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Structural and Catalytic Properties of Ag- and Co₃O₄-Impregnated Strontium Titanium Ferrite SrTi_{0.7}Fe_{0.3}O_{3-δ} (STF) in Methanol Steam Reforming

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Abstract

The catalytic performance of Ag- and Co_3O_4 -impregnated strontium titanium ferrite ($\text{SrTi}_{0.7}\text{Fe}_{0.3}\text{O}_{3-\delta}$, STF) has been assessed in methanol steam reforming as a test reaction and accordingly correlated with spectroscopic and structural characterization after each step of a *catalytic cycle* including pre-oxidation and pre-reduction. After pre-reduction in hydrogen at 400 °C, metallic silver and oxidized Co in the form of Co_3O_4 are present. As for catalysis, it was observed that both Ag and Co_3O_4 are strongly promoting the methanol chemistry with respect to pure STF already at low temperatures (230 °C for both materials). As a consequence, the selectivity towards carbon monoxide is strongly enhanced in comparison to pure STF. On Co_3O_4 -STF, the catalytic profile is basically dominated by a temperature-dependent complex interplay between methanol steam reforming, methanol dehydrogenation and the water-gas shift equilibrium. The results also prove that despite the obvious inadequacy of H_2 -prereduced Ag-STF to act as a highly CO_2 -selective steam reforming catalyst, a potential use as a low-temperature fuel cell anode material might be envisioned. It is shown that Ag effectively lowers the activation barrier for the total oxidation of methanol to CO_2 , if the reaction is started from the fully pre-oxidized catalyst. This is explained by fast and efficient supply of lattice oxygen from STF toward Ag via the perovskite-metal phase boundary, which is expected to prevail if Ag-STF is used as SOFC anode material with continuous electrochemical supply of lattice oxygen.

1. Introduction

The methanol or hydrocarbon steam reforming reactions are excellent ways to achieve high hydrogen-to-carbon ratios and accordingly obtain large quantities of hydrogen in the product feed.^{1,2} As catalysts, a large number of materials, usually metals supported on various oxides, are employed.³ The choice is thereby related to the specific requirements of methanol or hydrocarbon activation on the metal and water usually on the oxide or at special interfacial sites. As for methanol steam reforming, the technically used catalyst is a Cu/ZnO material stabilized with alumina.¹ Also other supporting oxides apart from ZnO, such as ZrO₂, have been successfully used.² Here, while Cu acts as a material for methanol activation, ZnO and/or ZrO₂ is at least partially responsible for water activation through reversible surface hydroxylation.⁴ Hydrocarbon, *e.g.* methane, activation usually requires metals capable of C-H bond breaking, such as Pt group metals or Ni, which subsequently yield H₂ or CO-rich H₂-CO mixtures, respectively.⁵ However, the use of the catalyst entities does not come without drawbacks. Especially for Cu-containing particles supported on ZnO, particle sintering is a serious issue.⁶ This can be improved by the use of ZrO₂, but the latter itself leads to a higher structural complexity due to the polymorphism-dependent catalytic behavior.⁷ Speaking of the catalytic materials used in *e.g.* methane steam reforming, Ni is an often-used obvious choice due to its abundance, low price and reasonable activity.⁵ Its use, however, offers one serious drawback: it is very prone to de-activation by coking, as the reaction has to run at high temperatures.^{3,5} To overcome this dilemma, precious metals such as Cu, Ag or Au have been used as promoters to suppress the coke formation.^{5,8,9} The suppression of coking has been directly proven for Ag on alumina-supported Ni catalysts in methane steam reforming.⁵ Recently, also metals on complex oxides, such as perovskite systems, have been successfully studied.^{3,10} In this special case, however, exsolution phenomena might lead to either altered catalytic properties or simple de-activation *via* surface/bulk alloying with the catalytically

