Activation of Carbon Dioxide by a Silica-supported Platinum–Tin Bimetallic Complex

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Simultaneous coordination of carbon dioxide and ethylene and their coupling over a silica-supported Pt–Sn bimetallic complex is reported.

Reactions involving CO_2 and transition metals have been extensively studied due to their importance in the potential activation of CO_2 *via* complexation on metal centres.[1,2] Among them, stoichiometric reactions of carbon dioxide with transition metal complexes,[3] insertion reactions into metal–carbon bonds of well-defined complexes,[4] and formation of metallaheterocycles from the coupling reaction of CO_2 with unsaturated compounds on metal centres[5,6] have been described in the literature. The relevance of all these reactions lies in the fact that they may lead to products that could be postulated as intermediates in catalytic processes.[7]

We report here, for the first time, the activation of the CO_2 molecule and its coupling to ethylene over a silica-supported Pt–Sn complex. The methyl 3-hydroxypropanoate was the only product detected after reaction between CO_2 and C_2H_4 over *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$–silica when the sample was treated with a water–methanol mixture. On the other hand, by FT–IR spectroscopy, simultaneous coordination of CO_2 and C_2H_4 to the supported complex was observed.

Complex *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$, prepared and characterized according to literature methods,[8] was impregnated from a methylene chloride solution on a Degussa Aerosil-type silica (BET surface area of 200 $m^2\ g^{-1}$) treated under high vacuum (10^{-5} mbar) at 473 K for 16 h. The impregnation was performed to yield 10^{-4} mol complex per gram of silica. The anchoring of the complex was followed by *in situ* IR spectroscopy and accomplished after impregnation by a high vacuum treatment at 373 K for 16 h, as described elsewhere.[9]

Reaction was carried out in an 80 cm^3 inconel batch reactor over 0.5 g of sample at 42 bar of a 1 : 1 CO_2–C_2H_4 mixture and 393 K. After 12 h the reactor was cooled to 195 K and vented, then in order to extract the reaction products the solid was treated with 5 cm^3 of a 1 : 1 water–methanol mixture at room temperature. The resulting suspension was filtered and the emerging solution was acidified with HCl, analysed by gas chromatography and the products were characterized by mass spectrometry. The only product detected was the methyl 3-hydroxypropanoate (1.9×10^{-6} mol g^{-1} sample), presumably coming from a carboxylate produced in the reaction between CO_2 and C_2H_4 on the supported complex. Blank runs with non-impregnated silica were carried out under the same reaction conditions and no transformation products were detected in any case.

To carry out infrared experiments a sample was prepared *in situ* from a methylene dichloride solution of *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$ and a thin disk of the silica support in a special greaseless infrared cell using break-seal techniques.

After impregnation, sample was evacuated at 373 K, cooled to 294 K, and then CO_2 was introduced. The IR spectrum is shown in Fig. 1(*a*), an asymmetric band with two peaks clearly developed after 1 hour can be observed. Deconvolution of this band gave two well-resolved absorption maxima at 2345 and 2339 cm^{-1} [Fig. 1(*b*)]. A vacuum treatment produced the disappearance of the absorption at higher wavenumbers and only the band at 2339 cm^{-1} remained [Fig. 1(*c*)]. Prolonged high vacuum treatment at room temperature (2 h) was necessary to complete the elimination of this band. In a blank experiment CO_2 was admitted on silica support, and only one band at 2344 cm^{-1} appeared [Fig. 1(*d*)]. These findings indicate that the band at 2345 cm^{-1} in Fig. 1(*b*) can be assigned to physisorbed CO_2 on silica, in good agreement with literature data,[10,11] and the band at 2339 cm^{-1} can reasonably be assigned to CO_2 coordinated to the supported metallic complex without lost of linearity on the CO_2 molecule. Indeed, the appearance of a band at 2337 cm^{-1}, attributable to

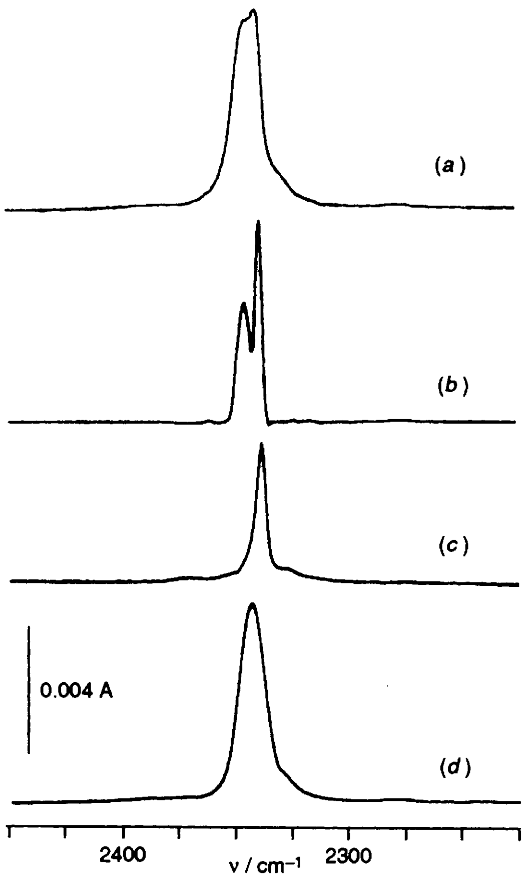

Fig. 1 Infrared spectra of CO_2: (*a*) CO_2 (60 mbar) over *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$–SiO_2 system at 294 K; (*b*) deconvolution of spectrum (*a*); (*c*) After spectrum (*a*), sample evacuated to 10^{-2} mbar; (*d*) CO_2 (40 mbar) over SiO_2 support at 294 K

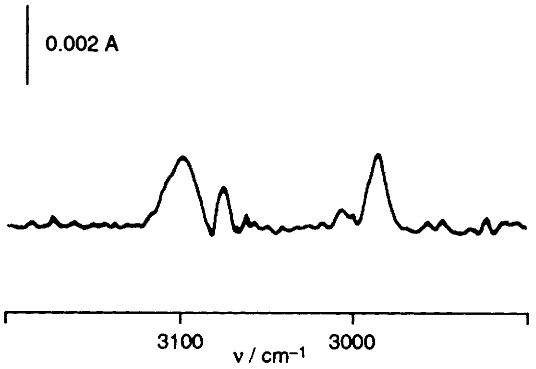

Fig. 2 Infrared spectrum in the ν(C–H) region of coordinated C_2H_4 to *cis*-$[PtCl(SnCl_3)(PPh_3)_2]$–SiO_2 system. After C_2H_4 admission at 294 K (20 mbar), the sample was evacuated to 10^{-3} mbar.

coordinated CO_2 on metallic silver surface, has recently been reported.[12]

An independent infrared study of the interaction of ethylene with the supported Pt–Sn complex revealed bands in the ν(C–H) region at 3098, 3076, 3008 and 2987 cm^{-1} (Fig. 2). The spectrum is very similar to that of Zeisse's salt[13] and indicates a possible π interaction between ethylene and the supported Pt–Sn complex.

The FT–IR spectrum obtained when sample was exposed to CO_2 after ethylene treatment and then evacuated at room temperature is analogous to those of CO_2 and ethylene coordinated in separate experiments, indicating simultaneous coordination of CO_2 and ethylene. These results support the observed coupling reaction between CO_2 and ethylene over this supported Pt–Sn complex.

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