

THE CO-ADSORPTION OF HYDROGEN 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 H₂ + CO₂ on Re supported by Al₂O₃, TiO₂, MgO and SiO₂ have been investigated by FT-IR 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 H₂ to CO₂, 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 format species. No bands due to format were detected on Re/SiO₂ and 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. The possible pathways of the occurrence of format complex on the oxides are described.

Keywords: catalyst, support, co-adsorption, H₂ + CO₂ reaction, formate

INTRODUCTION

The number of chemical products produced in the world moves about 30,000 nowadays (WEISSERMEL AND ARPE, 1997, 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 (NH₄)₂ReO₄·4H₂O (Merck). The following supports were used: SiO₂ (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 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. 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 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 $\pm 4 \text{ cm}^{-1}$ (Figure 1). Typically 128 scans were collected. All of the spectra were taken without the use of a scaling factor ($f = 1.0$).

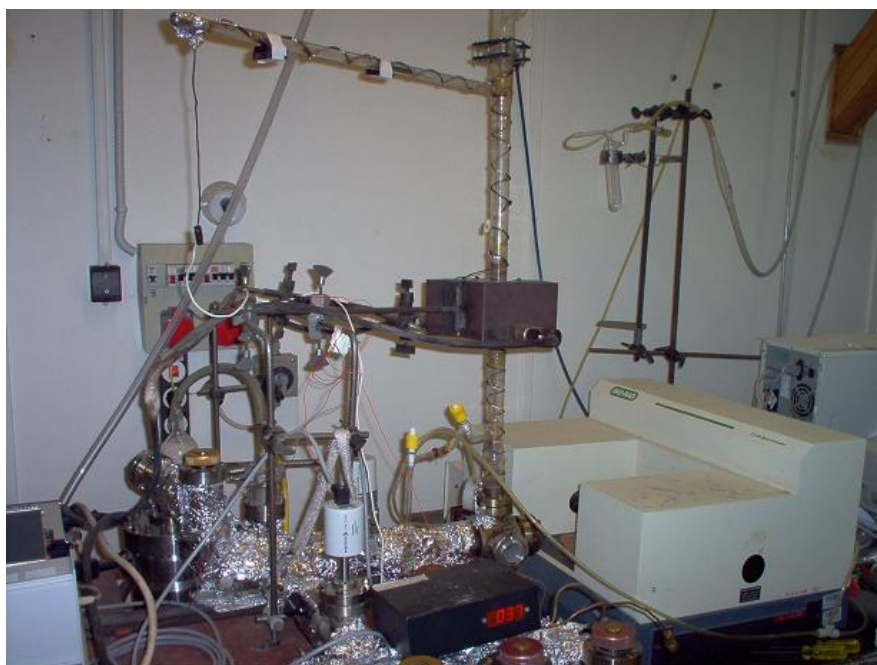


Figure 1. FTIR 155 set

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 2A.

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 2B). For Re/MgO , we measured absorption at ~ 2334 , 1660-1670, 1450, 1543, 1310 and 1220 cm^{-1} at 300 K. Admission of CO_2 on

Re/TiO₂ 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/SiO₂, 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.

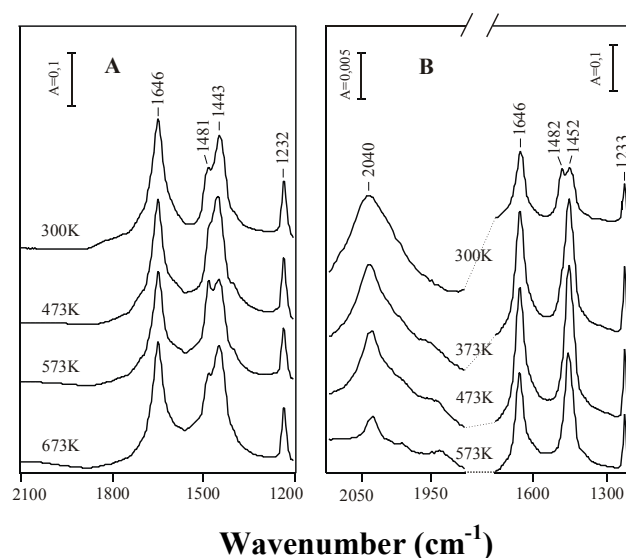


Figure 2. FTIR spectra of Re/Al₂O₃ following the adsorption of CO₂ (50 Torr) at different temperatures for 15 min ($T_R = 673$ K) Reduction temperature: 673 K (A) and 1073 K (B).

H₂ + CO₂ adsorption

Adding H₂ to CO₂ caused a change in the IR spectra of adsorbed CO₂ registered by Re/Al₂O₃ ($T_R = 673$ K) (Figure 3A).

