High Selectivity of Supported Ru Catalysts in the Selective CO Methanation—Water Makes the Difference

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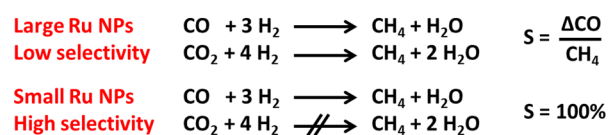[‡]Clariant Produkte (Deutschland) GmbH/Clariant SE, Lenbachplatz 6, D-80333 München, Germany

Ⓢ *Supporting Information*

ABSTRACT: The selectivity for CO methanation is a decisive aspect for the practical application of the methanation reaction for the removal of CO from CO_2-rich H_2 fuel gases produced via hydrocarbon reforming. We show that increasing the water content in the feed gas, up to technically relevant levels of 30%, significantly increases the selectivity of supported Ru catalysts compared with operation in (almost) dry gas, while in operando EXAFS measurements reveal a gradual decrease in the Ru particle size with increasing amounts of water in the gas feed. Consequences of these findings and related IR spectroscopic data for the mechanistic understanding and practical applications are outlined.

The successful introduction of low-temperature polymer electrolyte membrane fuel cells (PEMFCs) relies decisively on an inexpensive and reliable supply of contamination-free hydrogen, where in particular CO levels have to be in the low parts per million range to avoid poisoning of the anode catalyst. For the removal of CO from H_2-rich feed gases to below these levels in small-scale applications, e.g., in domestic operation, selective methanation of CO is a highly attractive and promising alternative to the commonly used preferential oxidation of CO (PROX) because of its simpler operation.[1−5] In the presence of high CO_2 concentrations in the feed gas, which are typical for H_2 generation by reforming processes, e.g., from natural gas, the methanation of CO must be highly selective to avoid intolerable losses of H_2 due to CO_2 methanation (see the equation below). Therefore, a very high selectivity for CO methanation over the entire lifetime of the catalyst is an important if not the most important aspect for a successful catalyst.

We recently demonstrated that for supported Ru catalysts the selectivity for CO methanation, which is defined as the ratio of the rate of CO conversion to the overall rate of CH_4 formation (conversion of CO + CO_2), depends sensitively on the Ru particle size.[6,7] Ru/zeolite catalysts with Ru particle sizes below 1 nm were found to exhibit CO_2 conversions just at the detection limit of the gas chromatograph (∼5 ppm for CH_4) even at very low CO levels, where high selectivities are no longer enforced by a surface-blocking CO adlayer, as is the case for higher CO contents. In contrast, Ru/γ-Al_2O_3 catalysts with Ru particle sizes of 2 nm or more were found to be highly selective only at these higher CO concentrations, while at lower CO contents the CO_2 conversion increased significantly.[6] The high selectivity of the Ru/zeolite catalysts was explained by an inherent inactivity of the very small Ru particles for CO_2 dissociation as a first step for CO_2 methanation, while for larger Ru particles this was found to be facile.[6]

Large Ru NPs **Low selectivity**	$CO + 3 H_2 \longrightarrow CH_4 + H_2O$ $CO_2 + 4 H_2 \longrightarrow CH_4 + 2 H_2O$	$S = \dfrac{\Delta CO}{CH_4}$
Small Ru NPs **High selectivity**	$CO + 3 H_2 \longrightarrow CH_4 + H_2O$ $CO_2 + 4 H_2 \xrightarrow{\;/\!/\;} CH_4 + 2 H_2O$	$S = 100\%$

Our previous studies[6−10] were performed in idealized reaction gas mixtures with no or low water content in the reaction gas mixture. Here we report on changes in the reaction behavior, in particular in the selectivity for CO methanation over supported Ru catalysts, that occur when changing from idealized to technically relevant reaction gas mixtures by stepwise increases in the amount of water in the reformate gas from 0 to 30% (see Table S1 in the Supporting Information). To gain further insight into the physical origin of any changes in the reaction behavior, the catalytic performance was followed by combined kinetic and in operando extended X-ray absorption fine structure (EXAFS) measurements in the presence of increasing amounts of water in the reaction gas mixture. In addition, time-resolved in situ IR spectroscopic (diffuse-reflection FTIR spectroscopy (DRIFTS)) measurements were employed to resolve changes in the CO_{ad} vibrational characteristics correlated with the change of Ru particle size and in the selectivity. The Ru catalysts used in this study (Ru/zeolite and Ru/Al_2O_3) were identical to those investigated previously,[6−10] and information on their characteristic properties and the experimental setups and procedures is given in the Supporting Information.

