



# Mechanistic study of low temperature CO<sub>2</sub> methanation over Rh/TiO<sub>2</sub> catalysts

Alejandro Karelovic\*, Patricio Ruiz

Institute of Condensed Matter and Nanosciences – Molecules, Solids and Reactivity (IMCN/MOST), Université catholique de Louvain, Croix du Sud 2/17, 1348 Louvain-La-Neuve, Belgium

## ARTICLE INFO

### Article history:

Received 12 November 2012  
Revised 7 February 2013  
Accepted 11 February 2013  
Available online 20 March 2013

### Keywords:

CO<sub>2</sub> methanation  
Operando-DRIFTS  
Effect of particle size  
Rh/TiO<sub>2</sub>  
Low temperature  
Hydrogenation  
Reaction order

## ABSTRACT

CO<sub>2</sub> methanation at low temperature and atmospheric pressure was studied over Rh/TiO<sub>2</sub> catalysts focusing on the effect of Rh particle size on the activity and reaction mechanism. Catalysts with different Rh contents (0.5–5 wt.%) were prepared in order to obtain different mean cluster sizes. The activity was measured between 85 and 165 °C, with a H<sub>2</sub>/CO<sub>2</sub> ratio equal to 4. The rate of methane production per surface Rh atoms increases as metal particle size increases up to ca. 7 nm. Beyond this size, the rate does not change appreciably. Higher activation energies (up to 28.7 kcal/mol) are obtained for catalysts with small cluster size (ca. 2 nm), whereas for larger particles (>7 nm), the activation energy is lower and does not change with size (ca. 17 kcal/mol). Reaction order with respect to CO<sub>2</sub> is near zero for large clusters, whereas it decreases to –0.36 for lower size clusters. From the analysis of adsorbed species using operando-DRIFTS, it is proposed that smaller Rh particles tend to bind CO(ads) intermediate stronger than larger ones. The activation energy for the dissociation of adsorbed CO species does not vary with Rh particle size, which suggests that smaller particles are not intrinsically less active, but they present less active sites than larger ones. The study of the kinetic parameters permits to propose that CO(ads) dissociation is aided by the presence of H species and that a likely surface intermediate is Rh carbonyl hydrides.

© 2013 Elsevier Inc. All rights reserved.

## 1. Introduction

The recycling of CO<sub>2</sub> has become an important topic in recent years. As carbon dioxide is one of the main contributors to greenhouse effect and hence to climate change, there is a growing interest in its use as a feedstock in chemical processes [1–3]. Although CO<sub>2</sub> can be converted to valuable chemical products through organic syntheses, the volume of such a production cannot even approach the large volumes of fuels consumed in the world whose production is two orders of magnitude larger [1,2]. Hence, it is important to convert CO<sub>2</sub> to fuels or raw materials which must be also easily transportable. Methane is suitable for this because it benefits from the existing infrastructure for transport and storage of natural gas.

CO<sub>2</sub> methanation (CO<sub>2</sub> + 4H<sub>2</sub> ↔ CH<sub>4</sub> + 2H<sub>2</sub>O) has been studied extensively, using different types of metals and supports. Noble metals, especially Ru and Rh, are very active and selective at low temperatures [4–8]. Regarding the choice of support, it has been shown that Rh/TiO<sub>2</sub> is one of the most active catalysts for the reaction, being up to one order of magnitude more active than Rh/SiO<sub>2</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> [9]. The enhanced activity of Rh/TiO<sub>2</sub> systems has been attributed to an electronic interaction between the metal and the support [10,11] or to the interaction of Ti<sup>3+</sup> ions located

at the edge of TiO<sub>2</sub> islands with the CO adsorbed on Rh. It has been suggested that these interactions facilitate the breaking of C=O bond, thus increasing the overall activity [12,13].

Different mechanisms have been proposed for CO<sub>2</sub> methanation. The first mechanism involves the adsorption of CO<sub>2</sub> on the support and its reaction with H(ads) species formed in the metal which leads to formate intermediate (COOH) at the metal–support interface. The formates can give rise to CO(ads) species which are subsequently hydrogenated to methane [14–17]. The second mechanism involves the direct dissociation of CO<sub>2</sub> to CO(ads) and O(ads) on the metal surface, with CO(ads) being subsequently hydrogenated to CH<sub>4</sub> [4,8,18,19]. The dissociation of CO(ads) has been generally recognized as the rate-determining step of the reaction [7,13,18,20]. The question whether the dissociation of CO(ads) proceeds via an step assisted by hydrogen or not has also been discussed [21–25]. Additionally, few works have addressed the effect of metal particle size in CO<sub>2</sub> methanation reaction. Some authors have shown that smaller particles give the higher intrinsic activity [6], whereas others reported increased rates when metallic clusters are large [26–29].

