Influence of the catalyst loading on the activity and the CO selectivity of supported Ru catalysts in the selective methanation of CO in CO_2 containing feed gases

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ABSTRACT

We have investigated the methanation of CO and CO_2 over Ru/zeolite catalysts with different Ru loading in semi-realistic reformate gases by *in situ* X-ray absorption spectroscopy (XAS), *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and kinetic measurements. Increasing the Ru loading causes an increase of the mean particle size from 0.9 nm (2.2 wt.% Ru) to 1.9 nm (5.6 wt.% Ru). At the same time, also the activity for CO methanation increases, while the selectivity for CO methanation, which is constant at 100% for reformate gases with 0.6% CO, decreases at low CO contents. The latter findings are interpreted in terms of a change in the physical effects governing the selectivity for CO methanation with increasing Ru particle size, from an inherently low activity for CO_2 dissociation and subsequent CO_{ad} methanation on very small Ru nanoparticles to a site blocking mechanism on larger Ru nanoparticles. In the latter mechanism, CO_2 methanation is hindered by a reaction inhibiting adlayer of CO at higher CO_{ad} coverages, i.e., at not too low CO concentrations, but facile in the absence of a CO adlayer, at lower CO concentrations in the reaction gas mixture.

1. Introduction

The methanation of CO has attracted increasing interest in recent years because of its potential as simple technique for CO removal from H_2-rich feed gases for low temperature fuel cells produced by steam reforming of fossil fuels or biomass based fuels [1]. It is an attractive alternative to the more commonly used selective CO oxidation (PROX) reaction in cost sensitive small scale applications, since it avoids the controlled addition of a second gas (O_2). Since the resulting reformates typically contain also considerable amounts of CO_2 (15–20%) [1–5], the reaction must be highly selective for CO methanation, with CO_2 methanation essentially being inhibited, otherwise the losses of H_2 would become intolerable [1,6]. Therefore, the mechanisms of these reactions, CO methanation and CO_2 methanation, as well the physical effects controlling the selectivity for the selective methanation of CO in CO_2-rich gas mixtures, are of obvious importance for industrial applications.

In addition to the commonly used Ni, Fe or Co-based catalysts for the Fischer-Tropsch reaction, also supported Ru catalysts are highly active for CO methanation [7–10]. For supported Ru catalysts, it was established in a number of studies that in addition to the nature of the support material, such as Al_2O_3, TiO_2 or zeolites, the Ru particle size has a pronounced effect on their activity for CO methanation [11–14]. The Ru mass normalized reaction rate was found to increase with increasing Ru particle size. For very small Ru nanoparticles with diameters <1 nm, the activity decreased steeply. This was associated with the higher fraction of Ru terrace sites on larger Ru nanoparticles, which were considered to be more active for this reaction [11–14]. While the above studies were conducted under Fischer-Tropsch reaction conditions in a typical syngas mixture (H_2:CO = 3), this trend was confirmed also in more recent studies performed under conditions more relevant for feed gas processing (H_2:CO = 14) [10,15,16].

The selectivity for CO methanation in the selective methanation of CO_2-rich gas mixtures was attributed to surface blocking by adsorbed CO, due to the much higher adsorption energy of CO compared to CO_2. The CO adlayer was proposed to inhibit the (dissociative) adsorption of CO_2 and thus the subsequent methanation reaction [17,18]. In that mechanism, CO_2 methanation will be inhibited as long as the CO partial pressure is sufficiently high to maintain the reaction inhibiting CO adlayer. Increasing the selectivity and activity of Ru supported catalysts has already been tried in many different ways, including the use of different support materials such as TiO_2, Al_2O_3, SiO_2 [16,19], or of dopants [20,21], or by varying the Ru particle size [22]. In the latter study on Ru/Al_2O_3 catalysts, the Ru particle sizes were varied between 7.5 and 34 nm, and a decrease in

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the temperature for maximum methane formation with decreasing particle size was reported. Also the use of zeolite supports was proposed as an alternative to standard supports such as TiO_2 or Al_2O_3; the zeolite supported Ru catalysts showed indeed a higher selectivity for the methanation of CO compared to Ru/Al_2O_3 or Ru/SiO_2 catalysts [23,24]. This was explained by a stronger metal-support interaction.

Recently, we reported on a zeolite supported, commercial Ru catalyst, which showed an extremely high selectivity, essentially 100%, over a wide range of CO concentrations [25–27]. We could demonstrate that for a 2.2 wt.% Ru/zeolite catalyst this selectivity was maintained even in reaction gases with a very low CO content (100 ppm), where the CO_{ad} coverage on the Ru nanoparticles (NPs) was far below saturation. Moreover, this catalyst shows 100% CO selectivity and full CO conversion at 190 °C even under integral reaction conditions. CO_2 is methanated only at higher temperatures and exhibits 50% conversion at 350 °C [26]. In contrast, on a 5 wt.% Ru/Al_2O_3 catalyst, which was investigated for comparison, the selectivity decayed rapidly once the CO_{ad} coverage, as detected by its IR signal intensity, fell significantly below its saturation value [26]. This was tentatively attributed to an inherently low activity of the very small Ru NPs in the Ru/zeolite catalyst for CO_2 dissociation, which results in very low CO_2 methanation rates even at low CO_{ad} coverages, while on the Ru/Al_2O_3 catalyst with its much larger Ru particles (mean particle size around 2.5 nm), the inherent activity for CO_2 decomposition and methanation is quite high and high selectivities are only obtained by surface blocking by CO_{ad}. In that picture, the selectivity was primarily attributed to the Ru particle size, hence, to a particle size effect. This explanation, though convincing, was preliminary, since the Ru particle size in the Ru/zeolite catalysts was unknown. The Ru particles appeared to be too small for transmission electron microscopy (TEM) imaging and X-ray diffraction (XRD). Furthermore, since catalysts with two different supports were compared, support effects on the selectivity, due to metal-support interactions, cannot be ruled out.

