Review
Hydrogenation of Carbon Dioxide on Supported Rh Catalysts

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Abstract: The constant increase in the CO₂ concentration in the atmosphere requires us to look for opportunities to convert CO₂ into more valuable compounds. In this review, the activity and selectivity of different supported metal catalysts were compared in the hydrogenation of carbon dioxide, and found that Rh is one of the best samples. The possibility of the CO₂ dissociation on clean metal and on supported Rh was discussed separately. The hydrogenation of CO₂ produces mainly CH₄ and CO, but the selectivity of the reaction is affected by the support, in some cases the reduction of the support, the particle size of Rh, and the different additives. At higher pressure methanol, ethanol, and acetic acid could be also formed. The activity of the various supported Rh catalysts was compared and the results obtained for TiO₂-, SiO₂-, and Al₂O₃-supported catalysts were discussed in a separate chapter. The compounds formed on the surface of the catalysts during the reaction are shown in detail; mostly, different CO species, adsorbed formate groups, and different carbonates were detected. In a separate chapter the mechanism of the reaction was also discussed.

Keywords: supported Rh catalysts; hydrogenation of CO₂; CO₂ + H₂ reaction; methanation of CO₂

1. Introduction

The carbon dioxide concentration in the atmosphere increased dramatically since the industrial revolution. The levels of CO₂ in the atmosphere underwent slow fluctuations in the last few 100,000 years, but always remained below 300 ppm. In the last century, the burning of fossil fuels and new technologies (cement production, iron, steel industry etc.) have rapidly driven atmospheric CO₂ levels to new heights. In approximately 1910, the CO₂ concentration exceeded 300 ppm, in 2014 it reached 400 ppm, and now the CO₂ concentration is over 415 ppm [1,2]. According to lots of scientists the higher CO₂ concentration resulted in climate change, the rise in temperature. If we want to prevent the further increase of CO₂ concentration in the atmosphere we have to hinder the enhancement of the carbon dioxide emission and we need to increase the conversion of CO₂ to other more valuable compounds. The amount of all products that could be produced nowadays using CO₂ is only a few hundred Mt, whereas the carbon emission only from the large stationary sources is more than 10 Gt. It means that conventional products and technologies for CO₂ utilization do not influence the CO₂ concentration in the atmosphere.

This means that new procedures should be applied especially where CO₂ emissions are significant. The highest carbon emission sector is the energy industry and the transportation so we have to look for the solution in these fields.

Products that can be produced in the hydrogenation of carbon dioxide, methane, and methanol could be used directly either in the energy industry or in the transportation. Another important product is CO which is the component of synthesis gas and from it plenty of products can be produced including gasoline.
These processes could help the storage of electricity, too, whereas the greatest problem with the renewable energy (wind and solar) production is their fluctuation and the energy consumption is also uneven. The H$_2$ could come from the electrolysis of water and if the electricity has a renewable source on the one hand, then it is an environmentally friendly process, and on the other hand, by the conversion of products (for example burning of methane), the energy invested can be recovered. Extensive research work has been conducted on different catalytic systems for CO$_2$ conversion. Recently, various metal catalysts have been developed that demonstrated CO$_2$ methanation at low temperatures and atmospheric pressure.

Knowing the above, it is not surprising that the hydrogenation of carbon dioxide is in the focus of academic and industrial research again.

2. Hydrogenation of CO$_2$ on Supported Metal Catalysts

The CO$_2$ methanation was discovered by Sabatier and Senderens in 1902 [3], and has been investigated now and developed for more than a hundred years. A variety of different metals were used as catalysts in the CO$_2$ hydrogenation. The results obtained are summarized in different reviews [4–9]. Based on the metal catalysts’ activities and selectivities, different activity orders have been published by different research groups. Analyzing these orders and the previous literature, the following order of activity for various metals in CO$_2$ methanation is revealed [10].

Ru > Rh > Ni > Fe > Co > Os > Pt > Ir > Mo > Pd > Ag

Among these catalysts, Ru, Rh, and Ni exhibited the highest activity and selectivity. Metal-promoted mesostructured silica nanoparticles have been studied for CO$_2$ methanation. The rate of methane formation (related to the metal content) was the highest on the Rh containing sample; however, on an area basis, Ni was the most active catalyst [11].

On alumina supported noble metal catalysts the activity order was Ru > Rh > Pt > Ir > Pd [12]. In another paper, it was found that the turnover frequency of CO$_2$ conversion on Rh supported on TiO$_2$ [13] was higher than on Ru samples but others found that Rh/Al$_2$O$_3$ activity exceeded only at higher temperatures the activity of Pt [14]. The highest CO$_2$ conversion was obtained on supported Rh compared with Pd and Ni catalysts supported on various oxides (SiO$_2$, Al$_2$O$_3$, and CeO$_2$) and zeolites (ZSM-5 and MCM-41) under the same experimental conditions [15].

The selectivity of methane formation depends strongly on the metal. It was significantly higher on Rh and Ru than on Pt and Pd. The methane selectivity was also the highest on Rh/Al$_2$O$_3$ and on Rh/CeO$_2$ followed by Ni/CeO$_2$. 2% Rh/PSAC (palm shell activated carbon) was also more active in the methanation of CO$_2$ than 2% Ni/PSAC [16].

Different metal-promoted mesostructured silica nanoparticles (MSN) have been studied for CO$_2$ methanation under atmospheric pressure. High activity was observed on Rh/MSN, Ru/MSN, Ni/MSN, and the CH$_4$ selectivity was 100% on Rh and Ru sample. However, on a metal basis, Rh/MSN was the most active catalyst, whereas Cu/MSN and Fe/MSN were the poorest samples [11].

The products formed in the CO$_2$ hydrogenation on different metals supported on zirconia depended strongly on the nature of the metal. Cu and Ag are suitable for methanol production, and Ni, Rh, and Ru yield methane. CH$_4$, CH$_3$OH, and CO formed on Pd, Re, Pt, and also on Au. In this case, Rh along with Pd, Au and Pt were considered less reactive metals [17].

The steady-state activity of CeO$_2$ supported noble metals were also compared [18]. According to these results, the catalyst can be divided into two groups: Ru and Rh, which give CH$_4$ only as the reaction product, and Pt, Pd, and Ir, which give mainly CO and the CH$_4$ selectivity was below 10%.

High-throughput screening methods were used for the heterogeneously catalyzed gas phase hydrogenation of CO and CO$_2$ over zirconia and ceria supported noble and base metal catalysts at 573–673 K and ambient pressure. Ru, Rh, and Ni were found to promote methanation, whereas Pt tends to catalyze the reverse water gas shift reaction. Methanation activity can be enhanced by some
acidic and redox dopants or suppressed by basic additives. However, Rh and Ru were the most active methanizers [19].

The brief summary above clearly shows that Rh is one of the best catalysts for CO$_2$ hydrogenation. Despite the high costs of rhodium, their superior catalytic properties at low temperature still make them indispensable to understand the interaction between the metal and the support, to check the surface compounds formed during the reaction and to show the elementary steps of the reaction.

3. Adsorption and Dissociation of CO$_2$ on Rh and on Supported Rh Catalysts

The adsorption and activation of CO$_2$ on Rh has also been widely investigated [20,21]. In the early studies, the adsorption of CO$_2$ was claimed to be weak and associative on Rh films [22], polycrystalline Rh [23], and alumina-supported Rh [24].

The Somorjai group [25–27] reported CO$_2$ dissociation on a Rh foil and on several Rh single crystal planes above critical CO$_2$ exposures, but Weinberg [28] and Goodman [29], on the basis of thermodynamic and kinetic results available at that time, indicated that the CO$_2$ sticking probability under the experimental conditions used (at low pressures and room temperature) would be by orders of magnitude smaller than needed to observe dissociation using surface analytical techniques like vibrational and thermal desorption spectroscopy (TDS). It was found that CO$_2$ adsorbed on the (111) and (110) faces of Rh single crystal at 100 K completely desorbs below 300 K without detectable dissociation [30,31]. However, deposition of potassium adatoms, an electron-donating promoter, on the Rh (111) surface activated the CO$_2$ molecule and caused its dissociation even at 150–200 K [32,33].

Using field electron microscopy (FEM), the Nieuwenhuys group [34,35] demonstrated that the crystallography of the surface Rh field emitter tip influenced the adsorption and dissociation of CO$_2$. By comparing TDS spectra with FEM patterns, a mechanism was proposed for the dissociative adsorption of CO$_2$ on Rh nanocrystals [34,35]. It was found the CO$_2$ dissociative adsorption to be the fastest on {012} facets [36].

On supported Rh catalysts the situation is basically different; the CO band appeared on the infrared spectra during CO$_2$ adsorption indicating the dissociation of CO$_2$, but it depends on the nature of the support [24,37–40]. Note that not everyone has noticed the appearance of CO bands after or during CO$_2$ adsorption, that is, the dissociation of CO$_2$ on supported Rh samples [41].

The preparation of the catalysts, the dispersity of Rh, the nature of the support, the adsorption temperature, and the CO$_2$ pressure all have an influence on this process.

The most effective support was TiO$_2$ but even on these samples the CO$_2$ dissociation was detected only above 373 K [37,38]. It was found that on Rh/TiO$_2$ reduced at 673 K CO formation was observed already at 423 K, but when this sample was reduced at 473 K, the dissociation was also observed at 423 K but only after 20 min of adsorption [42]. It means that the CO$_2$ dissociation depends on the reduction temperature of the TiO$_2$ supported samples, which could be attributed to the formation of oxygen vacancies on the perimeter of the Rh-TiO$_2$ interface during the reduction.

