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.
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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 suffi-

ciently 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).

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, ~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
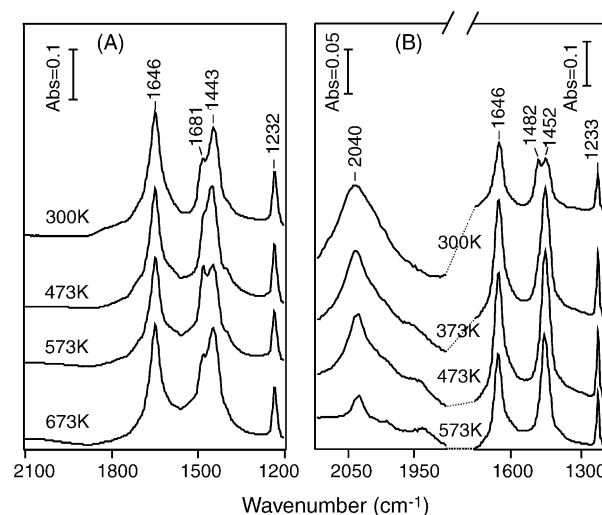

Fig. 1. FT-IR spectra of Re/Al_2O_3 ($T_R = 673$ K) following the adsorption of CO_2 (50 Torr) at different temperatures for 15 min. Reduction temperature: 673 K (A) and 1073 K (B).

absorption band at 2040 cm^{-1}, in addition to the previously observed peaks (Fig. 1B). 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/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

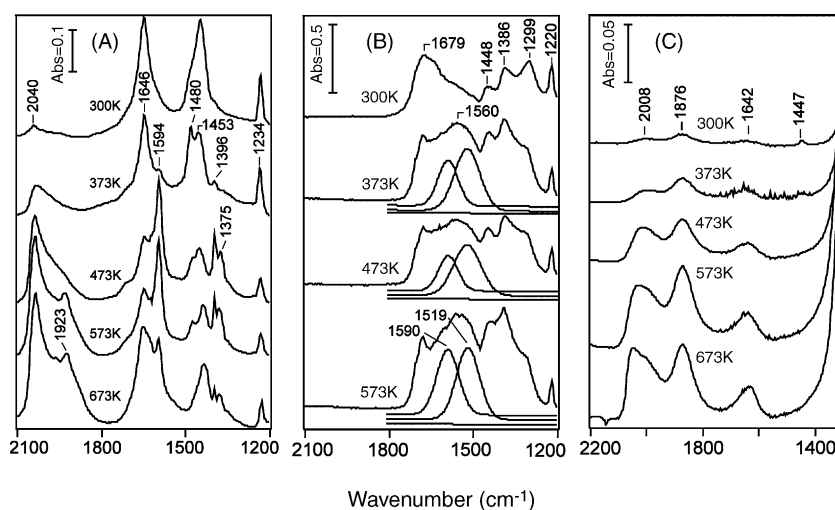
Fig. 2. FT-IR spectra of Re catalysts following the adsorption of $H_2 + CO_2$ (1:1) gas mixture at different temperatures for 15 min. (A) Re/Al_2O_3; (B) Re/MgO; (C) Re/SiO_2 ($T_R = 673$ K).

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 1928 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 $H_2 + CO_2$ on Rh/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 at 1519 and 1590 cm^{-1} (Fig. 2B). In the case of Re/SiO_2 weaker absorption bands appeared at 2010 and 1876 cm^{-1} at 300 K. An increase in the temperature caused an intensification and a slight shift of these bands (Fig. 2B). It is important to note that no new spectral features developed in the low frequency region. In certain cases a band was seen at ∼1620 cm^{-1}, which is very likely due to the adsorbed H_2O.

