Dynamical Properties of a Ru/MgAl₂O₄ Catalyst during Reduction and Dry Methane Reforming

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ABSTRACT: Combined in situ small- and wide-angle X-ray scattering (SAXS/WAXS) studies were performed in a new laboratory setup to investigate the dynamical properties of a ruthenium/spinel (Ru/MgAl₂O₄) catalyst, *w*(Ru) = 4 wt %, during the reduction and subsequent dry methane reforming. The Ru particles in the fresh catalyst sample were found to be partially oxidized. High-resolution transmission electron microscopy (HRTEM) indicated a coexistence of pure Ru and RuO₂ nanoparticles. Reduction in hydrogen occurred at a temperature between 373 and 393 K. The mean particle diameter as refined from SAXS of the size regime attributed to scattering from Ru/RuO₂-particles decreases slightly by about 0.2 nm during the reduction. Dry methane reforming experiments were performed in a temperature interval from 723 to 1023 K by applying a gas mixture of carbon dioxide and methane in molar ratio of 3:1. The catalyst did not show any deactivation during the experiment of overall 32 h, indicated by stable turnover frequencies for methane. The mean Ru-particle diameter remained constant during the dry methane reforming experiments, revealing a high sintering stability of the Ru/MgAl₂O₄ catalyst.

INTRODUCTION

Methane reforming with carbon dioxide yields a synthesis gas with a molar ratio of H₂/CO = 1 and is an ideal feedstock for various large-scale processes such as Fischer–Tropsch, hydroformylation, and synthesis of methanol.^{1–3}

However, the obtained H₂/CO ratio is in practice less than 1 because H₂, produced by dry methane reforming, reacts with CO₂ in the reverse water gas shift reaction (RWGS) to form water and carbon monoxide.^{4–6}

H₂/CO ratios close to 1 are only obtained at high temperatures where water produced by the RWGS reacts in the steam reforming reaction to yield CO and H₂.

Many transition metals such as Ni, Ru, Rh, Pd, Ir, and Pt^{7–10} have been found to show good catalytic activity for the methane reforming reaction. Although Ni-based catalysts are commercially more interesting due to low price,¹¹ their main drawback is that Ni catalysts form carbon at milder conditions than those where most of the active noble metals can be used.⁸ The doping of Ni catalysts with small amounts of Ru was reported to suppress carbon formation.^{12,13} Ru and Rh were reported to

be the most active catalysts for the methane reforming reaction,^{8,9,14} and this was confirmed by first-principle calculations.¹⁵

The choice of the support material also influences the catalyst performance, but it is controversial whether the support actively influences the reaction pathway^{4,16,17} or only the dispersion of the metal nanoparticles.¹⁰ Moreover, the impact of the metal dispersion on the activity is contentious. Correlations between metal particle dispersion and the activity were reported by Jones et al.¹⁵ and Wei and Iglesia,¹⁸ suggesting structure sensitivity of the methane reforming reaction. Mark and Maier reported the activity to be independent of the dispersion and exclusively related to the accessible metal particle surface area.¹⁰

Irrespective of the assumption of whether solely the dispersion or the accessible metal surface area affects the activity and which influence the support might have on the reaction pathway, it is essential that highly active and long-term stable dry methane reforming catalysts exhibit, besides a low affinity for carbon formation, only a marginal tendency of particle growth to retain its nanostructure.

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This Article is focused on the dynamical changes of a 4 wt % Ru/MgAl₂O₄ catalyst during reduction and subsequent dry methane reforming to understand changes such as phase transitions and particle growth due to sintering in connection with the gas atmosphere and sample temperature. A suitable technique to resolve these changes is combined in situ small- and wide-angle X-ray scattering, small-angle X-ray scattering (SAXS) to follow the particle growth and wide-angle X-ray scattering (WAXS) to detect phase transitions and crystalline growth. Additionally, online mass spectroscopy of the product gas enables relating these changes to variations in the methane conversion level.

■ EXPERIMENTAL SECTION

Experimental Setup. Simultaneous in situ SAXS/WAXS was performed using a laboratory pinhole camera setup with sample-to-SAXS detector distances of 1494 (short geometry) and 4679 (long geometry) mm covering a q -range of $0.002 < q < 0.45 \text{ \AA}^{-1}$ by using Mo $K\alpha$ $\lambda = 0.7107 \text{ \AA}$ in the short and Cu $K\alpha$ radiation $\lambda = 1.5418 \text{ \AA}$ in the long geometry. SAXS patterns were acquired with a 2D “Gabriel” type gas detector¹⁹ and WAXS patterns with an image intensified Gemstar 125 CCD camera mounted 30° off-axis to the direct beam to avoid shadowing the SAXS. The 125 mm CCD scintillator screen permits in that setup the resolution of a q -range from 2 to $6.5 \text{ \AA}^{-1}$ by using Mo $K\alpha$ radiation. The instrumental resolution of the CCD camera was determined from powder diffraction of a silicon standard (NIST SRM 640c) and is on the order of $\Delta q/q = 4 \times 10^{-3}$.

