



## Selective methanation of CO over supported Ru catalysts

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### ABSTRACT

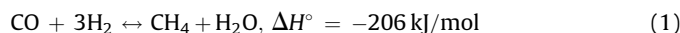
The catalytic performance of supported ruthenium catalysts for the selective methanation of CO in the presence of excess CO<sub>2</sub> has been investigated with respect to the loading (0.5–5.0 wt.%) and mean crystallite size (1.3–13.6 nm) of the metallic phase as well as with respect to the nature of the support (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, YSZ, CeO<sub>2</sub> and SiO<sub>2</sub>). Experiments were conducted in the temperature range of 170–470 °C using a feed composition consisting of 1%CO, 50% H<sub>2</sub>, 15% CO<sub>2</sub> and 0–30% H<sub>2</sub>O (balance He). It has been found that, for all catalysts investigated, conversion of CO<sub>2</sub> is completely suppressed until conversion of CO reaches its maximum value. Selectivity toward methane, which is typically higher than 70%, increases with increasing temperature and becomes 100% when the CO<sub>2</sub> methanation reaction is initiated. Increasing metal loading results in a significant shift of the CO conversion curve toward lower temperatures, where the undesired reverse water–gas shift reaction becomes less significant. Results of kinetic measurements show that CO/CO<sub>2</sub> hydrogenation reactions over Ru catalysts are structure sensitive, i.e., the reaction rate per surface metal atom (turnover frequency, TOF) depends on metal crystallite size. In particular, for Ru/TiO<sub>2</sub> catalysts, TOFs of both CO (at 215 °C) and CO<sub>2</sub> (at 330 °C) increase by a factor of 40 and 25, respectively, with increasing mean crystallite size of Ru from 2.1 to 4.5 nm, which is accompanied by an increase of selectivity to methane. Qualitatively similar results were obtained from Ru catalysts supported on Al<sub>2</sub>O<sub>3</sub>. Experiments conducted with the use of Ru catalyst of the same metal loading (5 wt.%) and comparable crystallite size show that the nature of the metal oxide support affects significantly catalytic performance. In particular, the turnover frequency of CO is 1–2 orders of magnitude higher when Ru is supported on TiO<sub>2</sub>, compared to YSZ or SiO<sub>2</sub>, whereas CeO<sub>2</sub>- and Al<sub>2</sub>O<sub>3</sub>-supported catalysts exhibit intermediate performance. Optimal results were obtained over the 5%Ru/TiO<sub>2</sub> catalyst, which is able to completely and selectively convert CO at temperatures around 230 °C. Addition of water vapor in the feed does not affect CO hydrogenation but shifts the CO<sub>2</sub> conversion curve toward higher temperatures, thereby further improving the performance of this catalyst for the title reaction. In addition, long-term stability tests conducted under realistic reaction conditions show that the 5%Ru/TiO<sub>2</sub> catalyst is very stable and, therefore, is a promising candidate for use in the selective methanation of CO for fuel cell applications.

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### 1. Introduction

The methanation reaction has been widely used in industry as an efficient method for the removal of carbon oxides from inlet streams in hydrogen or ammonia plants [1]. The interest for the reaction has grown significantly during the last few years as a result of recent advancements in fuel cell technology and the need for development of fuel processors capable of converting carbonaceous fuels into hydrogen [2,3]. In such systems, the CO methanation reaction (Eq. (1)) could be used as the final purification step of reformat gas to reduce concentration of CO

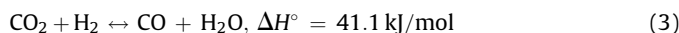
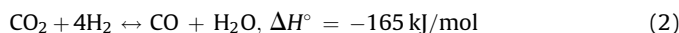
to the extremely low levels (<50 ppm) dictated by the poisoning limit of PEM fuel cell electrodes [4–7].



