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### Hydrogenation of CO<sub>2</sub> over supported noble metal catalysts

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### **Graphical abstract**



#### **Research Highlights:**

- Rh and Ru catalysts are more active for the CO<sub>2</sub> methanation compared to Pt and Pd catalysts, which promote the RWGS.
- CO<sub>2</sub> methanation reaction is structure sensitive and is enhanced with increasing mean Ru crystallite size.
- The reactive surface intermediates could potentially be CO species linearly bonded on reduced Ru crystallites (Ru<sub>x</sub>-CO).
- The relative intensity of the band due to Ru<sub>x</sub>-CO species increases with increasing Ru particle size.

### ABSTRACT

The catalytic activity of supported noble metal catalysts for the CO<sub>2</sub> methanation reaction has been investigated with respect to the nature (Rh, Ru, Pt, Pd), loading (0.1-5.0 wt.%) and mean crystallite size (1.3-13.6 nm) of the dispersed metallic phase. It has been found that the turnover frequency (TOF) of CO<sub>2</sub> conversion for TiO<sub>2</sub>-supported catalysts increases following the order of Pd < Pt < Ru < Rh, with Rh being about 3 times more active than Pd. Selectivity toward methane depends strongly on the noble metal catalyst employed and is significantly higher for Rh and Ru catalysts compared to Pt and Pd, which mainly promote production of CO via the RWGS reaction. Conversion of CO<sub>2</sub> at a given temperature increases significantly with increasing Ru loading in the range of 0.1-5.0 wt.%. Results of kinetic measurements show that the CO<sub>2</sub> hydrogenation reaction is structure sensitive, i.e., catalytic activity is strongly influenced by metal crystallite size. In particular, for Ru/TiO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts, the normalized turnover frequency (TOF divided by the length of the perimeter of the metal-support interface) increases by two orders of magnitude with increasing ruthenium crystallite size in the range of 0.9-4.2 nm and 1.3-13.6 nm, respectively. FTIR experiments provide evidences that CO<sub>2</sub> hydrogenation reaction occurs via intermediate formation of adsorbed CO species (Rux-CO, Ru<sup>n+</sup>(CO)x, (TiO<sub>2</sub>)Ru-CO) produced via the RWGS reaction. Part of this species interacts with adsorbed hydrogen atoms producing

methane, whereas the remaining species desorbs to yield CO in the gas phase. The CO<sub>2</sub> hydrogenation pathway does not change with variation of Ru crystallite size. However, the relative intensity of the band due to CO species linearly bonded on reduced Ru crystallites (Ru<sub>x</sub>-CO) increases significantly with increasing Ru particle size, indicating that Ru<sub>x</sub>-CO species could potentially being the reactive surface intermediates.

Keywords: CO<sub>2</sub> methanation; Ru, Rh, Pt, Pd; TiO<sub>2</sub>; Al<sub>2</sub>O<sub>3</sub>; structure sensitivity; DRIFTS

#### **1. INTRODUCTION**

Fossil fuels consumption is responsible for the significant emissions of CO<sub>2</sub> in the atmosphere, which, in nowadays, is considered as one of the main greenhouse gases resulting in global warming and therefore, major climate changes [1-3]. Thus, efforts have been made during the last decades in order to eliminate and utilize CO<sub>2</sub>. Among the proposed utilization processes, CO<sub>2</sub> hydrogenation is of special interest, since it is not only able to reduce effectively carbon dioxide, but also opens up novel pathways for producing high added value chemicals and fuels [4-6]. Depending on the operating conditions and catalyst employed, the interaction of CO<sub>2</sub> with hydrogen results in the formation of a variety of products, including carbon monoxide, methanol, formic acid and C<sub>2</sub> hydrocarbons [2, 6].

Methanation of CO<sub>2</sub> (Eq. 1) takes place efficiently at atmospheric pressure and moderate temperatures (300-400°C) and offers certain advantages provided that hydrogen is generated from renewable energy sources (e.g. water electrolysis, biomass etc.) [1, 2, 4-7].

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$$
  $\Delta H^\circ = -165 \text{ kJ/mol}$  (Eq. 1)

In particular, methane produced can be used as synthetic substitute of natural gas in chemical and petrochemical industry and/or as energy carrier in power plants following well established methods for its storage and transfer [3-5].

It is generally accepted that the CO<sub>2</sub> hydrogenation proceeds through intermediate formation of CO via the reverse water-gas shift (RWGS) reaction (Eq. 2), followed by CO hydrogenation to methane [8-10].

$$CO_2 + H_2 \leftrightarrow CO + H_2O$$
  $\Delta H^0 = 41.1 \text{ kJ/mol}$  (Eq. 2)

However, depending on the reaction conditions and catalyst employed, part of the produced CO cannot be further hydrogenated toward CH<sub>4</sub> and is desorbed in the gas phase, resulting in low methane selectivities. Thus, it is important to develop active and stable CO<sub>2</sub> methanation catalysts, able to convert selectively CO<sub>2</sub> to CH<sub>4</sub> at relative low temperatures (< 400°C).

Hydrogenation of carbon dioxide toward methane can be catalyzed by several metal catalysts, including Ni [2, 3, 11-14], Ru [7, 15-21], Rh [1, 4, 5, 15, 22], Pt [15], Pd [6, 15, 23] Ir [24] and Co [25] supported on various metal oxides (e.g. TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>). Generally, Ru, Rh and Ni catalysts exhibit high activity for the reaction, which is also affected by the nature of the support [13, 15, 26-28]. Alumina and titania supported catalysts present high activity and selectivity toward methane and thus, they are widely studied. It has been found that metal-support interactions can modify the catalytic properties of the active metallic phase (i.e. morphology, dispersion etc.) and thus, affect the CO<sub>2</sub> hydrogenation activity [26, 27]. Metal loading and crystallite size affect catalytic performance of supported metal catalysts in a manner which depends on operating conditions and metal-support combination employed [4, 6, 18, 26, 29-31]. For example, it is generally accepted that a high Ru or Pd loading is necessary to produce selectively methane in CO<sub>2</sub> hydrogenation [6, 18, 26]. On the other hand, although catalysts with high Ni loadings exhibit high CO<sub>2</sub> conversions they tend to enhance the RWGS reaction, resulting in lower methane selectivities [26]. In the case of Rh/Al<sub>2</sub>O<sub>3</sub> catalysts, CO<sub>2</sub> methanation activity is favored over large Rh particles at low reaction temperatures (<185°C), whereas at high reaction temperatures no effect has been observed [4].