Heating experiments were performed in a special designed in situ cell, which was described in detail previously.²⁰ The cell was adapted to the laboratory pinhole camera with modified X-ray windows to cover the wide-angle scattering and a new designed heater permitting sample temperatures in an interval of 298–1073 K.²¹ Constant gas flows were applied to the sample using a gas system including a mass flow controller. The product gas was monitored by a quadrupole mass spectrometer (Balzers ThermoStar GSD 300) on the outlet of the in situ cell.

Transmission Electron Microscopy. High-resolution transmission electron microscopy (HRTEM) micrographs were acquired with a JEOL 3000 F microscope with an acceleration voltage of 300 kV of fresh catalyst samples. For the HRTEM studies, the 4 wt % Ru/MgAl₂O₄ catalyst was dispersed in ethanol with a dilution of 1:1500 using ultrasonic treatment. Ten microliters of this dispersion was coated on a 400 mesh holey carbon grid.

Bright-field transmission electron microscopy (BF TEM) and high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were performed with a FEI Titan 80-300 ETEM, equipped with in situ capabilities at 300 kV.²² For the in situ HAADF-STEM, the sample was heated to 773 K in 1.3 mbar H₂, and the samples were dry dispersed on Au TEM grids.

Catalyst Preparation. The 4 wt % Ru/MgAl₂O₄ catalyst was prepared by incipient wetness impregnation of MgAl₂O₄ (45 m² g⁻¹) support with an 8.1 wt % Ru(NO)(NO₃) aqueous solution. The sample was dried in air at 353 K for 4 h. Subsequently, the catalyst was reduced in pure hydrogen at 873 K at a gas pressure of 1 bar for 4 h and afterward aged for 225 h at 1103 K in H₂O/H₂ (1:1) at 31 bar to achieve a stable catalyst.²⁷

Reduction and Dry Methane Reforming Experiments. The 4 wt % Ru/MgAl₂O₄ catalyst sample, of approximately 6

mg, was inserted in a 0.7 mm quartz capillary, embedded between two glass wool plugs, and mounted gastight between two Swagelok fittings using graphite ferrules. The in situ reduction experiments were performed in a constant gas flow of 2 mL min⁻¹ hydrogen (alphagaz 1, Air Liquide, >99.999 vol %) at standard temperature and pressure (STP). Three combined SAXS/WAXS patterns were acquired at 298, 393 K, and in an interval from 473 to 873 K in steps of 100 K.

For the methane reforming experiments, a catalyst sample of 0.8 mg was reduced in pure hydrogen for 1.5 h at 723 K. Subsequently, a constant flow of 15 mL min⁻¹ pre-mixed gas composed of 25 vol % CH₄, 74 vol % CO₂, and 1 vol % Ar was applied; Ar was used as an internal standard to trace fluctuations of the sensitivity changes from the quadrupole mass analyzer due to variations of the pressure. The sample was heated in an interval from 723 to 1023 K, afterward cooled to 723 K, and heated again to 1023 K. The temperature was increased and decreased gradually in steps of 50 K during these experiments. At each temperature, three combined SAXS/WAXS patterns were acquired to follow the dynamical properties of the catalyst at different conversion levels.

The approximately 1 order of magnitude larger amount of catalyst for the in situ reduction study as compared to the methane reforming experiments was chosen for convenience, because it was easier to position the longer catalyst bed correctly in the X-ray beam. In contrast to the in situ methane reforming, where experiments with small amounts of catalyst are indispensable to work outside of mass transport limitations inside the catalyst bed, the amount of catalyst for the in situ reduction experiments has a secondary role. Even if all Ru in the approximately 6 mg of catalyst would be oxidized, the selected hydrogen flow would allow a complete reduction in less than 2 s, and this is far below the time resolution of the simultaneous SAXS/WAXS data acquisition of 1800 s for one pattern in the specific experiment.

Data Treatment. Data Transformation. The 2D SAXS data were azimuthally averaged using the Fit2d software package from ESRF.²⁸ The SAXS data of the fresh catalysts sample, acquired in both geometries, were scaled to interpolate intensities in the overlapping angular region, calculating the quotient for the individual data points and using the mean to determine a scaling factor.

To transform the WAXS data to 1D diffraction patterns, a silicon standard (NIST SRM 640c) was measured in the sample position before the experiment. From a fit of the silicon powder rings, the camera position relative to the sample was determined, and a matrix was generated relating each detector pixel to a certain scattering angle. Subsequently, this matrix was applied for data binning of the 2D powder pattern of the Ru/MgAl₂O₄ catalyst.

For clarity, the scattered intensity I is plotted in all figures as a function of the scattering vector q , which is related to the scattering angle θ and X-ray wavelength λ by $q = 4\pi \sin \theta / \lambda$ in units of $\text{\AA}^{-1}$.

