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Carbon Monoxide Oxidation on Cobalt Oxides at 80 K: an FT-IR Study

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FTIR spectroscopy has been used to demonstrate that at 80 K carbon monoxide reacts on the surface of cobalt oxides to form molecular CO_2, the readsorption of which leads to the formation of stable carbonate complexes.

The catalytic oxidation of CO over transition metal oxides is known to be accompanied by the formation of surface carbonate complexes, which have been detected by IR spectroscopy. These species were thought to be formed by the interaction of CO with surface oxygen, their subsequent decomposition leading to the evolution of CO_2. Therefore, surface carbonates were regarded as intermediates.[1,2] However, we have shown recently that, in the case of cobalt oxides, the surface carbonates are characterized by high thermal stability and low reactivity towards the components of the reaction mixture (CO, O_2), thus raising doubt about their role as intermediates.[3] Thus, a scheme was proposed whereby molecules of CO adsorbed on reduced centres could be oxidized to CO_2 by surface oxygen, while the carbonates detected by IR spectroscopy are formed by CO_2 readsorption, and bear no relation to the catalytic cycle. In order to verify this scheme it was of interest to study the dynamics of formation of various surface species, primarily surface carbonates, after the introduction of CO or $CO + O_2$ compared with the dynamics of CO_2 evolution. In this communication, we report the results obtained for CoO and Co_3O_4. The experiments were carried out at low temperatures so that the rates of the processes under investigation were slow enough to be measurable.

The experiments were carried out in a high vacuum cell designed by Infraspac[4] using an IFS-113v Bruker spectrometer with a mercury cadmium telluride (MCT) detector, at 4 cm^{-1} resolution.

The samples of Co_3O_4 and CoO were prepared by decomposition of the basic carbonate in air or helium, respectively, with subsequent vacuum pretreatment in the IR cell at 673 K. The adsorption was carried out at 80 K. In the spectra presented the background absorption has been subtracted on the optical density scale.

Immediately after admission of CO a group of absorption bands in the carbonyl stretching region were detected, the most intense one located at 2137–2141 cm^{-1} for Co_3O_4 (depending on the pretreatment of the sample) and at 2125 cm^{-1} for CoO, together with very weak peaks due to the surface carbonates (1650, 1625, 1275, 1050 cm^{-1}). The spectra of the surface carbonates differed considerably from those observed at 300 K, their intensities being considerably lower. For *ca.* 200 min there were no variations in the carbonate absorption region for either oxide (Figs. 1, 2). At the same time a new band appeared and grew at 2345 cm^{-1}, caused by physically adsorbed molecular CO_2. Changes were also developing in the carbonyl region. In the case of Co_3O_4 the band at 2137 cm^{-1} was shifted by 3–4 cm^{-1} to higher frequency. For CoO the behaviour was more complicated: for *ca.* 50 min the 2125 cm^{-1} band diminished until it disappeared, this was accompanied by a simultaneous increase in intensity of the 2151 cm^{-1} band. For Co_3O_4, carbon dioxide appeared in the very first minutes after CO admission, while for CoO an induction period of *ca.* 50 min

