



Activity, selectivity, and adsorbed reaction intermediates/reaction side products in the selective methanation of CO in reformat gases on supported Ru catalysts

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ABSTRACT

The reaction behavior and mechanistic aspects of the selective methanation of CO over two supported Ru catalysts, a Ru/zeolite catalyst and a Ru/Al₂O₃ catalyst, in CO₂ containing reaction gas mixtures were investigated by temperature-screening measurements, kinetic measurements and in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements. The influence of other components present in realistic reformat gases, such as H₂O and high amounts of CO₂, on the reaction behavior was evaluated via measurements in increasingly realistic gas mixtures. Temperature screening and kinetic measurements revealed a high activity of both catalysts, with the Ru mass-normalized activity of the Ru/zeolite catalyst exceeding that of the Ru/Al₂O₃ catalyst by about one order of magnitude. Approaching more realistic conditions, the conversion–temperature curve was shifted slightly upwards for the Ru/Al₂O₃ catalyst, whereas for the Ru/zeolite catalyst it remained unaffected. The selectivity was highest for the Ru/zeolite catalyst, where in parallel to full conversion of CO the conversion of CO₂ remained below 10% over a 40 °C temperature window. During selective methanation on the Ru/Al₂O₃ catalyst, CO₂ was converted even though CO was not completely removed from the feed. Transient DRIFTS measurements, following the build-up and decomposition of adsorbed surface species in different reaction atmospheres and in the corresponding CO-free gas mixtures, respectively, provide information on the formation and removal/stability of the respective adsorbed species and, by comparison with the kinetic data, on their role in the reaction mechanism. Consequences on the mechanism and physical reasons underlying the observed selectivity are discussed.

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1. Introduction

Economically and ecologically efficient techniques for the production of sufficiently pure H₂ are a prerequisite for the introduction of H₂ based energy technologies [1]. Today, H₂ is mainly produced by steam reforming/partial oxidation of fossil fuels [2–7], which, among other components, leaves CO (1–8%) and substantial amounts of CO₂ (up to 20%) in the resulting H₂-rich gas mixture ('reformat'). For the operation of low-temperature polymer electrolyte fuel cells (PEFCs), the resulting H₂-rich gas should be free of catalyst poisons, in particular the CO content has to be reduced to ≤10 ppm under steady-state conditions [8] (<1 ppm after 2015 [9]) [10], which is most commonly achieved catalytically, by a combination of the water gas shift (WGS) reaction and the preferential oxidation of CO (PROX) [2,3,6,11,12]. In cost sensitive, small scale applications, however, methanation of the CO may be a more attractive process for CO removal compared to the PROX reaction, since it uses the H₂ present in the feed gas and avoids the

need for an additional unit for O₂ dosing [4]. The losses of H₂ are tolerable, as long as the initial CO contents, after the WGS reaction, are low (0.5%). Precondition for this concept, however, is that the reaction is highly selective for the methanation of CO and that CO₂ methanation is essentially inhibited, otherwise the losses of hydrogen would become intolerable [4,13]. This is the background of the present study, where we investigated (i) the performance of two commercial-supported Ru catalysts, a zeolite-supported catalyst developed for these purposes and, for comparison, a standard Ru/Al₂O₃ catalyst, in the selective methanation of CO and (ii) mechanistic details of the reaction, aiming at a physical understanding of the reaction and the resulting high selectivities.

The CO methanation reaction is closely related to the Fischer–Tropsch reaction, where higher hydrocarbons are produced by the reaction of CO and H₂ [14,15], and accordingly, the most active catalysts in the Fischer–Tropsch reaction, oxide supported Fe, Co, Ni, and Ru catalysts [14,15], were identified also as the most active catalysts for the CO methanation reaction [16–22]. Also the methanation of CO₂ over Ru catalysts was investigated in a number of studies, e.g., in [23,24]. Catalysts with Ru as active component showed a high selectivity towards CO methanation in CO₂ containing gas mixtures [17,21,22,25–27]. Several authors [28–30]

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proposed that the use of zeolites as support for Ru catalysts results in a higher selectivity for the selective methanation of CO compared to Ru/Al₂O₃ or Ru/SiO₂ catalysts, which they explained by a stronger metal-support interaction. Furthermore, because of their large surface areas, zeolites are likely to favor the formation of small Ru particles and to stabilize these against sintering; and, their well-defined pore structure may result in a narrower particle size distribution [31]. The resulting small Ru particle size was suggested to have a positive effect on the catalyst's activity [27,32,33]. Other groups, however, assumed that small particles and a high dispersion are counterproductive for the activity [21,34,35]. The surface species formed during reaction were characterized by in situ infrared spectroscopy studies on different Ru-catalysts. Different types of adsorbed CO adsorbed on the Ru particles, e.g., CO_{ad} on oxidized Ru, linear and bridged CO_{ad} on Ru⁰, surface formates and/or surface carbonates as well as adsorbed CH_{x,ad} species were observed during CO methanation on the catalysts [25,36–41]. From these studies it was not clear, however, whether there is a preference for a specific type of CO_{ad} as active species, and if so, for which of them. Formates and carbonates are commonly interpreted as side products.

