Carriers Selective Methanation of CO in CO2–rich feed Gases on Supported Ru Catalysts

S. Eckle, H. G. Anfang, R.J. Behm

This document appeared in

Detlef Stolten, Thomas Grube (Eds.):
18th World Hydrogen Energy Conference 2010 - WHEC 2010
Parallel Sessions Book 3: Hydrogen Production Technologies - Part 2
Proceedings of the WHEC, May 16.-21. 2010, Essen
Schriften des Forschungszentrums Jülich / Energy & Environment, Vol. 78-3
Institute of Energy Research - Fuel Cells (IEF-3)
Forschungszentrum Jülich GmbH, Zentralbibliothek, Verlag, 2010
ISBN: 978-3-89336-653-8

Carriers Selective Methanation of CO in CO_2–rich feed Gases on Supported Ru Catalysts

Stephan Eckle, Institute of Surface Science and Catalysis, Ulm University, Ulm, Germany
H. G. Anfang, Süd-Chemie A.G., Bruckmühl, Germany
R.J. Behm, Institute of Surface Science and Catalysis, Ulm University, Ulm, Germany

1 Objective

Economically and ecologically efficient techniques for the production of sufficiently pure H_2 are a prerequisite for the introduction of H_2 based energy technologies [1]. Today, H_2 is mainly produced by steam reforming / partial oxidation of fossil fuels [2][3], which, among other components, leaves CO (1-8 %) and substantial amounts of CO_2 (up to 20 %) in the resulting H_2-rich gas mixture ('reformate'). For the operation of low-temperature Polymer Electrolyte Fuel Cells (PEFCs), the resulting H_2-rich gas should be free of (anode) catalyst poisons, in particular the CO content has to be reduced to $\leq$10 ppm [4], which is most commonly achieved catalytically, by a combination of the Water Gas Shift (WGS) reaction and the Preferential Oxidation of CO (PROX) [5]. In cost sensitive, small scale applications, however, methanation of the CO may be a more attractive alternative for CO removal compared to the PROX reaction, since it uses the H_2 present in the feed gas and avoids the need for an additional dosing unit for O_2 dosing [6]. The losses of H_2 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 oxidation of CO and that CO_2 methanation is essentially inhibited, otherwise the losses of hydrogen would become intolerable [6].

The selectivity for CO methanation in the selective methanation in CO_2-rich gas mixtures is generally attributed to a surface blocking by adsorbed CO, which is driven by the much higher adsorption energy of CO compared to CO_2. In this model CO_{ad} blocks the surface for (dissociative) adsorption of CO_2 and subsequent methanation reaction [7][8]. In that case, CO_2 methanation will be inhibited, as long as the CO partial pressure and hence the CO_{ad} coverage on the catalyst are sufficiently high [9][10][11]. However, most of the previous studies were conducted under conditions, where only little mechanistic insight on the reaction could be gained. Increasing the selectivity of Ru supported catalysts was also already tried in many different ways, including the use of different support materials such as TiO_2, Al_2O_3, SiO_2 [12] or of dopants [13], or varying the Ru particle size [14]. Also the use of zeolite supports was proposed as a promising alternative to standard supports such as TiO_2 or Al_2O_3, and the catalysts showed indeed a higher selectivity for the selective methanation of CO compared to Ru/Al_2O_3 or Ru/SiO_2 catalysts [15]. However, the physical origin, for improvement of the selectivity remained still unclear.

On the other hand the exact mechanism of the selective methanation of CO is still not solved yet. A large number of studies, mostly performed in the 1980's, state active carbon species as reactive intermediate [16]. In this concept, adsorbed CO_{ad} surface species dissociate to C_{ad}, which subsequently hydrogenates to CH_{ad}, $CH_{2,ad}$ $CH_{3,\,ad}$ and CH_4. In that case, care has to be taken that the steady-state carbon coverage is not too high to avoid deactivation of the catalyst [16]. Another mechanistic suggestion involves a hydrogen-assisted CO dissociation step [16]. Here, adsorbed H reacts with CO to an "HCO" formyl type species, which will dissociate either to CH_{ad} or react with another H atom to H_2CO. This is followed by subsequent CO bond scission to yield $CH_{2,ad}$. The produced $CH_{x,ad}$ surface species are hydrogenated to CH_4 afterwards. This „HCO" species, however, has not been observed spectroscopically so far.

