlayers of MnO_x in a series of supports (*6*) and reported in detail about their oxidative catalytic properties (*7*). Ceria-supported MnO_x shows the highest activity for the oxidation of carbon monoxide and methanol at high temperatures.

An ir spectroscopic study was made of the adsorbed species and the gas-phase products from the reactive chemisorption of O_2 and CO on the catalyst surface (*8*).

The present communication reports the formation of highly stable manganese carbonyls on MnO_x/CeO_2 during CO adsorption at high temperature.

Infrared measurements were carried out in a quartz cell with water-cooled NaCl windows using a Nicolet 7199 FT-IR spectrometer at a resolution of 4 cm^{-1}. The cells were attached to a conventional high-vacuum system equipped with a manifold for gas flow which permitted performing pretreatments and measurements *in situ*. The cells could be heated to 673 K with flowing gases for pretreatments. Calcined samples were pressed into wafers (~15 mg/cm^2) and placed in a quartz sample holder inside the cells.

Two fresh specimens were used, both undergoing a preoxidation with 20% O_2 in a balance of He at 473 K for 4 h and then at 573 K for 2 h.

The first specimen was used to study the reactive chemisorption of CO on the surface after evacuation (10^{-5} Torr) at 573 K of the preadsorbed oxygen used to pretreat the wafer. The second one was cooled to room temperature and outgassed at 298 K under high vacuum prior to the adsorption of carbon monoxide. Additional details are given elsewhere (*8*).

The adsorption of CO at room temperature on MnO_x/CeO_2 is a chemical reaction. Exposure to 1 Torr gave spectral bands at 2356, 2342, and 2190 cm^{-1}. They correspond to physisorbed CO_2 and surface "carbonyls" associated with surface Ce^{3+} cations (*2*), more properly designated as σ-bonded species. After adsorption of 15 Torr CO new bands at 2186, 2153, 2133, and 2111 cm^{-1} also appeared, indicating that CO bonds to manganese cations at the catalyst surface (*8*). Carbon dioxide was associated with a single type of surface site or surface geometry (only *one* band at 2350 cm^{-1} was present), in opposition with the presence of more than one site or geometrical arrangement on specimens outgassed at low temperatures (see below).

The adsorption of CO (100 Torr) at higher temperatures caused further surface transformations. When the temperature was raised to 373 K the band at ~2190 cm^{-1} disappeared; CO was no longer able to bond to Ce^{3+} through the labile electrostatic interactions as it did at low temperature. However, then the adsorption temperature was increased to 573 K, a broad band centered around 2176 cm^{-1} was formed (Fig. 1), and persisted as a broad shoulder even after the desorption of CO at 473 K (see below). Massive evolution of CO_2 followed the increases in temperature under this atmosphere of pure CO.

The desorption of CO (2×10^{-5} Torr) at

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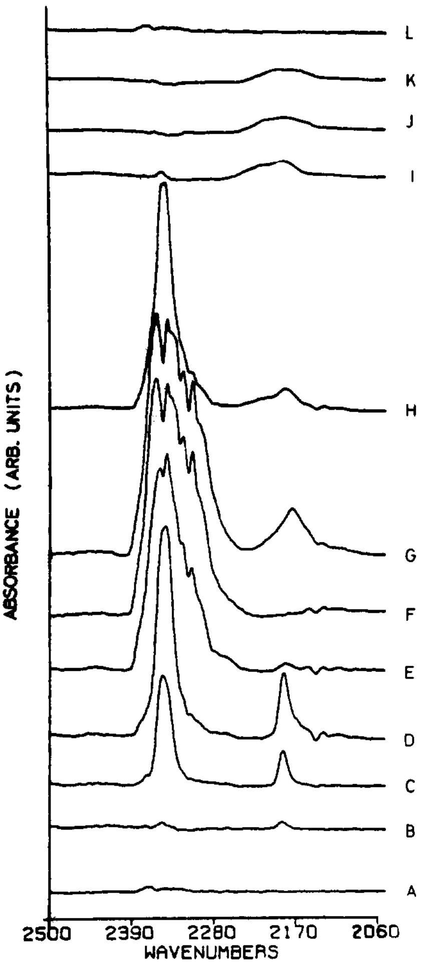