active metals.^{3,11} Using lanthanum-strontium ferrite (LSF), formation of Rh-Fe or Ni-Fe alloys significantly lowers the catalytic activity.^{3,11} For perovskites that are more difficult to reduce (containing less Fe), such as strontium titanium ferrite (STF), this de-activation through alloying is less pronounced or even suppressed altogether.^{3,11} For alcohol steam reforming (*e.g.* methanol) and other (partial) oxidation reactions, cobalt oxides (CoO or Co₃O₄) are also often employed.¹² The Co-containing materials are unique in a way that the activity of those oxides is strongly dependent on the degree of reduction and specific ratio of Co²⁺/Co³⁺.¹² Studies of methanol interaction both with metallic Co and cobalt oxides are abundant.^{13,14} It is therefore of specific interest, if the combination of cobalt oxides with a complex oxide, such as STF, which is itself capable of the formation of oxygen vacancies and to alter the oxidation levels of the constituting elements, does induce a change in catalytic properties. Silver-perovskite systems have so far only been used as nanocomposites in solid-oxide fuel cell cathodes and current collectors due to their promising conduction and oxygen diffusion properties as well as improved catalytic activity in the oxygen reduction reaction.¹⁵ In general, silver has become important in various oxidation reactions,¹⁶ whereby – similarly to the Co-containing systems – the performance is very delicately depending on the chemical nature of the surface sites, which itself is steered by the preparation, pre-treatment and reaction conditions, as well as the size of the Ag particles. As such, especially the interaction of silver with oxygen is the dominant factor for the activation of silver surfaces, including molecularly adsorbed and subsurface oxygen.¹⁷ One therefore might expect a considerable influence on the catalytic properties in Ag-containing composite materials, when Ag is combined with a material that itself is capable of oxygen release at the Ag-supporting oxide boundary, such as Gd-doped ceria, which strongly promotes selective methanol oxidation.⁹ A similar promotional mechanism is thus expected for the Ag-STF phase boundary, which can moreover act as an electrocatalytically promoted triple phase boundary in SOFC anode applications, since STF exhibits favorable mixed anionic-electronic conducting properties.

Practically, fast electrochemical supply of lattice oxygen from STF to Ag can be combined with lowered reaction barriers for methanol oxidation to CO₂ on the Ag surface, and the intrinsically beneficial protection of the electrode against coking linked to the use of pure Ag instead of *e.g.* Ni.

Consequently, the work presented herein is focused on the catalytic properties of two modified STF catalysts, namely Co₃O₄-STF and Ag-STF, respectively. As a test reaction, methanol steam reforming has been selected, since water activation on STF is possible and well-studied¹⁸, giving eventually rise to enhanced activity and moderate CO₂ selectivity. For possible further improvement of the catalytic properties, an oxide-oxide composite (Co₃O₄-STF) and a metal-oxide system (Ag-STF) will be comparatively assessed. An eventual structure-activity correlation will be established by combined structural (X-ray and electron diffraction, electron microscopy), spectroscopic (X-ray photoelectron spectroscopy) and catalytic studies.

2. Experimental

2.1. Materials and Synthesis

Strontium titanium ferrite (STF, SrTi_{0.7}Fe_{0.3}O_{3-δ}, particle size 0.2 – 10 μm) was synthesized following a solid state synthesis routine from SrCO₃, TiO₂ and Fe₂O₃ (99.98 % purity, Sigma-Aldrich). The educts were thoroughly mixed, calcined at 1000 °C for 2 h, ground in a mortar and again calcined at 1250 °C for 2 h. Surface areas of 0.4 m² g⁻¹ result. For surface area determination, a Quantachrome Nova 2000 surface and pore size analyzer was exploited. For preparation of the Ag- and Co₃O₄-STF samples, a simple impregnation technique was employed. As catalytic pre-cursor materials, the corresponding nitrate compounds AgNO₃ and Co(NO₃)₂•6 H₂O were used. Following their dissolution in ~50 mL H₂O (for approximately

3 g of nitrate starting material at 25 °C), the resulting solutions were slowly dropped under vigorous stirring to suspensions of approximately 2 g STF in ca. 150 mL H₂O under ambient conditions (no dispersants were used, preparation at 25 °C). Subsequent calcination at 600 °C in air for 1 h finally yields the Ag-STF and Co₃O₄-STF starting materials with a nominal loading of ~8 wt.-% Ag and Co₃O₄, respectively.