The present work aims to clarify some aspects of the activity of Rh catalysts toward CO<sub>2</sub> methanation. The objective is to study the effect of Rh particle size on the activity and mechanism of CO<sub>2</sub> methanation at low temperatures using kinetic measurements and operando-DRIFTS experiments. We show that large metal particles (>7 nm) provide the higher intrinsic activities. The study of

\* Corresponding author.

E-mail address: [alejandrokarelovic@uclouvain.be](mailto:alejandrokarelovic@uclouvain.be) (A. Karelovic).

the reactivity of surface reaction intermediates allows us to propose that smaller metal particles bind CO(ads) intermediates stronger than larger ones, leading to more negative reaction orders with respect to CO<sub>2</sub> and higher apparent activation energies. Moreover, the energy barrier for CO(ads) dissociation does not seem to depend on particle size.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

The catalysts were prepared by wet impregnation. RhCl<sub>3</sub>·H<sub>2</sub>O (Alfa Aesar, CAS 20765-98-4) was used as metallic precursor, and the support was TiO<sub>2</sub> (Degussa P-25). Five grams of support was suspended in 250 ml of distilled water. Appropriate amounts of Rh precursor were added to obtain catalysts with varying metal contents (0.5, 0.8, 1, 2, 3, and 5 wt.%). After stirring for 4 h and evaporating the solvent under reduced pressure in a rotavapor at 40 °C, the samples were dried at 110 °C overnight and then calcined in a static-air oven at 450 °C for 4 h (heating ramp 10 °C/min). Catalysts were afterward ground and sieved to obtain the appropriate grain size to be used in catalytic tests.

H<sub>2</sub> chemisorption at 35 °C was used to measure the amount of exposed Rh atoms. Experiments were performed with an ASAP 2010C apparatus from Micromeritics. Ca. 0.15 g of catalyst was loaded into a Pyrex tube and subsequently heated in He (Praxair 4.8, 20 ml/min) at 120 °C for 1 h. After evacuation, the sample was reduced at 350 °C during 1 h in pure H<sub>2</sub> (Praxair 4.8, 30 ml/min) followed by purging with He at the same temperature for 1 h and cooling in He to adsorption temperature. Two isotherms were measured in the range 0.07–90 kPa, the first corresponding to total (irreversible + reversible) adsorption and the second to reversible H<sub>2</sub> adsorption. The subtraction of the two isotherms gave the total amount of irreversibly adsorbed (chemisorbed) hydrogen. The amount of surface Rh atoms (μmol/g) was calculated from the amount of chemisorbed hydrogen assuming that the chemisorption stoichiometry is H:Rh = 1 [26]. Dispersion is defined as surface Rh atoms divided by total Rh atoms in the catalyst. The mean particle size of Rh was calculated, supposing they are hemispherical in shape, by the following equation:

$$d_p = \frac{6M}{D\rho\sigma N_0} \quad (1)$$

where  $M$  is the molecular weight of Rh (102.91 g/mol),  $D$  is the Rh fractional dispersion obtained as explained above,  $\rho$  is the Rh metal density (12.4 g/cm<sup>3</sup>),  $\sigma$  is the area occupied by a surface Rh atom (7.58 Å<sup>2</sup>/atom), and  $N_0$  is the Avogadro constant.

X-ray photoelectron spectroscopy (XPS) analyses were performed with a SSI-X-probe (SSX-100/206) photoelectron spectrometer equipped with a monochromatic microfocused Al K $\alpha$  X-ray source (1486.6 eV) from Surface Science Instruments. The sample powders were pressed into small stainless steel troughs mounted on a multi-specimen holder. The samples were outgassed overnight under vacuum (10<sup>-5</sup> Pa) and then introduced into the analysis chamber where the pressure was around 10<sup>-7</sup> Pa. An electron flood gun set at 8 eV and a Ni grid placed at 3 mm above the sample were used to standardize charging effects. Pass energy of the analyzer was 150 eV, and the spot size was approximately 1.4 mm<sup>2</sup>. The atomic concentration ratios were calculated by normalizing surface area ratios with sensitivity factors based on Scofield cross-sections. In addition, all binding energies were calculated taking as reference the C—(C, H) component of the C 1s adventitious carbon peak fixed at 284.8 eV. Peak decomposition was performed using the CasaXPS program (Casa Software Ltd., UK) with a Gaussian/Lorentzian (85/15) product function and a

Shirley non-linear sigmoid-type baseline. The following peaks were used for the quantitative analysis: O 1s, C 1s, Ti 2p, and Rh 3d.

