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# FT-IR study on the interaction of $CO_2$ with $H_2$ and hydrocarbons over supported Re

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## Abstract

The adsorption of $CO_2$ and the co-adsorption of $H_2 + CO_2$, $C_1$–$C_2$ alkanes + $CO_2$ on Re supported by $Al_2O_3$, $TiO_2$, MgO and $SiO_2$ have been investigated by FT-IR spectroscopy. The dissociation of $CO_2$ was not experienced on the Re/$Al_2O_3$ reduced at 673 K, it occurred, however, on the sample reduced at 1073 K. Addition of $H_2$ to $CO_2$, initiated the dissociation on all catalysts as indicated by CO bands at 2022–2053 $cm^{-1}$. Besides, new spectral features were developed at 1600–1550, 1395 and 1365 $cm^{-1}$ attributed to formate species. This assumption was confirmed by the adsorption of HCOOH vapor on these solids. No bands due to formate were detected on Re/$SiO_2$. Adding methane and ethane to $CO_2$ also led to the appearance of CO bands, the intensities of which were much less compared to the $H_2 + CO_2$ co-adsorption. The formation of formate also occurred to a small extent. No formate was detected following the co-adsorption of $CO_2$-containing gas mixture on the supporting oxides alone. It was assumed that the formate species identified in the surface interactions is located on the support, where it is stabilized. The possible pathways of the occurrence of formate complex on the oxides are described.

*Keywords:* FT-IR study; Co-adsorption; Surface interactions

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## 1. Introduction

Supported Re is a widely used catalyst in several technological important reactions, such as the reforming of petroleum feedstock [1]. Re also exhibits oxygen storage properties in automotive three-way catalyst [2,3]. Recently it was found that Re is active in the conversion of methane into benzene at 873–1073 K [4,5]. The capability of Re/ZSM-5 in the aromatization of $CH_4$ approaches that of $Mo_2C$/ZSM-5, which exhibits the best catalytic performance in this process [6–12]. This is in contrast to the behaviour of supported Pt metals, which catalyses only the complete decomposition of methane [13–17]. Subsequent studies revealed that supported Re also effectively catalyzes the aromatization of other lower alkanes, ethane, propane and *n*-butane [18,19]. The catalytic performance of Re in the production of synthesis gas has received little attention, although it was shown that at sufficiently high reaction temperatures it is an active carbon free catalyst for dry reforming of methane [20].

In the present paper an account is given on the surface interaction of hydrogen and lower hydrocarbons with $CO_2$ studied by FT-IR spectroscopy. This work is strongly connected with the study of $CO_2$ reforming of hydrocarbons on supported Re catalysts. We want to find answers to the following questions: (i) can the hydrogen and hydrocarbons promote the dissociation of $CO_2$, (ii) can the compounds influence the bonding of CO to Re, and influence the CO-induced disruption of Re crystallites, (iii) what kind of surface complexes is formed in the surface interaction of the $CO_2$-containing gas mixture?

## 2. Experimental

### 2.1. Materials

Supported rhenium was prepared by impregnating the support in an aqueous solution of $(NH_4)_2ReO_4{\cdot}4H_2O$ (Merck).

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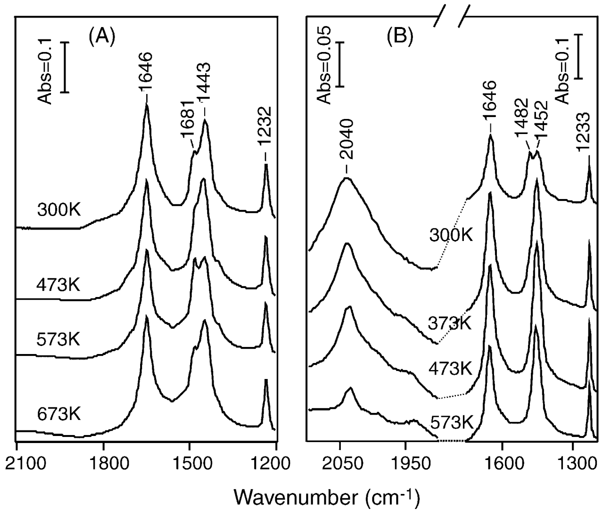

Fig. 1. FT-IR spectra of $Re/Al_2O_3$ ($T_R = 673\,K$) following the adsorption of $CO_2$ (50 Torr) at different temperatures for 15 min. Reduction temperature: 673 K (A) and 1073 K (B).