As regards the production of new spectral features Re/TiO_2 was more active than Re/Al_2O_3. Strong absorption bands appeared even at room temperature. Their positions were at 2053, 2010 and 1976 cm^{-1} (Fig. 3). 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 1945 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 1547–1550 cm^{-1}. At the same time another weak peak developed at 1360 cm^{-1}. It is an important observation that the co-adsorption of $H_2 + CO_2$ mixture on Re-free oxides did not produce the 1560–1595 and 1360–1395 cm^{-1} spectral features under similar conditions up to 573 K.
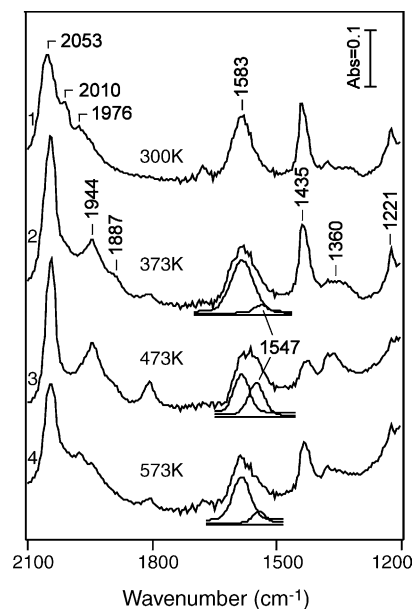

Fig. 3. FT-IR spectra of Re/TiO_2 ($T_R = 673$ K) following the adsorption of $H_2 + CO_2$ at different temperatures.

3.3. $CH_4 + CO_2$ adsorption

Adding methane to CO_2 caused the appearance of a CO band at 2041 cm^{-1} on Re/Al_2O_3 even at room temperature (Fig. 4A). The position of the bands in the low frequency region remained unaltered. Raising 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 473–573 K. More intense absorption bands were experienced on Re/TiO_2 sample (Fig. 4A). 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
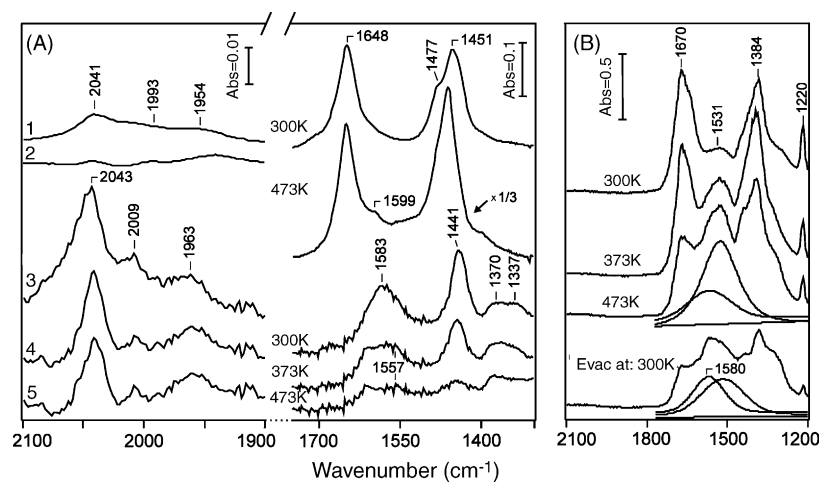