This approach offers certain advantages, compared to preferential oxidation (PROX) of CO [2,3,8,9], because it does not require addition of oxygen (air) in the hydrogen-rich gas stream, which may give rise to various problems related to reduced hydrogen yield, dilution, safety and restrictions in the operating parameters. In addition, methane produced is inert to the PEM fuel cell electrodes and can be utilized in the afterburner. However, depending on the operating conditions and catalyst employed, reaction (1) may run in parallel with the undesired methanation of CO<sub>2</sub>, which consumes significant quantities of valuable hydrogen

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(Eq. (2)), as well as with the reverse water–gas shift (RWGS) reaction (Eq. (3)), which shifts CO<sub>2</sub> to CO.



Consequently, it is important to develop stable and selective CO methanation catalysts with sufficiently high activity at low temperatures, able to suppress both CO<sub>2</sub> methanation and RWGS reactions.

Hydrogenation of carbon oxides toward methane and higher hydrocarbons can be catalyzed by several metal catalysts, including Ni [10–15], Ru [2,10,16–21] and Rh [18,21–23]. Ruthenium catalysts dispersed on metal oxide carriers have been found to exhibit high activity for the solo-methanation of CO [2,10,16,24] or CO<sub>2</sub> [17–20] as well as for the co-methanation of CO/CO<sub>2</sub> mixtures [9,16,21,25]. For instance, Vannice [24] reported that the specific activity of Ru/Al<sub>2</sub>O<sub>3</sub> for CO hydrogenation is about one order of magnitude higher, compared to that of Al<sub>2</sub>O<sub>3</sub>-supported Rh or Pd. Ruthenium (and also Rh and Ni) is also very active for hydrogenation of CO/CO<sub>2</sub> mixtures in contrast to Pt, which tends to catalyze the RWGS reaction [16,21,25]. A number of studies have shown that the nature of the support may play a crucial role in the mechanism of CO/CO<sub>2</sub> hydrogenation reactions, since metal–support interactions can modify the catalytic properties of the metallic phase [22,26–28]. In addition, catalytic performance of dispersed metal catalysts for methanation reactions is often affected by metal loading and crystallite size in a manner which depends on operating conditions used and metal–support combination employed [9,26,29–32].

In our recent study [21] we have investigated the effects of the nature of the metallic phase on the performance of Al<sub>2</sub>O<sub>3</sub>-supported Ru, Rh, Pt and Pd catalysts for the methanation of CO, CO<sub>2</sub> and their mixtures both in the absence and in the presence of water in the feed. It has been found that Ru and Rh are much more active hydrogenation catalysts, compared to Pt and Pd, which promote the undesired RWGS reaction. In the present study, the catalytic performance of Ru catalysts for the title reaction is investigated with respect to the loading and mean crystallite size of the metallic phase as well as with respect to the nature of the support (Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, YSZ, CeO<sub>2</sub> and SiO<sub>2</sub>). The aim is to identify key physicochemical parameters, which determine catalytic performance and to develop catalytic materials suitable for practical applications.

## 2. Experimental

Catalysts were prepared employing the wet impregnation method [21] with the use of Ru(NO)(NO<sub>3</sub>)<sub>3</sub> (Alfa) as metal precursor salt and the following commercial metal oxide powders as supports: TiO<sub>2</sub> (Degussa P25),  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Alfa products), CeO<sub>2</sub> (Alfa products), SiO<sub>2</sub> (Alfa products) and YSZ (Tosoh 8Y-SZ). The resulting slurry was heated slowly to 70 °C under continuous stirring and maintained at that temperature until nearly all the water evaporated. The solid residue was dried at 110 °C for 24 h and then reduced at 400 °C in H<sub>2</sub> flow for 2 h. The nominal metal loading of catalysts thus prepared varied between 0.5 and 5 wt.%. In certain cases, where synthesis of catalysts with large Ru crystallites was desired, the dried samples were calcined in air at 600, 650 or 700 °C for a period of 2 or 4 h and then reduced with H<sub>2</sub> as described above.