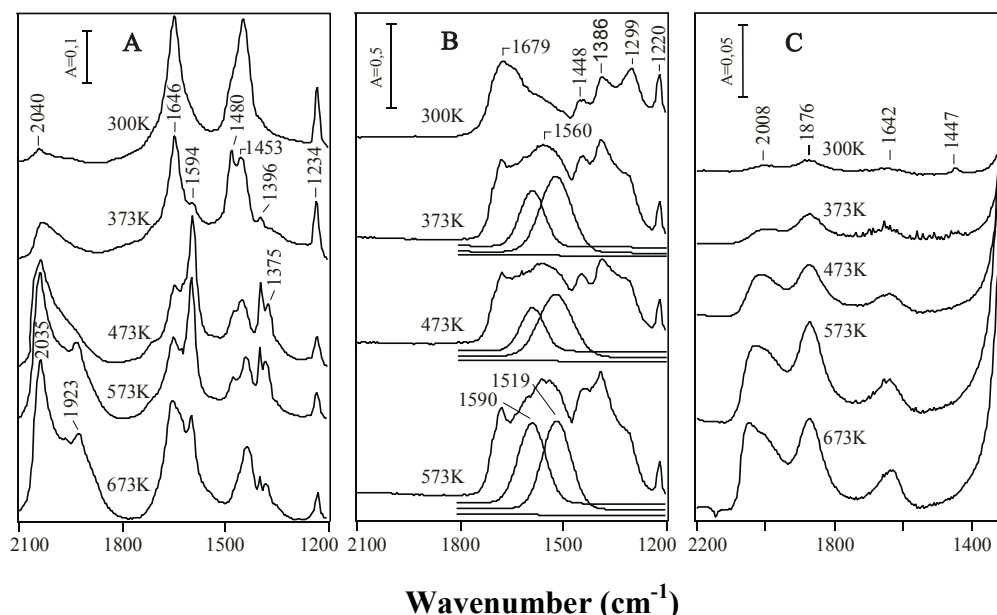


Figure 3. FTIR spectra of Re catalysts following the adsorption of H₂ + CO₂ (1:1) at different temperatures for 15 min ($T_R = 673$ K) Supports: Re/Al₂O₃ (A); Re/MgO (B); Re/SiO₂ (C)

In consequence of the bands of various carbonates detected after CO_2 adsorption, new spectral features appeared at 2040, 1594, 1396 and 1375 cm^{-1} . These new bands were seen even after adsorption at 300 K: their intensities increased in time of the adsorption. Raising the temperature resulted in an enhancement of all new bands, and produced another peak at 1923 cm^{-1} . Note that we also obtained a very weak signal at 2873 cm^{-1} . Degassing the catalyst at 300 K after above experiments caused a slight reduction of the bands in the low frequency region.

Co-adsorption of $\text{H}_2 + \text{CO}_2$ on Re/MgO yielded no bands in the CO stretching region. In the low frequency range a broad absorption was observed between 1500 and 1650 cm^{-1} consisting of several components. Deconvolution of this broad peak resulted in at least two bands between 1519 and 1590 cm^{-1} (Figure 3B).

In the case of Re/SiO₂ weaker absorption bands appeared at 2008 and 1876 cm^{-1} at 300 K. An increase in the temperature caused an intensification and a slight shift of these bands (Figure 3C).

It is important to note that no new spectral features developed in the low frequency region. In certain cases a band was seen at $\sim 1620\text{ cm}^{-1}$, which is very likely due to the adsorbed H_2O .

Compared the production of new spectral features, Re/TiO₂ was more active than Re/Al₂O₃. Strong absorption bands appeared even at room temperature. Their positions were at 2053, 2010 and 1976 cm^{-1} (Figure 4). An increase in the temperature caused a shift of the 2053 cm^{-1} band first to 2043 and then 2037 cm^{-1} , the disappearance of the bands at 2010 and 1976 cm^{-1} , and the formation of new band at 1944 cm^{-1} . In the low frequency region a band at 1583 cm^{-1} formed after CO_2 adsorption is broadened, particularly at 373-473 K. It clearly consisted of two components absorbing at 1585 and 1547 cm^{-1} . At the same time another weak peak developed at 1360 cm^{-1} . It is an important observation that the co-adsorption of $\text{H}_2 + \text{CO}_2$ mixture on Re-free oxides did not produce the 1590-1595 and $1360\text{--}1395\text{ cm}^{-1}$ spectral features under similar conditions up to 573 K.

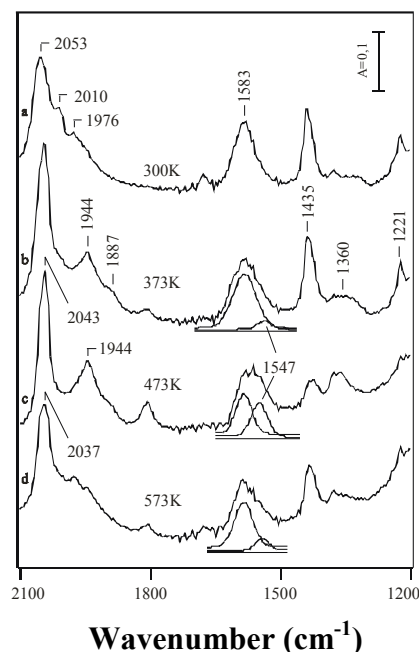


Figure 4. FTIR spectra of Re/TiO₂ following the adsorption of $\text{H}_2 + \text{CO}_2$ (1:1) at different temperatures for 15 min ($T_R=673\text{ K}$)

CONCLUSIONS

The adsorption of CO₂ on Re supported by Al₂O₃, TiO₂, MgO and SiO₂ have been investigated by FT-IR 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 H₂ to CO₂, 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 format species. This assumption was confirmed by the adsorption of HCOOH vapor on these solids.

REFERENCES

- ARPE, H.J. (2010): Industrial Organic Chemistry, 5th ed., VCH, Weinheim. 525 p.
- CIAPETTA F. G., WALLACE D.N. (1971): Catalytic Naphtha Reforming. Catal. Rev. 5: 67.
- LEITNER W. (1995): Carbon Dioxide as a Raw Material: The Synthesis of Formic Acid and Its Derivatives from CO₂. Angew. Chem. 34: 2207–2221.
- TAYLOR K.C., IN: ANDERSON M. J. R., BOUDART M. (EDS.) (1984): Automobile Catalytic Converters. Catalysis Science and Technology, 5, Springer Verlag, Berlin. 119 p.
- WEISSERMEL, K., ARPE, H.J. (1997): Industrial Organic Chemistry, 3rd ed., VCH, Weinheim. 439 p.