Fig. 4. FT-IR spectra of Re catalyst following the adsorption of $CH_4 + CO_2$ (1:1) gas mixture at different temperature for 15 min. (A) Re/Al_2O_3 (1,2); Re/TiO_2 (3–5) and (B) Re/MgO ($T_R = 673$ K).
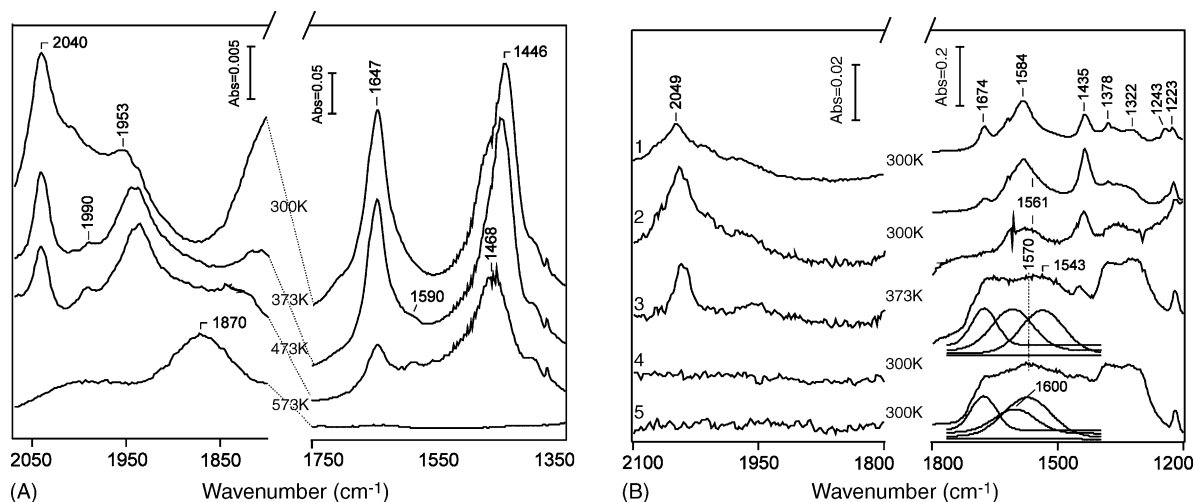
Fig. 5. (A) FT-IR spectra of Re/Al$_2$O$_3$ (T_R = 673 K) following the adsorption of C$_2$H$_6$ + CO$_2$ (1:1) gas mixture at different temperature for 15 min. (B) FT-IR spectra following the adsorption of CO$_2$ (1) and C$_2$H$_6$ + CO$_2$ (2,3) on Re/TiO$_2$ and CO$_2$ (4) and C$_2$H$_6$ + CO$_2$ (5) on Re/MgO (T_R = 673 K).

distinguished (Fig. 4A). Co-adsorption of CH$_4$ + CO$_2$ mixture on Re/MgO at 373–473 K resulted in a formation of a shoulder at ∼1580 cm^{-1} (Fig. 4B). On Re/SiO$_2$ we obtained only very weak absorption at 1877 cm^{-1}.

3.4. C$_2$H$_6$ + CO$_2$ adsorption

Adsorption of C$_2$H$_6$ + CO$_2$ gas mixture on Re/Al$_2$O$_3$ at 300 K produced two absorption bands at 2040 and 1953 cm^{-1}, the intensity of which decreased at higher temperatures (Fig. 5A). In the low frequency region a very weak band can be detected at 1590 cm^{-1} even at 373–473 K. Adsorption of C$_2$H$_6$ + CO$_2$ on Re/TiO$_2$ produced a band at 2049 cm^{-1}, the intensity of which was higher than that observed in the absence of C$_2$H$_6$ (Fig. 5B). A shoulder at 1561 cm^{-1} also developed even at 300–373 K. In the case of Re/MgO we obtained no CO band, but a new spectral feature at ∼1600 cm^{-1} can be clearly established in the deconvoluted spectrum (Fig. 5B). Co-adsorption of C$_2$H$_6$–CO$_2$ on Re/SiO$_2$ at 373 K produced two bands, a stronger one at 1871 and a weaker one at 1987 cm^{-1}.