SAXS. At sufficient low scattering vectors, $qR \ll 1$, the scattered intensity $I(q)$ can be approximated by Guinier's law:²⁹

$$I(q) = G \exp\left(\frac{q^2 R_g^2}{3}\right) \quad G = N r_e^2 \Delta \rho_e^2 V^2 \quad (4)$$

where R_g is the radius of gyration in terms of electron density of the particle in analogy to the radius of inertia in classical mechanics, N is the number density of primary particles, r_e is

the classical electron radius, $\Delta\rho_e$ is the average electron density difference between particles and matrix, and V is the average particle volume. In case of spherically symmetric particles, the radius of gyration is related to the radius by $R_g = (3/5R)^{1/2}$.^{29,30} At high scattering vectors, $qR \gg 1$, the scattered intensity decays with power law behavior scaling with the average surface area S of the primary particles:

$$I(q) = Bq^{-P} \quad B = 2\pi N\Delta\rho_e^2 S \quad (5)$$

where P is the power law coefficient. For sharp and smooth interfaces, $I(q)$ decays with $P = 4$, also known as Porod's law.²⁹ Deviations from Porod's law can be ascribed to surface fractals, $3 < P_i < 4$, diffuse interfaces, $P > 4$, and mass fractals, $1 < P < 3$.^{31,32}

The local scattering laws, described in eqs 4 and 5, can be combined to approximate scattering curves of n non interrelated structural levels with the unified approach proposed by Beaucage et al.:^{32,33}

$$I(q) = \sum_{i=1}^n G_i \exp\left(-\frac{q^2 R_{g,i}^2}{3}\right) + B_i \left(\frac{q}{(\text{erf}(qkR_{g,i}/\sqrt{6}))^3} \right) - P_i \quad (6)$$

where erf is an error function. The invariant Q , a quantity independent of particle shape and size distribution, can be obtained by integration of the scattered intensity over the complete q -range for a particular structure.^{29,33}

$$Q = \int_0^\infty q^2 I(q) dq = 2\pi^2 N \Delta\rho^2 V \quad (7)$$

The particle shape-independent average surface to volume ratio can be estimated from the ratio of the Porod prefactor B and the invariant:³³

$$\frac{\pi B}{Q} = \frac{\langle S \rangle}{\langle V \rangle} \quad (8)$$

TEM. The TEM micrographs were utilized to get an estimate of the particle size distribution (PSD) and the dispersion of the Ru catalyst particles. The particles were assumed to have a log-normal distribution:

$$f(d) = \frac{1}{d\sigma\sqrt{2\pi}} \exp\left\{-\frac{[\ln(d) - \mu]^2}{2\sigma^2}\right\} \quad (9)$$

where d is the particle diameter, μ is the mean, and σ is the standard deviation. The dispersion D of the catalyst particles in case of spherical symmetry can be calculated by:

$$D = \frac{6v \sum n_i d_i^2}{s \sum n_i d_i^3} \quad (10)$$

with the atomic volume and surface area v and s .³⁴ Under the assumption that the particle surface exhibits preferentially facets with the lowest surface energy, in case of ruthenium, the Ru(001) facets, D can be estimated from PSD and the lattice parameter c by:¹⁵

$$D = \frac{\sum n_i d_i^2}{\sum n_i d_i^3} \cdot 3 \cdot c \quad (11)$$

RESULTS AND DISCUSSION

Characterization of a Fresh Catalyst Sample. Fresh catalyst samples were characterized before the in situ reduction and dry reforming experiments. WAXS was used to identify the sample phases, BF TEM, HRTEM, and HAADF-STEM to get an estimate of particle shapes and sizes for the posterior data analysis, and SAXS to determine the initial particle sizes and surface to volume ratio.

The fresh catalyst sample consists of hexagonal Ru (space group no. 194: $P6_3/mmc$), tetragonal RuO_2 (space group no. 136: $P4_2/mnm$), and cubic MgAl_2O_4 (space group no. 227: $Fd-3m$). Figure 1 illustrates the WAXS pattern of a fresh catalyst

Figure 1. WAXS pattern of a fresh Ru/ MgAl_2O_4 catalyst at 298 K (black) and simulated contributions for the MgAl_2O_4 -support (red), RuO_2 (green), and Ru (blue). The contributions for the RuO_2 and Ru are simulated assuming a crystallite size of 3 nm.

with the simulated contributions of Ru- (blue), RuO_2 - (green), and MgAl_2O_4 -phase (red). The simulations were performed taking the instrumental resolution of the CCD detector refined from a Si standard (NIST SRM 640c) into account; the peak profiles were approximated by Voigt functions. The contributions of the Ru and RuO_2 -phases were simulated assuming a crystallite size of 3 nm. As the mean crystallite size of the MgAl_2O_4 support is assumed to exceed the maximum resolvable size of 18 nm of the CCD detector in the used experimental geometry, only the instrumental broadening refined from a Si standard was taken into account to simulate the contribution of the MgAl_2O_4 -phase.