These open questions are addressed in the present paper, where we report results of a systematic, combined kinetic and *in situ* spectroscopy study on the effect of Ru metal loading and Ru particle size on the activity and in particular on the selectivity of Ru/zeolite catalysts in the selective methanation of CO. The measurements were performed in a number of different idealized (H_2/CO, H_2/CO_2) and semi-realistic ($H_2/CO/CO_2$) reaction atmospheres, decreasing the CO content to as low as 100 ppm. *In situ* extended X ray absorption fine structure spectroscopy (EXAFS) and *in situ* diffuse reflectance IR spectroscopy (DRIFTS) measurements were employed, in addition to kinetic measurements, in order to gain information on the Ru particle sizes of the different catalysts during reaction under steady-state conditions (EXAFS) and on the temporal evolution of the adsorbate layer during the reaction (time-resolved DRIFTS). *In situ* EXAFS results, obtained after equilibration in idealized reformate (Table 1), are presented and discussed in Section 3.1. The time-resolved *in situ* DRIFTS measurements and their results are described in Section 3.2. In combination, the DRIFTS measurements allow us to not only determine the steady-state CO_{ad} coverages in the respective reaction atmospheres, but also to qualitatively assess the contribution from CO_2 decomposition to the CO_{ad} signal in semi-realistic reaction gases. The influence of the Ru loading and Ru particle size on the CO methanation activity and on the selectivity for CO methanation is topic of the following Section 3.3. The resulting correlations between CO_{ad} coverage and the selectivity for CO methanation and Ru particle size effects therein as well as consequences on the molecular scale mechanism responsible for the selectivity are discussed. Finally, we briefly comment on consequences of these findings for technical applications.

2. Experimental

Catalyst properties: The Ru/zeolite catalysts with metal loadings of 1, 2.2, 3.6, and 5.6 wt.% Ru were prepared by Süd-Chemie AG. BET specific surface areas of ~410 $m^2 g^{-1}$ for the Ru/zeolite catalysts were determined by N_2 adsorption, and the catalysts were free of additional dopants. Reliable Ru particle size determination of the zeolite supported catalysts had turned out to be problematic both for standard techniques such as TEM or XRD for structure determination (structure) and also for H_2 chemisorption, where only upper limits of the particle size could be estimated [26]. Hence, this question is still open. Further details of the catalyst characterization are given elsewhere [26].

XAS experiments: The EXAFS experiments were performed at the X1 beamline at Hasylab and BM26 at ESRF, using a Si-311 double crystal monochromator and a beam size of approximately 6 mm vertical and 2 mm horizontal. The reaction cell consisted of a stainless steel ring with a cylindrical channel (i.d. 4 mm) along the diameter, which contained the catalyst bed (length ca. 10 mm, ~25 mg catalyst, undiluted, conversion <15%). 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. In these directions, the reaction cell was closed by two Kapton windows. Sample heating was achieved by 4 wires, which passed through the ring in 4 small bores parallel to the reaction channel. A NiCr/Ni thermocouple was used to monitor the temperature. The reaction cell was placed between two He filled ionization chambers for collecting the spectra at the Ru K-edge (22,117 eV) in transmission geometry. A Ru metal foil placed in between the second and a subsequent third ionization chamber allowed for internal energy calibration during all measurements. The pre-edge region was measured from 21,867 to 22,087, the XANES region from 22,087 to 22,157 eV (XANES data not shown), and the EXAFS region from 22,157 to 23,317 eV. Processing of the EXAFS spectra followed standard procedures [28], using the program 'XDAP' [29]. In short, the spectra were pre-edge and background subtracted using a modified Victoreen function and a spline function, respectively. Normalization for constant signal intensity of the spectra was performed 50 eV above the edge. Multiple shell fitting of the EXAFS was done in r-space ($3.2 < k < 13.5 A^{-1}$, $1.0 < r < 3.2$), using a k weighting of 3. Theoretical references were calculated by FEFF 8.0 [30] and calibrated against a Ru foil and RuO_2 as experimental references, to obtain the damping factor S_0^2, the phase shift F and the mean free path of the electrons δ [28].

These *in situ* measurements were conducted with high purity gases (99.999%), which were passed through the reaction cell (gas flow 41.6 Nml min^{-1}). The reaction gas mixtures were prepared via mass flow controllers (Bronkhorst F201C-FA-88V). Prior to the *in situ* experiments, the catalysts were heated up in a N_2 stream to 150 °C, and subsequently heated within 10 min to the reaction temperature in the reaction gas atmosphere. The *in situ* EXAFS measurements were performed at 190 °C reaction temperature in idealized reformate at atmospheric pressure (0.6% CO, 3% N_2, balance H_2), until steady-state conditions were achieved, but at least for 500 min time on stream (max. 1000 min).

Kinetic measurements: The kinetic measurements were carried out at atmospheric pressure in a quartz tube micro reactor with the catalysts used as received. By diluting the catalyst with different amounts of SiO_2 (inactive under our reaction conditions), differential reaction conditions (maximum 15% conversion of the reactants) were obtained. The dilution of the catalyst with SiO_2 depended on the CO concentration and on the catalyst (0.6% CO: 1:5 (1 wt.% Ru/zeolite catalyst), 1:10 (2.2 wt.%), 1:30 (3.6 wt.%), 1:60 (5.6 wt.%); 100 ppm CO: 1:400 (3.6 wt.%) 1:600 (5.6 wt.%). In total, about 200 mg of diluted catalyst was used, resulting in a catalyst bed of 1 cm length. The experiments were carried out in a gas flow