

# Selective methanation of CO in CO<sub>2</sub>-rich H<sub>2</sub> feeds on supported Ru catalysts: Effect of water on activity and selectivity

Ali M. Abdel-Mageed, S. Eckle, J. Bansmann, and R.J. Behm

Institute of Surface Chemistry and Catalysis, Ulm University, Albert Einstein Allee 47, 89069 Ulm, Germany

**Introduction:** The conversion of H<sub>2</sub> into electric energy in fuel cells is the most promising substitute for burning of fossil fuels. The high sensitivity of low temperature fuel cells to CO in the H<sub>2</sub> feed, which poisons the Pt anodes, necessitates extremely low CO levels ( $\leq 10$  ppm) [1]. Currently, H<sub>2</sub>-rich feed gases are mainly produced by steam reforming of fossil fuels, which leaves substantial amounts of CO (>1%) in the gas feed (reformate) and up to 20% CO<sub>2</sub>. The methanation of CO [2] can be considered as an attractive alternative to the commonly used preferential oxidation of CO (PROX) for CO removal in a second step after decreasing CO down to 1 % using WGS reaction. This, however, is only true, if the reaction is highly selective for the CO methanation, ideally without methanation of CO<sub>2</sub> at the same time. In the present contribution, we investigated the effect of water on the reaction mechanism and the catalytic performance (activity and selectivity) of a Ru/Al<sub>2</sub>O<sub>3</sub> catalyst for the selective CO methanation. Combined kinetic and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements in the presence of up to 30% water revealed that the increase of water in the reaction gas mixture results in a decrease of activity at high. To get more insight into the physical reasons underlying the increase of the selectivity in the presence of water, these measurements were supplemented by *in situ* XAS measurements under similar reaction conditions.

**Experimental:** A commercial 5.0 wt.% Ru/Al<sub>2</sub>O<sub>3</sub> catalyst (Johnson Matthey) was studied by *in-situ* XAS measurements. The reaction was performed in idealized gas atmospheres (0.6 kPa CO, 3 kPa N<sub>2</sub>, balance H<sub>2</sub>; saturated with 5, 10 and 15% H<sub>2</sub>O) at 190°C until the coordination parameters did not change anymore (300 min). The effluent gases were analyzed by a GC, equipped with TCD detectors. EXAFS data were evaluated using the program XDAP {VAAR95}, the reference data were calculated by FEFF 8.1, calibrated against measured references [3]. Fitting of data was performed in *r* space after reduction of the spectra ( $k^3$  weighting).

**Results:** The observed increase in the selectivity of the Ru/Al<sub>2</sub>O<sub>3</sub> catalyst with increasing amount of water raised a question about the effect of water on the size and the oxidation state of Ru nanoparticles during the reaction, since in previous studies a trend of increasing CO selectivity with decreasing particle size was observed [4]. Fig. 1 shows the steady state EXAFS spectra for Ru K-edge including  $k^3$ -weighted  $\chi$ -functions in the *k*-range from 3.2 - 13.0 Å<sup>-1</sup> (left panels). The corresponding Fourier transforms in the *r*-space, in the range of the first shell (Ru-Ru scattering) (right panels (e-h)). The amplitude of the  $\chi$ -function decreases from the dry gas mixture progressively with increasing water content up to 15%. In the FT data (right panel), the data show a characteristic peak at 2.67 Å, which fits well to the Ru-Ru nearest neighbours distance.

EXAFS measurements of the fresh catalyst in air exhibited mainly oxidic Ru species. The oxidic species, which exists before reactive conditioning in feed gas is reduced after switching to the reaction gas at 150°C. The remaining oxidic Ru species vanishes shortly just after switching the catalyst to the reaction mixture. EXAFS spectra recorded 2 min after reaction in dry, 5% and 10% H<sub>2</sub>O saturated gas mixture showed mainly metallic Ru NPs. For a reaction gas mixture saturated with 15% water, however, a small oxidic feature can be observed until 28 minutes from the start of the reaction (Ru-O; 2.02 Å).