The CO$_2$ dissociation occurs on Rh/TiNT (titanate nanotube) and Rh/TiNW (titanate nanowire) at 493 K but at smaller extent than on Rh/TiO$_2$ under the same experimental conditions [43]. Other authors found that the CO$_2$ dissociation at room temperature does not occur; CO band was not detected on Rh/TiNT [44].

The interaction of CO$_2$ with Rh/TiO$_2$ (anatase) at 508 K results in the development of CO band at 1917 cm$^{-1}$ assigned to the bridge bonded CO indicating the CO$_2$ dissociation. When the TiO$_2$ was doped with W$^{6+}$, the CO band intensity increased with increasing the dopant concentration and at 0.45 at% W$^{6+}$ the linearly bonded CO is also appeared on the spectra at 2043 cm$^{-1}$ [45].

In the case of Rh/Al$_2$O$_3$, the dissociation of CO$_2$ to CO was also observed by infrared spectroscopy already at near room temperature [40,46,47], but others found that the dissociation occurs only at higher temperature above 373 K [48]. XPS measurements show that the CO$_2$ oxidized the Rh during the dissociative adsorption and this oxidation deactivates the catalyst [46,49].
The formation of CO band was also observed on Rh/ZrO$_2$ and Rh/MgO during CO$_2$ adsorption but the intensity of them was weaker. In this case, only a peak characteristic for linearly bonded CO was detected at lower wavenumber than recorded after CO adsorption from gas phase. This shift was explained by an earlier observation that the band frequency of CO stretching on Rh is a strong function of CO coverage [24] and so the low surface concentration of CO resulted the band shift [40].

Fisher and Bell compared the CO spectra obtained after CO adsorption with those registered during the CO$_2$ dissociation on Rh/SiO$_2$ [39]. Similar spectra were observed in both cases. After CO adsorption linearly bonded CO (2067–2039 cm$^{-1}$) and a broad feature centered at 1895–1856 cm$^{-1}$ assigned as bridge bonded CO were found. The spectrum exhibits a shoulder at 1949 cm$^{-1}$, which was attributed to Rh$_2$(CO)$_3$ species. The bands in the CO region registered after CO$_2$ adsorption are similar to those seen for adsorbed CO, only the peaks shifted to lower wavenumber. It is a questionable whether the twin structure is formed in this case during the adsorption of CO, although other studies reported about the di-carbonyl formation on Rh/SiO$_2$, too [50,51]. The formation of twin structured CO or gem-di-carbonyl on Rh is explained as the Rh$^0$ is oxidized with the surface OH groups of the support during the CO adsorption leading to the formation of this Rh$_2^+$ (CO)$_3$ complex [41,52]. According to others, as only linearly bonded CO species were found after CO$_2$ adsorption on different Rh catalysts, it was concluded that this CO species are not able to disaggregate the Rh clusters [47].

The interaction of CO$_2$ with Rh/CeO$_2$ was studied with temperature programmed desorption [18]. Significant differences were found in the behavior of the catalyst subjected to different reduction treatments; after reduction at 473 K, CO$_2$ was mainly desorbed and a small amount of CO was detected. The ratio of CO$_2$/CO in the desorbed gases was 10. By increasing the reduction temperature to 773 K, the presence of both CO and CO$_2$ was detected, and the ratio of desorbed CO$_2$ to CO was 3.3. It was found that, by increasing the reduction temperature, the reduction of the bulk CeO$_2$ increased, and this process is not promoted by the supported metal. The CO$_2$ could be activated on Ce$^{3+}$ sites with the formation of CO and Ce$^{3+}$ oxidized to Ce$^{4+}$. The presence of oxygen vacancies in the bulk will be an additional driving force for the reduction of CO$_2$ [18].

4. Reaction of CO$_2$ with H$_2$ on Unsupported Rh Catalysts

The CO$_2$ hydrogenation was studied on Rh foil [25]. It was found that the reaction rates at 700 Torr are nearly identical to those obtained on dispersed Rh catalysts, and it was approximately seven times higher than the CO hydrogenation rate at the same temperature, at 523 K. The oxygen pretreatment increases the CO$_2$ + H$_2$ reaction fivefold, acetylene pretreatment reduces the methane formation, but no chain growth was observed [25]. A similar effect of the pre-oxidation was found on Rh powder and on Rh ribbon [53]. Sub-monolayer deposit of titania on Rh foil increases the rate of CO$_2$ hydrogenation. The methane formation rate exhibits a maximum at Ti coverage of 0.5 ML, and this rate was 15 times higher than that over the unsupported Rh surface [54]. The increase in the rate in the presence of titania was attributed to an interaction between the adsorbed CO released by CO$_2$ dissociation and Ti$^{3+}$ ions located at the edge of TiO$_x$ islands covering the surface [54].

The efficiency and selectivity of mesoporous (meso-Rh) and nanoporous Rh (NP-Rh) was compared in the hydrogenation of CO$_2$ [55]. At 673 K, on NP-Rh, only CO was formed but on meso-Rh the methane selectivity was 100%, and the latter catalyst exhibits a higher reaction rate. Highly efficient performance and selectivity for CH$_4$ formation are achieved due to controllable crystallinity, high porosity, high surface energy, and large atomic step distribution of the sample [55].

Recently, it was found that the RhCo porous nanospheres exhibited enhanced catalytic activity for the hydrogenation of CO$_2$ to form methanol [56]. The turnover frequency on this sample reached 612 h$^{-1}$, which was 6.1 and 2.5 times higher than that of Rh/C and RhCo nanoparticles, respectively. In situ XPS results revealed that negatively charged Rh atoms are on the surface which promoted the activation of CO$_2$ to generate CO$_2$$^{5-}$ and methoxy intermediates [56].

A comparative study of the catalytic activity of polycrystalline Rh foil with Rh/SiO$_2$ and Rh/VO$_x$/SiO$_2$ model catalysts was carried out using the CO$_2$ hydrogenation as test reaction. The samples
were prepared by the evaporation of the components in UHV. The VO$_x$ promoted catalyst was more active than the unpromoted one, and the activity of Rh clusters on SiO$_2$ with a size of 1 to 2 nm was found to be on average 4 times for CO + H$_2$ and 27 times higher for CO$_2$ + H$_2$, as compared to the Rh foil. The higher activity of Rh/SiO$_2$ for CO$_2$ + H$_2$ as compared to CO + H$_2$ was explained by the differences in CO dissociation rates. The promotion effect of VO$_x$ was attributed to the oxygen vacancies on VO$_x$ which promote the dissociation of CO [57].

The hydrogenation of CO$_2$ was investigated over Rh foil decorated with sub monolayer quantities of different oxides [58]. With the exception of FeO, all of the metal oxides investigated enhanced the rate of CH$_4$ formation and the rate of it passes through maximum with increasing metal oxide coverage. The extent of rate enhancement for CO$_2$ hydrogenation decreases in the order TiO$_x$ of Lewis acid–base complexes between the oxygen and adsorbed CO or HCO and anionic vacancies present at the edge of the oxide metal boundary [58].

The deposition of vanadium oxide on Rh foil cause rate enhancement for CO$_2$ hydrogenation, the rate maximizes at 6 times that of the clean surface rate at a coverage of 0.6 ML. It was found that V$^{2+}$ species are responsible for increasing the CH$_4$ formation rate, whereas the V$^{2+}$ cations promote the dissociation of CO$_2$ to CO$_3$ and O$_x$ and of CO$_x$ to C$_x$ and O$_x$. The latter reaction is proposed to be critical for CH$_4$ formation [59].

5. Reaction of CO$_2$ with H$_2$ on Supported Rh Catalysts

The support exerted a significant influence on the activity and selectivity of Rh in the hydrogenation of CO$_2$. The reaction produced mainly CH$_4$ and CO. Using higher pressure methanol and ethanol production is favored [60–62]. Only a few papers report the formation of more than a trace amount of higher hydrocarbons [63,64]. Trovarelli et al. [64] found on Rh/TiO$_2$ and on Rh/Nb$_2$O$_5$ C$_1$–C$_5$ hydrocarbons and the amount of them follows the Anderson–Schulz–Flory statistic, whereas Nozaki et al. detected on Rh/Nb$_2$O$_5$ significant amounts of C$_2$ and C$_3$ (the C$_2s$, selectivity at 623 K was 37%), but on Rh/TiO$_2$ only CH$_4$ was observed [63].

Comparing the specific rate of CO$_2$ consumption on Al$_2$O$_3$, TiO$_2$, and SiO$_2$ supported Rh it was found that the most effective support was TiO$_2$ and the least effective one was SiO$_2$ [65]. The turnover frequency was more than 20 times higher on Rh/TiO$_2$ than on Rh/SiO$_2$. The high efficiency of Rh/TiO$_2$ was explained to different extent of electronic interaction between the Rh and the support, influencing the bonding and the reactivity of surface species [65]. As TiO$_2$ is an n-type semiconductor, a much greater electronic interaction can be expected than with alumina or silica [66].