In this contribution we report on the results of realistic field experiments and combined kinetic and *in situ* IR (DRIFTS) measurements under differential reaction conditions on Ru/supported catalysts, a Ru/zeolite catalyst and a Ru/Al_2O_3 catalyst. Measurements under realistic field conditions over the Ru/zeolite catalyst showed a high stability (100 % CO conversion) and CO selectivity (85 %) for over 1000 h. The latter measurements aimed at gaining more insight on the physical origin of the high selectivity for CO methanation and on the mechanism of the selective CO methanation reaction.

The combined kinetic and *in situ* DRIFTS measurements allowed us to not only determine the steady-state CO_{ad} coverages in different reaction atmospheres, but also to qualitatively assess the contribution from CO_2 decomposition to the CO_{ad} signal in the experiments performed under semi-realistic conditions. They were supported by additional experiments in a CO-free atmosphere (only CO_2 present).

SSITKA-type (*steady state isotope transient kinetic analysis*) DRIFTS transients, where one reactant is exchanged under steady-state conditions by its labelled isotopomer ($^{12}CO \rightarrow {}^{13}CO$) show a direct correlation between a possible formyl-type species with CO exchange and CH_4 production. The HCO species is likely to be the reaction intermediate of the selective CO methanation.

2 Experimental

The kinetic measurements were conducted at 190 °C under differential conditions in semi-realistic and idealized (CO_2 free) atmosphere (x kPa CO, 3 kPa N_2, 15.5 kPa CO_2, rest H_2) with varying CO concentration (6000 ppm, 3000 ppm, 1000 ppm, 100 ppm) and a gas flow of 41.6 Nml/min. The catalysts were diluted with SiO_2, which is inactive for the reaction under present reaction conditions. First they were heated in N_2 to 150 °C, subsequently the temperature was increased to 190 °C in reactive atmosphere. In-situ IR measurements were conducted in the same manner as described above. Background spectra were taken at 150 °C und N_2 atmosphere. SSITKA type measurements were conducted after 1000 min under idealized conditions to obtain a steady-state situation, before switching to the reactants isotopomer (i.e. $^{12}CO \rightarrow {}^{13}CO$).

3 Results

The Ru/zeolite showed a very high stability and selectivity over 1000 h time on stream in field experiments.

3.1 Mechanism for CO methanation

DRIFTS experiments on the Ru supported catalysts showed the typical CO_{ad} surface species with bands in the range of 2200 – 1900 cm^{-1}. Their coverage was correlated with the temporal evolution of the activity, indicating that these species or at least the related adsorption sites are directly involved in the CO methanation reaction. On the Ru/Al_2O_3 oxide catalyst, we also identified a surface species with a characteristic band at 1740 cm^{-1}, which we attribute to a formyl (HCO) molecule, as seen by formaldehyde adsorption on the catalyst. In transient experiments (exchange of ^{12}CO by ^{13}CO), the build-up and decay of this surface species was found to correlate with the build-up and decay of linearly adsorbed CO_{ad} and with the CH_4 formation as shown in Fig. 1.

On the Ru/zeolite catalyst, we could not identify such adsorbed formyl species under reaction conditions. However, due to the much higher activity of the latter catalyst compared to the Ru/Al_2O_3 catalyst, the steady-state coverage of the "HCO_{ad}" molecule may be too low for its detection. Nevertheless, we favor a similar reaction pathway and mechanism on both catalysts, with a similar activated complex, since the activation energies are similar in both cases [17].