FIG. 1. Infrared of the carbonyl region upon adsorption and desorption of CO on MnO_x/CeO_2 after O_2 desorption—2×10^{-5} Torr—at 573 K and cooling under vacuum to RT: *CO adsorption*, (A) 0.09 Torr, RT; (B) 1 Torr, RT; (C) 15 Torr, RT; (D) 100 Torr, RT; (E) 100 Torr, 373 K; (F) 100 Torr, 473 K; (G) 100 Torr, 573 K; (H) cell cooled to RT, 100 Torr; *CO desorption*, (I) 1 Torr, RT; (J) 2×10^{-5} Torr (HV), RT; (K) HV, 473 K; (L) HV, 573 K.

room temperature readily eliminated the physisorbed CO_2 and CO from the catalyst surface. Further heating to 573 K under vacuum finally eliminated the 2176-cm^{-1} shoulder.

Unlike the reactive chemisorption on MnO_x/CeO_2 preoxidized and evacuated at 573 K, the adsorption of CO at room temperature on the specimen outgassed at ambient temperature proceeded with very little interaction of the adsorbate with the catalyst surface.

After adsorption of CO (100 Torr) at room temperature only a very small amount of CO_2 (ads.) was produced; only metal–CO bonds associated with manganese were observed (Fig. 2). The adsorption of CO (100 Torr) at higher temperatures caused the formation of large amounts of carbon dioxide but on this specimen no Ce–CO bonds were formed and only a very small absorption band around 2170 cm^{-1} could be observed. These differences are due to the presence of more residual water—less coordinatively unsaturated cations—and less surface reduction—less anion vacancies—upon the evacuation of MnO_x/CeO_2 at low temperature (*4*, *8*).

The reactive chemisorption of CO produces various intermediates with intense bands in the carbonate region (1800–1200 cm^{-1}) which are bonded to the surface with variable strengths (*8*). The carbonate region showed that there is a close similarity in chemical surface transformations following the reactive chemisorption of CO (100 Torr) at higher temperatures on MnO_x/CeO_2 outgassed either at 573 K or room tempera-

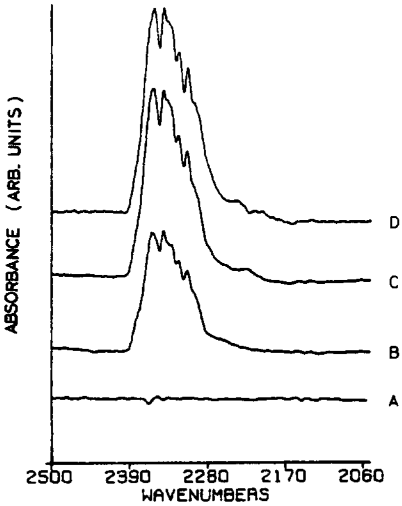

FIG. 2. Infrared spectra of the carbonyl region upon adsorption of CO on MnO_x/CeO_2, after desorption of O_2 at room temperature: (A) 100 Torr, RT; (B) 100 Torr, 373 K; (C) 100 Torr, 473 K; (D) 100 Torr, 573 K.

ture. The desorption process for CO from room temperature to 573 K was identical for both specimens as well.

The appearance of the broad band at 2176 cm^{-1} is a unique phenomenon. Neither MnO_x/CeO_2 outgassed at room temperature nor MnO_x supported on anatase or alumina exhibited such an absorbance band (*8*). One explanation associated with the high degree of reduction to which the catalyst was subjected under the CO atmosphere (Figs. 1 and 2) can be offered to justify this. Covalent manganese carbonyls are very stable under high vacuum and high temperatures. $Mn_2(CO)_{10}$ begins to decompose above 533 K (*9*).

Under reductive environments $[Mn(CO)_5]^- M^+$, with carbonyl bands around 2170 cm^{-1} have been observed (*10*). Therefore, it can be speculated that an ionic manganese carbonyl associated with neighbor cerium cations is formed after a high level of reduction on an initially unsaturated surface is reached, giving the 2170-cm^{-1} band. Additional studies are required to confirm this tentative assignment.

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