Carriers and catalysts were characterized with respect to their specific surface area, exposed metallic surface area and mean crystallite size employing nitrogen physisorption at liquid nitrogen

temperature and selective chemisorption of H<sub>2</sub> (CO for Ru/CeO<sub>2</sub>) at 100 °C. The mean crystallite size of the dispersed metal was estimated from hydrogen chemisorption data, assuming spherical particles, a H:Ru stoichiometry of 1:1, and an atomic surface area of Ru equal to 8.6 Å<sup>2</sup>, using the relation:

$$d_M = \frac{6}{\rho_M S_M} \quad (4)$$

where  $d_M$  is the mean crystallite diameter,  $\rho_M$  is the density of Ru (12.3 g cm<sup>-3</sup>) and  $S_M$  is the exposed surface area per gram of metal. Details on the equipment and procedures used for catalyst characterization can be found elsewhere [33].

Catalytic performance tests and kinetic measurements have been carried out using an apparatus, which consists of a flow measuring and control system, the reactor and an on-line analysis system [21]. The flow system is equipped with a set of mass-flow controllers (MKS) and a set of valves, which allows introduction of the gas mixture to the reactor or to a by-pass loop, through stainless steel tubing. When desired, water is introduced to the system with the use of an HPLC pump (Marathon Scientific Systems), vaporized in a stainless steel evaporator maintained at 170 °C and mixed with the gas stream coming from the mass-flow controllers. The resulting gas mixture is then fed to the reactor through stainless steel tubing maintained at 150 °C by means of heating tapes. The reactor consists of a 40-cm long quartz tube (6 mm OD) with an expanded 1-cm long section in the middle (8 mm ID), in which the catalyst sample is placed. Reaction temperature is measured in the middle of the catalyst bed by means of a K-type thermocouple placed within a quartz capillary well, which runs through the cell. The reactor is placed in an electric furnace, the temperature of which is controlled using a second K-type thermocouple placed between the reactor and the walls of the furnace. A pressure indicator is used to measure the pressure drop in the catalyst bed. The analysis system consists of a gas chromatograph (Shimadzu) equipped with two packed columns (Porapak-Q, Carboxen) and two detectors (TCD, FID) and operates with He as the carrier gas. The response factors of the detectors were determined with the use of gas streams of known composition (Scott specialty gas mixtures). Reaction gases (He, 15%CO/He, CO<sub>2</sub>, H<sub>2</sub>) are supplied from high-pressure gas cylinders (Messer Griesheim GMBH) and are of ultra-high purity.

The catalytic performance of the prepared samples for the selective methanation of CO has been investigated in the temperature range of 170–470 °C using a feed stream consisting of 1%CO, 15%CO<sub>2</sub> and 50%H<sub>2</sub> (balance He). When water was added in the feed, part of the balance gas (He) was replaced by water vapor (10–30% H<sub>2</sub>O). The mass of catalyst used in these experiments was typically 150 mg (particle size: 0.18 <  $d$  < 0.25 mm) and the total flow rate was 200 cm<sup>3</sup>/min. Prior to each experiment the catalyst sample was reduced *in situ* at 300 °C for 1 h under hydrogen flow (60 cm<sup>3</sup> min<sup>-1</sup>), purged with He, and then conditioned at 170 °C for 1 h with the reaction mixture. Conversions of reactants and selectivities toward products were then measured at that temperature using the analysis system described above. Selectivity to hydrogenation product “*i*” was calculated using the following expression:

$$S_i = \frac{C_{i,\text{out}}/v_i}{\sum_i C_{i,\text{out}}/v_i} \quad (5)$$

where  $v_i$  is the number of carbon atoms of product “*i*”. Similar measurements were obtained following a stepwise increase of temperature up to ca. 470 °C. A few more measurements were then obtained by stepwise decreasing temperature to check for possible catalyst deactivation. It should be noted that the system was left at

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