The reaction of CO$_2$ + H$_2$ and CO + H$_2$ was compared over Rh supported on ZrO$_2$, Al$_2$O$_3$, SiO$_2$, Nb$_2$O$_5$, and MgO. Among these catalysts, Rh/ZrO$_2$ was the most active and Rh/MgO was the least active one [67,68]. On Rh/ZrO$_2$ the CO$_2$ + H$_2$ reaction took place even at 323 K whereas the CO + H$_2$ reaction occurred only above 403 K. In the reaction of CO$_2$ + H$_2$ only CH$_4$ was formed up to 473 K but a small amount of CO was also detected above this temperature [68].

In the hydrogenation of CO Rh/Nb$_2$O$_5$ was more active than Rh/ZrO$_2$ but in all cases the CO$_2$ conversion was higher than that of CO [67]. The main product in the CO$_2$ + H$_2$ reaction at 10 bar on Rh/Nb$_2$O$_5$ and on Rh/ZrO$_2$ was methane but on Rh/TiO$_2$ a significant amount of methanol was also formed, the methanol selectivity at 513 K was 60.7% [61].

5.1. Reaction of CO$_2$ with H$_2$ on Titania-Supported Rh Catalysts

In the comparison of different supported Rh catalysts, Rh/TiO$_2$ was usually the most active sample. The initial rate of CO$_2$ hydrogenation depends on the reduction temperature of the catalyst; it increased significantly with increasing reduction temperature (between 473 and 673 K), but after some seconds, it drastically decreased [42]. The maximum initial rate of the methane formation on the sample reduced at 673 K was about twice of that in the presence of Rh/TiO$_2$ reduced at 473 K, whereas, in the steady state, the CH$_4$ production was nearly the same. When the sample was treated with water or with CO$_2$ at the reaction temperature before introducing CO$_2$ + H$_2$ mixture, the initial excess in the
methane formation was completely missing. The promotion effect of the reduction temperature was explained by the formation of oxygen vacancies on the perimeter of the Rh/TiO$_2$ interface, which can be re-oxidized by the adsorption of CO$_2$ and H$_2$O [42].

The particle size of Rh on TiO$_2$ influenced the efficiency of the catalyst; the CH$_4$ formation rate related to the number of surface Rh atoms increases with increasing the particle size of Rh up to ca. 7 nm. Beyond this size, the rate did not change. Higher activation energies were obtained for catalysts with small particle size (2 nm) whereas for larger clusters (>7 nm) the activation energy was lower and did not change with the size (Table 1) [69]. On the contrary, the CO formation rate increases with increasing the amount of isolated Rh sites on TiO$_2$ [70]. This suggested that the size of the Rh particles is a key factor in the selectivity of the catalyst. These experimental results obtained on Rh/TiO$_2$ were supported by DFT calculations [71].

The catalytic properties of Rh supported on TiO$_2$ as well as on titanate nanotube (TiNT) and nanowire (TiNW) formed in the hydrothermal conversion of titania were tested in the CO$_2$ hydrogenation at 493 K. The activity order of the catalysts at the beginning of the reaction decreased in the order Rh/TiNW > Rh/TiO$_2$ > Rh/TiNT. The conversion of CO$_2$ on Rh/TiO$_2$ and Rh/TiNT was relatively stable but on Rh/TiNW decreased significantly in time. Rh/TiO$_2$ displayed the highest steady state activity [43].

On Rh/TiNT at 363 K at atmospheric pressure, besides methane and CO, formic acid formation was detected in the CO$_2$ + H$_2$ reaction. The calculated turnover frequency for HCOOH formation was 7.210$^{-2}$ h$^{-1}$ [44]. It was proposed that the Na$^+$ content in TiNT plays an important role in the various carbonate formation processes. The reduced Rh/TiNT has the ability to form rhodium hydride complexes which can interact with bidentate carbonates to yield formate species and facilitates the further hydrogenation to formic acid [44]. This proposal was supported by the infrared spectroscopic results on Rh/MgO. In this case, the band characteristic for the bicarbonate species decreased and the formate band increased when the catalyst after CO$_2$ adsorption was treated with hydrogen at 373 K [37].

In the CO$_2$ + H$_2$ reaction, a dynamic decrease was observed in the rate of methane formation and increase of CO production on Rh/TiO$_2$ when the CO$_2$/H$_2$ ratios were greater than 1 [70].

The quantitative relationship between the concentration of isolated (iso) and nanoparticle-based (NP) Rh sites on TiO$_2$ and the selectivity of CO$_2$ hydrogenation toward CO and CH$_4$ formation was observed [70]. The relative fraction of these sites changes dynamically under reaction conditions from nanoparticles form isolated sites, and this process results in the unstable reactivity of the catalysts with higher Rh content under H$_2$-lean conditions in time. Ten percent CO$_2$ had no observable effect on site fractions; whereas 10% CO caused the Rh$_{iso}$ sites to convert to Rh$_{NP}$ sites, whereas CO can induce restructuring of Rh nanostructures, even at room temperature [71].

The Rh$_{iso}$ sites controls the CO formation rate (TOF), whereas the Rh$_{NP}$ controls the CH$_4$ production. Thus, selectivity of CO and CH$_4$ formation in CO$_2$ hydrogenation is controlled by the ratio of Rh$_{iso}$ and Rh$_{NP}$ sites [70].

Similar results were obtained on RhY zeolite [72]. CH$_4$ is the main product on this catalyst, because the surface concentration of CO on Rh particles is kept low by the CO induced disruption of Rh particles into atomically dispersed Rh. In the sample which was doped with Li, as adsorbed CO is accumulated on the surface of stable Rh particles, mainly CO production occurs.

Contrary to these observations on titanate nanotube supported Rh catalyst it was found that the intensity of the XPS peak (at 308.2 eV) characteristic of highly dispersed Rh gradually decreased and nearly completely vanished after 60 min of the H$_2$ + CO$_2$ (4:1) reaction at 498 K [43] indicating the agglomeration of Rh sites during the CO$_2$ + H$_2$ reaction.

The strong metal–support interaction was studied on CeO$_2$, TiO$_2$, and Nb$_2$O$_5$-supported Rh catalysts using CO$_2$ hydrogenation as a test reaction [73]. Tauster et al. [74] found and designated the phenomenon to strong metal–support interaction (SMSI) that high temperature hydrogen treatment of reducible oxides supported Pt–metals causes the reduction of the oxide and induced the migration
of the substoichiometric oxide on the metal particles which resulted in the decrease of the hydrogen adsorption capacity and the activity of the catalysts. On Rh/TiO$_2$, after high temperature reduction, a small positive effect was observed in the steady-state conditions, whereas Rh/Nb$_2$O$_5$ showed a remarkable decrease in activity and on Rh/CeO$_2$ ~50% reduction was recorded. When the reaction was studied with pulse technique under unsteady state conditions, a completely different behavior was observed. The initial activity of Rh/TiO$_2$ and Rh/Nb$_2$O$_5$ is totally suppressed after reduction at 773 K, whereas an enhancement was observed on Rh/CeO$_2$. The activity increase was explained by the formation of bulk vacancies in CeO$_2$. In the case of Rh/TiO$_2$ and Rh/Nb$_2$O$_5$, the samples lose their activity due to encapsulation by reduced oxides but the water and the oxygen formed in the CO$_2$ dissociation reoxidize the oxide [73].

In an earlier work, Christopher et al. reported the dynamic decrease in the rate of CH$_4$ production and increase in the rate of CO production when the CO$_2$/H$_2$ ratio was greater than 1. It was attributed to the changes in the particle size of Rh [70]. In situ X-ray absorption spectroscopy (XAS) on a 2% Rh/TiO$_2$ catalyst during the 20% CO$_2$:2% H$_2$ treatment showed no measurable difference between the reduced and the untreated catalysts, with a constant Rh–Rh coordination number. The XAS results were consistent with ex situ STEM images of 2% Rh/TiO$_2$ catalysts after reduction and 20% CO$_2$:2% H$_2$ treatment showed no evidence of Rh structural changes [75].

In situ spectroscopy and microscopy measurements show that the high concentration of adsorbates (HCO$_x$) on TiO$_2$ induces oxygen-vacancy formation, which facilitates the migration of the support covered by HCO$_x$ species onto the metal. This adsorbate-mediated SMSI (A-SMSI) encapsulation state is stabilized against reoxidation by H$_2$O and modifies the reactivity of all the remaining exposed Rh sites, and appears to be comprehensive in covering Rh, but amorphous and permeable to reactants. Formation of the A-SMSI state induces a selectivity switch in the CO$_2$-reduction reaction from CH$_4$ production on bare Rh particles to CO production in the A-SMSI state, which effectively renders Rh less active for C–H bond formation. A similar effect was found between the influences of 20% CO$_2$:2% H$_2$ and formic acid treatments on the reactivity of Rh/TiO$_2$ catalysts. These observations suggested the existence of an A-SMSI state; a high coverage of HCO$_x$ promotes the formation of oxygen vacancies at the TiO$_2$ surface, and thereby causes migration of the support onto Rh [75]. It is rare that a paper is valued in the same issue as in the present case [76].