2.2. X-ray Diffraction

X-ray powder diffraction measurements were carried out on a STOE Stadi P diffractometer in transmission geometry, including a MYTHEN2 DCS4 detector system and a molybdenum X-ray tube. Mo-K_{α1} radiation with a wavelength of 70.93 pm was selected using a curved Ge(111) crystal. Evaluation of the data was done using the WinX^{POW} software.¹⁹ Phase analysis was based on references from the ICDD database.²⁰

2.3. X-ray Photoelectron Spectroscopy

In order to investigate the surface-near chemistry, representative samples were analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific MultiLab 2000 spectrometer with a base pressure in the low 10⁻¹⁰ mbar range. The instrument is equipped with a monochromated Al-K_α X-ray source, an Alpha 110 hemispherical sector analyzer, as well as a flood gun for charge compensation, providing electrons with a kinetic energy of 6 eV. Where possible, the energy axis shift was calibrated relative to the C-C component of the C 1s peak (set to 284.8 eV). When there was no sufficient amount of adventitious carbon present on the surface, the bulk oxide peak of the Sr 3d_{5/2} component was set to 131.7 eV, according to previous experiments.¹¹ For the Ag 3d spectra, a symmetric peak shape corresponding to Ag₂O was fitted, as well as an asymmetric one for metallic silver. The spin-orbit splitting was

kept at 6.0 eV for all deconvolutions,²¹ and the area ratio of the 3d_{3/2} and 3d_{5/2} peaks was kept at 2/3.

For the cobalt-containing systems, the presence of Fe Auger peaks prohibited the determination of the relative concentrations of Co²⁺ and Co³⁺, but a qualitative assessment is possible via the location of the satellite feature in the Co 2p region, allowing the distinction between Co₃O₄ and CoO.²¹

2.4. Transmission Electron Microscopy

Transmission electron microscopy (TEM) measurements were carried out using two microscopes, namely a ZEISS EM 10 C (for overview imaging and selected area electron diffraction) and a FEI Tecnai F20 S-TWIN analytical (high-resolution) transmission electron microscope (200 kV), equipped with an Apollo XLTW SDD X-ray detector (for collecting energy-dispersive X-ray (EDX) data).

2.5. Catalysis

Catalytic characterization has been carried out using a well-established re-circulation batch-reactor, which is connected to a quadrupole mass spectrometer (MS) with a secondary electron multiplier in cross-beam geometry (Balzers QMG 311) and specialized for small sample amounts (reactor volume = 13.7 mL). The pressure in the mass spectrometer is monitored by both a hot cathode ionization gauge (IONIVAC IM 210 D, Leybold Heraeus) and established by a turbomolecular pump (TURBOVAC 151 C, Leybold Heraeus).

The reactor itself is a quartz glass tube (6 mm inner and 8 mm outer diameter; 260 mm in length) connected to two Swagelok[®] crosspieces with viton O-ring seals. To those elements, the circulating pump (Ansyco MB-21E) used for gas circulation, the sample holder (quartz

glass) as well as the thermocouple wires can be attached and/or inserted gas-tightly. Within the sample holder, the sample (usually around one hundred mg of finely ground powder) is supported by pre-annealed (800 °C) quartz wool.

The liquid methanol steam reforming mixture is prepared in a methanol:water = 1:10 composition to achieve a ratio of methanol:water = 1:2 in the gas phase to avoid the steam reforming reaction being stopped by simple water depletion. Several freeze-and-thaw cycles have been performed prior to the catalytic measurements to ensure purity of the reaction mixture.

A methanol steam reforming cycle usually consists of three steps: (1) pre-oxidation in 1 bar O₂ at 600 °C for 1 h (termed O600), (2) pre-reduction in 1 bar H₂ at 400 °C for 1 h (termed H400) and (3) reaction (termed K400). The latter consists of adding the reaction mixture and defined amounts of Ar for baseline correction (to account for the gas withdrawal through the leak) to the reactor and backfilling the latter by He to atmospheric pressure (to enhance the thermal conductivity and re-circulation efficiency) at 100 °C. A temperature ramp from 100 °C to 400 °C with a rate of 5 °C min⁻¹ is then applied with continuous detection by MS for quantification.

In order to quantify the reactant/product gas components in the reactor at any point of reaction, the thermal pressure change upon performing a temperature-programmed reaction and the pressure loss due to slow gas withdrawal *via* the leak to the QMS need to be compensated in the data analysis. A blind experiment without catalyst was performed in the presence of Ar in the admixture, and the observed effective Ar pressure change was used to re-normalize the QMS signals of the relevant reactant gases to their initial values. *I.e.*, a so-corrected blind experiment shows more or less constant “effective” pressure values for the whole experimental run. The traces of the main products H₂, CO₂ and CO in this blind experiment correspond to zero pressure and are used for subsequent background correction of

the analogously performed reaction experiments with the catalyst inside the reactor (*i.e.* with measurable reactant conversion and product formation). Finally, the baseline-corrected QMS intensity data were converted to effective catalyst-induced reactant/product pressure changes given in mbar by calibration of the QMS intensities with known partial pressures of the products. In addition, fragmentation correction of the CO $m/z = 28$ intensity for simultaneous presence of CO₂ (contributing at a fixed fragmentation ratio to the $m/z = 28$ signal) was performed.