The WAXS pattern does not show any distinct peaks for Ru and RuO_2 ; in fact, very broad reflections due to size effects were observed that are superimposed by peaks of the MgAl_2O_4 support. Simulations of theoretical scattering patterns with different Ru-crystallite sizes and a metal loading similar to that of the studied catalyst and taking the instrumental resolution into account reveal that the crystallite size has to be above 6 nm to resolve a distinct peak from the strongest Ru-reflection. The presence of RuO_2 in the fresh catalyst can be explained by the exposure to air between the sample preparation and the experiments.

Figure 2a and b shows BF TEM micrographs of the 4% wt Ru/ MgAl_2O_4 , as prepared, at different magnifications. Additional HRTEM images were acquired to obtain information about the particle morphology and from the lattice fringes about the sample phases; see Figure 2c. Because the discrimination of the larger Ru/ RuO_2 particles from the support was observed to be difficult, HAADF-STEM micrographs were acquired. Figure 2b and d shows BF TEM and HAADF-STEM, scaled to the same size. The Ru/ RuO_2

Figure 2. Bright-field TEM with different magnifications (a and b), HRTEM (c), and HAADF-STEM (d) of the 4% wt Ru/MgAl₂O₄ catalyst, as prepared.

particles appear bright in the HAADF-STEM images, while the MgAl₂O₄ support remains dark.

The Ru/RuO₂ catalyst particles of the as-prepared 4% wt Ru/MgAl₂O₄ showed close to spherical morphology, as observed by HRTEM (see Figure 2c) and by HAADF-STEM (see Figure 2d), while the MgAl₂O₄ support particles showed a more irregular shape (see Figure 2a). For the SAXS data analysis of both Ru nanoparticles and the MgAl₂O₄ support, we assumed spherical particle shapes. Although irregular shaped particles were noted in case of MgAl₂O₄, the assumption of spherical particle symmetries is expected to hold.

The PSD of the Ru/RuO₂ particles was determined by measuring 884 individual nanoparticles in the HAADF-STEM micrographs. To compare HAADF-STEM and BF TEM for the determination of the Ru/RuO₂ size distribution, a spot test was performed measuring 121 metal nanoparticles in the BF TEM micrographs. The size distributions of the Ru/RuO₂ particles, derived from analysis of micrographs acquired with both techniques, are shown in Figure 3. The PSD of the support was estimated from measuring 115 random distances over the MgAl₂O₄ particles in low magnification BF TEM micrographs.

The sizes of the small Ru/RuO₂ particles, obtained by both techniques, seem to obey a log-normal distribution. However, the log-normal distribution breaks down for the description of the larger Ru/RuO₂ particles. The parameters from a least-squares fit of eq 9, together with the mean particle diameters $\bar{d}$ calculated from the fit parameters and directly from the measured particle sizes, are listed in Table 1.

The mean Ru/RuO₂ particle diameter determined from the fit parameters of a log-normal distribution on the PSD obtained from HAADF-STEM was about 0.4 nm larger than the mean particle diameter achieved from BF TEM. A 0.8 nm larger mean particle diameter was obtained from HAADF-STEM when the directly measured particle sizes were used to calculate the mean particle diameter. Because the large Ru/RuO₂ were only poorly described by the log-normal size distribution, the

Figure 3. Particle size distribution (PSD) derived from HAADF-STEM (red Δ) and BF TEM (O) image analyses of a fresh Ru/MgAl₂O₄ catalyst plotted together with the log-normal fits (solid lines).

Table 1. Mean Particle Diameter Calculated from the Parameters from a Fit of the Log-Normal Distribution and Directly from the Measured Particle Sizes

technique	$\bar{d}$ (log-n. dist.) [nm]	$\bar{d}$ (direct) [nm]
HAADF-STEM	2.3 ± 0.9	2.7 ± 1.4
BF TEM	1.9 ± 0.8	1.9 ± 0.9

direct measured particles sizes were utilized to calculate the Ru dispersion using eq 11 with a lattice parameter of $c(\text{Ru}) = 4.282$ Å. We obtained a Ru dispersion of $D_{\text{HAADF}} = 0.28$ from analysis of the HAADF-STEM micrographs and $D_{\text{BF}} = 0.45$ from BF TEM. The estimated catalyst turnover frequencies (TOF) during the in situ methane reforming experiments would therefore be about 40% underestimated using the dispersion determined with BF TEM. This strongly emphasizes the advantage of using HAADF-STEM for the investigation of such catalyst systems, because this technique allows distinguishing the larger catalyst nanoparticles from the support and therefore taking them into account for the determination of the particle size distribution. The mean particle diameter for the support particles was determined directly from the measured distances as $d(\text{MgAl}_2\text{O}_4) = 39.0 \text{ nm} \pm 15.4 \text{ nm}$.

