

THE CO-ADSORPTION OF METHANE AND CARBON DIOXIDE ON CATALYSTS

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ABSTRACT

In the elucidation of the reaction mechanism of a catalytic process it is important to establish the reaction intermediates and their possible role in the reaction. In most cases, however, this is not an easy task as a real reaction intermediate exists only transitorily and in a very low concentration on the catalysts.

The adsorption of CO₂ and the co-adsorption of CH₄ + CO₂ on Re supported by Al₂O₃, TiO₂, SiO₂ and MgO have been investigated by FTIR spectroscopy. The dissociation of CO₂ was not experienced on the Re/Al₂O₃ reduced at 673 K, it occurred, however, on the sample reduced at 1073 K.

Addition of CH₄ to CO₂, initiated the dissociation on all catalysts as indicated by CO bands at 2041 cm⁻¹. Besides, new spectral features were developed at 1599 and 1397 cm⁻¹ attributed to formate species.

No bands due to formate were detected on Re/SiO₂ and no formate was detected following the co-adsorption of CO₂-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: co-adsorption, catalyst, support, CH₄ + CO₂ reaction, formate

INTRODUCTION

The number of organic chemical products produced in the world moves about 30000 nowadays (WEISSERMEL AND ARPE, 2010). But despite the relatively large numbers, they are just made from a few raw materials. The applied coal is obtained almost exclusively from fossil sources – namely mineral oil, natural gas and hard coal.

The limited resources of coal raised the problem of the exploitation of alternative carbon sources in the early 1970s.

Carbon dioxide has always enjoyed great attention because of the nature of synthetic building process used successfully during photosynthesis - which can be considered as the basis of life on Earth as well.

In our planet the amount of CO₂ and CO₃²⁻ forms are available several times higher than natural resources in the form of hard coal, oil or natural gas form. In addition, this source is virtually limitless, especially if we consider that since the middle of the 19th century at the beginning of industrialization – the amount of "anthropogenic" CO₂ has multiplied considerably in the atmosphere. In 1989 the amount of CO₂ emission due to industrial activities was approximately 7×10⁹ t (LEITNER, 1995).

Supported Re is a widely used catalyst in several technologically important reactions, such as the reforming of petroleum feedstock (CIAPETTA AND WALLANCE, 1971).

Re also exhibits oxygen storage properties in automatic three-way catalysts (TAYLOR ET AL., 1984).

MATERIAL AND METHOD

Supported rhenium was prepared by impregnating the support in aqueous solution of $(\text{NH}_4)_2\text{ReO}_4 \cdot 4\text{H}_2\text{O}$ (Merck). The following supports were used: SiO_2 (CAB-O-SiL, and MS Scintran BHD); Al_2O_3 (Degussa); 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 x 10 mm, $\sim 60 \text{ mg/cm}^2$). 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 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. As hydrogen can promote the dissociation of CO_2 , it was absolutely necessary to remove completely the hydrogen from the system after the reduction of Re catalyst, otherwise the appearance of CO bands cannot be avoided. The Re content was 5 wt% on all samples.

Infrared spectra were recorded with a Digilab. Div. FTS 155 by Biorad with a wave number accuracy of $\pm 4 \text{ cm}^{-1}$. Typically 128 scans were collected. All of the spectra were taken without the use of a scaling factor ($f = 1.0$).

RESULTS

CO_2 adsorption

The spectra obtained after adsorption of CO_2 on $\text{Re}/\text{Al}_2\text{O}_3$ ($T_R = 673 \text{ K}$) are displayed in *Figure 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.

There were no other spectral features following the adsorption at higher temperatures, 373-673 K. Similar experiment on the $\text{Re}/\text{Al}_2\text{O}_3$ reduced at 1073 K produced a weak absorption band at 2040 cm^{-1} , in addition to the previously observed peaks (*Figure 1B*).

For Re/MgO , we measured absorption at ~ 2334 , 1660-1670, 1450, 1543, 1310 and 1220 cm^{-1} at 300 K (results not shown).

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 (results not shown).