3. Results and Discussion

3.1. Structural and Spectroscopic Characterization

In close correlation to previous studies on Ni- and Rh-containing perovskite samples^{3,5}, the present Ag- and Co₃O₄-STF materials were subjected to a rigorous structural and spectroscopic characterization by X-ray diffraction, electron microscopy and X-ray photoelectron spectroscopy after each step of a *catalytic cycle*, *i.e.* after pre-oxidation, after pre-reduction and after a methanol steam reforming run.

Figure 1 A reveals that none of any studied catalytic pre- or catalytic treatments causes considerable changes in the bulk structure of either Ag or STF. The latter appears structurally intact and Ag, as expected, is bulk metallic (fcc structure). To assess the surface chemical state of the catalysts, correlated XP spectra (Figure 2 A-D) have been collected accordingly. After pre-oxidation (Figure 2 A), despite the bulk being clearly metallic, the surface appears oxidized. The binding energy position of the Ag 3d_{5/2} peak measured at 368.2 eV coincides with literature-reported values of Ag₂O (368.2 eV).²² Hence, one might assume that the Ag particles (see below) are covered by a thin layer of Ag₂O (at least 2.4 nm in thickness according to the escape depths as determined by the Gries formula²³), which is either too thin to be seen in XRD or the oxide layer is amorphous. After pre-reduction, the amount of

oxidized Ag is completely reduced and the particles are purely metallic again, with the Ag^0 component appearing at 367.6 eV, which coincides with the value of metallic Ag in literature measured at 367.9 eV.²⁴ Metallic Ag also appears after an MSR reaction using a fully oxidized sample (*i.e.* without pre-reduction) (Figure 2 C), indicating that the hydrogen formed during the methanol steam reforming reaction is able to fully reduce the oxidic hull formed after the pre-oxidation step. After a catalytic run with pre-reduction, the silver in the sample is fully reduced as well.

Figure 1: Panel A: X-ray diffraction experiments on Ag-STF and Panel B: X-ray diffraction experiments on Co_3O_4 -STF after selected catalytic (pre-) treatments: after pre-oxidation at 600 $^\circ\text{C}$ (pink traces); after subsequent pre-reduction at 400 $^\circ\text{C}$ (brown traces); after MSR up to 400 $^\circ\text{C}$ without a pre-reduction step (blue traces) and after MSR up to 400 $^\circ\text{C}$ with a pre-

reduction step up to 400 °C (purple traces). Reference diffractograms have been marked by red (Ag) and green (STF) bars.

Figure 2: Ag 3d X-ray photoelectron spectra of Ag-STF after selected catalytic (pre-) treatments. A) after pre-oxidation at 600 °C, B) after subsequent pre-reduction at 400 °C, C) after MSR up to 400 °C without a pre-reduction step and D) after MSR up to 400 °C with a pre-reduction step up to 400 °C. Component fits of the individual Ag^0 and Ag^+ contributions are also shown.

The corresponding X-ray diffractograms of Co-STF (Figure 1 B) reveal some interesting differences compared to Ag-STF. Although the STF support remains unchanged upon treatment in any gas atmosphere, no crystalline Co compound shows up in the diffractograms (metallic or oxidized). However, the respective XPS measurements (cf. Figure 3) and TEM analyses (cf. Figure 7) corroborate the presence of Co, albeit obviously in an X-ray invisible