CH_x species had been proposed by Ekerdt and Bell [37] and later by Yamasaki et al. [38] as reaction intermediates. The latter authors showed in a very detailed in situ IR study that upon changing from a ¹²CO/H₂ reaction atmosphere to a ¹³CO/H₂ gas mixture the signals related to ¹²CH_{x,ad} species disappeared, while signals related to the corresponding ¹³CH_{x,ad} species were growing in [38]. They also estimated concentrations of CH₂ and CH₃ groups present on the surface under steady-state conditions. Assuming that these groups belonged to adsorbed C_xH_y hydrocarbon chains, they could calculate the average length of the C_xH_y hydrocarbon chains. Based on these data they proposed a complex mechanism for the CO methanation reaction, where CH_{x,ad} species act as reaction intermediates and CH₄ formation proceeds via formation and decomposition of adsorbed hydrocarbon chains [38]. However, since in the SSITKA-type (steady-state isotope transient kinetic analysis) experiments the CH_{x,ad} removal rate in H₂ was not quantified and compared to the CH₄ formation rate, it is not clear, whether the reactive removal of the CH_{x,ad} species observed in IR is really the rate-limiting step in the dominant reaction pathway, which would mean that these species represent reaction intermediates in that pathway, or whether they should better be considered as spectator species or as reaction intermediates in a minority pathway (side reaction). Further information on mechanistic aspects can be derived from recent density functional theory (DFT) studies [42–46].

In the present paper, we investigated the CO methanation reaction in a number of different reaction atmospheres, going from pure H₂/CO and H₂/CO₂ mixtures to more realistic reaction mixtures, over a Ru/zeolite and a Ru/Al₂O₃ catalyst. In the first part, we characterized the activity, selectivity and stability of the two catalysts in conversion measurements and in kinetic measurements under differential reaction conditions, determining reaction rates, activation energies and reaction orders. In the second part, the formation and their accumulation with time of different surface species under reaction conditions as well as their decomposition in CO-free atmosphere (H₂/N₂ mixtures) was followed in transient in situ diffuse reflection IR Fourier transform spectroscopy (DRIFTS) measurements, performed under comparable reaction conditions (differential conversion, identical gas mixtures and reaction temperatures) as used in the kinetic measurements and compared to reaction and mass spectrometric transient data. The correlation between the activity and the build-up of surface species during the reaction under different reaction conditions and between the removal of adsorbates and CH₄ formation in transients in CO-free atmosphere on both

Ru catalysts as well as consequences for the reaction pathway are discussed.

2. Experimental

2.1. Catalyst properties

Two Ru catalysts were investigated, a Ru/zeolite catalyst prepared by Süd-Chemie AG with 2.2 wt.% Ru loading and a commercial 5.0 wt.% Ru/Al₂O₃ catalyst (Johnson Matthey). The BET surface areas were determined by N₂ adsorption to 100 and 410 m² g⁻¹ for the Ru/Al₂O₃ and the Ru/Zeolite catalyst, respectively. The Ru oxidation state was determined by X-ray photoelectron spectroscopy (XPS; PHI 5800 ESCA system), using monochromatized Al K α radiation. For the as-received catalysts, without additional pre-treatment, most of the surface Ru is present as Ru oxide, with a Ru⁴⁺/Ru⁰ ratio of 2:1. This is true for both catalysts. Similar results were obtained also after reactive pre-treatment (description see Section 2.2). Most likely, any changes induced by the reactive pre-treatment are counteracted by the transport through air from the reactor used for pre-treatment to the XPS spectrometer. The Ru particle size was investigated by different methods. For the Ru/zeolite catalyst, X-ray diffraction (XRD) showed reflections related to RuO₂ before reactive conditioning (used as received, conditioning see Section 2.2), corresponding to RuO₂ domain/nanoparticle sizes of 10 nm diameter (Debye–Scherrer). After reactive conditioning for 100 min., the RuO₂-related XRD reflection decreased significantly in intensity. On the other hand, except for a small shoulder at a support-related reflection, no signal related to metallic Ru was observed, indicative of very small (<1 nm diameter) Ru nanoparticles or grains. On a used catalyst, after 1800 h on stream, the diffractogram reveals metallic Ru nanoparticles or nanograins of 2 nm mean diameter.

For the Ru/Al₂O₃ catalyst, the Ru particle size was determined by TEM imaging to 2–3 nm diameter. On the Ru/zeolite catalyst, in contrast, high resolution TEM imaging was complicated by electron beam-induced decomposition of the zeolite. The images showed a very inhomogeneous distribution of Ru particles, with few individual particles (10–20 nm diameter) and agglomerates of Ru particles, in addition to larger areas without visible nanoparticles (representative TEM images are given as [Supplementary material, Fig. 1S](#)).

H₂ adsorption experiments performed on the two catalysts after reduction in H₂ (30 min, 200 °C) yielded active surface areas of 3.7 m² g⁻¹ (Ru/Al₂O₃) and 0.095 m² g⁻¹ (Ru/zeolite), which would correspond to dispersions/Ru particles sizes of 15%/6.5 nm and <1%/113 nm, respectively. (It should be noted that higher reduction temperatures up to 300 °C had no effect on the active surface area, above that temperature the active surface area decreases, probably due to agglomeration.) Additional adsorption experiments performed on a temporal analysis of products (TAP) reactor at –30 °C after reactive conditioning (100 min, see Section 2.2) yielded active surface areas of 2.8 m² g⁻¹ and 0.7 m² g⁻¹ for the Ru/Al₂O₃ and the Ru/zeolite catalyst, respectively, which would correspond to dispersions/particle sizes of 12.5%/8 nm (Ru/Al₂O₃) and 6.3%/15 nm (Ru/zeolite). After 1000 min reaction, the respective values were 2.35 m² g⁻¹/10.5%/10 nm (Ru/Al₂O₃) and 0.7 m² g⁻¹/6.5%/15 nm (Ru/zeolite). Obviously, the dispersions and particle sizes derived from the adsorption experiments are incompatible with those determined by TEM or XRD. We explain this discrepancy by assuming that also after conditioning a significant fraction of the Ru nanoparticle surface is still oxidized and therefore does not adsorb hydrogen. During reaction, the oxidized Ru surface is further reduced in the reaction atmosphere, but at the same time, an increasing fraction of the active Ru surface area is

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