The most sensitive method to detect the dissociation of CO_2 on supported metals is the FTIR spectroscopy. The spectra presented in *Figure 1* clearly show that the dissociation of CO_2 is very limited on $\text{Re}/\text{Al}_2\text{O}_3$. Admission of CO_2 on $\text{Re}/\text{Al}_2\text{O}_3$ ($T_R = 673 \text{ K}$) at 300 K produced a strong band at 2234 cm^{-1} due to CO_2 and several others at 1646, 1481, 1443 and 1233 cm^{-1} due to carbonate species. Other spectral feature in the CO stretching region was not seen even after adsorption at 573 K. Evacuation of the cell led to the disappearance of the CO_2 band at 2334 cm^{-1} and did not affect the other bands due to the vibration of carbonates. A CO band at 2040 cm^{-1} suggesting the dissociation of CO_2 , however, appeared on highly reduced $\text{Re}/\text{Al}_2\text{O}_3$ ($T_R = 1073 \text{ K}$).

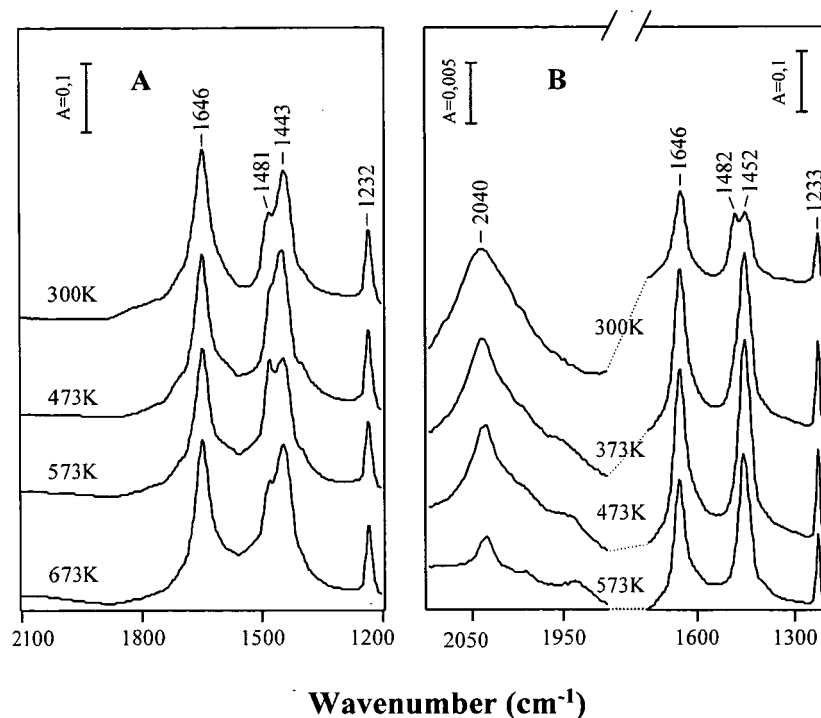


Figure 1. FTIR spectra of Re/Al₂O₃ following the adsorption of CO₂ (50 Torr) at different temperatures for 15 min ($T_R = 673$ K) Reduction temperature: 673 K (A) and 1073 K (B)

CH₄ + CO₂ adsorption

Adding methane along with CO₂ caused the appearance of CO band at 2041 cm⁻¹ on Re/Al₂O₃ even at room temperature (*Figure 2A*).

The position of the bands in the low frequency region remained unaltered. Raising of the adsorption temperature led to the attenuation of all bands. Weak spectral features were detected at 1599 and 1397 cm⁻¹ following the adsorption at 473 K. These weak spectral features were also detected at 573 K (not shown). More intense absorption bands were experienced on Re/TiO₂ sample (*Figure 2A*).

In addition to the band at 2043 cm⁻¹, weaker peaks appeared at 2009 and 1963 cm⁻¹. On this catalyst a widening of the band at 1583 cm⁻¹ also occurred at higher temperature and a peak at 1557 cm⁻¹ can be distinguished (*Figure 2A*). Co-adsorption of CH₄ + CO₂ mixture on Re/MgO at 373 – 473 K resulted in a formation of a shoulder at ~ 1580 cm⁻¹ (*Figure 2B*). On Re/SiO₂ we obtained only very weak absorption at 1877 cm⁻¹.