state. The chemical properties of Co are expected to be much more complicated due to the general possibility of the presence of at least three different oxide phases after pre-oxidation (CoO , Co_2O_3 , Co_3O_4), which might also lead to an altered catalytic behavior.¹² The respective XP spectra are shown in Figure 3. Before discussing the spectral details, it should be noted that especially CoO (Co^{2+}) and Co_3O_4 (Co^{2+} and Co^{3+}) can be easily distinguished based on the position of the satellite feature in the Co 2p region.²¹ CoO exhibits distinctive Co 2p satellite features (at 785 eV and 802 eV) which makes a discrimination easily possible. As such, the redox chemistry of Co upon pre-oxidation, pre-reduction and after catalysis follows the expected trend: after pre-oxidation at 600 °C (Figure 3 A), the Co particles mainly consist of Co_3O_4 , whereas after pre-reduction at 600 °C, CoO is predominantly present (Figure 3 B). It is furthermore worth noting that a catalytic treatment in MSR (up to 400 °C, Figures 3 C and D) does not lead to re-oxidation of the surface, if a pre-reduction is conducted. Confirming the reduction potential of the product feed once a large amount of hydrogen is formed during MSR, a fully oxidized sample (starting with Co_3O_4) is reduced to CoO in the course of the reaction. Note, however, that peak deconvolution of the complex region could not be performed, because the Co 2p region overlaps with an Fe-Auger peak originating from the perovskite.

Figure 3: Co 2p X-ray photoelectron spectra of Co_3O_4 -STF after selected catalytic (pre-) treatments. A) after pre-oxidation at 600 °C, B) after subsequent pre-reduction at 600 °C, C) after MSR up to 400 °C without a pre-reduction step and D) after MSR up to 400 °C with a pre-reduction step up to 400 °C.

To gain more insight into the structure of the catalysts after each step of a catalytic cycle, electron microscopy experiments have been carried out. Overview images have been collected to determine the particle sizes, morphology and distribution. As seen in the inset showing the particle size distribution, the mostly encountered Ag particle size is approximately 5 nm, based on the analysis of about 100 particles. The histogram, however, also reveals small additional maxima for larger particle sizes (approximately 12 nm, 23 nm and 40 nm). The Ag particles themselves appear mostly as somewhat rounded aggregates, which evenly decorate

the surface of the STF grains (Figure 4 A). The presence of Ag metal and a structurally unaltered STF perovskite independent of the pre-treatment are also corroborated by complementary selected area electron diffraction patterns (Figure 4 B). All of the rather faint rings or spots match either STF or Ag metal. The particle size distribution is better seen in combined HAADF/EDX measurements. Figure 5 directly compares the HAADF image (the intensity of which is proportional to approximately Z^2 , Z being the average atom number, constant thickness and density provided – it therefore basically reflects the chemical contrast) and the respective EDX mapping image. As Ag has a higher Z , it appears bright in the HAADF image. The particle's location is then directly verified in the EDX image (reflected by the Ag L-edge intensity depicted in orange color). The EDX maps once again also confirm that Ag is metallic, as no pronounced O-K intensity is observed at the location of Ag. Figure 6 depicts a high-resolution image of a single metallic Ag particle with a perfect hexagonal outline showing two sets of Ag{111} lattice spacings (measured at 0.24 and 0.22 nm, which almost perfectly match the theoretical value of 0.23 nm) forming a 60° angle, as theoretically expected.²⁵ This angle is better seen in the FFT (inset) of the particle, where the symmetrical {111} spots are clearly visible due to the [011] orientation of the particle to the electron beam.

Figure 4: TEM overview image of Ag-STF after pre-oxidation at 600 °C (Panel A, the inset shows the particle size distribution) and the corresponding selected area electron diffraction pattern (Panel B). The Ag particles can be seen as black and grey dots in A.

Figure 5: TEM image (Panel A), HAADF image (Panel B) and the corresponding EDX map (Panel C) of Ag-STF after pre-oxidation at 600 °C. Panel C is an overlay of O-K, Ag-L, Ti-L, Fe-L and Sr-L edge intensities. The elemental distributions are shown separately in the lower panels.

According to the TEM image (Figure 7 A and B), the Co-containing particles are on average much larger (19.2 ± 0.4 nm, based on the analysis of approximately 50 particles). Combined TEM, HAADF and EDX analyses (Figure 7 C-E) reveal that especially the grain edges are enriched in Co particles (Panel C). The principal presence of Co_3O_4 , as already determined by XP spectra, is now further corroborated by high-resolution images (Figure 7 E), clearly revealing $\text{Co}_3\text{O}_4(111)$ lattice spacings measured at 0.48 nm (space group Fd-3m; lattice constant: $a=0.8084$ nm, $d_{\text{theoretical}}(111) = 0.47$ nm).²⁶ Furthermore, the cobalt oxide particles

appear to contain a hollow void (see, for instance, the particle in the top right of panel E), which potentially arises from the nanoscale Kirkendall effect.²⁷ This phenomenon usually occurs during the reaction of the Co particles with oxygen from the surrounding atmosphere, forming an initial oxide shell around the particle. If, subsequently, the outward-diffusion of any Co species through this shell is faster than the inward-diffusion of oxygen, vacancies are left behind on the inside of the particles that coalesce into a single void.²⁸

Figure 6: High-resolution image of a metallic Ag particle in [011] orientation. The inset shows its Fast Fourier transform (FFT).