From the HRTEM images, atomic distances matching Ru, RuO₂, and MgAl₂O₄ crystallite planes were refined, see Table 2,

Table 2. Atomic Distances Extracted from HRTEM Images of a Fresh Ru/MgAl₂O₄ Catalyst

index	theoretical interplanar distance (Å)	measured interplanar distance (Å)
Ru(101)	2.08	2.08
Ru(100)	2.42	2.38
RuO ₂ (200)	2.25	2.28
RuO ₂ (101)	2.54	2.56
MgAl ₂ O ₄ (311)	2.44	2.45
MgAl ₂ O ₄ (220)	2.86	2.88
MgAl ₂ O ₄ (111)	4.67	4.78

confirming the phase composition observed from WAXS. HRTEM of the catalyst nanoparticles with spherical morphology indicates a coexistence of pure Ru and RuO₂ particles in the fresh sample. Partial oxidation of nanostructured Ru catalysts may occur at temperatures as low as room temperature, and the degree of oxidation increases with specimen temperature.²³ Oxidation studies on RuO₂/Ru bilayers²⁴ and Ru particles with mean crystallite sizes in the micrometer range^{25,26} revealed the oxidation of Ru to be a

thermally activated process, limited by oxygen diffusion through RuO₂. The limitations by oxygen diffusion are consistent with observations reported by Jakobsen et al., who recently observed Ru/RuO₂ core/shell-particles in a fresh Ru/ZrO₂ catalyst sample.²⁷ At the current stage, we are not able to give an explanation for the coexistence of the pure Ru and RuO₂ particles in our fresh catalyst sample, and a detailed study of this phenomenon is beyond the scope of this Article. However, we believe that the complete oxidation of some of the Ru particles might be explained by a size effect. Whereas Jakobsen et al. reported a mean Ru particle diameter of 3.5 nm for a fresh catalyst sample, we observe a mean particle diameter of 2.7 nm. Considering the oxidation of Ru to be a diffusion-limited process, a complete oxidation of smaller Ru nanoparticles would be facilitated.

The best description of the SAXS data, acquired for a fresh catalyst sample in short and long geometry at 298 K, was obtained with a unified equation comprising two structural levels for scattering from the MgAl₂O₄ support (second and third terms in eq 12) and the Ru catalyst particles (fourth and fifth terms). The first term describes power law scattering from large aggregates, close to the limit of resolution.

$$I(q) = B_0 q^{-4} + G_1 \exp\left(-\frac{q^2 R_{g,1}^2}{3}\right) + B_1 \left(\frac{q}{(\operatorname{erf}(q R_{g,1}/\sqrt{6}))^3}\right)^{-P_1} + G_2 \exp\left(-\frac{q^2 R_{g,2}^2}{3}\right) + B_2 \left(\frac{q}{(\operatorname{erf}(q R_{g,2}/\sqrt{6}))^3}\right)^{-P_2} \quad (12)$$

The power law coefficients P_1 and P_2 were fixed at a value of 4, corresponding to smooth particle interfaces. Least-square fitting leaving P_1 free led only to a slight deviation from the value of 4, indicating a marginal interface roughness of the MgAl₂O₄-support particles. Fits with P_2 as a free parameter were observed to be unstable because of the low intensity at high angles, where the power law scattering specific to the Ru/RuO₂ particle surface is strongly influenced by the background subtraction. Small fluctuations of the scattered intensity can lead to over- or underestimation of the background and thereby to an under- or overestimation of the surface to volume ratio. Figure 4 illustrates the previously described least-squares fit of eq 12 on data acquired at 298 K.

The mean particle diameter of the two size regimes was determined from the fitted radius of gyration by $d_{\text{SAXS}} = 2R = 2(5/3)^{1/2} R_g$. Particle diameters for both size regimes and the volume averaged particle diameters are compared in Table 3.

The mean particle diameters determined from SAXS and the diameter from HAADF-STEM and BF TEM show reasonable agreement. We conclude that the size regime at low q can be attributed mainly to scattering from the MgAl₂O₄ support, and the regime at high q to scattering mainly from Ru catalyst particles.

In Situ Reduction. In situ reduction experiments and dry methane reforming experiments were carried out in a short camera geometry to resolve only the q -range where scattering of the Ru-particles contributes to the SAXS data, because changes of the support material morphology at the chosen experimental conditions were not expected. The reduction of RuO₂ occurred at temperatures below 393 K indicated by an

Figure 4. Overlapped SAXS data of a fresh catalyst sample acquired in both geometries at 298 K and fitted by the unified approach (red) with contributions of power law scattering from large aggregates (green), the Guinier- and the Porod-term for a size regime related to the support particles (blue), and respectively for the Ru particles (magenta).