Interestingly, the dissociation of CO₂ was also facilitated by methane even at 300 K (*Figure 2*). The intensity of CO band was, however, much lower. This is not surprising, if we assume that adsorbed hydrogen is needed for dissociation of CO₂. As both CH₄ and CO₂ adsorb weakly over Re at 300 K, we can exclude the direct surface interaction between the two adsorbed species.

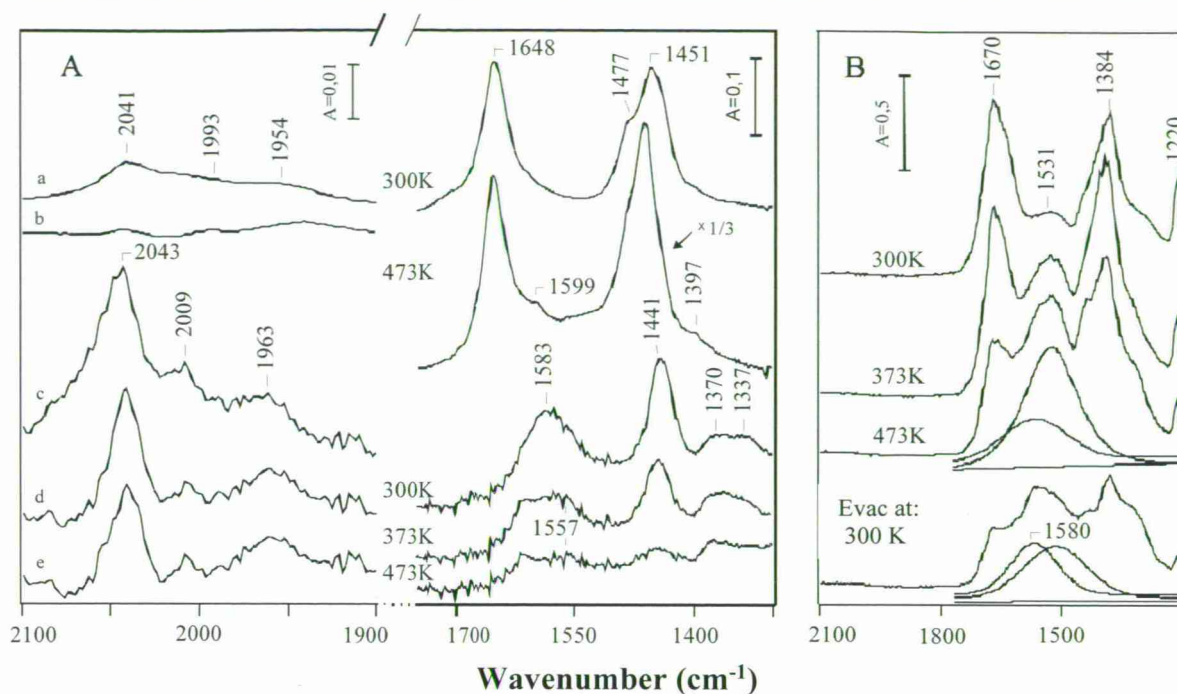


Figure 2. FTIR spectra of Re catalysts following the adsorption of CH₄ + CO₂ (1:1) gas mixture at different temperatures for 15 min ($T_R = 673\text{K}$)
Supports: (A) Re/Al₂O₃ (a, b); Re/TiO₂ (c-f);
(B) Re/MgO

CONCLUSIONS

The adsorption of CO₂ on Re supported by Al₂O₃, TiO₂, MgO and SiO₂ have been investigated by FTIR spectroscopy. The dissociation of CO₂ was not experienced on the Re/Al₂O₃ reduced at 673 K, it occurred, however, on the sample reduced at 1073 K.

No format was detected following the co-adsorption of CO₂-containing gas mixture on the supporting oxides alone. It was assumed that the format species identified in the surface interactions is located on the support, where it is stabilized.

Addition of CH₄ to CO₂, initiated the dissociation on all catalysts as indicated by CO bands at 2041 cm⁻¹. Besides, new spectral features were developed at 1599 and 1397 cm⁻¹ attributed to format species. This assumption was confirmed by the adsorption of HCOOH vapor on these solids.

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