

Experiment Report Form



Experiment title: Structural and chemical properties of Ru/Zeolite for the Selective Methanation of CO during reaction and their influence on the catalyst activity and selectivity	Experiment number: CH 3122	
Beamline: BM26A	Date of experiment: from: 25 Jun 2010 to: 01 Jul 2010	Date of report: 01.03.2011
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Report:

The selective methanation of CO in CO₂ excess represents a promising technique for the fine purification of H₂ rich feed gases for PEM Fuel Cells. Whereas Ru/Al₂O₃ catalysts show only a low selectivity at low CO partial pressures, Ru/zeolite supported catalysts are highly selective even at low CO concentrations. We proposed that very small Ru nanoparticles (NP), as expected for a zeolite catalyst, must be responsible for this behaviour, however, their particle size could not be determined by TEM and XRD.

Ru/zeolite catalysts with 2.2wt.% / 3.6wt.% were investigated in-situ by XAS spectroscopy in idealized gas atmospheres (0.6 kPa CO, 3 kPa N₂, balance H₂) at 190°C until the coordination parameters did not change anymore. The data evaluated with XDAP, the reference were calculated by FEFF 8.1 and calibrated to measured references.

The k³ weighted chi functions from the Ru/zeolite catalysts are displayed in the left part of Fig. 1, the right part show the resulting Fourier transforms. The prominent Ru-Ru signal at ~2.7 Å indicates that the particles are essentially metallic under steady-state conditions, although EXAFS data recorded prior to the experiment revealed that the Ru NPs are oxidic (Ru-O: 1.97 Å), however, they are reduced within 2 min after exposure to the reaction gas.

The EXAF spectra could be fitted with a single Ru-Ru shell. The result of metallic Ru NPs is compatible with previous findings in *in situ* DRIFTS measurements, which yielded vibrational frequencies for adsorbed CO similar to those characteristic for CO_{ad} on metallic Ru^{1;2}.

The Ru-Ru coordination number (CN), obtained by fitting the first shell to the Ru foil reference (see Fig. 1), can be directly correlated to the mean particle size of the Ru NPs³. Table 1 summarizes the structural parameters. Spectra recorded at 190°C showed a slightly smaller Ru-Ru bond length (~2.67 Å compared to 2.70 Å for bulk Ru), indicative of a contraction of the Ru lattice in the very small Ru NPs. The Ru CN value increases with increasing catalyst loading as expected for increasing Ru particle sizes (0.9 nm at 2.2 wt.% and 1.6 nm at 3.6 wt.%). The very small Ru particle size supports our proposal that most of the Ru NPs of the 2.2 wt.% Ru/zeolite catalyst are located in the pores (0.8 – 0.9 nm) of the zeolite². For the catalysts with higher Ru loading (3.6 wt.%), we suggest that the larger mean particle sizes results mainly from a higher fraction of larger particles present on the outer surface, in addition to the very small Ru NPs in the pores. Correlation with kinetic results show, that the CO methanation selectivity is particle size dependent.

Table 1: structural parameters of the different Ru/zeolites catalysts.

Catalyst	Coordination number	Debye Waller factor / 10^{-3} \AA^2	Distance / Å	E_0 /eV	particle size / nm
2.2wt.%	6.71 ± 0.21	6.6 ± 0.41	2.7 ± 0.007	6.1 ± 0.22	0.9
3.6wt.%	8.31 ± 0.24	7.7 ± 0.42	2.67 ± 0.007	7.1 ± 0.21	1.62
125°C/2.2wt.%	7.79 ± 0.21	7.2 ± 0.41	2.7 ± 0.007	6.1 ± 0.22	1.4
465°C/3.6wt.%	6.95 ± 0.24	7.7 ± 0.42	2.67 ± 0.007	5.1 ± 0.21	1.62

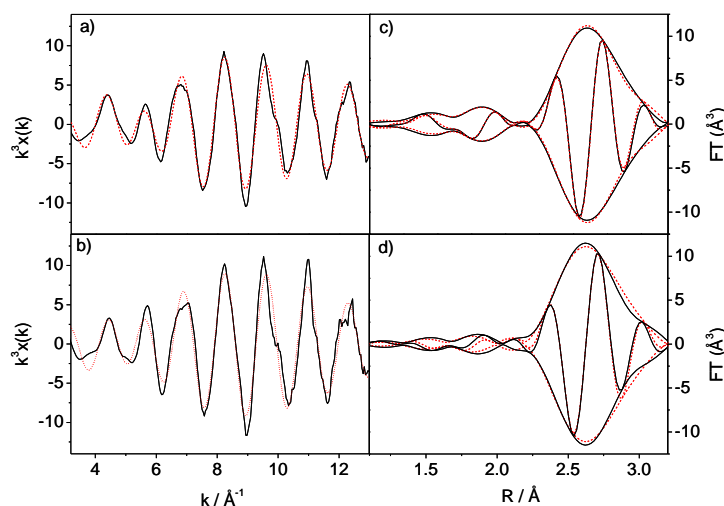


Fig. 1: left panels: k^3 weighted chi function, right panels: k^3 corresponding Fourier transform (k^3 -weighted, $3.2 < k < 13.0 \text{ \AA}^{-1}$) of (a), (c): 2.2 wt.% Ru/zeolite, (b), (d) 3.6 wt.% Ru/zeolite.

Evaluation of EXAFS spectra of catalysts calcined at different temperatures resulted in a particle size of ~1 nm (465°C calcined catalyst) and ~1.4 nm (125°C calcined catalyst). From previous kinetic measurements we know, that the catalyst calcined at the highest temperature showed the highest CO methanation selectivity (particle size dependent), a phenomenon ascribed as oxidative disruption of Ru bonds, which results in a redispersion of particles. These small nanoparticles inherit a low CO₂ methanation activity compared to the larger ones. A publication on these results is in preparation.

References:

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2. Eckle, S., Anfang, H.-G., and Behm, R. J., *Appl. Cat. A: General*, 391 (211) 325.
3. A.M. Karim, V. Prasad, G. Mpourmpakis, W.W. Lonergan, A.I. Frenkel, J.G. Chen, D.G. Vlachos, *J. Am. Chem. Soc.* 191 (2009) 12230.