Table 3. Particle Diameters Determined from SAXS with the Standard Errors Derived from the Least-Square Fits, from TEM for MgAl₂O₄ and from HAADF-STEM for the Ru Nanoparticles of a Fresh Catalyst Sample at 298 K

	d_{SAXS} (nm)	$D_{\text{electron microscopy}}$ (nm)
low q regime	49.7 ± 0.5	39.0
high q regime	3.4 ± 0.1	2.7

increase of the scattered intensity from the Ru- and correspondingly a decrease from the RuO₂-phase in WAXS (see Figure 5a and b), and this correlates with changes observed in the SAXS pattern at high q , in the size regime that is related to scattering of the Ru/RuO₂-particles (see Figure 5c). No further changes of the SAXS and WAXS patterns were observed at higher temperatures. The WAXS pattern acquired at 373 K during a second reduction experiment exhibits a scattered intensity of the Ru-phase similar to the WAXS pattern acquired at room temperature. During heating of this sample to 473 K, an increase in scattered intensity of the Ru-phase was observed in WAXS (see inset of Figure 5b). We conclude therefore that the reduction of RuO₂ starts in a temperature interval from 373 to 393 K.

Multiple peak fitting of all acquired WAXS patterns in a q -range from 2.1 to 3.4 Å⁻¹ was performed to follow the progress of the reduction and subsequent dry reforming reaction using the program Fityk.³⁵ The patterns were well described with six Lorentzian shaped peaks for the MgAl₂O₄ (220), (311), (222), (400), and the contributions of RuO₂ and Ru. The fitted Ru-peak mainly reflects the contributions of the Ru (101) reflection to the WAXS pattern, but simulations of the theoretical scattering patterns with particle sizes as determined by HAADF-STEM and SAXS show an overlap with the much weaker Ru (100) and (002) peaks. However, unconstrained peak fitting of the Ru (100) and (002) was not possible due to their relative low intensity and broad peaks. Contributions of the background over the limited q -range were assumed to be approximately constant and were therefore fitted with a straight line.

The center of the Ru (101) peak was fixed during the peak fitting and calculated from the ruthenium lattice parameters ($a = 2.7053$ Å, $c = 4.2820$ Å).³⁶ Shifts of the Ru (101) peak position due to sample annealing were taken into account by correcting the lattice parameters for linear thermal expansion

Figure 5. WAXS patterns acquired during two reduction experiments with different temperature steps (a) and (b) at 298 K (black line), 373 K (blue x), 393 K (green x), and 473 K (red line) and SAXS (c) at 298 K (x) and 393 K (red x).

using the polynomial reported by Shirasu et al.,³⁷ the best fits of patterns before and after reduction are illustrated in Figure 6.

The ratio of the integrated peak intensities of the Ru $\langle 101 \rangle$ and the MgAl_2O_4 $\langle 400 \rangle$ reflection, $I_{\text{Ru}} \langle 101 \rangle / I_{\text{support}} \langle 400 \rangle$, increased at temperatures between 298 and 393 K and remained constant at higher temperatures. This shows that the reduction of the RuO_2 -phase initiates and completes at temperatures below 393 K.

The SAXS data, acquired during the in situ experiments, were fitted using a unified equation comprising one size regime for the scattering Ru-particles and a term describing power law scattering of the MgAl_2O_4 support surface; a fit of the SAXS data at 298 K is shown in Figure 7. The surface to volume ratios of the Ru-catalysts particles were evaluated from eq 8, using the invariant calculated with eq 7.

The reduction was observed to be accompanied by a slight decrease of the Ru/ RuO_2 -particle diameter of 0.2 nm at temperatures below 473 K, from 3.4 ± 0.1 to 3.2 ± 0.1 nm. A similar trend was observed from a spot test of the particles diameter from in situ HAADF-STEM micrographs, acquired at 773 K in 1.3 mbar H_2 . The mean particle diameter was here determined to be around 2.6 nm, whereas the particle diameter of a fresh catalyst sample was determined to be 2.7 nm.

Figure 6. WAXS data (blue $\circ$) fitting with Lorentzian peak profiles before reduction (a) and after reduction at 393 K (b) with the fitted profiles of the MgAl_2O_4 support (—) and Ru (pink —).

Figure 7. SAXS data acquired in short geometries at 298 K and fitting with a unified approach (red) comprising power law scattering from the MgAl_2O_4 support particle surface (green) and the Guinier- and the Porod-terms for a size regime related to scattering from the Ru catalyst particles (blue).

The surface to volume ratio, determined from SAXS, increased in the same temperature interval from 5.0 to 5.3. Constant Ru-particle diameters and surface to volume ratios were obtained at higher temperatures, indicating the absence of sintering during heating in pure H_2 . The trend of the ratios of $I_{\text{Ru}} \langle 101 \rangle / I_{\text{support}} \langle 400 \rangle$ let us conclude that the complete reduction of RuO_2 occurs at temperatures below 393 K. Experiments with the same catalyst, but a different heating program, did not show any evidence of the reduction at temperatures up to 373 K, and we conclude that the reduction of the RuO_2 phase occurs in a temperature interval between 373 and 393 K. The reduction rate of unsupported RuO_2 is reported to be independent of the initial grain size and temperature and can begin at temperatures as low as 373 K after an induction period.²⁵ Temperature-programmed reduction (TPR) experiments of polycrystalline RuO_2 with a heating ramp of 2 K min^{-1} reported by Madhavaram et al.³⁸ showed that the reduction occurs promptly at a temperature of 391 K.