3.5. Adsorption of HCOOH

For the interpretation of the IR spectra obtained previously it seemed necessary to determine the interaction of HCOOH with various Re catalysts. Adsorption of HCOOH on Re/Al$_2$O$_3$, Re/TiO$_2$ and Re/MgO at 300 K produced strong absorption bands at 1600–1558, 1395 and 1373 cm^{-1}. Degassing the samples caused only slight attention of the bands. Heating the adsorbed layer to higher temperatures under continuous evacuation led to the decrease of the above bands above 573 K, and produced weak absorption features at 2020–2040 cm^{-1}. In contrast, adsorption of HCOOH on Re/SiO$_2$ at and above 300 K yielded only peaks at 1720 and 2040 cm^{-1}. The first one was eliminated by evacuation at
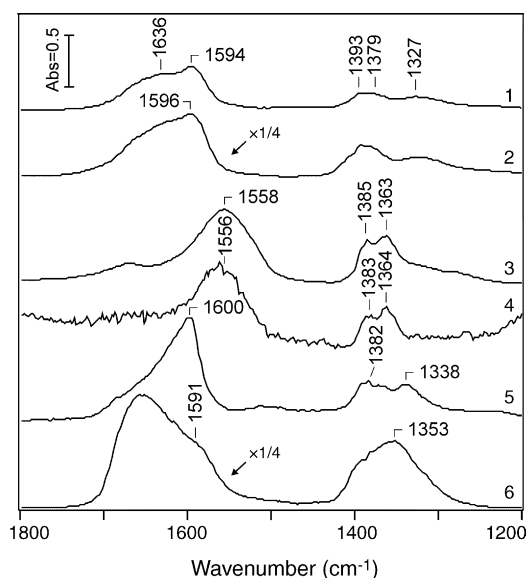

Fig. 6. FT-IR spectra following the adsorption and subsequent evacuation of HCOOH at 300 K, on Re/Al$_2$O$_3$ (1), Al$_2$O$_3$ (2), Re/TiO$_2$ (3), TiO$_2$ (4), Re/MgO (5), MgO (6).

300 K. Identical spectral features with the exception of CO band were obtained when only the supporting oxides were exposed to HCOOH. Some characteristic spectra are presented in Fig. 6.

4. Discussion

4.1. Characteristics of IR spectra of adsorbed CO

Before discussing the results of IR spectroscopic measurements we may summarize the main features of the CO–Re interaction. The IR study of the adsorption of CO on supported Re has been the subject of extensive research [21–25].

Very divergent IR spectra were obtained, which can be attributed to two main reasons: (i) the complete reduction of ReO_x on support is difficult and requires high temperature [26–29]; (ii) CO interacts strongly with Re_x crystallites leading to the disruption of Re_x and to the formation Re carbonyl species characterized by new absorption bands [25]. The assignment of the new bands was based on the vibrational characteristics of the Re carbonyl complexes [30–33]. The occurrence of the disruption process sensitively depends on the size of Re crystallites, and also on the adsorption temperature and time of CO [25]. Adsorbing CO on a completely reduced sample ($T_R = 1073$ K) at 100 K, when the disruption process can be excluded, produced two absorption bands at 2020–2050 and 1860 cm^{-1}[25]. The first one was assigned to linearly bonded CO, Re_x–CO, and the second one to bridged CO, Re_2–CO. Raising the adsorption temperature, or adsorbing CO at 300 K, new bands appeared at 2058, 2005 and 1960 cm^{-1} as a result of disruption of Re_x cluster, and the formation of $Re_2(CO)_{10}$ species. After a longer adsorption time at 300 K, or at 373–473 K, a new pair of bands was produced at 1920 and 2030 cm^{-1} assigned to Re tricarbonyl, $Re(CO)_3$ [25].

4.2. Dissociation of CO_2

The most sensitive method to detect the dissociation of CO_2 on supported metals is the FT-IR spectroscopy. The spectra presented in Fig. 1 clearly show that the dissociation of CO_2 is very limited on Re/Al$_2$O$_3$. Admission of CO_2 on Re/Al$_2$O$_3$ ($T_R = 673$ 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. New 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 the highly reduced Re/Al$_2$O$_3$ ($T_P = 1073$ K). Taking into account the features of the interaction of CO with supported Re described in the previous chapter, we may state that this small amount of adsorbed CO formed in the dissociation of CO_2 is not sufficient to cause the disruption of Re_x nanoparticles and the production of Re carbonyls. As regards the nature of the support, we obtained similar results with some variation of the positions of various carbonates.