When Rh/TiO$_2$ was prepared from Rh(NO$_3$)$_3$ and the sample was calcined at 1273 K, so the BET surface was low, ~8 m$^2$/g; the main product in the CO$_2$ hydrogenation was CO and the CH$_4$ selectivity was only ~30% [77]. The turnover frequency of methane formation increased significantly when W$^{6+}$ ions were incorporated into the TiO$_2$ support [77]. Increasing the W$^{6+}$ concentration increased the rate and selectivity of CH$_4$ formation and decreased the apparent activation energy of the reaction, but the donation did not influence the partial order of hydrogen and carbon dioxide [78,79]. The donation enhanced the electric conductivity of the oxide by one to two orders of magnitude. Doping the TiO$_2$ support with lower valence ions (Mg$^{2+}$, Al$^{3+}$), which hardly influenced the electron conductivity of the oxide, caused only little alteration in the specific activity of Rh. The effect of doping the support with W$^{6+}$ ions was attributed to the enhanced electron transfer from the TiO$_2$ to the Rh which promotes the dissociation of CO [45,77,78]. There is another possible explanation for the promoting effect of W$^{6+}$. The hydrogen chemisorption is favored on doped catalyst; there is an increase in the concentration of surface hydrogen participating in the rate determining step.

It was found that the activation energy for CO formation is much lower than that for CO$_2$ methanation (Table 1), indicating that the dissociation of CO$_2$ to CO is easier than methanation. A reduction in the apparent activation energy was observed when Rh was supported on W$^{6+}$-doped TiO$_2$ [77,78], but the value does not depend on the dopant concentration [78].

When the inlet pressure was increased to 10 bar on Rh/TiO$_2$ significant amount of methanol (the selectivity was 60.7%) and ethanol were formed at 513 K in the CO$_2$ + H$_2$ reaction, but the selectivity decreased as the reaction temperature increased. When 3% Rh/TiO$_2$ was promoted with Na (Rh/Na
ratio was 1/1.5), the methanol selectivity decreased but that of ethanol increased; at 533 K it was 13.3% [61].

Significant amount of ethanol was formed at 47 kPa pressure on Se doped Rh/TiO$_2$ catalyst ([Rh$_{10}$Se]/TiO$_2$). The selectivity of it was 83% at 523 K although problems of deactivation of the catalyst exist. Ethanol was not produced under the same experimental conditions on other supported Rh clusters on different (Al$_2$O$_3$, MgO, and SiO$_2$) oxide supported [Rh$_{10}$Se] samples [62,80]. Different factors were proposed to explain preferential ethanol synthesis: the structural e

The CO$_2$ feedstock often contains trace amounts of sulfur compounds. The effect of sulfur on the methanation of CO$_2$ was studied on different supported Rh catalysts [81]. It was found that a trace amount of H$_2$S (22 ppm) can promote the reaction on TiO$_2$- and CeO$_2$-supported Rh, whereas on other supports, such as SiO$_2$, ZrO$_2$, and MgO, or when the H$_2$S concentration was higher (116 ppm), the contamination poisons the reaction. TPD and XPS results show that the sulfur built into the support and so the catalysts became more active as a result of the formation of new active sites at the interface between the Rh and the support [81].

5.2. Reaction of CO$_2$ with H$_2$ on Silica Supported Rh Catalysts

A comparative study shows that the rate of methane formation over Rh/SiO$_2$ was higher for CO$_2$ than for CO hydrogenation [39] and the activation energy for CO$_2$ hydrogenation was lower than that for CO hydrogenation similarly as it was found on Rh/Al$_2$O$_3$ [65].

The difference in Rh loading [82] and in the precursor of the metal [83] significantly changed the product selectivity on SiO$_2$ supported Rh. The main product was CO for the low-loaded catalyst, whereas CH$_4$ was dominantly produced on Rh/SiO$_2$ when the Rh content was more than 5% [60,65,82]. Over the catalysts prepared from acetate and nitrate the main product was CO, but it was CH$_4$ over the samples prepared from chloride precursor. The ratio of hydroxyl groups to Rh particles on SiO$_2$ surface-determined by XPS, increased in the order of chloride < nitrate < acetate precursor, was expected to have a significant influence on the reactivity [83]. The effect of metal loading on the product distribution was explained in a similar way. For 1% Rh/SiO$_2$ catalyst, the Rh species were surrounded by hydroxyl groups of the support. CO-saturated Rh species, which were derived from CO$_2$, reacted with surface OH groups to form fine Rh carbonyl clusters. This type of adsorbed CO was not hydrogenated further, resulting in desorption as molecular CO. On the other hand, 10% Rh/SiO$_2$ catalyst achieved higher surface coverage of Rh than 1% Rh/SiO$_2$. Therefore, too few surface hydroxyl groups existed around Rh particles, insufficient to form Rh carbonyl clusters. The coverage of hydride species on this Rh surface was higher than that of CO species, resulting in CH$_4$ formation [82].

The turnover frequency for CO$_2$ methanation on highly dispersed Rh/SiO$_2$ ($514 \times 10^{-5}$ s$^{-1}$) prepared by cation exchange was about fifty times higher than on a low dispersion Rh/SiO$_2$ ($9.2 \times 10^{-5}$ s$^{-1}$) and comparable to a high dispersion Rh/TiO$_2$ catalyst ($803 \times 10^{-5}$ s$^{-1}$) [84].

Rh/SiO$_2$ promoted with CeO$_2$ also showed high activity in CO$_2$ methanation [85]. This is probably cause by the presence of vacancies at the Rh and the reduced CeO$_2$ interface. High temperature reduction of Rh/CeO$_2$ and Rh/CeO$_2$/SiO$_2$ enhanced the catalytic activity in CO$_2$ methanation. The presence of oxygen vacancies in the bulk, formed in the large CeO$_2$ crystallites after reduction at 773 K, is believed to be the driving force leading to CO$_2$ activation [85]. The mechanisms of interaction between the ceria supported metals and CO$_2$ and the activation of CO$_2$ in the presence of H$_2$ to CH$_4$ are strongly influenced by the reduction temperature. It was suggested that by increasing the reduction temperature increased the reduction of bulk CeO$_2$, which is not promoted by the presence of metal [18]. It was suggested that the interaction mechanism involves the activation of CO$_2$ on surface Ce$^{3+}$ sites with the formation of CO, followed by the oxidation of Ce$^{3+}$ to Ce$^{4+}$. The presence of oxygen bulk vacancies will create the additional driving force for the reduction of the CO$_2$ to CO and/or surface carbonaceous species, which then rapidly hydrogenated to CH$_4$ over the supported metal [18].
Earlier, it was found that silica-supported Rh catalysts are efficient above 25 bar for C₂ oxygenate (ethanol, acetaldehyde, and acetic acid) production from CO + H₂ mixture [86,87] and so it would be expected that Rh/SiO₂ can convert CO₂ + H₂ into oxygenates while there are some proposed mechanisms that the reaction proceeds through CO intermediate. However, against expectations, 5% Rh/SiO₂ produces almost exclusively methane [60,65]. The addition of more than 30 metal oxide promoters to the catalysts was tested in the case of Rh/SiO₂. It was found that only four additives (Li, Fe, Sr, and Ag) showed ethanol formation [60]. On Rh-Li/SiO₂ (T = 513 K, P = 5 MPa), 15.5% ethanol selectivity at 7% CO₂ conversion was achieved and 43.1% methanol selectivity was found at 2.8% CO₂ conversion on the Rh-Sn/SiO₂ sample [60]. The addition of Fe influenced the CO₂ conversion as well as the ethanol selectivity reaching a maximum at a Fe/Rh atomic ratio = 2. It was 16% and the CO₂ conversion was 26.7% over 5% Rh-Fe(1:2)/SiO₂ catalyst at 5MPa and 533 K [88,89]. The effect of the Fe was interpreted as Fe influenced the electronic states of Rh. A good correlation was observed between the oxidation state of Fe and the product selectivity. It was suggested that Fe⁺II promoted the methanation as well as the dissociation of adsorbed CO intermediate and the non-metallic Fe is responsible for the higher conversion and higher alcohol selectivity [88].

A comparative study of CO and CO₂ hydrogenation at 20 atm and 543 K shows that, although Rh and Rh-Fe/TiO₂ [90] and Rh-Fe/SiO₂ [87] catalysts exhibited appreciable selectivity to ethanol during CO hydrogenation, they functioned as a methanation catalyst during CO₂ hydrogenation, but ethanol (S_{EOH} = 6.4) and higher hydrocarbons (S_{C₂} = 6.18) were also formed [90].

In the catalytic hydrogenation of CO₂ over Rh-Co/SiO₂ catalysts, the amount of cobalt added influenced the methanol selectivity as well as the CO₂ conversion. By means of XRD and XPS results, Rh-Co alloy formation was proposed; this process changes the electronic states of rhodium, resulting in the increase of methanol formation [91,92]. A good correlation was found between selectivity of methanol production and the surface composition of Rh-Co/SiO₂ catalysts determined by XPS. It was suggested that methanol formation was promoted on the interface between Rh and Co [92].

Lanthana addition to the Rh/SiO₂ increases the CO formation in the CO₂ + H₂ reaction, which does not react further to oxygenated products as in the CO hydrogenation [93].

When the Rh/SiO₂ was promoted with Ag the main product was CO but acetic acid formation was observed at 2 MPa pressure [94]. Its selectivity, taking into account hydrogenated products, was 61.3%. In CO hydrogenation Ag addition to Rh/SiO₂ suppressed the formation of C₂-oxygenates while in the CO₂ + H₂ reaction it remarkably promoted the CH₃COOH production. The possible pathway to acetic acid from CO₂ is the direct incorporation of CO₂; the reaction of adsorbed CO₂ with methyl groups to form acetic acid was suggested as a possibility [95]. Similar mechanism was described for acetic acid synthesis in the CH₄ + CO₂ step-wise reaction over Rh/SiO₂ catalyst [96].