In the present study, the catalytic performance of TiO<sub>2</sub>- and Al<sub>2</sub>O<sub>3</sub>-supported noble metals for the title reaction is investigated with respect to the nature, loading and mean crystallite size of the metallic phase. The relation between CO<sub>2</sub> hydrogenation activity and physicochemical properties of the dispersed metallic phase is discussed. The effect of metal crystallite size on the nature and relative population of adsorbed surface species produced during CO<sub>2</sub> methanation is investigated over Ru/TiO<sub>2</sub> catalysts employing *in situ* FTIR spectroscopy technique.

#### 2. EXPERIMENTAL

#### 2.1 Catalyst preparation and characterization

Noble metal catalysts supported on TiO<sub>2</sub> (Degussa P25) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Alfa products) were synthesized employing the wet impregnation method [32]. The metal precursor salts used were Rh(NO<sub>3</sub>)<sub>3</sub>, Ru(NO)(NO<sub>3</sub>)<sub>3</sub>, (NH<sub>3</sub>)<sub>2</sub>Pt(NO<sub>2</sub>)<sub>2</sub> and (NH<sub>3</sub>)<sub>2</sub>Pd(NO<sub>2</sub>)<sub>2</sub>. Impregnation of catalysts was followed by drying at 110°C for 24 h and reduction at 300°C (400°C for Ru catalysts) in flowing hydrogen for 2 h. The nominal metal loading of the catalysts thus prepared varied between 0.1 and 5 wt.%. In the case of Ru/Al<sub>2</sub>O<sub>3</sub> catalysts, three additional samples with 5 wt.% Ru content were prepared in an attempt to increase Ru crystallite size. This was achieved by calcination of the dried samples in air at 600, 650 or 700°C for 2 or 4 h, followed by reduction with H<sub>2</sub> as described above.

Carriers and dispersed noble metal catalysts were characterized with respect to their specific surface area employing nitrogen physisorption at 77 K (B.E.T. technique) with the use of a Micromeritics (Gemini III 2375) instrument [32]. The exposed metallic surface area, metal dispersion and mean crystallite size were estimated employing selective chemisorption of H<sub>2</sub> with the use of a modified Fisons Instruments (Sorptomatic 1900) apparatus [32, 33]. Measurements have been conducted at 25°C for Rh and Pt, 60°C for Pd and 100°C for Ru

samples. Calculations of the exposed metallic surface area, metal dispersion and mean crystallite size have been performed using standard equations described in detail elsewhere [32, 33]. The structural characteristics of selected catalysts were also investigated employing Transmission Electron Microscopy (TEM) following standard procedures [10, 33].

#### 2.2 Catalytic performance tests

The catalytic performance for the CO<sub>2</sub> hydrogenation reaction was evaluated using a fixed bed reactor, operating at atmospheric pressure. The reactor consisted of two 6 mm O.D. sections (22-cm long) of quartz tube, which served as inlet and outlet to and from a quartz cell of 8 mm O.D. (1-cm long), in which the catalyst sample was placed by means of quartz wool. The temperature of the catalyst was measured by a K-type thermocouple, which ran through the cell. Heating of the reactor was provided by an electric furnace, the temperature of which was controlled using a second K-type thermocouple placed between the reactor and the walls of the furnace. The pressure drop in the catalyst bed was measured by means of a pressure indicator. The flow of the gases (CO<sub>2</sub>, H<sub>2</sub>, He) was measured and controlled with the use of three mass-flow controllers (M+W Instruments). The gas mixture was fed to the reactor through stainless steel tubing, whereas, when desired, the gas stream was introduced to a bypass loop by means of a common set of switch valves. The exit of the reactor was connected to a three-way valve, which allows selection of introduction of the gas stream to the GC or to a bubble flow meter, which was used for measuring the total flow rate at the exit of the reactor. The reactor effluent was analyzed using a gas chromatograph (Shimadzu) equipped with two packed columns (Porapak-Q, Carboxen) and two detectors (TCD, FID), operating with He as the carrier gas. Determination of the response factors for the TCD and FID detectors was achieved using gas streams of known compositions.

Catalytic performance tests were carried out in the temperature range of 170-450°C using 100 mg (particle size: 0.18 < d < 0.25 mm) of catalyst and a total flow rate of 150 cm<sup>3</sup>

min<sup>-1</sup>. Prior to each experiment the catalyst was reduced *in situ* at 300°C for 1 h under 50% H<sub>2</sub>/He flow (60 cm<sup>3</sup> min<sup>-1</sup>), followed by purging with He and decrease of temperature to 170°C. The sample was then exposed to the reaction mixture (150 cm<sup>3</sup> min<sup>-1</sup>) consisting of 5% CO<sub>2</sub>+20% H<sub>2</sub> (in He), and the conversions of reactants as well as the product distribution were determined using the gas chromatograph described above. The temperature was then stepwise increased up to 450 °C and similar measurements were obtained. It should be noted that the reaction was carried out for 1 hour in each temperature, so as steady state conditions to be achieved. Carbon dioxide conversion ( $X_{CO2}$ ) and selectivities toward CH<sub>4</sub> ( $S_{CH4}$ ) and CO ( $S_{CO}$ ) were calculated following the expressions described in detail in the SI.