The following supports were used: $Al_2O_3$ (Degussa); $SiO_2$ (CAB-O-SiL, MS Scintran BHD); $TiO_2$ (Degussa P25) and MgO (DAB). After impregnation, the suspensions were dried in air at 383 K. The dried and pulverized samples were pressed into thin self-supporting wafers (30 mm × 10 mm, $\sim$60 mg/cm$^2$). Further treatment was applied in situ: it consisted of oxidation at 573 K (100 Torr of $O_2$ for 30 min), evacuation at 573 K for 30 min, reduction at 673 K and in certain cases at 973–1073 K (100 Torr of $H_2$ for 60 min), and evacuation at the temperature of reduction for 30 min. Note that the heating of the sample from 573 K to the temperature of reduction was carried out in the presence of hydrogen. The Re content was 5 wt.% on all samples.

### 2.2. Methods

Infrared spectra were recorded at room temperature with a Biorad (Digilab. Div.FTS 155). Typically, 128 scans were collected with 2 cm$^{-1}$ spectral resolution. All of the spectra were taken without the use of a scaling factor ($f = 1.0$).

## 3. Results

### 3.1. $CO_2$ adsorption

As hydrogen can promote the dissociation of $CO_2$ (see next chapter), it was absolutely necessary to remove completely the hydrogen from the system after reduction of Re catalyst, otherwise the appearance of CO bands cannot avoided. Spectra obtained after adsorption of $CO_2$ on $Re/Al_2O_3$ ($T_R = 673\,K$) are displayed in Fig. 1A. Strong bands appeared at 2334, 1646, 1481, 1443 and 1232 cm$^{-1}$, the intensity of which only slightly decreased after degassing at 300 K. No new spectral features developed following the adsorption at higher temperatures, 373–673 K. Similar experiment on the $Re/Al_2O_3$ reduced at 1073 K produced a weak absorption band at 2040 cm$^{-1}$, in addition to the previously observed peaks (Fig. 1B). For Re/MgO, we measured absorption at $\sim$2334, 1660–1670, 1450, 1543, 1310 and 1220 cm$^{-1}$ at 300 K. Admission of $CO_2$ on $Re/TiO_2$ at 300 K produced bands at 2334, 1667, 1582, 1438, 1378 and 1322 cm$^{-1}$, the position of which was independent of the temperature in the range of 300–573 K. In the case of $Re/SiO_2$, we obtained only a band at 2334 cm$^{-1}$. Evacuation of the cell led to the elimination of the 2334 cm$^{-1}$ feature in all cases, but did not affect the other bands.

### 3.2. $H_2 + CO_2$ adsorption

Adding $H_2$ to $CO_2$ caused a dramatic change in the IR spectra of adsorbed $CO_2$ registered for $Re/Al_2O_3$ ($T_R = 673\,K$) (Fig. 2A). In addition to the bands of various

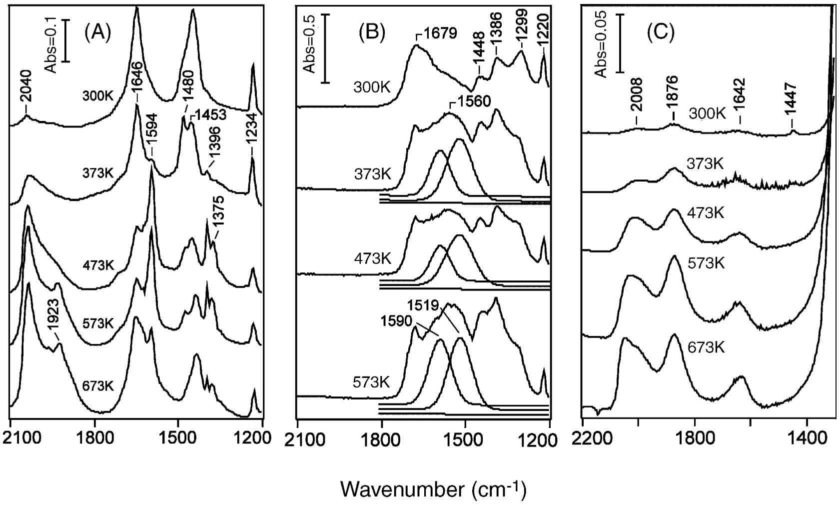

Fig. 2. FT-IR spectra of Re catalysts following the adsorption of $H_2 + CO_2$ (1:1) gas mixture at different temperatures for 15 min. (A) $Re/Al_2O_3$; (B) Re/MgO; (C) $Re/SiO_2$ ($T_R = 673\,K$).