### 5.3. Reaction of CO₂ with H₂ on Alumina Supported Rh Catalysts

The reaction of CO₂ + H₂ on Rh/Al₂O₃ produces almost exclusively methane [46,49,65,79,97]. From a comparison of the specific activities of Rh/Al₂O₃ in the H₂ + CO₂ and H₂ + CO reactions, it appears that the hydrogenation of CO₂ occurs much faster than that of CO [65]. It was found that the activity of Rh/Al₂O₃ to methane did not depend on the particle size at temperatures between 185 and 200 °C, whereas at lower temperature larger particles favored higher activity and on these species the activation energy was lower [79].

The CO and CO₂ hydrogenation was compared on Rh/Al₂O₃ using temperature programmed pulsed reaction experiments [98]. It was observed that the rate of hydrogenation of C(ads) from CO₂ was quicker than that of CO. This higher rate is probably due to easier availability of surface hydrogen because of reduced competition in the absence of adsorbed CO and less surface carbon [98].

The presence of oxygen could have a positive effect on the methanation of CO₂ [49]. When the oxygen concentration is higher than ~2%, it has a negative effect. DRIFT experiments explain that the positive effect of oxygen is due to the formation of more reactive species than the linearly bonded CO,
such as gem-dicarbonyl. On the contrary, the negative effect could be attributed to the oxidation of the catalyst [49].

On Rh/Al₂O₃, reversible structural changes were observed at atmospheric pressure and at relatively low temperatures (<350 °C) during the CO₂ methanation under transient operation conditions. Such changes were not observed for the Rh/SiO₂ catalyst, which also exhibits lower CO₂ conversion. Some of the Rh atoms are found to be in a low oxidation state (RhOₓ) for the highly active Rh/Al₂O₃ during the CO₂ methanation. According to the in situ DRIFTS results, mainly linearly and bridge-bonded CO are formed on the Rh surface during CO₂ hydrogenation over both alumina and silica supported catalysts suggesting that a metallic Rh phase is required for the dissociation of CO₂. However, the oxygen resulting from the CO₂ dissociation reacts with some other Rh atoms and form RhOₓ as revealed by XAS and XRD measurements. The linearly adsorbed CO species on metallic Rh are responsible for the higher activity of Rh/Al₂O₃. Thus, it is concluded that CO₂ methanation over Rh/Al₂O₃ proceeds by the dissociative adsorption of CO₂ giving rise to linearly adsorbed CO species on reduced Rh (Rh-CO₃), whereas the adsorbed O can interact with other Rh atoms forming RhOₓ [99].

The hydrogenation of CO₂ to methane was studied on Rh/Al₂O₃ doped with different metals (Cr, Fe, Co, Mo, P, Sn, and Pb). The additives lead to an increase in the binding energy of Rh 3d electrons and increase in the heat of hydrogen adsorption with the exception of Sn and Pb. The methanation rate has a maximum as a function of hydrogen adsorption heat [100].

The effect of Ba and K addition to Rh/Al₂O₃ catalysts in CO₂ hydrogenation reaction has been investigated by Büchel et al. [101]. Pure Rh/Al₂O₃ as well as the Ba-containing catalysts showed high CH₄ selectivity below 773 K with a maximum yield at 673 K, whereas, above this temperature, the reverse water gas shift reaction leading to CO and H₂ started to become dominant. In contrast, on K-containing catalysts CH₄ was not formed; all CO₂ was directly converted to CO in the whole temperature range of 573 to 1073 K. The effect of K was explained by the fact that due to the weak interaction between the catalysts and CO; CO was rapidly desorbed before being further reduced [101].

The hydrogenation of CO₂ on Rh/Al₂O₃ modified with Ni and K was also studied [41]. The catalytic tests show in these cases, too, that the K additive promotes the CO formation. On Rh/Al₂O₃, methane was the main product as found earlier [65,79,102], but the reaction was less selective to CH₄ on Rh/K/Al₂O₃ and on Rh,Ni/Al₂O₃; on Rh,K,Ni/Al₂O₃ CO formation was preferred [41]. It was found that K changes the surroundings of Rh affecting the adsorption sites of CO and influences the activation ability for H₂ dissociation as well as the strength of CO adsorption.

Mechanical mixture of Rh/Al₂O₃ and Ni/AC (activated carbon) shows a significant catalytic synergy in the methanation of CO₂ [103]. This observation was explained by the cooperation between the two components. Rh/Al₂O₃ is highly efficient in CO₂ adsorption and Ni/AC is able to adsorb high quantities of H₂. It was supposed that the activated hydrogen migrates from Ni/AC towards Rh/Al₂O₃ and reacts with the adsorbed CO₂ [103].

Similar results were obtained when the reaction was studied on the mechanical mixture of Rh/Al₂O₃ and Pd/Al₂O₃ catalyst. It was found that although Pd/Al₂O₃ is inert under these conditions, the activity of the mechanical mixtures of the two catalysts was higher up to 50% than that of the pure Rh/Al₂O₃ [102]. The oxidation state of Rh or Pd in mono and bimetallic catalysts was nearly the same. No indication of segregation of one metal to the surface of the other was observed that can lead to the formation of bimetallic structures in the mixtures. From the kinetic data it was concluded that H₂ activated mainly over Rh/Al₂O₃, but the activation of CO₂, its dissociation to CO(ads) and subsequent hydrogenation to methane can take place on both catalysts [102].

5.4. Reaction of CO₂ with H₂ on Other Supported Rh Catalysts

The reaction was studied not only on the aforementioned carriers (TiO₂, Al₂O₃, and SiO₂), but many other oxides were also used as catalyst supports, such as CO₂ [15,18,47,73,85,104], Nb₂O₅  [61,63,64,67,73,105], MgO [65,67,68,98,106], ZrO₂ [61,67,68,107], etc.
Table 1. Comparison of the kinetic data for CO$_2$ + H$_2$ reaction obtained on different Rh catalysts.

| D%  | Particle Size (nm) | $E_a$ kJ/mol | $x$  | $y$  | Reference |
|-----|--------------------|--------------|------|------|-----------|
| 5% Rh/SiO$_2$ | 22.8 | 72.4 | 0.64 | 0.27 | [66] |
| 3.4% Rh/SiO$_2$ | 45 | 2.2 | 69.5 | 0.53 | $-0.46$ | [39] |
| 2.3% Rh/SiO$_2$ | 27 | 66.6 | - | 0.4 | [68] |
| 1.047% Rh/SiO$_2$ | 99.2 | - | - | - | [84] |
| 2.3% Rh/ZrO$_2$ | 51 | 62.4 | 0.4 | - | [67,68] |
| 5% Rh/Al$_2$O$_3$ | 30.2 | 67.8 | 0.61 | 0.26 | [12,65] |
| 1% Rh/Al$_2$O$_3$ | 30 | 3.6 | 95 | - | [79] |
| 2% Rh/Al$_2$O$_3$ | 18 | 6.1 | 66.1 | - | [79] |
| 3% Rh/Al$_2$O$_3$ | 7.1 | 15.4 | 61.1 | - | [79] |
| 2.3% Rh/Al$_2$O$_3$ | 6 | 71.2 | - | - | [67,68] |
| 1% Rh/TiO$_2$ | 22.3 | 81.1 | - | - | [65] |
| 1% Rh/TiO$_2$ + 2% WO$_3$ | 16.9 | 72.8 | - | - | [77] |
| 0.5% Rh/TiO$_2$ | 102.8 for CH$_4$ | 54.8 for CO | 0 | 0.49 | [78] |
| 0.5% Rh/TiO$_2$ + 0.45% W$^{6+}$ | 69.4 for CH$_4$ | 26.3 for CO | 0 | 0.53 | [78] |
| 0.5% Rh/TiO$_2$ | 61 | 2 | 120.2 | 0.83 | $-0.36$ | [69] |
| 1% Rh/TiO$_2$ | 24 | 5 | 81.2 | 0.75 | $-0.15$ | [69] |
| 3% Rh/TiO$_2$ | 6 | 17 | 71.2 | 0.58 | 0.01 | [69] |
| 5% Rh/TiO$_2$ | 6 | 19 | 68.2 | - | - | [69] |
| 2.3% Rh/MgO | 27 | 96.7 | - | - | [67,68] |
| 0.67% Rh/MgO | 29 | 92 | - | - | [106] |
| 2.3% Rh/Nb$_2$O$_5$ | 6 | 69.9 | - | - | [67] |
| Rh foil | 71.2 | 0.5 | 0.2 | - | [54] |
| Rh foil | 67 | - | - | - | [25] |
| Rh foil | 75 | - | - | - | [57] |

$E_a$ apparent activation energy, $x$ and $y$ the partial order of H$_2$ and CO$_2$, respectively.

The role of the ceria based catalysts in the hydrogenation of CO$_2$ is summarized recently [108]. These samples have been found to have higher activity and selectivity to methane with respect to many other oxides [15,47,73]. This behavior was attributed to the presence of oxygen vacancies on the reduced ceria. It was suggested that by increasing the reduction temperature a progressive reduction of the bulk CeO$_2$ takes places which is not promoted by the metal. Please note, however, that others found that Rh promotes the reduction of the CeO$_2$ surface [109]. The oxygen vacancies which are formed in the large CeO$_2$ crystallites after reduction at 773 K but not after low temperature reduction are the driving force for CO$_2$ activation with the formation of CO and the oxidation of reduced ceria. The role of the supported metal is providing the active H species for hydrogenation [18,85].