Figure 7: TEM experiments on Co_3O_4 -STF after pre-oxidation at 600 °C. Panel A: Overview TEM image; Panel A-C: Combined TEM (Panel A), HAADF (Panel B) and EDX (Panel C) experiments. In Panel C, the Co-K line intensity is shown in blue; Panel D: Overview TEM image with several exemplary Co_3O_4 particles marked by white arrows; Panel E: High-resolution images of hollow Co_3O_4 particles exhibiting (111) lattice fringes.

3.2. Catalytic Characterization in Methanol Steam Reforming

Figure 8 and 9 show the methanol steam reforming experiments on Ag-STF and pure STF in a comparative fashion with and without an additional pre-reduction step at 400 °C in hydrogen for 1 h. Starting with the experiments on pre-oxidized Ag-STF without subsequent pre-reduction (Figure 8, left panel), the catalytic profile can be separated into two distinct regimes. From 170 °C to 270 °C, predominant CO_2 formation is observed, which goes

directly along with a small rate maximum peak and a high CO₂-selectivity (>95 %). Hence, in this temperature regime non-catalytic CO₂ formation via lattice oxygen supply from the STF perovskite takes place, *e.g. via* methanol dehydrogenation on Ag followed by fast onward oxidation of dehydrogenation intermediates such as CO to CO₂ *via* lattice oxygen spillover. Above 270 °C, the selectivity changes toward CO and considerable amounts of H₂ are formed, indicating that the supply of lattice oxygen from STF is ceasing. This indicates the onset of the catalytic methanol steam reforming reaction which leads to the rate maxima for both hydrogen and CO₂ in Figure 8 (left panel) at around 350 °C. A methanol conversion of approximately 93 % after 120 min has been determined. Compared to these observations on Ag-STF, the onset for CO₂ formation on Ag-free pure STF after pre-oxidation (Figure 8, right panel) is found at slightly above 250 °C and the rate maxima of CO₂ and hydrogen are spread over a larger time period. However, the maximum rate of CO is again located at approximately 300 °C and a final methanol conversion of 89 % is reached. Most importantly, the low-temperature CO₂ rate maximum is clearly absent and further confirms the promotion of the CO₂ formation and total oxidation *via* spillover to Ag. The fact that a spillover phenomenon is responsible for the low-temperature CO₂ rate maximum is derived from a semi-quantitative estimation of the possibility of oxygen removal by reduction of oxidic Ag species. In principle, this could also cause CO₂ formation via total oxidation. However, considering a meaningful amount of accessible oxygen bound within a thin Ag-oxide layer covering the Ag particles (the bulk of the particles still consist of metallic Ag, as proven by XRD), it turns out that such a layer is only able to provide about 3 % of the oxygen atoms required to explain the amount of CO₂ formed up to about 200 °C. Thus, we conclude that indeed oxygen spillover from STF to Ag must take place. For the analogous Co₃O₄-STF system, the situation is slightly more complex, as discussed below.

Figure 8: Catalytic methanol steam reforming profiles on Ag-STF (left) and pure STF (right) after pre-oxidation at 600 °C in O₂ for 1 h.

The catalytic patterns change considerably if a pre-reduction step is carried out (Figure 9). The low-temperature CO₂ peak assigned to non-catalytic methanol total oxidation at approximately 200 °C is entirely removed and the signals of CO₂, CO and hydrogen rise almost in line. Rate maxima of CO₂ and hydrogen are observed at about 330 °C, but the selectivity towards CO₂ has decreased considerably (to approximately 20 %) due to increased CO formation. This indicates that the H₂ pre-reduction step completely depletes the reactive lattice oxygen reservoir within STF, which is available only in the pre-oxidized state for low-temperature total oxidation/CO₂ formation. As for the influence of Ag on the catalytic behavior of pre-reduced STF in methanol steam reforming, a comparison to Figure 9 (right panel, pure STF) clearly shows that Ag even detrimentally affects the CO₂ selectivity of pure STF (between 70 and 50 %) by enhancing the CO-forming pathways (*i.e.* direct dehydrogenation to CO and/or i-WGSR) already at lower temperatures. Mechanistically, the data may be interpreted in terms of a mix of methanol dehydrogenation and reforming, occurring both on STF and Ag-STF, whereby the formed hydrogen desorbs with a lowered

barrier on the latter. This may be due to reverse hydrogen spillover effects from STF to Ag and/or to the intrinsic catalytic action of the Ag surface.

