

CO Disproportionation at Mild Temperatures over Partially Reduced Cerium Oxide

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Direct dissociation and disproportionation of carbon monoxide over partially reduced cerium oxide are demonstrated, even at room temperature, by Fourier-transform IR spectroscopy.

CO hydrogenation over metal catalysts has been extensively studied in the last decades, and CO disproportionation has been commonly found for most of the group VIII metal catalysts, especially at high temperatures. However, studies of CO hydrogenation over pure metal oxide catalysts are relatively limited. In general, CO is not activated as readily on oxides as it is on metal catalysts; accordingly, CO disproportionation on oxides at mild temperatures has been considered to be impossible. We have found that the CO hydrogenation over cerium oxide produces hydrocarbons rather than oxygen-containing compounds as over other oxides.^{1,2} Here we report on the direct dissociation of CO over partially reduced cerium oxide studied by FTIR spectroscopy. Partially reduced cerium oxide exhibits high activity for cleavage of CO even at room temperature, and the activity is proportional to the extent of reduction of the cerium oxide.³ A similar result for rare earth oxides has not been reported.

Cerium oxide was obtained by the thermal decomposition of cerium hydroxide gel at 773 K in air for 3 h. The cerium hydroxide was prepared through precipitation from an aqueous solution of cerium(III) nitrate with NH_4OH . H_2 was purified *via* a Deoxo arrangement and then through a liquid-nitrogen trap in a circulating system. CO_2 was prepared from the decomposition of NaHCO_3 . IR spectra were recorded on a JEOL JIR-100 FTIR spectrometer. The sample was pressed into a self-supporting disc. The disc was placed in an IR cell with a furnace capable of heating the disc *in situ* up to 1000 K.

Surface contaminants including carbonate-like species were removed by treating the cerium oxide disc in O_2 at 873 K and outgassing at 1000 K [referred to as CeO_2 (1000 K)]. The sample was reduced in H_2 at 673 K for 1–4 h then dehydroxylated by evacuation at 1000 K for 30 min, to give CeO_2 (673-H). After the sample was cooled to room temperature it was exposed to CO (30 Torr) and IR spectra were recorded immediately. Fig. 1 shows the IR spectra followed after admission of CO at room temperature. A number of bands were clearly observed in the 1700–800 cm^{-1} region while no bands were observed in the 2000–3500 cm^{-1} region. These bands grew slowly with time as shown in Fig. 1. From their growth in intensities, these bands can be roughly grouped into three kinds of surface species: (I) sharp bands at 1691 and 1078 cm^{-1} , (II) a sharp band at 1597 and a broad band at around 1315 cm^{-1} , and (III) broad and weak bands at 1489 and 1390 cm^{-1} . When isotopically labelled ^{13}CO was introduced onto the partially reduced cerium oxide, all these bands shifted to the lower frequency region but the outline of

the spectrum remained unchanged. The isotope results indicated that these bands observed after CO adsorption on the partially reduced cerium oxide at room temperature were derived from CO. In a separate experiment, when CO_2 was adsorbed on the partially reduced cerium oxide, an almost identical spectrum of the species (II) and (III) as shown in Fig.

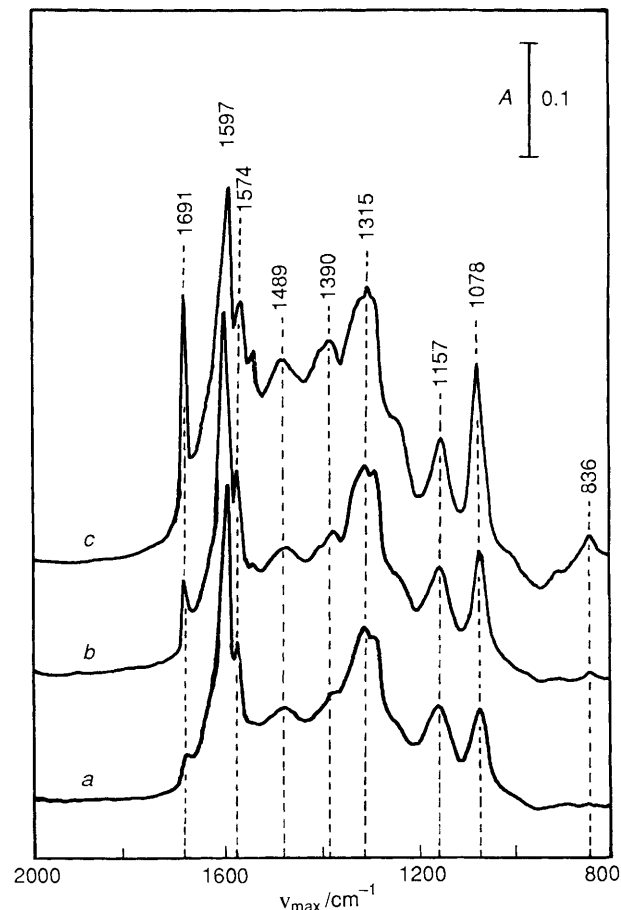
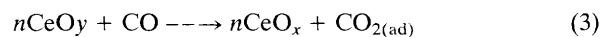
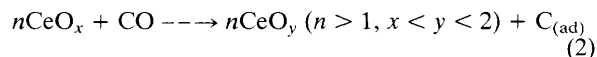
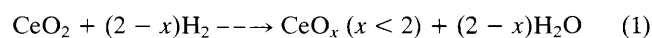


Fig. 1 IR spectra of adsorbed species derived from CO adsorption at room temperature on partially reduced cerium oxide (dehydroxylated): (a) after admission of CO for 2 min; (b) for 5 min and (c) for 12 h

1 was obtained while the bands at 1691 and 1078 cm^{-1} of species (I) were absent. Accordingly, the bands in Fig. 1 were due to the adsorbed species formed from CO_2 adsorption. In detail, the species (I), (II) and (III) can be respectively assigned a bridged carbonate, bidentate carbonate and inorganic carboxylate according to our previous work.⁴

The above results demonstrated that the CO_2 was produced even at room temperature when CO reacts with the partially reduced cerium oxide. Because the surface was reduced at 673 K in H_2 prior to the CO adsorption, the possibility of CO oxidation by the surface oxygen was ruled out; therefore, the surface species of adsorbed CO_2 was formed from the CO disproportionation reaction ($2\text{CO} \rightarrow \text{C} + \text{CO}_2$). The IR spectra of adsorbed CO on CeO_2 (100–1000 K) are different from those over CeO_2 (673-H).³ The intensities of these IR bands grew markedly when the CO adsorption temperature was elevated. It was also found that the band intensities increased with the reduction time of cerium oxide. This proved that the partially reduced cerium oxide can activate the CO dissociation even at mild temperatures, and accordingly

the partially reduced surface underwent a redox cycle [see eqns. (1)–(3)].



Received, 7th November 1990; Com. 0105014H

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