The intrinsic reaction rates were measured under differential reaction conditions, i.e. for conversions of reactants lower than 10%. These results, along with the measurements of metal dispersion, were used to calculate the turnover frequencies (TOFs) of carbon dioxide conversion, defined as moles of  $CO_2$  converted per moles of surface noble metal atom per second (s<sup>-1</sup>). The equations used are described in the SI.

#### 2.3 In situ FTIR spectroscopy

The CO<sub>2</sub> hydrogenation reaction was investigated by performing in situ FTIR spectroscopy experiments under continuous flow conditions with the use of a Nicolet 6700 FTIR spectrometer. The spectrometer was equipped with a diffuse reflectance (DRIFT) cell (Spectra Tech), an MCT detector and a KBr beam splitter [8]. Briefly, the catalyst powder was placed into the sample holder and heated at 450°C under He flow (30 cm<sup>3</sup> min<sup>-1</sup>) for 10 min followed by reduction with 20%H<sub>2</sub> in He (30 cm<sup>3</sup> min<sup>-1</sup>) at 300°C for 60 min. The reduced sample was then heated in flowing helium (30 cm<sup>3</sup> min<sup>-1</sup>) at 450°C for 10 min and subsequently cooled down to room temperature (RT). In the cooling stage, background spectra were recorded at selected temperatures. Finally, the flow was switched to the reaction mixture, which consisted of 1%CO<sub>2</sub>+4%H<sub>2</sub> (in He) (30 cm<sup>3</sup> min<sup>-1</sup>) and the first spectrum was

recorded at RT after 15 minutes-on-stream. The temperature was then increased in a stepwise mode up to 450°C and spectra were collected at selected temperatures. In each temperature an equilibration for 15 minutes-on-stream was carried out prior to spectrum recording.

#### **3. RESULTS AND DISCUSSION**

#### **3.1 Catalyst characterization**

The specific surface areas of commercial TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> used as supports in the present study were measured with the BET method and found to be 42 m<sup>2</sup>/g and 83 m<sup>2</sup>/g, respectively. Similar measurements have been conducted over the dispersed noble metal catalysts and results showed that the specific surface areas were not altered upon addition of metal. The physicochemical characteristics of synthesized catalysts are summarized in Table 1, where metal loading ( $X_{Me}$ ), dispersion (D) and mean crystallite size ( $d_{Me}$ ) are listed for all samples investigated. It is observed that metal dispersion and crystallite size vary significantly in the range of 7-99% and 0.9-13.6 nm, respectively, depending on the nature and loading of the metallic phase, as well as on the nature of the support employed.

The structural characteristics of 0.5% and 5% Ru/TiO<sub>2</sub> catalysts were also investigated by HRTEM and the images obtained are shown in Fig. S1. It is observed that both 0.5% and 5% Ru/TiO<sub>2</sub> catalysts comprise fairly homogeneously dispersed spherical Ru particles of approximately 1.8 and 4.0 nm diameter, respectively. Ruthenium crystallite sizes obtained by TEM analysis agree well with those estimated based on H<sub>2</sub> chemisorption measurements (Table 1).

#### 3.2 Effect of the nature of the metallic phase on CO<sub>2</sub> methanation activity

The effect of the nature of the dispersed metal on catalytic performance for the CO<sub>2</sub> hydrogenation reaction was investigated over Rh, Ru, Pd and Pt catalysts of the same metal loading (0.5 wt.%) supported on TiO<sub>2</sub>. Results obtained are summarized in Fig. 1A, where the conversion of CO<sub>2</sub> obtained over noble metal catalysts is plotted as a function of reaction

temperature. Under the present experimental conditions both CO<sub>2</sub> methanation and RWGS reactions are equilibrium limited. Thus, the equilibrium conversion, predicted by thermodynamics, is also shown for comparison.

It is observed that, under the experimental conditions employed, Rh catalyst exhibits significantly higher CO<sub>2</sub> conversions, in the entire temperature range, compared to Ru and Pt, whereas Pd is significantly less active than the other samples examined. In particular, Rh-loaded sample is activated at temperatures higher than 150°C and  $X_{CO2}$  reaches equilibrium at ca 380°C. The conversions curves of Ru and Pt catalysts are shifted toward higher temperatures, compared to that of Rh, while temperatures higher than 450°C are required to achieve equilibrium CO<sub>2</sub> conversions. For the least active Pd catalyst,  $X_{CO2}$  is lower than 10% at temperatures as high as 440 °C.

In addition to methane, hydrogenation of CO<sub>2</sub> also results in the production of appreciable amounts CO, via the RWGS reaction, which is strongly affected by the nature of the dispersed metallic phase. Representative results can be seen in Fig. 1B where selectivities toward CO and CH<sub>4</sub> at 350 °C are plotted for the investigated catalysts. Interestingly, methane selectivity at 350 °C is 100% for Rh, 86% for Ru, 1% for Pt and practically zero for Pd catalyst. It should be noted that *S*<sub>CH4</sub> decreases from 90 to 79% with increasing temperature for Ru/TiO<sub>2</sub> catalysts (not shown for clarity), whereas it remains practically unaffected by temperature for Rh, Pt and Pd/TiO<sub>2</sub> catalysts. Results indicate that the RWGS is strongly favored over Pt and Pd catalysts, which are not able to methanate CO<sub>2</sub> at least under the present experimental conditions employed. Results are in agreement with previous studies over noble metal catalysts (Rh, Ru, Pt, Pd) supported on Al<sub>2</sub>O<sub>3</sub>[15] and CeO<sub>2</sub> [34], and can be explained considering the mechanistic pathway proposed for the title reaction. It has been suggested that CO<sub>2</sub> hydrogenation proceeds through intermediate formation of CO at the metal-support interface via the RWGS reaction. Part of CO interacts with hydrogen

leading to methane production, whereas the rest is desorbed to yield CO in the gas phase. The enhancement of each pathway depends on the catalyst and experimental conditions employed, and determines selectivity toward CH<sub>4</sub> (methanation) or CO (RWGS) [8]. Results of Fig.1B suggest that the adsorbed CO species produced via the RWGS reaction at the interface between Pt (or Pd) and TiO<sub>2</sub> support prefer to desorb yielding CO in the gas phase rather than to interact with hydrogen producing CH<sub>4</sub>.