Different in situ measurements (AP-XPS, HE-XRD, and DRIFT) revealed that the Ce$^{3+}$ species are likely the active sites in CO$_2$ methanation for ceria-based catalysts [104].

The hydrogenation of CO$_2$ was investigated over Rh catalyst prepared from amorphous Rh$_{20}$Zr$_{80}$ alloy and the results were compared with Rh/ZrO$_2$ prepared by conventional impregnation method. It was found that the CH$_4$ formation rate related to surface Rh was slightly higher for the alloy precursor catalyst [110]. When the reduction temperature was raised, the CH$_4$ selectivity decreased above 620 K for the impregnated Rh/ZrO$_2$ and above 720 K for the alloy precursor catalyst [110]. The activities of Rh/ZrO$_2$ prepared by different methods were compared [111]. The product was mainly CH$_4$ but on the impregnated sample CO was formed. The highest CO$_2$ conversion was found on the
The selectivity of it drastically decreased as the temperature increased. The selectivity was lower than preferential adsorption produced. When the CO hydrogenation was studied in the presence of CO$_2$, the turnover number for methanol formation decreased indicating that CO$_2$ may partially blocked the sites required for the CO hydrogenation [107]. On Rh/ZrO$_2$ at atmospheric pressure in the CO$_2$ + H$_2$ reaction the CO$_2$ conversion (23% at 453 K) was more than 20 times higher than the CO conversion in CO hydrogenation (1% at 453 K) [68].

Rh/Nb$_2$O$_5$ catalyst gives C$_2$+ hydrocarbons consisting mainly of C$_2$H$_6$ and C$_3$H$_8$ with 30–50% selectivity at temperatures ranging from 250 to 350°C even at atmospheric pressure [63]. The conversion of CO$_2$ on this catalyst was significantly lower (4% at 523 K) than on Rh/TiO$_2$ (29%) or RhZrO$_2$ (8%), but on the former sample, only CH$_4$ was produced, whereas on the latter catalyst, the selectivity for C$_2$+ hydrocarbons was significantly lower [63]. It was found that the C$_2$+ hydrocarbon formation was influenced by the structure of the Nb$_2$O$_5$ support [105] and the selectivity increased with increasing the reduction temperature [64,105]. Comparing the activity of different supported Rh catalysts in the CO and CO$_2$ hydrogenation only on Rh/Nb$_2$O$_5$ was found higher activity for CO conversion than that of CO$_2$ [67]. When the pressure was increased to 10 bar methanol was formed on Rh/Nb$_2$O$_5$ catalyst [61]. The selectivity of it drastically decreased as the temperature increased. The selectivity was lower than on Rh/TiO$_2$ but the rate of methanol formation was higher (100 µmol h$^{-1}$ g-catal$^{-1}$).

Rh/MgO is not one of the most active catalysts [65,67,68]; in this case, different results were obtained by different research groups. Some have reported that Rh/MgO activity decreases continuously in time and does not reach steady state [65]. The reaction product was almost exclusively CH$_4$ below and at 473 K [67,106], but above 523 K, CO was the main product [67]. The apparent activation energies of CO$_2$ and CO hydrogenation to form CH$_4$ at the steady-state reaction were nearly the same, 92 kJ/mol, however the rate of CO$_2$ conversion was eight times higher than that of CO. These observations strongly suggested that common intermediates form CH$_4$ with the same kinetic structure in both reactions. In CO hydrogenation an appreciable amount of adsorbed CO is accumulated on the surface during the reaction inhibiting the reaction of the intermediates with H$_2$ and this resulted in the higher rate for CO$_2$ hydrogenation [106].

When Rh was supported on La$_2$O$_3$ in the CO$_2$ hydrogenation mainly CO was formed (S$_{CO}$ % = 82.5% at 513 K) and the conversion was much higher (30.3% at 513 K) than in the CO + H$_2$ reaction (5.6%), but in the latter case, besides methane and CO$_2$, C$_2$+ hydrocarbons, methanol, ethanol, and acetic acid (S$_{CH_3}$ [%] = 39.3% at 513 K) were also formed [93].

Rh-doped SrTiO$_3$ synthetized by hydrothermal methods shows better activity, higher yield, and selectivity for CO formation in the CO$_2$ + H$_2$ reaction than the conventional Rh/SrTiO$_3$ catalyst. The excellent activity is attributed to the cooperative effect between the sub-nanometer Rh clusters, which are effective in the dissociation of H$_2$ and the reconstructed SrTiO$_3$ with oxygen vacancies for preferential adsorption/activation of CO$_2$ [112].

Rh ion-exchanged Y-type zeolite showed 10 times higher activity in the CO$_2$ hydrogenation (H$_2$/CO$_2$ = 3, total pressure 3 MPa, 423 K) than a conventional impregnated Rh/SiO$_2$ [113].

Significant amount of methanol formation was detected in the reaction, but after 100 min serious deactivation was observed; it was attributed to the deposition of water inside the zeolite cage. The active Rh sites were determined as Rh particles (2-3 nm) located outside of the cage. It was supposed that the zeolite cage played a role to condense CO$_2$ and to supply to Rh sites outside the cage [113].

The catalytic selectivity is strongly related to the environment of the Rh nanoparticles. Pure silica MFI-fixed Rh nanoparticles exhibited maximized CO selectivity at high CO$_2$ conversion, whereas aluminiumsilicate MFI zeolite (ZSM-5)-supported Rh nanoparticles displayed high CH$_4$ selectivity.
under equivalent conditions. When K ions were introduced by ion exchange into the HZSM-5 preparing Rh/KZSM-5 catalyst, the CO selectivity markedly enhanced; the CO selectivity strongly depended on the amount of K\(^+\) in the catalyst. It was concluded when the hydrogen spill over is hindered then the CO formation is favorable, and the significant spill over should be attributed to the abundant acidic sites of Rh/ZSM-5 \cite{114}.

The CO\(_2\) hydrogenation was performed over Li promoted Rh ion-exchanged zeolite catalysts at 3 MPa pressure \cite{72,115}. As the amount of added Li increased, the selectivity of methane formation decreased and CO was formed. When the Li/Rh ratio was 10 the selectivity for CO reached 87\% and alcohol formation was also observed, the methanol and ethanol selectivity was 2.3\% and 2.7\%, respectively.

6. Surface Species Formed in the Interaction and in the Reaction of CO\(_2\) with H\(_2\) on Supported Rh

To understand the mechanism of a reaction, it is necessary to investigate the interaction of the reaction partners on the surface of the catalysts, to identify the species formed and exist on the reaction surface during the reaction and to determine their reactivity.

The adsorption measurements revealed that, with the exception of Rh/SiO\(_2\), the presence of H\(_2\) greatly enhances the uptake of CO\(_2\) by Rh supported on different oxides (TiO\(_2\), Al\(_2\)O\(_3\), and MgO) \cite{37,48}.

Infrared spectroscopic measurements show that besides different carbonates, formate groups (except for SiO\(_2\) supported sample) and CO are formed in the low temperature interaction \cite{37,41,48} and during the CO\(_2\) hydrogenation. Comparing the IR spectra of adsorbed CO\(_2\) and formic acid on clean supports, similar spectra were registered as on the supported Rh samples. It means that the carbonates and the formate are located not on the Rh but rather on the supports. In this case, the only interesting question may be why the absorption bands of one form or the other are missing from the spectrum. The amount and the nature of the adsorbed species are dependent on the annealing temperature of the support, on the nature of the surface OH groups, i.e., on the basicity of the surface \cite{116}. For example, on \(\gamma\)-Al\(_2\)O\(_3\) annealed at 473 K, mostly bicarbonates formed, whereas no adsorbed CO\(_2\) was detected on this highly hydroxylated surface. With increasing calcination temperature the surface concentration of carbonates and linearly adsorbed CO\(_2\) increased but bicarbonates remained the most abundant surface species \cite{117}. When the Rh/Al\(_2\)O\(_3\) was promoted with K it was assumed that no potassium formates were formed, but rather formates that were adsorbed at the alumina surface in the vicinity of K \cite{41}. Some groups suggested that carbonates and formates are only spectator molecules, whereas, in the opinion of others, these surface species, despite the location of their adsorption centers, are actively involved in the CO\(_2\) + H\(_2\) reaction. The formate species formed after the adsorption of HCOOH at room temperature on Rh/Al\(_2\)O\(_3\) at 423 K decomposed to CO\(_2\) and H\(_2\) (70\%) and to CO and H\(_2\)O (30\%), CH\(_4\) was formed only in traces. When the formate ion was treated with H\(_2\) at the same temperature, 70\% of the adsorbed species was converted to CH\(_4\) \cite{118}. Similar results were found on lanthanide-oxide promoted Rh/Al\(_2\)O\(_3\) \cite{119}. The admission of H\(_2\) onto preadsorbed CO\(_2\) on Rh/MgO results in a decrease of the 1650 cm\(^{-1}\) band due to the hydrogen carbonate band and at the same time in the appearance of formate band at 1600 cm\(^{-1}\) \cite{37}. These observations clearly show that the hydrogen carbonate could be converted to formate and the formate to CH\(_4\).

Before examining the spectra of adsorbed CO formed in the reaction or in the interaction, let us examine first the forms in which the CO gas is adsorbed. The linearly bonded CO (Rh-CO) absorbs at 2040–2075 cm\(^{-1}\) depending on the coverage, the characteristic bands for the twin or dicarboxyl (Rh(CO)\(_2\)) structure are at ~2100 and ~2030 cm\(^{-1}\), and the peak due to the bridge bonded form Rh\(_2\)CO can be detected at 1830–1850 cm\(^{-1}\). The Rh\(_2\)(CO)\(_3\) form absorbs at 1905–1925 cm\(^{-1}\). There are some minor species bonded to the oxidized Rh surface \cite{120,121}.