However, a variety of reduction temperatures observed from TPR measurements for supported RuO₂ particles can be found in the literature,^{5,9,12,39} ranging from 358 to 466 K, depending on metal–support interactions, catalyst loading, and heating ramp. The temperature interval where we observed the reduction of the RuO₂-phase agrees well with the temperatures reported for unsupported RuO₂. However, the variety of reported reduction temperatures suggests that the reducibility is influenced by interactions of the RuO₂ particles with the support. For a more accurate determination of the reduction temperature, powder diffraction experiments with a constant heating ramp on a Synchrotron facility could be performed, as shown for the reduction of NiO by Rodriguez et al.⁴⁰

The increase in SAXS intensity in a q -range where the Ru-particles contribute to the pattern can be explained by an increase in the average electron density difference $\Delta\rho^2$ because the electron density of RuO₂ is only around one-half of Ru. The slight decrease in the Ru-particle diameter might be explained by the following. Coexisting spherical Ru and RuO₂ particles, as observed by HRTEM, exhibited approximately similar diameters. Because of the difference in mass density, the RuO₂ particles will shrink around 25% during the reduction. Because the mean particle size from SAXS includes both Ru and RuO₂, a decrease in the mean particle diameter of only 0.2 nm is conceivable.

Dry Reforming Experiments. In situ dry methane reforming experiments were performed in a premixed gas containing CO₂/CH₄ in a ratio of 3:1. The premixed gas, with an excess of CO₂, was chosen from thermodynamic considerations. Carbon deposition on the metal catalyst particles occurs by decomposition of CH₄ and CO. Hence, a premixed gas with a lower CH₄ concentration will also show lower carbon formation rates. Dry methane reforming experiments were performed with a high weight hourly space velocity, WHSV = 1 250 000 cm³ g⁻¹ h⁻¹, to observe the intrinsic kinetics of the catalysts. CH₄ conversion levels only exceeded 20% of the thermodynamic equilibrium at temperatures above 923 K. Mass spectroscopy was performed to analyze the composition of the product gas. All signals detected in the mass spectra were normalized by the argon molecule peak to correct for time- and pressure-dependent fluctuations of the sensitivity from the quadrupole mass spectrometer. The CH₄ content was determined from the CH₃⁺ fragment peak ($m/z = 15$) because this signal can be related solely to methane and shows no cross correlations with other fragments from the product gas.

CH₄ turnover frequencies (TOF) were evaluated assuming every surface atom of the Ru-clusters to be an active center; however, this is not necessarily true considering observations made by Jones et al.¹⁵ and Wei and Iglesia,¹⁸ who reported a dependency of D_{Ru} on the turnover frequency. A plot of the turnover frequencies during the first and second heating cycles is shown in Figure 8.

H₂/CO ratios were determined from the molecule peaks of hydrogen (H₂⁺, $m/z = 2$) and the carbon monoxide (CO⁺, $m/z = 28$). The carbon monoxide molecule peak is cross correlated with the CO⁺ fragment peak from excess CO₂ in the product gas. Therefore, the ratio of the carbon dioxide molecule (CO₂⁺, $m/z = 44$) and fragment peak (CO⁺, $m/z = 28$) was determined before acquisition, and the data were corrected accordingly. The H₂/CO ratio increased during the sample heating from 0.21 at 723 K to 0.64 at 1023 K.

Mean Ru particle diameters, during the in situ dry methane reforming experiments, were evaluated from the SAXS data; see

Figure 8. Methane turnover frequencies during the first (○) and second heating cycles (red △) evaluated from the CH₃⁺ fragment peak ($m/z = 15$).

Figure 9. Ru particle diameters remained constant around 3.1 nm during sample heating and cooling.

Figure 9. Mean particle diameter for the Ru particles during the methane reforming experiment refined from the SAXS; the error bars represent the estimated standard error from the least-squares fit.

The turnover frequencies for CH₄ were observed to be stable during the complete experiment with an overall duration of 32 h. The CH₄ turnover frequency increased during the first sample heating from 0.4 s⁻¹ at 723 K to 14.0 s⁻¹ at 1023 K and followed the same trend during cooling and reheating. During the reheating, the TOF increased by less than 10% to 15.2 s⁻¹. The turnover frequencies during our in situ dry methane reforming experiments were in reasonable agreement with the TOFs, reported for similar catalysts in the literature.^{4,8,16,18} When the observed TOFs for the dry methane reforming are comparable to those reported in the literature, they are, however, significantly lower than those reported for methane reforming with steam. Jones et al.¹⁵ reported TOFs for steam reforming of methane of 1.1 and 19.9 s⁻¹ for Ru/ZrO₂ catalyst at 773 K with metal dispersion of 0.11 and 0.48. Jakobsen et al.²⁷ observed for a similar catalyst, with a metal dispersion of 0.25, at the same temperature a TOF of 11 s⁻¹. We obtained TOFs between 0.8 and 1.0 s⁻¹ during dry methane reforming at the same temperature. Rostrup-Nielsen and Hansen⁸ reported by a factor of 2–3 lower TOFs for methane reforming with CO₂ as compared to steam from experiments on a series of noble metal catalysts. The lower TOFs were attributed to higher CO partial pressures during reforming with CO₂, leading to higher CO coverage on the metal particle surface and thereby to a partial blocking of the active sites. Jakobsen et al.²⁷ reported that their experimentally observed results from studies of steam and CO₂ reforming of methane over Ru/ZrO₂ were described well by a kinetic model assuming partial blockage of the active sites by adsorbed CO and H. If we consider the by a