Turnover frequencies of CO<sub>2</sub> conversion (TOF<sub>CO2</sub>) over the four catalysts are summarized in the Arrhenius-type diagram of Fig. 1C. It is observed that the intrinsic activity per exposed metal atom varies by a factor of 2.9 at 250°C in the order of Rh > Ru ~ Pt > Pd. However, the specific activity takes completely different values taking into account the selectivity toward methane formation. In particular, the specific reaction rate of methane formation (not shown for clarity) is 1.5 times higher for Rh catalyst compared to Ru and practically zero for Pt and Pd catalysts. The high activity of Rh and Ru catalysts for CO<sub>2</sub> methanation has been reported by several authors and has been attributed to the rapid hydrogenation of the intermediate CO, resulting in higher methane production [15, 26, 28, 34].

The apparent activation energies (*E*<sub>a</sub>) of the CO<sub>2</sub> methanation reaction over the four catalysts examined were calculated from the slopes of the fitted lines shown in Fig. 1C and results are summarized in Table 1. It is observed that the apparent activation energy depends on the nature of the metallic phase, taking values between 55.6 kJ/mol for Ru and 71.1 kJ/mol for Rh. Similar values have been previously reported over Al<sub>2</sub>O<sub>3</sub>-supported noble metal catalysts [15, 24].

#### **3.3 Effect of metal loading and crystallite size**

#### 3.3.1 CO<sub>2</sub> methanation activity

The effect of metal loading on catalytic performance was investigated over ruthenium

catalysts (0.1-5.0 wt.%) supported on TiO<sub>2</sub>. The mean crystallite size of Ru ( $d_{Ru}$ ) in this series of catalysts increases from 0.9 to 4.2 nm with increasing ruthenium content from 0.1 to 5.0 wt.%, respectively (Table 1). Results obtained are shown in Fig. 2A, where it is observed that increasing Ru loading from 0.1 to 5.0 wt.% results in a progressive and significant shift of the CO<sub>2</sub> conversion curve toward lower temperatures. In particular, the catalyst with the lowest Ru loading (0.1 wt.%) is activated at temperatures higher than 250 °C, whereas temperatures higher than 450 °C are required in order  $X_{CO2}$  to reach equilibrium conversions. On the other hand, the 5 wt.% Ru-loaded sample is already active at 165 °C and  $X_{CO2}$  reaches equilibrium conversions at 375°C (Fig. 2A).

The specific reaction rate of CO<sub>2</sub> conversion over the Ru/TiO<sub>2</sub> samples of variable metal loading and crystallite size are shown in the Arrhenius-type diagram of Fig. 2B. It is observed that the rate per surface Ru atom does not follow a monotonic trend with respect to the size of Ru crystallites. Turnover frequency takes similar values for the 0.1 and 0.5 wt.% loaded catalysts, which characterized by Ru crystallite size of 0.9 and 2.2 nm, respectively. TOF increases with increasing metal crystallite size up to 3.2 nm and decreases for the sample with larger Ru particles of 4.2 nm (5.0 wt.%). As discussed above, CO<sub>2</sub> hydrogenation proceeds through the formation of CO, as an intermediate, via the RWGS, followed by CO hydrogenation to methane. The RWGS reaction has been found to take place at the metal carrier interface [35]. This implies that the interface between the Ru and TiO<sub>2</sub> is promoting this catalytic step. Therefore, the interfacial area between the metal particles and the support material participates directly in the reaction pathway, and influences the observed catalytic activity.

The length of the metal/support interface decreases with increasing metal particle size, and therefore, the specific rate would be expected to decrease with increasing metal particle size. However, if specific activity is enhanced with the size of the metal crystallites, the

opposite tendency is expected. In order to eliminate the factor attributed to the length of the interface, TOF was normalized with respect to the interfacial length. The total perimeter of the metal/support interface per Ru surface area, *I*<sub>0</sub>, was calculated following Eq. 3, which is based on our previous study [33] and developments reported by Duprez et al. [36], assuming hemispherical particles.

$$I_{0} = \frac{A_{m}^{2} \cdot \beta \cdot \rho \cdot AW_{Ru}}{N_{AV} \cdot S_{Ru}} \qquad \qquad \left[m_{\text{interface}} / m_{Ru}^{2}\right] \qquad (\text{Eq. 3})$$

 $[m_{Ru}^2 \,\langle \, g_{Ri}]$  the specific weight of the metal Where:  $A_m$  is the metallic surface area  $(12.3 \times 10^6 g_{Ru} / m_{Ru}^3)$ ,  $AW_{Ru}$  is the atomic weight of the metal  $(101.07 g_{Ru} / mol_{Ra})$   $W_{AV}$  is the Avogadro number (6.023×10<sup>23</sup> atom<sub>Ru</sub>/mol<sub>Ru</sub>), S<sub>Ru</sub> is the surface area occupied by a surface metal atom (8.6·10<sup>-20</sup>  $m_{Ru}^2/Ru$  atom) and  $\beta$  is the coefficient depending on the particle shape  $(\beta=33.3 \text{ for a hemispherical particle})$ . As it was expected the length of the metal/support interface (I<sub>0</sub>) decreases progressively with increasing ruthenium crystallite size (Fig.S2A). Turnover frequencies presented in Fig. 2B were normalized with respect to Io and results obtained,  $TOF/I_0$ , are presented in the Arrhenius-type diagram of Fig. 3A. It is observed that normalized specific activity for the CO<sub>2</sub> hydrogenation reaction at a given temperature increases progressively (by two orders of magnitude) with increasing ruthenium crystallite size, from 0.9 to 3.2 nm, whereas it does not change appreciably for particle sizes up to 4.2 nm. This can be clearly seen in Fig. 3B, where the TOF/Io at 250 °C is plotted as a function of mean Ru crystallite size ( $d_{Ru}$ ) for all TiO<sub>2</sub>-supported catalysts investigated. The increase of the normalized TOF which is observed in Fig. 3A and B can be attributed to the influence of Ru crystallite size alone on specific catalytic activity. Based on previous studies, the WGS reaction over supported Ru catalysts is structure insensitive with respect to the metal, i.e. the TOF does not depend on metal loading or crystallite size [32, 35]. Thus, although the RWGS and CO<sub>2</sub> hydrogenation reactions run in parallel under the present experimental conditions,

