



Selective CO methanation in CO₂-rich H₂ atmospheres over a Ru/zeolite catalyst: The influence of catalyst calcination

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ABSTRACT

The pre-treatment of highly active and selective Ru/zeolite catalysts for the selective CO methanation in CO₂-rich H₂ atmospheres involves a calcination step before the catalyst activation to reach their high activity and selectivity. In this study, we investigated the impact of the calcination procedure on a 2.2 wt.% Ru/zeolite catalyst by evaluating the resulting changes in the catalyst structure and reaction characteristics by combined kinetic, *in situ* extended X-ray absorption fine structure (EXAFS) and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements. Calcination in synthetic air, followed by the standard activation procedure in reaction gas, results in a decrease in mean Ru particle size with increasing calcination temperature, from ~1.5 nm to ~1.0 nm. The increase in dispersion goes along with a distinct increase in selectivity of the Ru/zeolite catalyst for CO methanation at extremely low concentrations of CO (100 ppm). Possible mechanisms and the physical origin responsible for these changes in catalyst structure and reaction characteristics are discussed.

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1. Introduction

The direct conversion of hydrogen into electric energy in fuel cells, in particular in proton exchange membrane fuel cells (PEMFCs), is one of the most promising processes for energy conversion, with various applications, including transportation, stationary applications, and mobile applications [1]. The high sensitivity of low-temperature fuel cells to carbon monoxide in the H₂ feed, which acts as catalyst poison for the anode catalyst, requires that the CO concentration is kept at very low levels (≤ 10 ppm) [2]. Currently, H₂-rich feed gases are mainly produced by steam reforming of fossil fuels, which leaves substantial amounts of CO in the gas feed (reformate) and up to 20% CO₂. The methanation of CO in reformate gases [3–6] may be an attractive alternative to the commonly used preferential oxidation of CO (PROX) for CO removal [7,8]. It is economically feasible, however, only if the reaction is highly selective for CO methanation, and reaction of the abundant CO₂ with hydrogen is inhibited. In response to the increasing interest in using selective methanation (SelMeth) for complete removal of CO, the mechanistic understanding and the identification of the physical reasons underlying the high selectivity for CO

methanation in CO₂-rich H₂ gas feeds have been the subject of various studies [9–14].

We have recently studied the mechanism of the selective methanation reaction over highly active and selective Ru/zeolites catalysts, being particularly interested in the physical origin of the high selectivity [15–18]. Main results of these studies were (i) that these catalysts exhibit very small Ru particles (mean particle size 0.9 nm), (ii) that the reaction proceeds via a formyl intermediate, and (iii) that the high selectivity results from an inherently low activity of the very small Ru particles for CO₂ dissociation and hence for CO₂ methanation, in combination with a high activity of these nanoparticles (NPs) for CO methanation. For larger NPs, in contrast, the selectivity originates from CO_{ad} surface blocking of the active Ru surface. This effect decays at low CO partial pressures, leading to a decreasing selectivity at lower CO concentrations, as experienced, for example, at the end of the reactor in practical applications. Further details as well as a comprehensive literature overview on the selective methanation reaction are given in our previous papers [15–18].

In the present study, we aim at a mechanistic understanding of the role of the calcination procedure which is applied after catalyst synthesis, before activation of the pre-catalyst, and its further use. It is known that this calcination step leads to a significant improvement of the activity and selectivity of the catalyst after subsequent reactive activation. The mechanisms and physical origin for the observed increase in catalytic performance, however, are largely

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unknown. These are the topics of the present contribution. The structural changes of the catalyst imposed by the calcination procedure were determined by *in situ* X-ray absorption spectroscopy (XAS) for different calcination temperatures. The resulting changes in catalytic reaction characteristics were evaluated by combined kinetic and *in situ* IR spectroscopic measurements (diffuse reflection FTIR spectroscopy – DRIFTS). The reaction measurements were performed in different reaction mixtures including idealized (CO and H₂), and semi-realistic (CO, H₂, and CO₂) gas streams. Coupled with activity measurements, *in situ* spectroscopic DRIFTS measurements were used to follow the evolution of different intermediates formed on the catalyst surface during the reaction, in particular the steady-state coverage of CO_{ad}, which acts as a precursor leading to the active intermediates involved in both CO and CO₂ methanation.

2. Experimental section

2.1. Catalysts

The 2.2 wt.% Ru/zeolite catalyst was prepared by an elaborate ion exchange procedure. Afterward, the loaded catalysts were calcined in synthetic air at different temperatures up to 500 °C (samples A–D, with increasing calcination temperature) [19]. All samples were prepared at Süd-Chemie AG. A BET specific surface area of 410 m² g⁻¹ was determined for the zeolite catalyst support using N₂ adsorption. X-ray diffraction (XRD) and high-resolution transmission electron microscopy (TEM) indicate the presence of rather large RuO₂ nanoparticles with sizes around 10 nm after reactive reduction. Due to electron-induced decomposition of the support during the TEM measurements, and because of the too low sensitivity of XRD, these methods were not suited to determine the size of the very small Ru nanoparticles resulting after activation [15,18]. Comparing XPS measurements for two different Ru catalyst supports, Ru/zeolite and Ru/Al₂O₃, the lower Ru(2p) and O(1s) peak intensities for the Ru/zeolite catalyst indicate that in this case, the Ru particles are mainly located in the pores of the zeolite rather than on the (outer) surface of the zeolite particles [16].