The changes in activity and selectivity over both catalysts were followed in a reformate gas mixture with a very low CO content (SR-ref 100 gas mixture: 0.01% CO + 3% N_2 + 15.5 CO_2 + balance H_2) with different amounts of water (0−30%) added. The measurements were performed at a fixed reaction temperature (190 °C) under differential reaction conditions. The low CO concentration results in a rather low CO_{ad} coverage, far below saturation, which allows us to test the inherent selectivity of the catalyst in the presence of high CO_2 concentrations. At higher CO contents and hence high CO_{ad} coverages, in contrast, blocking of active sites by adsorbed CO species hinders the dissociation of CO_2 and leads to high

selectivities of up to 100%, even for catalysts that at low CO_{ad} coverages would be active for CO_2 dissociation.

For the Ru/γ-Al$_2$O$_3$ catalyst, addition of water to the reaction gas mixture caused only small changes in the activity for CO conversion, which decreased by up to 16% in the presence of 30% H$_2$O (Figure 1a). At the same time, however, it resulted in
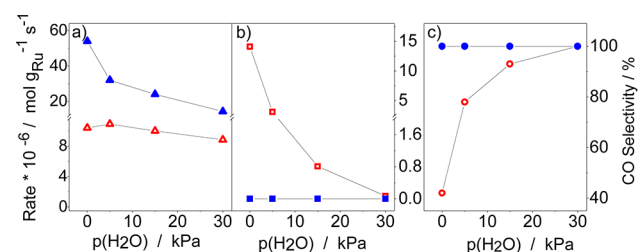

Figure 1. (a, b) Steady-state Ru-mass-normalized reaction rates for (a) CO methanation and (b) CO$_2$ methanation and (c) selectivities for CO methanation obtained over a 5.0 wt % Ru/Al$_2$O$_3$ catalyst (CO conversion, red △; CO$_2$ conversion, red □; selectivity, red ○) and over a 2.2 wt % Ru/zeolite catalyst (CO conversion, blue ▲; CO$_2$ conversion, blue ■; selectivity, blue ●) in an SR-ref 100 gas mixture (0.01% CO + 3% N$_2$ + 15.5 CO$_2$ + balance H$_2$) at 190 °C after 1000 min on stream.

a tremendous decrease in the CO$_2$ conversion. The additions of 5, 15, and 30% water to the reaction gas mixture lowered the rate of CO$_2$ conversion to 22.0, 5.7, and ~0% of the value obtained in dry reformate, respectively (Figure 1b). The decrease in the CO$_2$ methanation rate corresponds to an increase in the selectivity from 42% in dry atmosphere to 78, 92, and 100% in reaction atmospheres with 5, 15, and 30% H$_2$O, respectively (Figure 1c).

Similar measurements performed with the Ru/zeolite catalyst revealed decreases in the steady-state activity for CO conversion by ~41% (5% H$_2$O) and ~75% (30% H$_2$O) (Figure 1a), while the CO$_2$ conversion and the selectivity for CO methanation, which were below the detection limit of the GC (5 ppm) and already at 100% in dry reformate, respectively, were not measurably affected (Figure 1b,c).