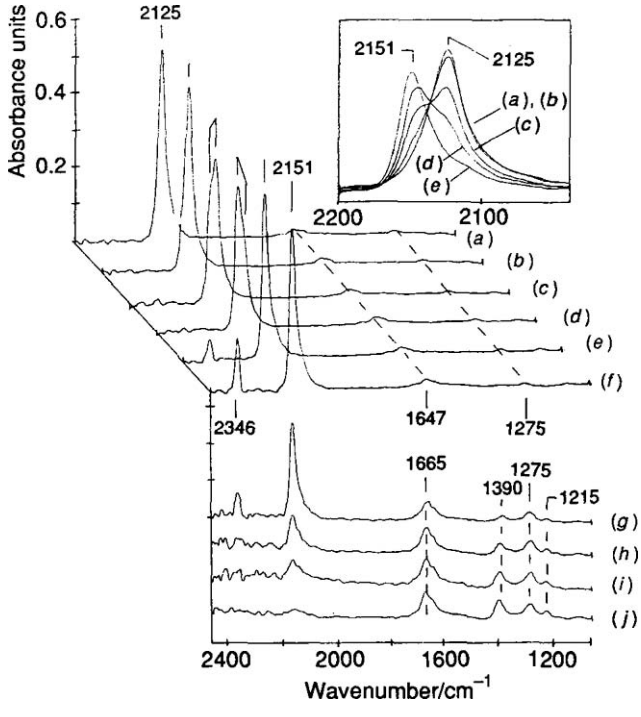

Fig. 1 CO adsorption on CoO at 80 K ($P_{CO} = 0.1$ Torr) after (*a*) 1, (*b*) 8, (*c*) 18, (*d*) 30, (*e*) 48 and (*f*) 100 min; (*g*)–(*j*) with subsequent evacuation: (*g*) 30 s, (*h*) 1, (*i*) 1.5 and (*j*) 2.5 min

was observed, *i.e.* CO_2 evolution began only after the changes in the carbonyl absorption region were complete.

The interaction of Co_3O_4 with a $CO + O_2$ mixture has also been studied. As in the case of pure CO, immediately after the introduction of the reaction mixture absorptions due to carbonyls and negligible amounts of surface carbonates were observed. However, in this case the most intense carbonyl absorption was situated at 2143 cm^{-1}, while the weak bands at 2080, 2050, 1980 cm^{-1} assigned previously to Co^0CO (ref. 3) were absent [Fig. 2(*d*)]. The formation of CO_2 was also observed, the initial rate being considerably higher than that for pure CO, but a pronounced decline in the rate was later observed. The spectra of the surface carbonates, as in the previous experiments, do not change with time.

Further experiments (keeping the pre-evacuated cell at 80 K, admitting CO_2 at 80 K, admitting a ^{12}CO–^{13}CO mixture) demonstrated that the appearance of CO_2 could not be attributed to methodical errors (*e.g.* air leakage) and were, therefore, the result of CO oxidation.

Pumping of CO leads to rapid disappearance of both the

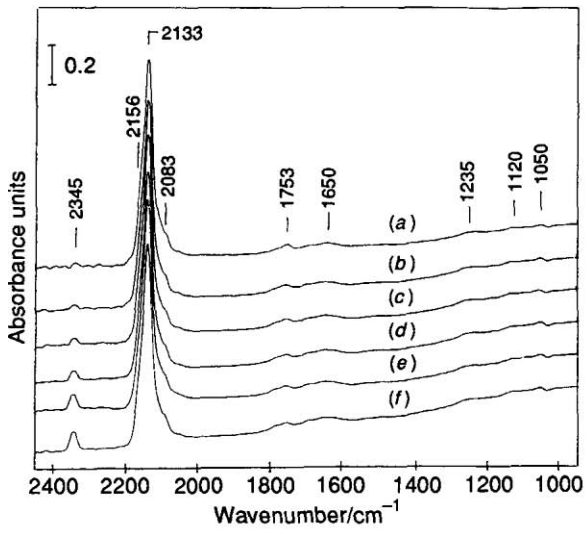

Fig. 2 CO adsorption on Co_3O_4 at 80 K ($P_{CO} = 0.1$ Torr) after (*a*) 1, (*b*) 8, (*c*) 20, (*d*) 45, (*e*) 100 and (*f*) 170 min

carbonyl and CO_2 peaks and to a substantial increase in the intensity of the bands due to the surface carbonates, the spectra of the latter being different to those observed before evacuation (Figs. 1, 4). For Co_3O_4 these carbonates are similar to those detected previously at 300 K.[3] In our opinion, this fact may be explained only by supposing that the observed surface carbonates are formed *via* CO_2 readsorption. At 80 K CO molecules block the surface centres necessary for the formation of the surface carbonates, while they do not prevent CO oxidation. On evacuation, these centres become vacant and some of the CO_2 molecules can then adsorb onto the surface.

The surface carbonates formed during the first moments after the introduction of CO did not appear to be involved in the subsequent reaction dynamics since their concentration does not change over time. The same is true for surface carbonates formed after CO evacuation. Indeed, after the reintroduction of CO, the rate of CO_2 formation is close to that before evacuation (Fig. 4). Therefore, the increase in surface carbonate coverage is accompanied neither by acceleration of the reaction, nor by blocking of the active centres, although the carbonates were previously shown to be localized on the reduced centres.