only the rate of CO<sub>2</sub> hydrogenation is affected by the size of Ru particles. It may then be argued that CO<sub>2</sub> hydrogenation reaction is structure sensitive and is enhanced with increasing mean Ru crystallite size.

The effect of Ru crystallite size on catalytic activity has been also investigated over Ru/Al<sub>2</sub>O<sub>3</sub> catalysts of variable ruthenium content (Fig.4). Results of H<sub>2</sub> chemisorption measurements showed that increasing Ru loading from 0.5 to 5 wt.% results in an increase of Ru particles size in the narrow range of 1.3-1.6 nm (Table 1). In order to increase metal crystallite size, 5%Ru/Al<sub>2</sub>O<sub>3</sub> catalysts were calcined at 600-700°C for 2-4 hours and investigated for the CO<sub>2</sub> hydrogenation reaction. An increase of Ru particles up to 13.6 nm was achieved (Table 1), which was accompanied by a decrease of the length of the metal/support interface (Fig. S2B). Results of kinetic measurements are shown in Figs.4A and B, where it is observed that the normalized specific activity, *TOF/I<sub>0</sub>*, is significantly improved with increasing Ru crystallite size from 1.3 to 13.6 nm. Obviously, the beneficial effect of increasing the size of Ru particles on catalytic activity is also operable for Al<sub>2</sub>O<sub>3</sub> support. Comparison of Figs.4 and 5 shows that the effect is higher in the case of Ru/TiO<sub>2</sub> catalyst, taking into account that the size of Ru crystallites varies in the narrow range of 0.9-4.2 nm compared to the wider range of 1.3-13.6 nm for Ru/Al<sub>2</sub>O<sub>3</sub> catalysts.

It is of interest to know that, for both TiO<sub>2</sub>- and Al<sub>2</sub>O<sub>3</sub>-supported catalysts, the increase of intrinsic activity with increasing ruthenium crystallite size, at a given temperature, is accompanied by an increase of methane selectivity from 90 to 100% and from 80 to 100%, respectively (Fig 5). Catalysts with low ruthenium content (or small Ru particles) favor the formation of CO, which is diminished substantially for higher ruthenium loadings (or large Ru particles). Results agree well with the above discussion indicating that the hydrogenation of the intermediate produced carbon monoxide takes place faster with increasing Ru crystallite size (decreasing the length of the metal/support interface). Results of Fig.5 are in

agreement with previous studies over Pd/Al<sub>2</sub>O<sub>3</sub> catalysts, where selectivity toward methane was found to be higher (by a factor of 2-3) over 5%Pd/Al<sub>2</sub>O<sub>3</sub> compared to that measured over 0.5%Pd/Al<sub>2</sub>O<sub>3</sub>[6]. Similarly, *S*<sub>CH4</sub> has been found to be improved over large Ru particles dispersed on TiO<sub>2</sub> [37] or Al<sub>2</sub>O<sub>3</sub> [37, 38].

It can be concluded that CO<sub>2</sub> hydrogenation on Ru is structure sensitive and increases with increasing mean Ru crystallite size or that larger Ru particles are significantly more efficient in catalyzing CO<sub>2</sub> hydrogenation. The structure sensitivity of dispersed noble metals for the CO<sub>2</sub> methanation reaction has been investigated by several authors and results seems to depend on the metal-support combination employed, the experimental conditions and the range of metal particles size investigated [4, 6, 18, 31, 38, 39]. For example, Karelovic et al. [4] found that large Rh particles supported on Al<sub>2</sub>O<sub>3</sub> are more active than smaller particles at temperatures lower than 150 °C, whereas above 200 °C the intrinsic activity does not depend on metal particle size. Kowalczyk et al. [39] reported that TOF for CO<sub>2</sub> methanation reaction increases with decreasing Ru dispersion over Ru/Al<sub>2</sub>O<sub>3</sub>, Ru/MgO and Ru/MgAl<sub>2</sub>O<sub>4</sub> catalysts. Moreover, it has been found that the rate of methane production per surface Rh atoms increases with increasing metal particle size up to 7 nm, whereas it does not vary significantly for larger Rh particles [31]. As it will be discussed below, most of the studies agree that the beneficial effect of large metal particles on catalytic activity is attributed to the higher population of active sites which is enhanced over catalysts of high metal content.