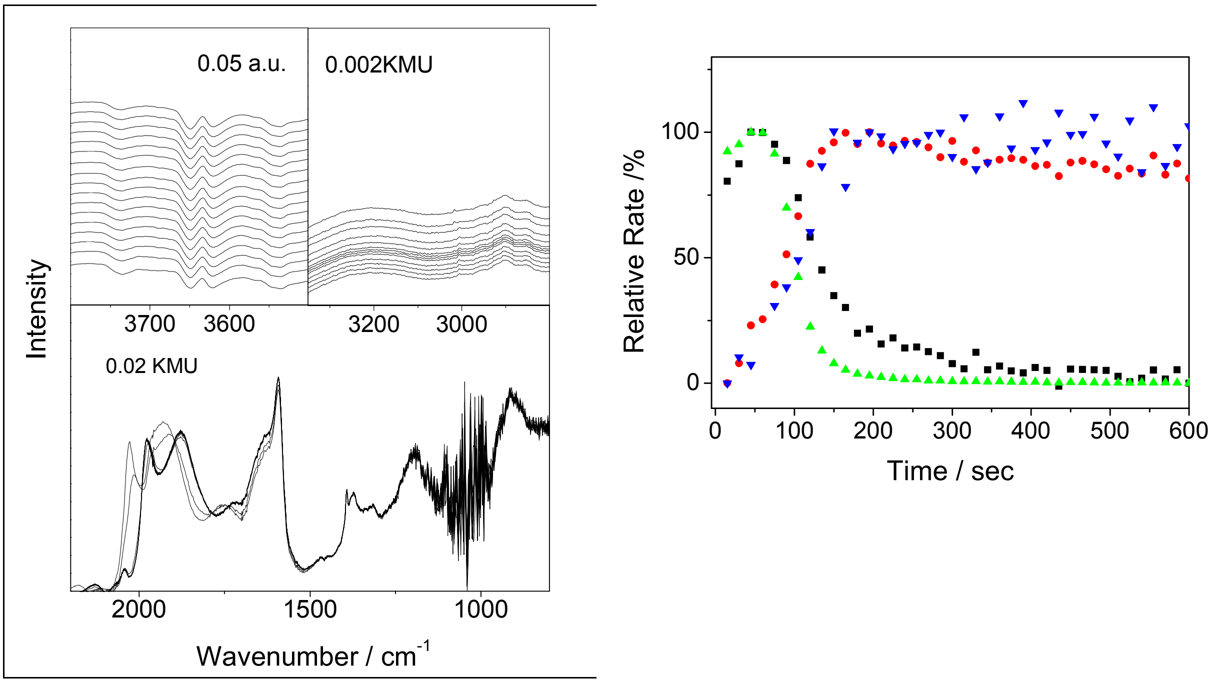

Figure 1: left: DRIFTS transients after 1000 min reaction under idealized conditions and subsequent switch from ^{12}CO to ^{13}CO. right: signal intensities of respective peaks: (■) ^{12}CO, (▲) ^{12}CHO, (▼) $^{13}CH4$, (,) ^{13}CHO

3.2 Selectivity for CO methanation

In the kinetic and *in situ* spectroscopy studies it was found, that at low CO concentrations (100 ppm) the CO_{ad} coverage is very low, also in the presence of 15.5 kPa CO_2, while on the Ru/Al_2O_3 catalyst, the CO_{ad} coverage is much higher. The resulting value of the CO_{ad} band intensity on that catalyst is the same as that in a “normal” reaction gas mixture with 0.6 kPa CO, where full coverage can be assumed. Hence, on the Ru/Al_2O_3 catalyst, dissociation of adsorbing CO_2 provides another channel for the formation of CO_{ad}, in addition to CO adsorption. Facile decomposition of CO_2 to CO_{ad} on this catalyst is supported by the fact that also in (CO-free) CO_2 reformate CO_{ad} saturation coverage is reached. In the kinetic experiment, the CO selectivity reached a value of 100%. In total, the CO_{ad} band intensity correlates with the selectivity value, therefore CO_{ad} blocking of active sites is held responsible for the prevention of CO_2 methanation.