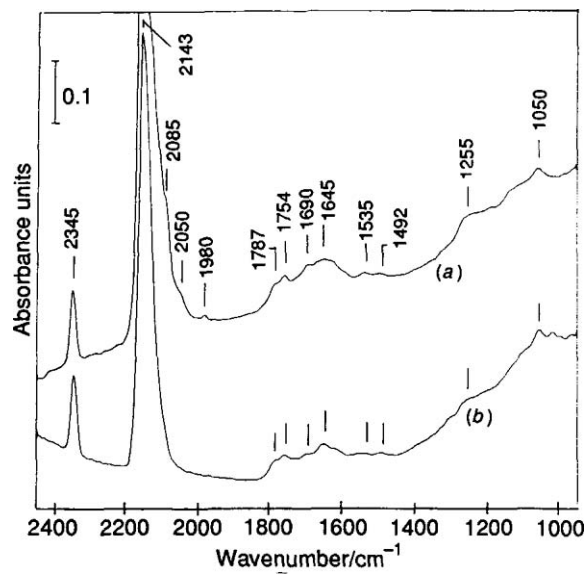

Fig. 3 IR spectra of Co_3O_4 after 50 min exposure to (*a*) CO and (*b*) $CO + O_2$ at 80 K; $P_{CO} = 0.1$ Torr, $CO:O_2 = 1:1$

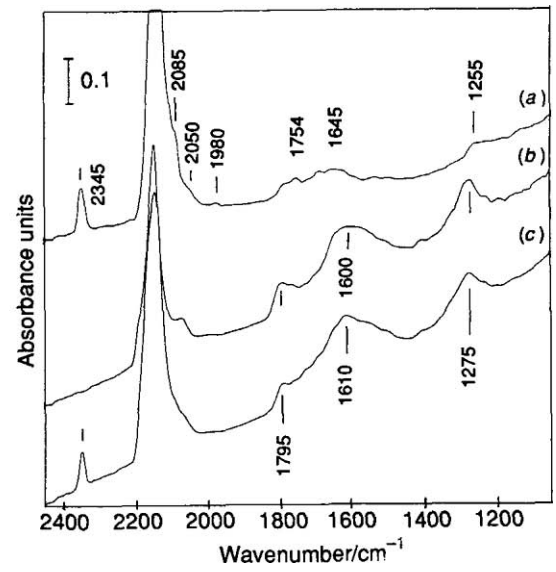

Fig. 4 IR spectra of Co_3O_4 after (*a*) 50 min exposure to CO, (*b*) evacuation to 10^{-5} Torr and (*c*) repeated CO exposure for 50 min

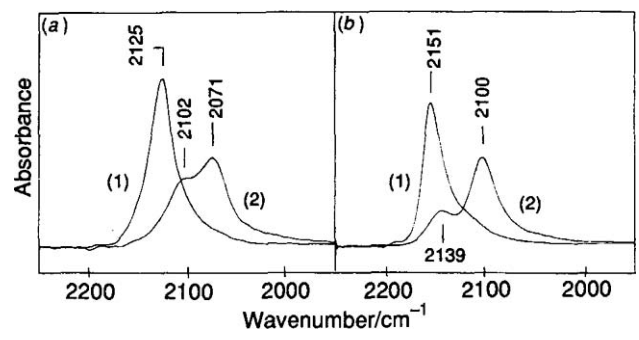

Fig. 5 Isotopic dilution experiments on CoO: (*a*) after 1 min and (*b*) after 100 min exposure; (1) ^{12}CO adsorption (2) $^{12}CO + {}^{13}CO$ (1:7) adsorption

(*i*) For the first time it has been found that at 80 K oxidation of CO (either in a pure CO atmosphere or in a $CO + O_2$ mixture) takes place on the surface of cobalt oxides.

(*ii*) This reaction proceeds without the participation of surface carbonates, which appear to be strongly bound surface complexes formed as a result of molecular CO_2 chemisorption.

(*iii*) In addition to CO_2 formation, changes in the carbonyl regions of the spectra were observed indicating, probably, a rearrangement of the adsorption layer.

Moreover, isotope dilution experiments (Fig. 5) enabled us to observe a high-frequency shift of the carbonyl bands due to dynamic dipole–dipole coupling in the adsorbed layer, indicating the probable 'island' character of the CO chemisorption. This might be associated with aggregation of the adsorption sites on the surface of cobalt oxides.

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