Regarding the apparent activation energy of CO<sub>2</sub> hydrogenation, results (Table 1) show that it varies in the range of 51.5-71.1 kJ/mol for Ru/TiO<sub>2</sub> and 61.9-93.7 kJ/mol for Ru/Al<sub>2</sub>O<sub>3</sub> without presenting any trend with respect to metal particle size. This can be attributed to the fact that two reactions, RWGS and CO<sub>2</sub> hydrogenation, run simultaneously under the present conditions, each one of which depends in a different manner on temperature, nature of the support and metal crystallite size. This is in accordance to the

results of Aksoylu et al.[40], who found that  $E_a$  varies in the range of 59.4-72.8 kJ/mol over Ni/Al<sub>2</sub>O<sub>3</sub> catalysts without depending on Ni loading (5-25 wt.%). Similar values of the apparent activation energy have been previously reported for Rh/Al<sub>2</sub>O<sub>3</sub> (60.7-95.0 kJ/mol) [4] and Rh/TiO<sub>2</sub> (71.1-120.1 kJ/mol) [31] catalysts. However, the authors found that  $E_a$  depends on Rh crystallite size and that smaller Rh particles exhibit higher activation energies. Interestingly, Kwak et al. [38] found that the apparent activation energy of CO formation was lower (by ~20 kJ/mol) than that of CH<sub>4</sub> formation, regardless of Ru loading. The authors suggested that the formation of CO and CH<sub>4</sub> follows different pathways or takes place on different active sites, indicating that CO cannot be considered as an intermediate of methane formation. This should not be the case for the results of the present study. Although the apparent activation energy of CO formation was not possible to be estimated for all catalysts examined, in most cases it takes values lower or equal to that of methane formation implying that methanation of CO<sub>2</sub> proceeds through intermediate CO formation.

#### 3.3.2 CO<sub>2</sub> methanation studied by DRIFTS

Results of Figs.2-5 clearly show that ruthenium crystallite size affects strongly CO<sub>2</sub> methanation activity. In an attempt to identify the nature of active sites and adsorbed species, which drives selectivity for CO<sub>2</sub> hydrogenation reaction with respect to Ru crystallite size, the interaction of CO<sub>2</sub>/H<sub>2</sub> mixture with the catalyst surface was investigated over 0.5% and 5% Ru/TiO<sub>2</sub> catalysts employing *in situ* FTIR spectroscopy. It should be noted that, with the exception of the CO<sub>2</sub>/H<sub>2</sub> ratio (1/4), the experimental conditions (e.g. mass of catalyst, total flow rate, feed composition etc.) used in DRIFT experiments are not identical with those used during catalytic performance tests under steady state conditions. Moreover, previous studies have shown that DRIFT cells may present some bypass of the catalyst bed [41]. Therefore, FTIR results of the present study cannot be used to extract kinetic information, but only qualitative information related to the nature and variation of the relative population of

adsorbed surface species with reaction temperature and catalyst employed.

In Figure 6A are shown DRIFT spectra obtained over the 0.5% Ru/TiO<sub>2</sub> catalyst under CO<sub>2</sub> hydrogenation reaction conditions in the temperature range of 25-450°C. It is observed that interaction of the catalyst with 1%CO<sub>2</sub>+4%H<sub>2</sub> mixture at temperatures lower than 100°C results only in the development of bands below 1700 cm<sup>-1</sup> (trace a) which, are due to formate (bands at ca. 1553, 1382 and 1318 cm<sup>-1</sup>) and bicarbonate (bands at ca. 1660, 1646 and 1426 cm<sup>-1</sup>) species associated with the support [8, 31, 42-44]. However, increase of temperature at 150°C (trace c) results in the development of a band at 2060 cm<sup>-1</sup>, two overlapping peaks located at 2020 and 1967 cm<sup>-1</sup>, and a broad weak band at 1837 cm<sup>-1</sup>, indicating the formation of Ru-bonded carbonyl species. The band at 2060 cm<sup>-1</sup> is due to multicarbonyl species adsorbed on partially oxidized  $Ru^{n+}$  sites ( $Ru^{n+}(CO)_x$ ) [8-10, 45], which disappears from the catalyst surface upon heating at temperatures higher than 300°C. The latter sites can be formed by the oxidative disruption of small Ru clusters with the participation of hydroxyl groups of the support, which is enhanced over well-dispersed Ru catalysts [10, 46, 47]. The broad band at 1837 cm<sup>-1</sup> can be attributed to bridge-bonded CO on reduced Ru crystallites [8, 19]. The peak at 2020 cm<sup>-1</sup> appears at wavenumbers corresponding to CO species linearlybonded on reduced Ru sites (Ru<sub>x</sub>-CO) [8-10, 19, 45, 46], whereas the peak at 1967 cm<sup>-1</sup> can be attributed to terminal CO species adsorbed on Ru sites located at the metal-support interface ((TiO<sub>2</sub>)Ru-CO) [8-10, 48]. The relative intensity of the (TiO<sub>2</sub>)Ru-CO band decreases with increasing temperature up to 250°C, whereas the opposite is observed for the band assigned to Rux-CO, which dominates in the spectra obtained up to 450°C. The red shift of the Ru<sub>x</sub>-CO band from 2020 cm<sup>-1</sup> at 150°C (trace c) to 1991 cm<sup>-1</sup> at 450°C (trace i) is consistent with the decrease of the dipole-dipole coupling with decreasing coverage [9, 49].

In our previous study, under CO/H<sub>2</sub> conditions, it has been found that  $Ru^{n+}(CO)_x$ species are interconverted to  $Ru_x$ -CO species most probably due to H<sub>2</sub>-induced reductive

agglomeration of  $\operatorname{Ru}^{n+}$  sites to  $\operatorname{Ru}_{x}$  [8, 10]. This may also be the case for the results of the present study since the decrease of the relative intensity of the band at 2060 cm<sup>-1</sup> is accompanied by an increase of the band at 2020 cm<sup>-1</sup>. The intensity of the latter band starts decreasing above 300°C, where a new weak band at 3015 cm<sup>-1</sup> assigned to gas-phase CH<sub>4</sub> (not shown) [9] appears, indicating the onset of CO<sub>2</sub> methanation reaction.