Figure 9: Catalytic methanol steam reforming profiles of Ag-STF (left) and pure STF (right) after pre-reduction at 400 °C in H₂ for 1 h following the pre-oxidation treatment.

As for the catalytic methanol steam reforming profiles of Co₃O₄-STF (Figure 10), also differences between an only pre-oxidized sample (left) and one with subsequent pre-reduction (right) are evident. Starting from a fully oxidized sample, total oxidation of methanol to CO₂ is clearly predominant, amounting to a final methanol conversion of 96 % at almost 100 % CO₂ selectivity throughout the whole experiment. H₂ formation is obviously unstoichiometric, starting at around 200 °C, but this small amount of H₂ is being entirely consumed again in the course of the reaction (pronounced negative reaction rate in Figure 10 left). Again, this strongly points to non-catalytic reduction of both STF (as shown previously for pure STF^{3,5}) and/or Co₃O₄. The reduction to CoO is directly proven by the XP spectra taken after the methanol steam reforming reaction (*cf.* Figure 3, Panel C), which in accordance reveal the presence of CoO. Starting the MSR reaction from a pre-reduced sample (Figure 10, right panel) reveals only methanol dehydrogenation (rise of both hydrogen and carbon monoxide

signals in accordance with its reaction stoichiometry) up to a temperature of about 300 °C, above which the water-gas shift reaction consumes a part of the already produced carbon monoxide and carbon dioxide is formed. The water-gas shift reaction reaches its equilibrium very quickly at around 350 °C. Note that up to 350 °C the entire reaction network most probably proceeds on CoO, as STF (*cf.* Figure 9, right panel) is essentially inactive in the corresponding temperature regime. The observed catalytic action of Co₃O₄/CoO is in accordance with literature reports. In methanol oxidation, Co₃O₄ is reported to be unstable in the reaction mixtures and a partial CoO_x (surface) phase is formed. Corroborating literature reports, CoO and CoO_x with $1 > x > 1.33$ yield oxidized products such as formaldehyde and total oxidation products. As for the water-gas shift reactivity, it has been reported that cobalt oxides are very attractive catalysts for CO oxidation reactions due to the presence of reactive lattice oxygen, including also the water-gas shift reaction.¹² This necessarily also includes a vital redox chemistry of Co₃O₄/CoO. Following the XPS interpretation, we might infer that the active catalyst for the water-gas shift equilibrium is in fact CoO.

Again, a qualitative comparison to Co₃O₄-free STF indicates low-temperature promotion of total oxidation, as after pre-oxidation without pre-reduction a distinct CO₂ rate maximum at around 200 °C on the Co₃O₄-containing catalyst is observed. If this is merely an effect of pure reverse lattice oxygen spillover from STF to Co₃O₄ or if a contribution of Co₃O₄ reduction to CoO must be also considered, is subject to further studies. Here, estimations on the basis of geometric analyses of the accessible Co₃O₄ area are severely hampered by the fact that it does not exhibit a crystalline state in XRD and analysis of TEM data is difficult due the pronounced contrast of STF. Hence, the estimation of the Co₃O₄ particle size distribution is not straightforward, further preventing the establishment of correlated structure-catalytic analyses.

Figure 10: Catalytic methanol steam reforming profiles of Co_3O_4 -STF after pre-oxidation at 600 °C in O_2 for 1 h (left) and after subsequent pre-reduction at 400 °C in H_2 for 1 h (right).