To explore the physical origin of the enhanced selectivity upon increasing the amount of water in the reaction gas mixture on the Ru/Al$_2$O$_3$ catalyst, we performed in operando EXAFS measurements under similar reaction conditions in the presence of 0, 5, and 15% water in the reaction gas mixture (higher water contents were not possible for technical reasons). Data evaluation and EXAFS parameters are given in the Supporting Information. EXAFS spectra of the Ru K-edge recorded on the Ru/Al$_2$O$_3$ catalyst under steady-state reaction conditions are presented in Figure 2. They include the k^3-weighed χ functions in the k range of the first Ru−Ru shell (Figure 2a,b) as well as the corresponding Fourier transforms (Figure 2c,d). The data indicate a distinct decrease in the Ru−Ru coordination number (CN) upon reaction in the presence of 15% water compared with reaction under dry conditions, from 8.93 (dry reformate) to 7.45 (reformate containing 15% water) (the complete set of structural parameters resulting from the data evaluation is listed in Table S2 in the Supporting Information). From the commonly used relationship between coordination number and particle size, which is based on the assumption of a hemispherical particle shape,[11] the decrease in CN corresponds to a decrease in the Ru particle size from 2 nm
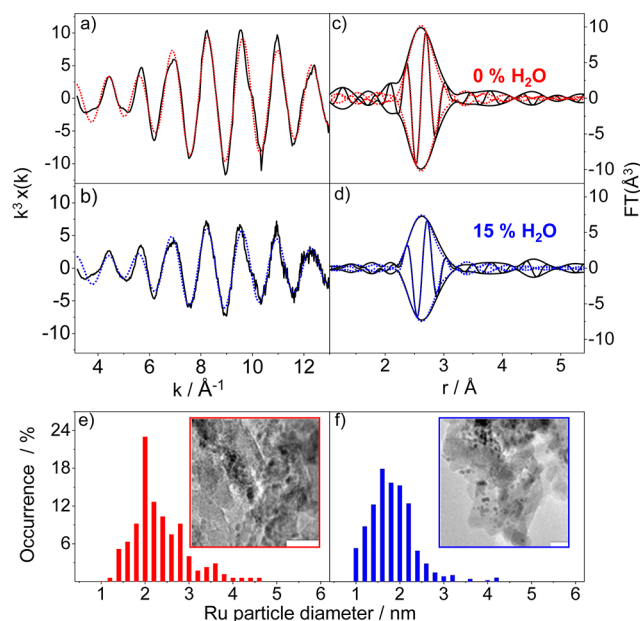

Figure 2. (a, b) k^3-weighted χ function and (c, d) corresponding Fourier transforms (3.2−13.0 Å^{-1}) obtained on a 5.0 wt % Ru/Al$_2$O$_3$ catalyst during reaction in an idealized reformate gas mixture (0.6% CO, balance H$_2$) containing 0% water (upper panels) or 15% water (lower panels). Solid lines are EXAFS data, and dashed lines are fits. (e, f) Typical TEM images/particle size distributions of the catalysts after reaction for 1000 min in the same atmospheres. Scale bars indicate 10 nm.

in dry reformate gas to 1.2 nm in reformate gas containing 15% H$_2$O under steady-state conditions (Figure 3a).

Transmission electron microscopy (TEM) measurements of the Ru particle size distribution on the Ru/γ-Al$_2$O$_3$ catalyst, performed once after reaction in dry reformate and once after

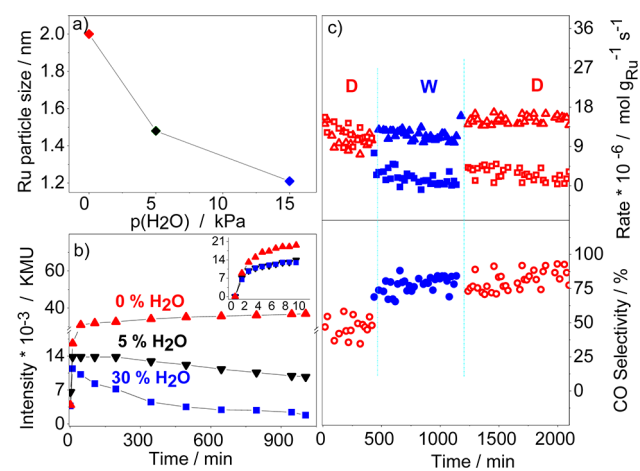**Figure 3.** (a) Ru particle size in a Ru/Al$_2$O$_3$ catalyst as a function of the amount of water in the SR-ref 6000 reaction gas mixture. (b) Intensity evolution of the band related to on-top adsorbed CO in CO$_2$-ref gas mixture containing different amounts of water: dry CO$_2$-ref, red ▲; CO$_2$-ref containing 5% H$_2$O, black ▼; CO$_2$-ref containing 30% H$_2$O, blue ■. (c) Reaction rates for CO methanation (triangles) and CO$_2$ methanation (squares) and selectivities for CO methanation (circles) during reaction first in dry SR-ref 100 reformate (D) at 190 °C, then in wet SR-ref 100 reformate (W) (15% H$_2$O in the feed gas), and then back again to dry (D) SR-ref 100 reformate (open red symbols, dry; solid blue symbols, wet).