4.3. Co-adsorption of $H_2 + CO_2$

Co-adsorption of $H_2 + CO_2$ mixture on Re/Al$_2$O$_3$ ($T_R = 673$ K) at 300–473 K produced several new spectral features at 2022, 1594, 1395 and 1375 cm^{-1}. Raising the temperature led to the intensification of these bands, and to the shift of the 2022 cm^{-1} band to 2035 cm^{-1} (Fig. 2A). Accordingly, the presence of hydrogen or more precisely the adsorbed H promoted the dissociation of CO_2 and the formation of Re_x–CO species characterized by a band at
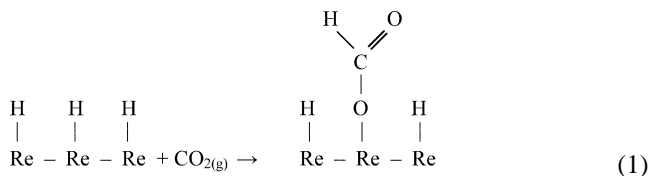
Table 1
Positions of the asymmetric stretch of formate species formed in the surface interaction of $H_2 + CO_2$ and HCOOH adsorption

| Catalyst	$H_2 + CO_2$ adsorption (cm^{-1})	HCOOH adsorption (cm^{-1})	
Re/Al$_2$O$_3$	1594	1594	1596[a]
Re/TiO$_2$	1550	1558	1556[a]
Re/MgO	1590	1600	1591[a]
Re/SiO$_2$	–	–	–

[a] On Re-free oxides.

2022–2035 cm^{-1}. Somewhat different spectra were obtained for other Re samples. On Re/TiO$_2$ intense CO bands appeared at 2053, 2010 and 1976 cm^{-1} suggesting the occurrence of the disruption of Re_x crystallite, and the formation of Re carbonyl, $Re_2(CO)_{10}$ [25]. This surface complex, however, transformed into $Re(CO)_3$ at and above 373 K, as indicated by the appearance CO bands at 2037 and 1945–1929 cm^{-1} (Fig. 3). The fact that the most intense CO band was produced on Re/TiO$_2$ may be attributed to the occurrence of an electronic interaction between Re and n-type TiO$_2$, e.g. to the charge transfer from the titania to the Re [34]. This is in harmony with the previous findings that titania-supported metals are more efficient in the activation of CO_2, and in the reactions involving CO_2 [35,36]. The possible reason is the facilitation of the formation of partially negatively charged $CO_2^{\delta-}$ [37]. In addition, new bands at 1547 and 1360 cm^{-1} were developed at 373–573 K. On Re/MgO, CO bands were produced only on the high temperature ($T_R = 973$ K) reduced sample, while in the low frequency region a new feature appeared at 1590 cm^{-1} (Fig. 2B). Weakest CO bands at 2008–2012 and 1876 cm^{-1} were produced on Re/SiO$_2$, the intensity of which increased with the rise of the adsorption temperature (Fig. 2C). There was, however, no sign of absorption at 1594–1550 and 1360–1395 cm^{-1}, belonging to the asymmetric and symmetric stretch of the vibration of formate group [38–42]. The formation of this surface complex on other catalysts suggests that in addition to the extended dissociation of CO_2, adsorbed hydrogen interacts with CO_2 producing formate species:

$$
\begin{array}{ccc}
& & \overset{\displaystyle H}{\underset{\displaystyle |}{}} \overset{\displaystyle O}{} \\
\end{array}
$$

$$
\underset{Re - Re - Re + CO_{2(g)} \;\rightarrow}{\overset{\displaystyle H\quad H\quad H}{\underset{\displaystyle |\quad\;\; |\quad\;\; |}{}}}\quad
\underset{Re - Re - Re}{\overset{\displaystyle H\quad O\quad H}{\underset{\displaystyle |\quad\;\; |\quad\;\; |}{}}} \tag{1}
$$

As regards the location of this surface complex the following findings should be considered: (i) coadsorption of $H_2 + CO_2$ at 300–573 K on Re-free supports does not produce formate, (ii) adsorption of HCOOH on Re/Al$_2$O$_3$, Re/MgO and Re/TiO$_2$ as well as on the metal-free oxides gave strong bands at the same positions (Table 1), (iii) neither the $H_2 + CO_2$ interaction nor HCOOH adsorption led to the formation of formate groups on Re/SiO$_2$.