Based on our previous studies, in the absence of H<sub>2</sub> in the feed, the interaction of CO<sub>2</sub> with Ru/TiO<sub>2</sub> catalyst results only in the development of bands due to carbonate species associated with TiO<sub>2</sub> support, whereas no bands are detected in the v(CO) frequency region [8, 9]. This indicates that CO<sub>2</sub> is mainly adsorbed on the support surface [50], and that dissociation of CO<sub>2</sub> does not take place, in agreement with results obtained over Pd/Al<sub>2</sub>O<sub>3</sub> [6], Ru/Al<sub>2</sub>O<sub>3</sub> [18] and Rh/Al<sub>2</sub>O<sub>3</sub> [51] catalysts. Results of Fig.6A show that Ru-bonded carbonyl species can be detected in the presence of H<sub>2</sub> in the gas stream, indicating that hydrogen facilitates the conversion of CO<sub>2</sub> to CO. It has been previously suggested that hydrogen adsorbed on Ru surface is diffused at the metal-support interface where it reacts with CO<sub>2</sub>, which is mainly adsorbed on TiO<sub>2</sub>, yielding formate and, eventually, adsorbed CO species according to [6, 9, 10, 18, 42, 51]:

$$CO_{2(TiO_{2})} + H_{(Ru)} \rightarrow (COOH)_{(Ru-TiO_{2})} \rightarrow CO_{(Ru)} + OH_{(TiO_{2})}$$
(Eq. 4)

This scheme is consistent with the results of Fig. 6A, where the relative population of formate species associated with the support starts decreasing at temperature higher than 150°C where the adsorbed CO species start to be developed. Part of this species may interact with adsorbed hydrogen atoms to form methane in the gas phase, whereas the rest is possibly desorbed yielding CO in the gas phase, in a manner which depends on the catalyst and experimental conditions employed [10]. The elimination of (TiO<sub>2</sub>)Ru-CO species from the catalyst surface already at 250°C, i.e. prior to initiation of CO<sub>2</sub> methanation reaction provides evidence that

this species cannot be further hydrogenated toward methane and most probably is desorbed producing gas phase CO.

In Figure 6B are shown the *in situ* DRIFT spectra obtained from 5%Ru/TiO<sub>2</sub> catalyst under CO<sub>2</sub> hydrogenation reaction conditions. Qualitative comparison with results obtained from 0.5%Ru/TiO<sub>2</sub> (Fig. 6A) shows the following differences: (a) The formation of Rubonded carbonyls species takes place at lower temperatures for the 5%Ru/TiO<sub>2</sub> catalyst; (b) The relative intensity of the band due to Ru<sup>*n*+</sup>(CO)<sub>*x*</sub> species (band at ca. 2060 cm<sup>-1</sup>) is significantly lower over the catalyst of higher Ru content; (c) The relative intensity of the Ru<sub>*x*</sub>-CO band (ca. 2015 cm<sup>-1</sup>) is significantly higher over the 5%Ru/TiO<sub>2</sub> catalyst, whereas the band attributable to (TiO<sub>2</sub>)Ru-CO species is either significantly lower and superimposed by that of Ru<sub>*x*</sub>-CO species or it does not appear at all; (d) The relative population of formate/carbonate species (<1700 cm<sup>-1</sup>) is higher over the sample with smaller Ru crystallites due to the higher exposed surface of TiO<sub>2</sub> support.

The formation of adsorbed CO species at lower temperatures for the catalyst containing 5% Ru implies that CO<sub>2</sub> conversion initiates at lower temperatures with increasing Ru crystallite size in agreement with results of Figs. 2 and 3. The higher relative intensity of the band due to multicarbonyl species on partially oxidized Ru<sup>*n*+</sup> sites over the 0.5%Ru/TiO<sub>2</sub> catalyst can be explained taking into account that the catalyst with smaller Ru particles is characterized by higher metal/support interface. As a result, the interaction of ruthenium atoms with the hydroxyl groups of TiO<sub>2</sub> support is enhanced, leading to the creation of partially oxidized Ru sites. The higher metal/support interface is also responsible for the detection of (TiO<sub>2</sub>)Ru-CO species on the surface of 0.5%Ru/TiO<sub>2</sub> catalyst. On the other hand, the observed increase of the relative intensity of the band assigned to Ru<sub>x</sub>-CO species on the surface of the most active 5%Ru/TiO<sub>2</sub> catalyst implies that CO species linearly bonded on reduced Ru crystallites could potentially being precursors of methane. This agrees well with

results reported in our recent publication, using a different CO<sub>2</sub>/H<sub>2</sub> reaction mixture, where it has been found that the mechanistic pathway for the CO<sub>2</sub> methanation reaction does not change with increasing Ru crystallite size, and that the key factor which determines catalytic activity is the relative population of the active intermediate carbonyl species [10]. As suggested above, in the case of 0.5%Ru/TiO<sub>2</sub> catalyst, the adsorbed CO species at the metalsupport interface ((TiO<sub>2</sub>)Ru-CO) most possibly prefer to desorb producing gas phase CO rather than to interact with adsorbed hydrogen atoms producing CH<sub>4</sub>, indicating that they are inactive for the title reaction [10]. However, the formation of (TiO<sub>2</sub>)Ru-CO species is eliminated with increasing Ru loading or crystallite size. This is accompanied by an increase of the relative intensity of the band due to the potentially active Ru<sub>x</sub>-CO species, which dominates on the surface of 5%Ru/TiO<sub>2</sub> catalyst, and may be related to the higher methane selectivity observed in Fig.5. Results are in agreement with previous studies over Rh/TiO<sub>2</sub> [31], Ru/Al<sub>2</sub>O<sub>3</sub> [18] and Pd/Al<sub>2</sub>O<sub>3</sub> [6] catalysts, which have demonstrated that the different relative population of reactive sites/intermediates is responsible for the structure sensitivity of the CO<sub>2</sub> methanation reaction.