factor of 2–3 lowered activities for CO₂ reforming, reported by Rostrup-Nielsen and Hansen,⁸ and the TOF of 11 s⁻¹ for steam reforming at 773 K over a Ru/ZrO₂ catalyst with nearly similar metal dispersion, reported by Jakobsen et al.,²⁷ we would expect TOFs of 4 and 6 s⁻¹ during our CO₂ reforming at similar temperature. However, our experimentally observed TOF at similar temperature is a factor of 4–7 lower than expected from the TOF for steam reforming reported by Jakobsen et al.²⁷ One reason for the low TOFs observed here may be experimental uncertainties, that is, the comparable small amount of catalyst of 0.8 mg used in our in situ experiments resulting in weighing errors. The low TOFs may also be due to inhomogeneities of catalyst material, due to incipient wetness impregnation of MgAl₂O₄ pellets, or bypass of the gas might have a huge impact on the observed TOF. Finally, increase and stabilization of the catalyst activity at high temperature was previously observed to be important for the activity of noble metal catalysts at lower temperature,^{27,41} and this may also be the reason for the increase in activity observed here during the second measurement cycle. However, the main focus in this work is to follow the dynamics of catalysts in situ under conditions comparable to large-scale industrial processes and correlate changes in the catalyst activity to changes in the particle morphology, size distribution, and crystalline phase, rather than obtaining absolute numbers for the TOFs. Even if the obtained TOF during in situ experiments might deviate from those obtained under similar conditions in larger plug flow reactors at steady-state condition, they will still show the changes in the catalyst activity.

The temperature dependency of the reaction rate for CO₂ reforming is shown in Figure 10. The apparent activation

Figure 10. Temperature dependency of the reaction rate for CO₂ reforming plotted in an Arrhenius graph and straight line fit used to determine the activation energy.

energy for methane dissociation, E_a , estimated from the Arrhenius plot, was 75 ± 1 kJ mol⁻¹. The E_a determined from our experimental data during the dry reforming is lower than the ones reported in refs 18 and 23 of 96 and 102 kJ mol⁻¹, where either the measurements were carried out at conditions where there are no or only a few adsorbates on the Ru particle surface or they corrected for it.

From the stoichiometry of the dry methane reaction, one could expect a H₂/CO level close to 1. Deviation from this ratio can be explained by the RWGS.^{5–7} The H₂/CO ratio increases with the temperature, because water produced by the RWGS is consumed via steam reforming (3) to yield hydrogen and carbon monoxide.⁶ An indication for the RWGS in our experiments was observed by a water molecule peak in the mass spectrum (H₂O⁺, $m/z = 18$). However, the quantification of the water concentration in the product gas stream was not

possible because water condensates in the cold metal tubing connecting the mass spectrometer with the vent of the in situ cell.

The catalyst did not show any effect of deactivation, and this is in good agreement with the high sintering stability observed by SAXS and the low tendency of carbon deposition on Ru.⁸ BF TEM micrographs of the same catalysts sample, probed in a similar experiment, but with a different WHSV, did not show any indication for carbon whisker formation.

CONCLUSION

In this study, combined SAXS/WAXS was utilized to follow the dynamical changes of a 4% wt Ru/MgAl₂O₄ catalyst during reduction in pure hydrogen and subsequent dry methane reforming. The onset of the reduction of the RuO₂-phase during the in situ experiments in pure hydrogen was observed at a sample temperature below or equal to 393 K by increasing intensity of the Ru peaks in the WAXS. At the same temperature, an increase of the scattered intensity in the SAXS pattern was observed in a q -range related to scattering of the Ru-particles, and the mean particle size refined from SAXS was noted to decrease by around 0.2 nm. The particle diameter was found to remain stable during repeated methane reforming experiments, thus preserving the nanostructure. The high sintering stability of the Ru catalyst nanoparticles was also reflected in stable methane conversion levels. No catalyst deactivation was observed at any time and temperature during the whole experiment. The apparent activation energy for methane dissociation at the experimentally applied conditions was determined to be 75 ± 1 kJ mol⁻¹. The experiments showed the applicability of the instrumental setup to test catalysts under conditions comparable to large-scale processes. It permits simultaneous in situ determinations of changes in the crystalline structure, particle morphology, and reactivity of nanoscale catalysts to resolve their correlations with the sample temperature and reactant gas composition.

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Notes

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