Infrared Spectrophotometry Study of Hydrogen Interaction with Carbonates Adsorbed on ThO$_2$

Contrary to hydrogenation of CO, which has been the subject of many publications and reviews (*1, 2*), hydrogenation of CO$_2$ has been scarcely studied. However, the latter reaction is potentially interesting owing to the possibility which it offers to substitute CO$_2$ for CO in a number of applications (*3*). Thorium dioxide has been widely used in CO hydrogenations, either as a promoter of Fischer–Tropsch catalysts (*1*) or as the sole component of isosynthesis catalyst (*4*).

In CO$_2$ hydrogenation, ThO$_2$ has been used as a promoter of nickel in an earlier investigation (*5*) in which its role was ascribed to dehydrating properties. To the best of our knowledge there is no publication on CO$_2$ methanation on ThO$_2$ alone. This is why it seems worthwhile to report observations made during an infrared spectrophotometry study of hydrogen interaction with carbonated thorium dioxide surface.

Thoria has been obtained from the thermal decomposition of thorium oxalate in air at 450°C during 48 hr. The starting material has been prepared according to the procedure described by Breysse (*6*) in order to ensure a large enough specific surface area (40 m^2 g^{-1}) for the oxide. As this oxide is very difficult to shape as a wafer, it has been compressed on an electrolytic gold grid so as to obtain a mechanically coherent and optically transparent layer. The sample was located in a holder which could slide in a cell made of two parts, one where thermal treatments were carried out, and the other which comprised two KBr windows and through which the ir radiation was passed.

The successive treatments undergone by the solid were as follows:

—an evacuation at room temperature,
—a temperature increase up to 450°C *in vacuo*,
—a heating at 450°C under oxygen for 16 hr in order to burn the eventually adsorbed hydrocarbons,
—a desorption at 450°C for a few hours.

After this preliminary sequence, the temperature of the solid was fixed at the value desired for investigating the hydrogen action. The infrared absorption spectra were recorded by means of a Perkin–Elmer 580 spectrophotometer with an average resolution of 2.8 cm^{-1}.

The spectra of the starting solid exposed to air and of the solid *in vacuo* at room temperature show the absorption bands of carbonates and the vibration band ν_2 of water at 1630 cm^{-1}. For the solid degassed at 450°C for 16 hours there remain only the bands at 850, 1060, 1410, and 1470 cm^{-1}, characteristic of monodentate carbonate, resulting from adsorption of ambient CO$_2$. These results confirm a previous study on CO$_2$ adsorption on thoria (*8*), which has shown that at temperatures over 100°C, CO$_2$ is adsorbed as a monodentate species.

The oxygen treatment at 450°C followed by a desorption at the same temperature does not introduce any noticeable change with respect to the previous spectrum. Interaction of hydrogen with such a surface at room temperature does not modify the spectrum.

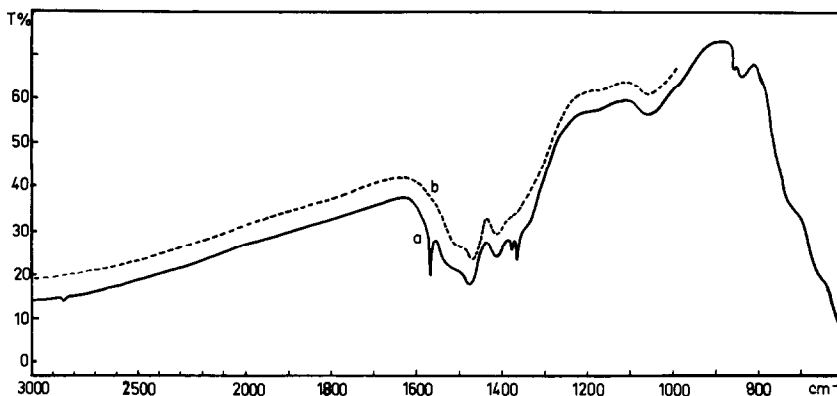Modifications are noted above 250°C (Fig. 1). Spectrum (a) is that of the solid

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FIG. 1. Infrared spectra of ThO_2 (a) after interaction with hydrogen at 250°C and in the presence of the gas phase; (b) after evacuation at 450°C.

having interacted with hydrogen at 250°C for 16 hr and left in the presence of the gas: narrow bands appear at 2845, 1565, 1365, and 1375 cm^{-1} and are ascribed respectively to the ν(CH), ν_{as}(COO$^-$), ν_s(COO$^-$) stretchings, and δ(CH) bending of the formate ion (9). These absorption bands have also been reported for formic acid adsorption on several oxides (10).

Spectrum (b) is obtained with the preceding solid vacuum-treated at 450°C: it reveals the disappearance of these formate bands. Formate formation also occurs at 350 and 450°C. In the gas phase at 350°C only one hydrocarbon is detected by infrared spectroscopy and by mass spectrometry, namely, methane (absorption bands at 1305 and 3015 cm^{-1}). The methane amount grows with the temperature. At 450°C a small amount of CO is revealed by absorption at 2140 cm^{-1} and by its mass spectrometry peak.

This observation prompted us to study the reaction of CO with H_2 on ThO_2 surface thoroughly cleared of its adsorbed carbonates by repeated hydrogen treatments and desorption at 550°C. From 350°C a mixture $(H_2)/(CO) = 7$ causes both formate formation on the surface and exclusive appearance of methane in the gas phase.

All the above observations are in agreement with a mechanism in which CO_2 (adsorbed as a carbonate) is first reduced to CO by hydrogen, CO being manifested on the surface as a formate. The hydrogenation of CO in a later stage then leads exclusively to methane.

This mechanism is supported by the following facts:

(1) ThO_2 is known as a catalyst for the water gas conversion (11) and therefore of the reverse reaction

$$CO_2 + H_2 \rightarrow CO + H_2O.$$
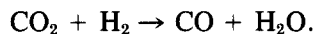
(2) CO is adsorbed on surface oxygen ions as a formate, as already reported (8). This is why the carbon monoxide resulting from the above reaction is revealed as a formate and appears in the gas phase only at higher temperatures (whereas the adsorbed water is evidenced by the broad hydroxyl bands between 3400 and 3700 cm^{-1}). These observations are in agreement with the previous work of Ueno and coworkers (12) who also provided evidence for the formate ion as an intermediate species in the water gas shift reaction on MgO.

(3) The exclusive formation of methane by CO_2 hydrogenation has been observed on most Fischer–Tropsch catalysts (13–15) and CO formation is widely accepted as an intermediate step (13–15).

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