4. Conclusions

The outlined results prove that both Ag and Co_3O_4 are very efficiently influencing the methanol chemistry with respect to pure STF already at comparably low temperatures (starting at about 170 °C for both materials). On the pre-reduced catalysts, the selectivity is strongly shifted towards carbon monoxide both by Ag and CoO compared to pure pre-reduced STF. On Co_3O_4 -STF, a complex catalytic network, encompassing a delicate temperature-dependent interplay between methanol steam reforming, methanol dehydrogenation and the water-gas shift reaction is observed. Despite the obvious unsuitability of both pre-reduced samples to act as highly CO_2 selective methanol steam reforming catalysts, a potential use as SOFC anode materials is envisioned, as fast and selective total oxidation of methanol to CO_2 is observed already at low temperatures (starting at about 170 °C) starting from the pre-oxidized initial states. In such an application, the observed non-catalytic consumption of STF-lattice oxygen could easily be compensated by continuous electrochemical supply of lattice oxygen at comparably low SOFC operating temperatures, as STF is an efficient mixed

electron and oxygen anion conductor. However, for a potential use as anode materials, the coking tendency has to be assessed separately, as Co-containing catalysts are especially prone to coking, in contrast to Ag-containing materials. As such, direct use of *e.g.* methanol as internal fuel in an SOFC might be more efficient using Ag-based materials.

5. Acknowledgments

The work was financially supported by the Austrian Science Foundation (FWF) via SFB projects F4501-N16 and F4503-N16 within the SFB “Functional Oxide Surfaces and Interfaces “FOXSI”, and performed within the framework of the platform Materials- and Nanoscience and the special PhD program “Reactivity and Catalysis” at the University of Innsbruck.

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Figure 1: Panel A: X-ray diffraction experiments on Ag-STF and Panel B: X-ray diffraction experiments on Co_3O_4 -STF after selected catalytic (pre-) treatments: after pre-oxidation at 600 °C (pink traces); after subsequent pre-reduction at 400 °C (brown traces); after MSR up to 400 °C without a pre-reduction step (blue traces) and after MSR up to 400 °C with a pre-reduction step up to 400 °C (purple traces). Reference diffractograms have been marked by red (Ag) and green (STF) bars.

Figure 2: Ag 3d X-ray photoelectron spectra of Ag-STF after selected catalytic (pre-) treatments. A) after pre-oxidation at 600 °C, B) after subsequent pre-reduction at 400 °C, C) after MSR up to 400 °C without a pre-reduction step and D) after MSR up to 400 °C with a pre-reduction step up to 400 °C. Component fits of the individual Ag^0 and Ag^+ contributions are also shown.

Figure 3: Co 2p X-ray photoelectron spectra of Co_3O_4 -STF after selected catalytic (pre-) treatments. A) after pre-oxidation at 600 °C, B) after subsequent pre-reduction at 600 °C, C) after MSR up to 400 °C without a pre-reduction step and D) after MSR up to 400 °C with a pre-reduction step up to 400 °C.

Figure 4: TEM overview image of Ag-STF after pre-oxidation at 600 °C (Panel A, the inset shows the particle size distribution) and the corresponding selected area electron diffraction pattern (Panel B). The Ag particles can be seen as black and grey dots in A.

Figure 5: TEM image (Panel A), HAADF image (Panel B) and the corresponding EDX map (Panel C) of Ag-STF after pre-oxidation at 600 °C. Panel C is an overlay of O-K, Ag-L, Ti-L, Fe-L and Sr-L edge intensities. The elemental distributions are shown separately in the lower panels.

Figure 6: High-resolution image of a metallic Ag particle in [011] orientation. The inset shows its Fast Fourier transform (FFT).

Figure 7: TEM experiments on Co₃O₄-STF after pre-oxidation at 600 °C. Panel A: Overview TEM image; Panel A-C: Combined TEM (Panel A), HAADF (Panel B) and EDX (Panel C) experiments. In Panel C, the Co-K line intensity is shown in blue; Panel D: Overview TEM image with several exemplary Co₃O₄ particles marked by white arrows; Panel E: High-resolution images of hollow Co₃O₄ particles exhibiting (111) lattice fringes.

Figure 8: Catalytic methanol steam reforming profiles on Ag-STF (left) and pure STF (right) after pre-oxidation at 600 °C in O₂ for 1 h.

Figure 9: Catalytic methanol steam reforming profiles of Ag-STF (left) and pure STF (right) after pre-reduction at 400 °C in H₂ for 1 h following the pre-oxidation treatment.

Figure 10: Catalytic methanol steam reforming profiles of Co₃O₄-STF after pre-oxidation at 600 °C in O₂ for 1 h (left) and after subsequent pre-reduction at 400 °C in H₂ for 1 h (right).