reaction in reformate containing 15% H_2O, support the above findings. Typical TEM images and particle size distributions are presented in Figure 2e,f. After reaction in dry reformate we obtained a mean particle size of 2.2 nm, while after reaction in reformate containing 15% H_2O the particle size distribution was shifted to lower values, yielding a mean particle size of 1.68 nm. Hence, the ex situ TEM measurements reveal a similar trend as the in operando EXAFS measurements, and even the absolute values are rather similar considering that very small Ru nanoparticles, in the subnanometer range, are not detected in these TEM images but contribute fully to the coordination number and hence to the mean particle size derived from the EXAFS measurements.

Similar EXAFS measurements performed with the Ru/zeolite catalyst showed a decrease in the Ru particle size from 1.05 to 0.86 nm upon addition of 5% H_2O to the reaction gas mixture (see Table S3 and Figure S1 in the Supporting Information), equivalent to an increase in the dispersion of the Ru NPs from 68% (dry reformate) to 82.5% (reformate containing 5% H_2O).

Using differently loaded and differently calcined Ru/zeolite catalysts, we had shown earlier that the mean Ru particle size and the selectivity for CO methanation in dry, CO_2-rich reformate gas (SR-ref 100) but under otherwise similar reaction conditions are strictly correlated with each other. The selectivity was found to increase with decreasing mean particle size of the Ru nanoparticles,[6,7] and similar trends were also reported by other groups.[12,13] Considering also the observed lower stability of adsorbed CO on very small Ru nanoparticles, the enhanced selectivity for CO methanation was interpreted to be a result of a decrease of the inherent activity for CO_2 dissociation on very small Ru NPs.[6,7] According to the Brønstedt−Evans−Polanyi (BEP) relation,[14] the activation barrier for this step increases with decreasing stabilization of the final product CO_{ad}.

We propose that the decrease in Ru particle size during reaction in wet reaction gas mixtures is caused by a water assisted rupture of Ru−Ru bonds, which eventually leads to smaller Ru NP sizes and thus a higher dispersion of the catalyst. Solymosi and Raskó[15] had shown previously that the adsorption of CO on Ru catalysts results in the formation of Ru−dicarbonyl species, which goes along with the disruption of Ru−Ru bonds, and that this process is accelerated by the presence of water. Ru−dicarbonyl-related bands were observed also in the present work, but their intensities were very low because of the presence of H_2, consistent with the earlier observations of Solymosi and Pasztor.[16] Similar observations were reported by Mitsushima et al.[17,18] By following the changes in the Ru K-edge spectra, these authors found that CO adsorption results in a decrease in the coordination number and the disappearance of the extended oscillations characteristic of Ru backscatterers, together with the appearance of Ru−O and Ru−C peaks in the Fourier transform. They concluded that small Ru nanoparticles are formed and that they are stabilized by adsorbed OH species.

Our proposal is strongly supported by the results of a series of DRIFTS measurements, where we monitored changes in the adlayer, in particular the evolution of the CO_{ad} coverage, with time on stream on the Ru/Al_2O_3 catalyst during exposure to CO-free reformate gas containing 15.5% CO_2 (no CO) and different contents of water vapor (CO_2-ref, balance H_2). As shown in Figure 3b, the intensity of the bands related to linearly adsorbed CO_{ad}, which is thought to be an intermediate in the CO_2 methanation reaction,[10] initially increased with time on

stream and then saturated for the dry CO_2-ref (Figure 3b inset). For CO_2-ref containing 5% water, it initially increased and then decreased with longer time on stream. Finally, for the CO_2-ref mixture containing 30% water the general behavior of the CO_{ad}-related intensity is rather similar, but the decay at longer times is more pronounced. The CO_{ad}-related intensities reached after 1000 min on stream in CO_2-ref containing 5% and 30% water were only $^1/_4$ and $^1/_{12}$, respectively, of that observed in dry CO_2-ref reformate. The latter amount of CO_{ad} is comparable to findings for Ru/zeolite in dry CO_2-ref reformate, which is known to be 100% selective even at very low CO contents (SR-ref 100) under those conditions.[6]