From these results we may infer that formate species is formed on Re crystallites, and after its formation it migrates

onto the support, where it is stabilized:

$$\text{(2)}$$
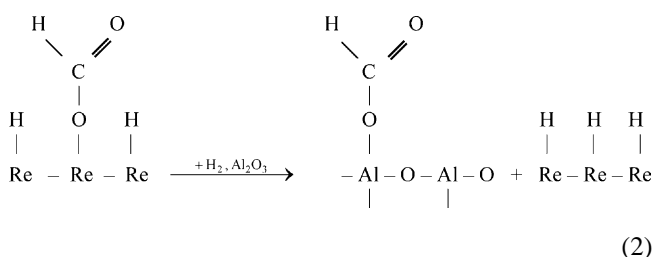
Alternatively, we may assume that adsorbed H atoms spill over onto oxides and reacts with carbonate or hydrocarbonate species to yield formate:

$$\text{(3)}$$
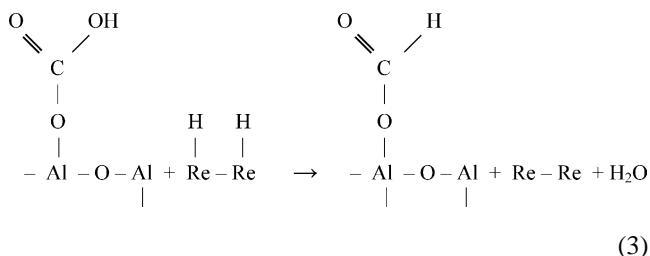
Exposing the CO_2-saturated Re/Al_2O_3 containing carbonates to hydrogen at 370–473 K produced no formate bands. This occurred only to a limited extent at and above 573 K indicating that this way can contribute only a little to the formation of formate established in the $H_2 + CO_2$ interaction. The missing formate on Re/SiO_2 is in harmony with the previous findings, namely that formate does not exist on silica surface [43–45]. Its absence also indicates that formate is not stable on Re.

4.4. Coadsorption of hydrocarbons and CO_2

Interestingly, the dissociation of CO_2 was also facilitated by methane even at 300 K (Fig. 4). The intensity of CO band was, however, much lower. This is not surprising, if we assume that adsorbed hydrogen is needed for the dissociation of CO_2. As both CH_4 and CO_2 adsorb weakly over Re at 300 K, we can exclude the direct surface interaction between the two adsorbed species.

Same phenomena were observed when ethane was added to CO_2 (Fig. 5). The linearly bonded CO at 2040–2049 cm^{-1} appeared at 300 K in the IR spectra of the samples. At the same time weak signs of the formation of formate were seen at higher temperatures on all samples except on Re/SiO_2 (Fig. 5).

5. Conclusions

(i) The dissociation of CO_2 is very limited on supported Re reduced at 673 K. The formation of adsorbed CO characterized by absorption band at 2020–2040 cm^{-1} was observed only on the high temperature (1073 K) reduced Re/Al_2O_3.

(ii) Adding H_2 to CO_2 greatly promoted the dissociation of CO_2 at and above 373 K on the samples reduced at 673 K as shown by the strong CO band at 2020–2040 cm^{-1}.

(iii) In addition, formate species was also produced by the $H_2 + CO_2$ interaction on the Re, which after formation on the metal migrated onto the support, where it was stabilized.

(iv) Formate bands were not identified either after coadsorption of $H_2 + CO_2$ or after adsorption of HCOOH on Re/SiO_2 at and above 300 K.

(v) Addition of C_1−C_2 alkanes to CO_2 also facilitated its dissociation very likely by means of adsorbed hydrogen formed in the decomposition of hydrocarbons. Formate species also formed in the surface interaction.

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