The spectral feature of CO formed in the co-adsorption or in the reaction of CO\(_2\) + H\(_2\) differed basically from that observed during the adsorption of gaseous CO. The IR spectra of adsorbed CO on different supported Rh have been the subject of several papers; the doublet due to the twin structure (Rh(CO)\(_2\)) was missing and the linearly bonded CO absorbed at lower frequencies (~2030–2020 cm\(^{-1}\)).
It was suggested that the adsorbed hydrogen prevents the formation of the twin structure and Rh carbonyl hydride was formed \(^{[37,41,42,48,122]}\).

\[
\text{Rh} \quad \begin{array}{c} \text{CO} \\ \text{H} \end{array} \quad \text{Rh} \quad \begin{array}{c} \text{H} \\ \text{CO} \end{array}
\]

The chemisorbed H is electron donating, the \(\pi\) back-donation from Rh into the antibonding orbital of CO increases, and thus the carbonyl band appears at lower frequencies \(^{[37,41,48]}\). Iizuka and Tanaka \(^{[68,123]}\) stated that the bands observed in the 2020–2040 cm\(^{-1}\) region on the infrared spectra, over supported Rh were due to a linear CO species at low coverage rather than to a carbonyl hydride. Henderson and Worley using \(D_2\), instead of \(H_2\), confirmed the Rh carbonyl hydride formation \(^{[122]}\). The absorption frequency of linearly bonded CO formed in the reaction depends on the Rh dispersion, i.e., on the Rh particle size. Catalysts with low Rh dispersion have a higher frequency of absorption compared with the catalysts with higher Rh dispersion \(^{[79]}\).

When 10% Rh/SiO\(_2\) was reduced and cooled down in hydrogen after CO\(_2\) adsorption linear CO was observed at 2029 cm\(^{-1}\). Upon \(H_2\) introduction the peak moved to higher frequency and a broad band at 1795 cm\(^{-1}\) was also found. This was also observed during CO\(_2\) hydrogenation. The frequency of this band red-shifted to 1749 cm\(^{-1}\) as the temperature increased. This absorption was attributed to the formation of hydroxicarbonyl species \(^{[82]}\).

\[
\text{Rh} \quad \begin{array}{c} \text{CO} \\ \text{OH} \end{array}
\]

When Rh/Al\(_2\)O\(_3\) was not reduced before the reaction the structure of the adsorbed CO changed during the reaction due to the progressing reduction of Rh\(^+\) and agglomeration effects. First at 523 K geminal dicarbonyl species are present, Rh\(^0\)-CO are observable at 573 K and then the band around 2020 cm\(^{-1}\) becomes dominant \(^{[41]}\).

On lanthanide-promoted Rh/Al\(_2\)O\(_3\), two peaks were observed in the CO region at ~2050 and ~2030 cm\(^{-1}\) in the CO\(_2\) + \(H_2\) reaction, but only one peak was detected at 2023 cm\(^{-1}\) on the unpromoted catalyst \(^{[124]}\). The band at ~2020 cm\(^{-1}\) was assigned to adsorbed CO on Rh(1) sites.

The formation and adsorption of CO from CO\(_2\) + \(H_2\) occurs according to high pressure FTIR measurements on Rh/Al\(_2\)O\(_3\). The main CO species, hydride CO, increase with increasing the CO\(_2\) pressure. In the presence of water vapor the absorption band of hydride CO is shifted to the lower frequency range of 2000 to 1880 cm\(^{-1}\); such a significant change was not observed for the bridged CO absorption at 1880–1740 cm\(^{-1}\) \(^{[125]}\). The direct interaction between the CO and the water was excluded, the shift was explained that the CO was displaced preferentially by water from atomically rough surface.

On Rh/TiO\(_2\) \(^{[42]}\), formyl groups were also found absorbing at 1720 cm\(^{-1}\). The intensity of this band shows a maximum as a function of reduction temperature. These results could be explained by the observation that the interfacial sites in TiO\(_2\)/Pt promote the decomposition of CH\(_3\)O intermediates \(^{[126]}\). As the higher reduction temperature increases both the formation and the decomposition rate of formyl groups the resultant is the maximum in the surface concentration.

On Fe-promoted 5% Rh/SiO\(_2\) catalysts (Fe/Rh = 0–0.5), in the CO\(_2\) + \(H_2\) reaction, as was mentioned earlier, ethanol was also formed. Infrared spectroscopic measurements revealed that adsorbed CO species were observed on each catalyst. Linear CO species at 2020–2050 cm\(^{-1}\) shifted to higher wave number with an added amount of Fe in the range of Fe/Rh = 0–0.1. The shift corresponds to a decrease in reverse donation from Rh to adsorbed CO and an increase in the C–O bond strength. In contrast the linear species shifted to lower wave number again with added Fe in the rage Fe/Rh = 0.3–0.5. The Fe
additives influenced not only the linear but the bridge bonded CO, too. The ratio of the bridge and linearly bonded CO increased with increasing the amount of Fe. By comparing this ratio with the ethanol selectivity, it was concluded that the ethanol selectivity correlates with the intensity of the bridged CO [88].

In situ ED-XAS and HE-XRD studies demonstrated that on Rh/Al2O3 the Rh is not in a pure metallic state; it was in a low oxidation state (RhOx) during the methanation reaction. This is a strong indication that CO2 dissociates forming adsorbed CO and O [99]. Such changes were not observed for the Rh/SiO2 catalyst, which exhibits lower CO2 conversion. In situ DRIFTS results indicated that mainly the linearly (~2020 cm⁻¹) and bridge bonded CO (1780 cm⁻¹) were formed during the CO2 hydrogenation over both Al2O3 and SiO2 supported samples, but the intensity of the Rh-CO species band was much stronger on Rh/Al2O3 than on Rh/SiO2. It was also accepted that the shift in the CO absorption frequency is due to the Rh-carbonyl-hydride formation [99].

On 1% Rh/Al2O3, under reaction conditions at 323 K, the CO band appeared at 2036 cm⁻¹ (Rh0-CO). When the temperature increased the band intensities increased and at the same time they shifted to lower wave numbers reaching 2021 cm⁻¹ at 473 K [79]. At this temperature, a broad band at 1805 cm⁻¹ attributed to bridge-bonded CO (Rh1/2CO) was also detected. On catalysts containing 2% or more Rh supported on Al2O3 a weak band was also observed at 1905 cm⁻¹, which was related to the formation of Rh2(CO)3 [79]. On potassium promoted Rh/Al2O3 the intensity of the linearly bonded CO was negligible and an additional band was observed at 1794 cm⁻¹ at 623 K. This band is only observable under reaction conditions and vanishes during flushing with He and it was attributed to adsorbed formyl (HCO) species [41].

During the CO2 + H2 reaction on Rh/TiNT and on Rh/TiNW, peaks were registered in the CO region not only at 2030–2050 cm⁻¹, but at 1760–1770 cm⁻¹, too. This feature was assigned to such type of tilted CO which bonded to the Rh and interacts with the oxygen vacancy of the titanate support. This suggestion was based on the earlier observations that Lewis acid sites interact with the oxygen atom of CO which resulted in a downward shift of the CO absorption wave number [127,128]. The other possible assignment of this peak would be the C=O band in the adsorbed HCHO. This was ruled out because this species on Rh/TiO2 absorbs at 1727 cm⁻¹ [129].

7. The Proposed Mechanism for the CO2 Hydrogenation on Supported Rh Catalysts

Regarding the reaction mechanism for CO2 hydrogenation basically two different, but same in a few steps reaction mechanisms were proposed. The first involves the adsorption of CO2 on the support and its reaction with H(ads) formed on the metal, which leads to the formation of formate (HCOO) or formyl (HCO) at the metal support interface [39,54,104]. The second mechanism involves the direct or hydrogen assisted dissociation of CO2 on the metal surface and the subsequent hydrogenation of adsorbed CO through surface carbon forming CHx and then CH4 [45,65]. There is a general agreement in this case that the dissociation of the adsorbed CO is the rate determining step. Many variations of both main directions have been described. Still, there is discussion on the nature of the intermediate compounds involved in the reaction process and on the products formation scheme. It is not so easy to distinguish between the real reaction intermediate and the spectator molecules, whereas, in most publications, the same surface species were found. Support dependent reaction mechanisms were suggested for CO2 hydrogenation via either a CO route for catalyst supported on non-reducible support [99] or the formate route for catalysts supported on reducible oxides [104,130,131]. Others suggested that oxygen vacancies play an important and major role in the dissociation of CO2 in the case of reducible oxide supported catalysts [59,85]. It was assumed that the CO evolved in the CO2 dissociation reacts further by the same mechanism as in the CO + H2 reaction.