2.2. XAS experiments

XAS experiments were performed at the X1 beamline at HASY-SLAB, using a Si-311 double crystal monochromator with a beam size of roughly 6 mm vertical and 2 mm horizontal. The reaction cell consisted of a stainless steel tube with a cylindrical channel (i.d. 4 mm) along the diameter, which contained the catalyst bed (length ca. 10 mm, around 25 mg catalyst, undiluted, conversion <20%), allowing the gases to flow through. A second bore along the central axis of the ring and perpendicular to the catalyst bed allowed the X-ray beam to pass through the catalyst bed. Under working conditions, the reaction cell is closed off by two kapton windows. Heating of the cell was achieved via wires passing along the reactor ring through 4 small bores parallel and aside to the reaction tube. The temperature was adjusted and varied during reaction with a NiCr/Ni thermocouple and temperature controller. The spectra (Ru k-edge, 22,117 eV) were collected in transmission using two filled with a Ar/N₂ mixture ionization chambers. A ruthenium metal foil placed in between the second and an additional ionization chamber allowed for internal and simultaneous calibration during all measurements. The pre-edge region was measured in the range of 21,867–22,087 eV with a step size of 10 eV. For the XANES region (22,087–22,157 eV) and EXAFS region (22,157–23,317 eV), step widths of 0.5 and 0.98 eV, respectively, were used. EXAFS spectra evaluation was carried out using the program XDAP with standard procedures described elsewhere [20].

Theoretical references were calculated by FEFF 8.0 [21] and calibrated against a Ru foil and RuO₂ as experimental references, to determine the damping factor S₀², the phase shift F, and the mean free path of the electrons δ [20]. When evaluating the fits, both the Ru–Ru bond distances and E₀ were allowed to relax. The resulting distances were very close to each other and also the E₀ values were reasonable and close to each other. k³ weighting was used to be more sensitive to higher shell contributions as expected from larger particles and to Ru–Ru scattering (>Z element) [22]. Following the literature [20,23,24], we assumed an error in the coordination numbers of 10%, which is mostly due to systematic errors.

The XAS *in situ* measurements were conducted with high-purity gases (99.999%), passed through the reaction cell at a gas flow of 41.6 N ml·min⁻¹. The reaction gas flow was adjusted via mass flow controllers for different gas sources (Bronkhorst F201C-FA-88V). Prior to the *in situ* experiments, the catalyst was heated to 150 °C in a N₂ flow and then heated up, within 10 min, to the reaction temperature of 190 °C in reactive gas atmosphere. All XAS measurements were performed in idealized reformat at atmospheric pressure (0.6% CO, 3% N₂, balance H₂). Since the presence of CO₂ did not lead to other reactivity, we expect similar Ru particle sizes also for reaction in realistic reformat (SR-ref 6000) [15].

2.3. Kinetic measurements

The kinetic measurements were carried out in a quartz tube microreactor contacted by a NiCr/Ni thermocouple in the central range for temperature monitoring and control during reaction. The reactor was filled with the calcined catalyst, which was diluted with SiO₂ to form a catalyst bed of 1 cm length (~200 mg of diluted catalyst). SiO₂ is inactive under reaction conditions. The dilution of the catalyst with SiO₂ depended on the CO concentration in the reaction mixture (for 0.6% CO: 1:10, for 0.01% CO: 1:250). Since the catalyst bed is unchanged in almost all measurements, the space velocity can be considered as constant in these measurements. Conditioning of the catalyst prior to the reaction was carried out before all kinetic measurements, following the procedure described for the EXAFS measurements. The activation/deactivation measurements were performed at 190 °C in the same way as described above, for the differently calcined catalysts A–D, following the reaction over 800 min in SR-ref 6000 and SR-ref 100 reformates (see Table 1) with a gas flow of 41.6 N ml min⁻¹. Reaction rates and selectivities of the different catalysts were calculated after reaching steady-state conditions, 400 min after the start of the reaction. Influent and effluent gases were analyzed by on-line gas chromatography-mass with a CO detection limit of ca. 10 ppm (DANI 86.10), using H₂ as carrier gas.

2.4. *In situ* IR spectroscopy measurements

In situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) measurements were performed using a commercial *in situ* reaction cell (Harricks, HV-DR2). The spectra were recorded using a Magna 6700 spectrometer (Thermo) equipped with a MCT

Table 1
Composition of the different reaction gas mixtures used in the kinetic and DRIFTS measurements.

| Reaction gas (reformat) | Reaction gas composition | | |
|-------------------------|--------------------------|---------------------|-----------------------------|
| | CO (ppm) | CO ₂ (%) | N ₂ (%) |
| CO ₂ -ref | 0 | 15.5 | 3.0, balance H ₂ |
| ID-ref 100 | 100 | 0.0 | 3.0, balance H ₂ |
| SR-ref 100 | 100 | 15.5 | 3.0, balance H ₂ |
| SR-ref 6000 | 6000 | 15.5 | 3.0, balance H ₂ |

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