Moreover, since the formation of Ru-bonded carbonyl species takes place via interaction of CO<sub>2</sub> adsorbed on TiO<sub>2</sub> with hydrogen atoms adsorbed on Ru surface (Eq. 4), the higher methanation activity observed with increasing Ru crystallite size (Fig.3) can be at least in part attributed to the higher population of adsorbed hydrogen species on the surface of the catalyst with higher Ru loading. This is in agreement with results reported by Wang et al. [6], who suggested that formate reduction to CO is facilitated on the surface of 5%Pd/Al<sub>2</sub>O<sub>3</sub> catalyst due to the catalyst ability to provide higher concentration of activated hydrogen species compared to that of 0.5%Pd/Al<sub>2</sub>O<sub>3</sub> catalyst.

#### **4. CONCLUSIONS**

Results of the present study show that catalytic performance and selectivity to reaction products for the CO<sub>2</sub> methanation reaction depend strongly on the nature of the metallic phase. Methanation activity is higher for Rh catalyst compared to Ru, whereas Pd and Pt are practically inactive for the title reaction, since they tend to enhance the RWGS reaction. Catalytic performance and selectivity toward methane are greatly enhanced with increasing Ru loading. Turnover frequency of CO<sub>2</sub> conversion, normalized with the perimeter of the metal/support interface, is significantly improved with increasing ruthenium crystallite size from 0.9 to 4.2 nm for Ru/TiO<sub>2</sub> catalysts, and from 1.3-13.6 nm for Ru/Al<sub>2</sub>O<sub>3</sub> catalysts. DRIFTS experiments carried out over 0.5% and 5% Ru/TiO<sub>2</sub> catalysts showed that the interaction of CO<sub>2</sub>/H<sub>2</sub> mixture with the catalyst surface results in the development of Rubonded carbonyl species, the nature of which does not depend on metal loading or crystallite size, implying that the reaction pathway is the same for both catalysts examined. Methanation of CO<sub>2</sub> proceeds via intermediate formation of adsorbed CO species produced via the RWGS reaction, followed by their hydrogenation to methane. The reactive surface intermediates could potentially be CO species linearly bonded on reduced Ru crystallites (Ru<sub>x</sub>-CO), as indicated by the increase of the relative intensity of the band assigned to Rux-CO species with increasing Ru crystallite size. It can be proposed that the structure sensitivity of the reaction may be related to variation of the relative population of reactive surface intermediates.

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#### Figure captions

- *Figure 1.* (A) Conversions of CO<sub>2</sub> as a function of reaction temperature, (B) selectivity toward CH<sub>4</sub> and CO at 350°C and (C) Arrhenius plots of turnover frequencies of CO<sub>2</sub> conversion obtained over Rh, Ru, Pt and Pd catalysts (0.5 wt.%) supported on TiO<sub>2</sub>. Experimental conditions: Mass of catalyst: 100 mg; particle diameter: 0.18<*d*<sub>p</sub><0.25 mm; Feed composition: 5%CO, 20% H<sub>2</sub> (balance He); Total flow rate: 150 cm<sup>3</sup> min<sup>-1</sup>.
- Figure 2. Effect of metal loading on the (A) catalytic performance and (B) turnover frequency of CO<sub>2</sub> conversion obtained over Ru catalysts supported on TiO<sub>2</sub>.
  Experimental conditions: same as in Fig. 1.
- Figure 3. (A) Arrhenius plots of normalized reaction rates obtained over Ru/TiO<sub>2</sub> catalysts with various crystallite sizes. (B) Effect of Ru crystallite size on the normalized reaction rates obtained over Ru/TiO<sub>2</sub> catalysts at 250°C. Experimental conditions: same as in Fig. 1.
- Figure 4. (A) Arrhenius plots of normalized reaction rates obtained over Ru/Al<sub>2</sub>O<sub>3</sub> catalysts with various crystallite sizes. (B) Effect of Ru crystallite size on the normalized reaction rates obtained over Ru/Al<sub>2</sub>O<sub>3</sub> catalysts at 250°C. Experimental conditions: same as in Fig. 1.
- *Figure 5.* Effect of mean Ru crystallite size ( $d_{Ru}$ ) of (A) TiO<sub>2</sub>- and (B) Al<sub>2</sub>O<sub>3</sub>-supported catalysts on the selectivity toward CH<sub>4</sub> and CO at 250°C. Experimental conditions: same as in Fig. 1.
- *Figure 6.* DRIFT spectra obtained over the (A) 0.5% Ru and (B) 5% Ru/TiO<sub>2</sub> catalysts following interaction with 1%CO<sub>2</sub>+4%H<sub>2</sub> (in He) at 25 °C for 15 minutes and subsequent stepwise heating at 450 °C under the same flow.



Figure 1





Figure 2





Figure 3





Figure 4



Figure 5



Figure 6

Table 1. Physicochemical characteristics of synthesized catalysts and their apparent

Catalyst	Nominal metal	Metal	Mean metal	
	loading	dispersion	crystallite size	Activation Energy
	(wt.%)		(nm)	(kJ/mol)
		(%)		
Pt/TiO <sub>2</sub>	0.5	47	2.2	63.2
Pd/TiO <sub>2</sub>	0.5	22	5.1	58.6
Rh/TiO <sub>2</sub>	0.5	99	1.1	71.1
Ru/TiO2	0.1	98	0.9	71.1
	0.5	46	2.1	55.6
	1.0	40	2.4	51.5
	2.0	29	3.2	55.2
	5.0	23	4.2	56.9
Ru/Al <sub>2</sub> O <sub>3</sub>	0.5	70	1.3	79.5
	2.0	63	1.5	75.7
	5.0	58	1.6	93.7
Calcined at: 600°C (2h)	5.0	13	7.4	64.4
650°C (4h)	5.0	10	9.4	61.9
700°C (4h)	5.0	7	13.6	69.0

activation energies for CO<sub>2</sub> hydrogenation reaction.