If the adsorbed CO species play an important role in the hydrogenation of CO2, the question arises as to why the formation of CH4 is faster in the CO2 + H2 reaction than when the H2 + CO mixture was used. There is an assumption that CO absorbs on the metal sites thus reducing the possibility of hydrogen dissociation [72]. It was supported by the finding that the partial order of CO at
relatively high CO concentration (33%) was negative [132]. It is another suggestion [11,45,65] whether the surface concentrations of adsorbed CO and the surface C play the key roles. When CO$_2$ was used, the concentration of adsorbed CO, and therefore the concentration of surface carbon produced in the direct or in the hydrogen induced dissociation of CO, was relatively low. The carbon formed can react quickly with the large excess of H$_2$, and there is less possibility for the accumulation and aging of surface C. In contrast, when a H$_2$ + CO gas mixture was used, the surface concentration of adsorbed CO is higher and so the formation of surface carbon will be much larger during a given time. Consequently, not all the surface carbon reacts immediately with hydrogen and a part of the surface carbon transformed to less reactive forms [C$_x$]. The hydrogenation rate of this species is slower and requires probably higher activation energy. The aging of carbon is well demonstrated by the study of the reaction of carbon deposit (formed in the H$_2$ + CO$_2$ or in the H$_2$ + CO reaction [133] or in CO disproportionation [132]) with H$_2$ on different supported Rh catalysts. The reactivity of the surface carbon formed in the dissociation or in the disproportionation of CO depended on the temperature of its formation and also on the time between its formation and its coming into contact with H$_2$ [132]. On the other hand, when a H$_2$ + CO mixture was used, CO adsorbed on Rh can function as a poison toward hydrogen chemisorption, therefore resulting in a decreased methanation rate, and the surface carbon has time to age.

In the previous chapter we have shown that different adsorbed CO species were detected during the reaction. There is even no consent in which detected CO form is actually involved in the hydrogenation of CO$_2$. There are groups that have suggested that linearly bonded CO [54,72] or the carbonyl-hydride form [65] is the most important surface intermediate, while others have proposed the bridge bonded CO [60,88] but there is also example that the dicarbonyl structure reacts further to methane [49]. There is another assumption that the intermediate species in the CO$_2$ hydrogenation on Rh/MgO, Rh/Al$_2$O$_3$, and Rh/CeO$_2$ is the [M$_y$]Rh$_x$H$_n$(CO)$_p$ (M = Mg, Al, Ce) complex [47].

In the following, some specific examples are presented in which the mechanism of the CO$_2$ + H$_2$ reaction is described in different ways.

The methanation of CO$_2$ on titania deposited Rh foils [51] and Rh/SiO$_2$ [39] is proposed to start with the dissociation of CO$_2$ into CO$_{(a)}$ and O$_{(a)}$ and then proceeds through steps which are identical to those for CO hydrogenation.

\[
\begin{align*}
\text{CO}_2(g) + 2S &\rightleftharpoons \text{CO}_{(a)} + \text{O}_{(a)} \\
\text{H}_2(g) + 2S &\rightleftharpoons 2\text{H}_{(a)} \\
2\text{H}_{(a)} + \text{CO}_{(a)} &\rightleftharpoons \text{H}_2\text{CO}_{(a)} + 2S \\
\text{H}_2\text{CO}_{(a)} + S &\rightarrow \text{CH}_2_{(a)} + \text{O}_{(a)} \\
\text{O}_{(a)} + \text{H}_{(a)} &\rightleftharpoons \text{OH}_{(a)} + S \\
\text{CH}_2_{(a)} + \text{H}_{(a)} &\rightleftharpoons \text{CH}_3_{(a)} + S \\
\text{CH}_3_{(a)} + \text{H}_{(a)} &\rightleftharpoons \text{CH}_4(g) + 2S
\end{align*}
\]

It was assumed that the rate limiting step is the dissociation H$_2$.

\[
\begin{align*}
\text{CH}_4(\text{ads}) &\rightarrow \text{C}_{(\text{ads})} + 4\text{H}_{(\text{ads})} \\
\text{CO}_2(\text{ads}) &\rightarrow \text{CO} + \text{O}_{(\text{ads})}
\end{align*}
\]

Kusama et al. [83] proposed that the first step of CO$_2$ hydrogenation on Rh/SiO$_2$ is the reaction of CO$_2$ with H$_2$ and the formation of adsorbed CO on Rh surface. CO saturated Rh surface species react with the surface hydroxyl groups and form Rh-carbonyl clusters

\[
[Rh]_n + 2\text{CO} + x\text{HO-Si} [Rh]_{n-1} + \text{Rh(CO)}_2(O-Si)_x + x2\text{H}_2
\]
Adsorbed CO was not subjected to further hydrogenation and just desorbed as CO. With this theory, the high CO selectivity on Rh/SiO₂ could be explained.

Earlier, it was suggested that the CO in Rh carbonyl hydride dissociates to surface carbon which reacts further to methane, but the carbon lost its activity in time [65].

\[
\text{H}_2(g) + \text{CO}_2(g) \rightarrow \text{CO}(g) + \text{H}_2\text{O}(l)
\]

Similar reaction scheme was suggested for CO₂ hydrogenation on Rh/TiO₂ catalyst [45].

\[
\text{CO}(g) \leftrightarrow \text{CO}_2(g) \rightarrow \text{C} \leftrightarrow \text{C} \leftrightarrow \text{hydrocarbons}(g)
\]

It was supposed based on the results of ambient-pressure XPS, DRIFT, and high-energy XRD measurements that the ceria phase is partially reduced during the CO₂ methanation on Rh/CeO₂, and, in particular, Ce³⁺ species seem to facilitate the activation of CO₂ molecules. The activated CO₂ species then react with hydrogen atom produced from H₂ dissociation on Rh sites and formate species are formed. The higher methane selectivity on Rh/CeO₂ is explained by the stronger metal–support interaction [104].

Several works proposed that CO dissociation is assisted by hydrogen and carbonyl-hydride can be formed which weakens the C–O bond related to that in carbonyl [65].

This suggestion is supported by the CO spectra registered during the reaction, while the CO band appeared at lower wave number than after CO adsorption. Although this is a significant difference in the hydrogen assisted C–O bond cleavage, but there is no direct evidence for the existence of H₄CO surface species during the hydrogenation of CO₂.

On Li promoted Rh/SiO₂ ethanol formed in the CO₂ + H₂ reaction but on Rh/SiO₂ the methane selectivity was 99.7%. The effect of Li in the ethanol formation was explained with the difference observed in the adsorbed CO formed during the reaction. On the IR spectra of Rh-Li/SiO₂, the intensity of bridge bonded CO was higher than that of the linear one, while on the undoped sample the intensities were the same. The more bridged CO (which occupies 2 Rh atoms) provide smaller number of unoccupied Rh sites for H₂ adsorption and thus the hydrogenation ability of the catalyst will be suppressed. Therefore, the CO species can be inserted into a CH₃-Rh bond more easily than on Rh/SiO₂ [60]. In the case of Rh-Fe/TiO₂, the ethanol production was also assumed through the formation of CH₃CO⁺ (acyl) groups [90].
The formation of acetic acid on Ag promoted Rh/SiO₂ was explained with the direct insertion of CO₂ to surface methyl species on Rh which led to acetate formation, followed by hydrogenation to acetic acid. Acetic acid formation suppresses remarkably the CO₂ dissociation and desorption over highly dispersed Rh catalyst at lower reaction temperature [94].

The adsorbed CO could be detected already at temperatures as low at which the gas phase products CO or CH₄ are not formed yet on Rh/TiO₂ [69], or on Rh/Al₂O₃ [48]. Some authors proposed a mechanism for CO(ads) production through the formation of formate species.

\[
CO₂ + H(\text{metal}) \rightarrow COOH(\text{interface}) \rightarrow CO(\text{metal}) + OH(\text{support})
\]  

(11)

Others suggested the direct dissociation of CO₂ on Rh in the interaction of CO₂ + H₂ [28]. It was assumed that the formates are mainly spectators and form in the reaction of CO(ads) with the OH groups of the support [69]

\[
CO(\text{metal}) + OH(\text{support}) \rightleftharpoons COOH(\text{interface})
\]  

(12)

As we have seen in recent years, many ideas have been developed for the hydrogenation of CO₂, but, to date, there is no clear explanation as to what and why influences the activity and selectivity of Rh catalysts.

8. Conclusions

This review summarizes the studies on the hydrogenation of CO₂ on supported Rh catalysts. Comparing the activity and selectivity of different supported metal catalysts, it was found that Rh is one of the best samples. The possibility of the CO₂ dissociation on clean metal and on supported Rh was discussed separately. The results are not clear there are groups who have detected the dissociation of CO₂ while others have not observed this process. The hydrogenation of CO₂ produces mainly CH₄ and CO, but the selectivity of the reaction is affected by the support, in some cases the reduction of the support; the particle size of Rh; and the different additives. At higher pressure methanol, ethanol and acetic acid could be also formed. The activity of the various supported Rh catalysts was compared and in general, the TiO₂ and CeO₂ supported samples were the best. Results obtained for TiO₂-, SiO₂-, and Al₂O₃-supported catalysts were discussed in a separate chapter. The compounds formed on the surface of the catalysts during the reaction are shown in detail; mostly different CO species, adsorbed formate groups, and different carbonates were detected. In a separate chapter, the mechanism of the reaction was also discussed. Basically, two different, but similar in a few steps, reaction mechanisms were proposed. The first involves the adsorption of CO₂ on the support and its reaction with H(ads) which leads to the formation of formate (HCOO) or formyl (HCO). The other involves the direct or hydrogen assisted dissociation of CO₂ on the Rh surface and the subsequent hydrogenation of adsorbed CO through surface carbon-forming CHₓ and then CH₄.

Conflicts of Interest: The authors declare no conflict of interest.

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