In contrast, on the Ru/zeolite catalyst, such correlation was not observed. At very low CO concentration (100 ppm) and in the absence of CO_2, the CO_{ad} band intensity is only 6 % of the saturation value obtained under normal reaction conditions (0.6 kPa CO, rest H_2). The same CO_{ad} band intensity and hence the same CO_{ad} coverage was obtained also in the presence of CO_2 (15.5 kPa CO_2). In this case, the blocking mechanism can not explain the experimental finding of a very high selectivity for CO methanation. Instead, the high selectivity is attributed to an inherently low activity of the Ru/zeolite catalyst for CO_2 methanation, which was tentatively attributed to the very small size of the Ru nanoparticles on the catalyst [18].

The proposed mechanism fully explains the high selectivity of the Ru/zeolite in practical applications, where the Ru/zeolite catalyst shows complete CO removal (<10 ppm) with negligible CO_2 methanation, whereas for the Ru/Al_2O_3 catalyst CO_2 methanation will start to contribute as soon as the CO partial pressure / coverage drops below a critical value.

References

[1] W. Lubitz, W. Tumas, Chem.Rev. 2007, 107 3900-3903.

[2] S. Kawatsu, J.Power Sources 1998, 71 150-155.

[3] D. R. Palo, R. A. Dagle, J. D. Holladay, Chem.Rev. 2007, 107 3992-4021.

[4] W. Vielstich, in Encyclopedia of Electrochemistry - Interfacial Kinetics and Mass Transport ,Vol. 2, (Eds.: A. J. Bard, M. Stratmann, E. J. Calvo), VCH, Weinheim 2003.

[5] J. R. Ladebeck, J. P. Wagner, in Handbook of Fuel Cells - Fundamentals Technology and Applications ,Vol. 3, (Eds.: W. Vielstich, A. Lamm, H. A. Gasteiger), Wiley, Chichester 2003, p. pp. 190-201.

[6] J. R. Rostrup-Nielsen, K. Aasberg-Petersen, in Fuel Cell technology and applications ,Vol. 3, (Eds.: W. Vielstich, H. A. Gasteiger, A. Lamm), Wiley, Chichester 2003, p. pp. 159-176.

[7] T. Inui, M. Funabiki, Y. Takegami, Ind.Eng.Chem.Prod.Res.Dev. 1980, 19 385-388.

[8] M. B. I. Choudhury, S. Ahmed, M. A. Shalabi, Appl.Catal.A 2006, 314 47-53.

[9] A. Rehmat, S. S. Randhava, Ind.Eng.Chem.Prod.Res.Dev. 1970, 9 512-515.

[10] M. Echigo, T. Tabata, J.Chem.Eng.Japan 2004, 37 75-81.

[11] M. Krämer, M. Duisberg, K. Stöwe, WF. Maier, J.Catal. 2007, 251 410-422.

[12] P. Panagiotopoulou, D. I. Kondarides, X. E. Verykios, Appl.Catal.B 2009, 88 470-478.

[13] M. Krämer, K. Stöwe, M. Duisberg, F. Müller, M. Reiser, S. Sticher, WF. Maier, Appl.Catal.A 2009, 369 42-52.

[14] A. R. Dagle, Y. Wang, G.-G. Xia, J. J. Strohm, J. Holladay, D. R. Palo, Appl.Catal.A 2007, 326 213-218.

[15] S. Scirè, C. Crisafulli, R. Maggiore, S. Minico, S. Galvagno, Catal.Lett. 1998, 51 41-45.

[16] G. A. Mills, F. W. Steffgen, Catal.Rev.Sci.Eng. 1974, 8 159-210.

[17] S. Eckle, Y. Denkwitz, R. J. Behm, J.Catal. 2010, 269 255-268.

[18] Eckle, S., Anfang, H.-G., and Behm, R. J. What drives the selectivity for CO methanation in the methanation of CO_2-rich reformate gases on supported Ru catalysts? Applied Catalysis A: General . 2010., submitted