### 2.2. Operando-DRIFTS

In situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) spectra were collected on a Bruker Equinox 55 infrared spectrometer equipped with an air-cooled MIR source with KBr optics and a MCT detector. Spectra were obtained by collecting 200 scans with a resolution of 4 cm<sup>-1</sup> and are presented in absorbance mode without any manipulation. A background was recorded before starting the experiment by placing an Al mirror in the sample holder. In that way, the signals due to impurities in the cell windows or gases inside the spectrometer were subtracted. Samples were placed without packing or dilution inside a cell with controlled temperature and environment reflectance (Spectra-Tech 0030-103) equipped with ZnSe windows. Different mixtures of gases could be sent to the cell (He, H<sub>2</sub>, CO<sub>2</sub>) whose flow rates were controlled by high precision gas rotameters. The gases at the outlet of the cell were analyzed by a quadrupole mass spectrometer (Balzers QMS 200) by following the evolution of the  $m/z = 2$  (H<sub>2</sub>), 15 (CH<sub>4</sub>), 18 (H<sub>2</sub>O), 28 (CO), and 44 (CO<sub>2</sub>).

The catalysts used in these experiments were previously reduced under H<sub>2</sub> flow (30 ml/min) in a fixed-bed reactor at 350 °C for 1 h and then grounded finely, before infrared experiments. Once the catalyst was placed in the cell, it was flushed in He (20 ml/min) for 10 min and then reduced again in a flow (20 ml/min) of a reactive mixture consisting of H<sub>2</sub> (5 vol.%) with He (95 vol.%), during 1 h at 300 °C. After that, the cell was cooled to 50 °C in the same gas mixture. Reaction was carried out introducing to the cell 20 ml/min of a mixture of CO<sub>2</sub> (10 vol.%), H<sub>2</sub> (40 vol.%) diluted in He. The sample was kept at 50 °C for 20 min, which was sufficient to ensure constant spectra.

- Steady-state experiments:* The system was then stepwise heated (5 °C/min) to 100 °C and 150 °C maintaining the sample 20 min at each temperature.
- Transient experiments:* The catalyst was heated under reactive mixture at 5 °C/min to the desired temperature (100, 130, or 150 °C), and after 20 min at that temperature, the flow was changed to H<sub>2</sub> (8 ml/min) diluted in He (10 ml/min) or pure He (18 ml/min). Spectra were recorded every 5 min. The response time of the mass spectrometer following a change in gas concentration was less than 60 s.

### 2.3. Catalytic activity measurements

Catalytic tests were carried out using a quartz reactor (U-shaped) with 0.4 cm internal diameter. A section in the center of the tube is expanded with a diameter of 1 cm, in which the catalyst (200 mg, 200–315 μm particle size) was placed and supported by a quartz frit. A thermocouple was in contact with the central part of the catalyst bed and was used to measure and control the temperature. Heat and mass-transfer effects were ruled out using the criteria recommended by Vannice [30]. Thus, one can safely assume that the reaction took place in fully kinetic regime.

The reaction was carried out at atmospheric pressure, by reducing the catalyst in a 30 ml/min flow of pure H<sub>2</sub> during 1 h (ramp 10 °C/min). Afterward, the reactor was cooled to 50 °C, and the reaction mixture (20 ml/min) was admitted (CO<sub>2</sub> (10 vol.%), H<sub>2</sub> (40 vol.%) diluted in He). Measurements were performed at various temperatures between 50 and 200 °C (with 1 h at each temperature to ensure steady state). Exit gases were analyzed with a Varian CP-3800 gas chromatograph (CH<sub>4</sub> and CO<sub>2</sub> were detected using FID and TCD detectors, respectively). All transfer lines were maintained at 120 °C to avoid water condensation.

Download English Version:

<https://daneshyari.com/en/article/61288>

Download Persian Version:

<https://daneshyari.com/article/61288>

[Daneshyari.com](https://daneshyari.com)