This observation directly indicates that the presence of water reduces the formation of CO_{ad} from CO_2, in perfect agreement with the mechanistic explanation presented above, where we had proposed that the water-assisted dispersion of the Ru nanoparticles leads to a decreasing probability for CO_2 dissociation and hence an inherently lower activity for CO_2 methanation with increasing H_2O content/decreasing Ru particle size. The different trends observed for increasing time on stream in Figure 3b can be explained on the same basis. In the absence of water, it takes some time before the steady-state CO_{ad} coverage is reached. In that case, the CO_{ad} intensity increases steadily with time and then saturates. We assume that this induction period is needed for the formation of the appropriate Ru particles (~2.0 nm) supporting the observed CO_{ad} coverage. With increasing water content, the water-assisted dispersion of the Ru nanoparticles becomes more effective. This leads to a counteracting decrease in the size of the Ru nanoparticles due to the increasing water-assisted dispersion and thus to decreasing CO_{ad} formation on the smaller Ru NPs than in the dry reaction gas mixture. As a result, the maximum CO_{ad} band intensity is lower and followed by a steady decline of the CO_{ad} band intensity. For 30% water content, these effects are more pronounced than for 5% water content. These results fully support the mechanistic proposal described above.

Finally, in order to test for a direct influence of adsorbed water on the reaction characteristics by site-blocking effects, which was proposed by Panagiotopoulou et al. as the origin of the improved selectivity for CO methanation in the presence of water,[13,19] we performed transient experiments starting with reaction in dry SR-ref 100, then switching to SR-ref 100 reaction gas containing 15% water, and finally switching back again to dry SR-ref 100 reformate (Figure 3c), where the latter was demonstrated before to have a rather high activity for CO_2 conversion, equivalent to a low selectivity for CO methanation (see Figure 1). Interestingly, after the change back to the dry reaction gas mixture the catalyst maintained the high selectivity observed in the presence of water, with a very low rate for CO_2 methanation, and did not return to the relatively high CO_2 methanation rate and low selectivity for CO methanation typical for reaction in dry SR-ref 100 reformate. Apparently, the changes induced by the reaction in water-containing reformate gas are irreversible on the time scale of these experiments (1000 min). This result also points to a structural change as the origin of the increased selectivity, fully supporting the previous conclusions, rather than to water-induced modifications in the adlayer. The latter should quickly approach a new steady-state composition under the present reaction conditions (190 °C), in particular for weakly adsorbed species such as H_2O.

These findings of a distinct and stable improvement in the selectivity for CO methanation are highly relevant for technical

applications of these catalysts for the selective methanation of CO in CO_2-rich reformate gases, e.g., for the removal of CO trace impurities from H_2-rich feed gases for PEMFCs. First, the contents of H_2O in technical reformates tend to drive the Ru catalysts to smaller particle sizes and hence to higher selectivities. Second, the high stability of the small Ru NPs generated upon temporary addition of H_2O to the feed gas allows for a simple procedure for the regeneration of the catalyst, which mainly means reimproving the selectivity rather than the activity of the catalyst. The present data strongly suggest that this can be achieved by occasional addition of water to the feed for a long enough time to redisperse the Ru particles, followed by operation again with the technical reaction gas mixture (without addition of water) over an extended time. This would be particularly important for applications of PEMFCs for house heating (domestic applications), where the catalyst system should survive 50 000 h of operation.

In summary, we have shown for Ru/Al_2O_3 that a Ru catalyst that is poorly selective for the methanation of CO in CO_2-rich reformate gases at low CO contents becomes highly selective, with up to 100% selectivity, in the presence of higher amounts of H_2O in the gas feed, as is typical for technical applications. This behavior is explained by a combination of two effects: (i) a pronounced H_2O-induced decrease in the mean Ru particle size and (ii) a pronounced decrease in the activity for CO_2 dissociation with decreasing Ru particle size, which we had explained earlier by decreased stabilization of CO_{ad} and hence, according to the BEP principle, an increasing barrier for $CO_{2,ad}$ dissociation with decreasing Ru particle size. We consider the dispersive effect of water to be a general effect for supported Ru catalysts that would allow simple reactivation of these catalysts in technical applications of selective CO methanation, e.g., in fuel gas processing for PEMFCs, by occasional addition of water.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and supporting data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b03689.

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Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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