Based on the steady state values of the Ru coordination number (CN), the average particle size and the dispersion of the Ru nanoparticles (NPs) were calculated using the coordination number – particle size relationship determined by Karim et al. [5] considering hemispherical Ru nanoparticles. Comparison of the coordination number of Ru-Ru shell during dry and wet measurements indicated a decrease of CN of Ru NPs in the presence of water (see table 1). A decrease in CN hints to a higher dispersion for the Ru NPs compared to the situation during dry reaction conditions. This can be attributed to an oxidative disruption process of Ru NPs in the presence of water in the gas feed [6]. The (in situ) observed decrease of the Ru particle size (Fig. 2, black columns) fits well with the increase of the selectivity (red columns) which correlates to an increase of the amount of water in the reaction gas mixture.

Fig.1 Left:  $k^3$  weighted  $\chi$ -function, right: corresponding Fourier transforms (3.2 – 13.0 k space) for Ru/Al<sub>2</sub>O<sub>3</sub> catalyst in idealized gas mixture (0.6 % CO, 3% N<sub>2</sub> in H<sub>2</sub>) saturated with a, e) 0% water; b, f) 5% water; c, g) 10% water; d, h) 15% water (190°C).

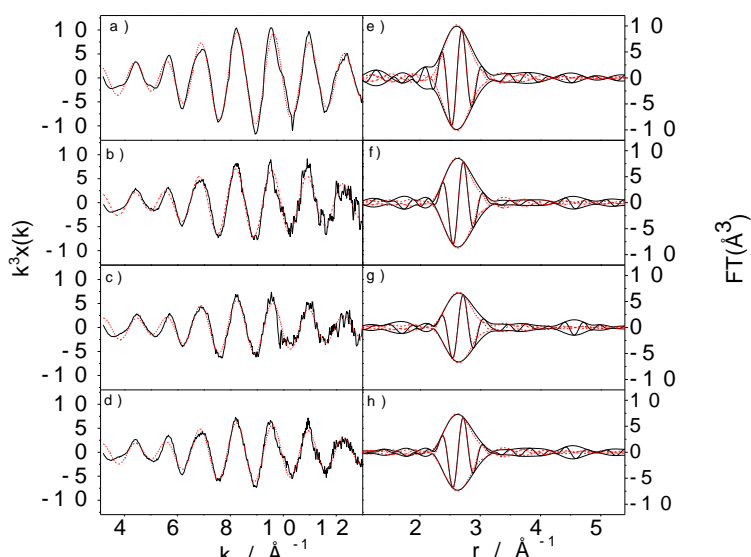


Fig. 2 Ru particle size calculated from coordination number as a function of the amount of water in the reaction gas mixture and corresponding selectivities for CO methanation during kinetic measurements.

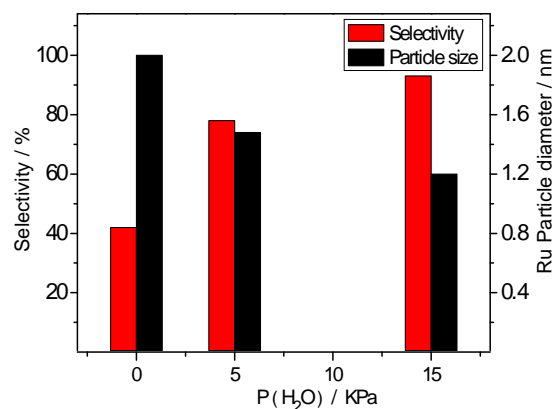


Table 1: results extracted from EXAFS measurements (steady state conditions, 190°C) in gas mixtures with different amounts of water (idealized reaction reformat: 0.6 % CO, balance H<sub>2</sub>).

% H <sub>2</sub> O	CN	DW / Å <sup>2</sup>	Ru-Ru / Å	E <sub>0</sub> / eV	Dispersion / %	size / nm
0	9.0 ± 0.9	0.00323	2.67	7.80	36 ± 3	2.0 ± 0.6
5	8.0 ± 0.8	0.00323	2.68	8.67	50 ± 12	1.5 ± 0.4
10	7.6 ± 0.8	0.00453	2.68	6.70	58 ± 15	1.3 ± 0.3
15	7.5 ± 0.8	0.00376	2.67	8.65	59 ± 15	1.2 ± 0.3

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