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Metastable Corundum-Type In₂O₃: Phase Stability, Reduction Properties and Catalytic Characterization

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Abstract

The phase stability, reduction and catalytic properties of corundum-type rhombohedral In_2O_3 have been comparatively studied with respect to its thermodynamically more stable cubic In_2O_3 counterpart. Phase stability and transformation were observed to be strongly dependent on the gas environment and the reduction potential of the gas phase. As such, reduction in hydrogen caused both the efficient transformation into the cubic polymorph as well as the formation of metallic In especially at high reduction temperatures between 573 K and 673 K. In contrast, reduction in CO suppresses the transformation into cubic In_2O_3 , but leads to a larger quantity of In metal at comparable reduction temperatures. This difference is also directly reflected in temperature-dependent conductivity measurements. Catalytic characterization of rh- In_2O_3 reveals activity in both routes of the water-gas shift equilibrium, which gives rise to a diminished CO_2 -selectivity of $\sim 60\%$ in methanol steam reforming. This is in strong contrast to its cubic counterpart, where CO_2 selectivities of close to 100 %, due to the suppressed inverse water-gas shift reaction, have been obtained. Most importantly, rh- In_2O_3 in fact is structurally stable during catalytic characterization and no unwanted phase transformations are triggered. Thus, the results directly reveal the application-relevant physico-chemical properties of rh- In_2O_3 which might encourage subsequent studies on other less-common In_2O_3 polymorphs.

1. Introduction

The understanding of the polymorphism of In_2O_3 has evoked recent interest both due to fundamental scientific¹⁻⁶ and technological aspects⁷⁻¹⁶. As for the latter, promising use in solar cells, as UV lasers sensors or for catalytic applications has been reported⁷⁻¹⁷. Interest from a basic scientific viewpoint is mainly fuelled by both novel synthesis routes to metastable In_2O_3 modifications and morphologies and understanding of the phase transitions between them^{1-4,17,18}. The In_2O_3 phase diagram thereby is currently comprised of five polymorphs, namely cubic bixbyite-type In_2O_3 (thermodynamically stable under ambient conditions), rhombohedral corundum-type rh- In_2O_3 and three orthorhombic modifications, i.e. Rh_2O_3 (II), (III)- and $\alpha\text{-Gd}_2\text{S}_3$ -type^{4,5,19-22}. While rh- In_2O_3 is accessible at ambient pressure, the orthorhombic polymorphs can only be synthesized via dedicated high pressure and high-temperature treatments and usually undergo partial phase transitions upon decompression^{4,18-22}. Therefore, physico-chemical characterization is severely hampered and consequently very limited. A recent exception, however, represents the rhombohedral polymorph. Due to the existing and envisioned applications of In_2O_3 as e.g. promising gas sensor and recent advances in morphological control of nanosized oxide particles and crystals, much effort has been placed in obtaining large quantities of rh- In_2O_3 exposing different crystal facets by dedicated and simplified synthesis procedures^{1,3,17,23}. Despite this progress, severe limitations still prevail due to the inherent instability also of the rhombohedral modification towards phase transition to the thermodynamically stable cubic phase. The stability range is extremely dependent on a variety of experimental parameters, including gas phase environment and annealing temperature³. This limits the available time period to between 30 minutes at 650 °C to hours and days at temperatures between room temperature and 350 °C²⁴. Therefore, not much is known about the intrinsic physico-chemical properties of the rhombohedral polymorph, except limited spectroscopic information (FT-IR and Raman¹⁷), as well as

structural characterization of dedicated morphologies and theoretical calculations of the electronic structure^{1,3,17,23,25,26}. Its properties, nevertheless, play a keyrole in the understanding and further directed knowledge-based synthesis and research. The studies are also partially fuelled by the outstanding reduction behavior and catalytic properties of its cubic counterpart^{8,9}, which readily loses oxygen upon treatment with various reducing gases (especially hydrogen and carbon monoxide) and therefore gives rise to exceptional properties in the water-gas shift reaction and a very pronounced CO₂-selectivity in the methanol steam reforming reaction^{8,9,27}.

Thus, the transfer of the experiments to the corresponding rhombohedral phase is most rewarding with respect to elucidating the common properties and differences of the two In₂O₃ modifications. In due course, a rhombohedral sample synthesized via a dedicated non-aqueous solvothermal route will be subjected to identical treatment as its cubic counterpart and studied by an array of spectroscopic (FT-IR spectroscopy, electrochemical impedance spectroscopy, EIS), structural (X-ray diffraction, XRD) and catalytic techniques (water-gas shift reaction, WGSR, and methanol steam reforming, MSR). Applying this pool of methods will, thus, reveal its intrinsic properties and especially also the influence of the eventual phase transition on the physico-chemical properties.

2. Experimental

2.1. Synthesis of the materials

Corundum-type rh-In₂O₃ was obtained by the calcination of metastable indium oxyhydroxide (InOOH) for 30 min at 673 K in ambient air. Phase-pure InOOH was synthesized by a solvothermal route, as described in²⁴. The synthesis route allows for the reproducible synthesis of about 3500 mg phase-pure InOOH per synthesis run. The as-synthesized

nanocrystalline rh-In₂O₃ sample has a BET specific surface area of 43.5 m² g⁻¹. The reference sample is a cubic In₂O₃ material from Alfa Aesar (99.99%) with a BET specific surface area of ~ 0.74 m² g⁻¹, measured on a Quantachrome Nova 2000 Surface and Pore Size Analyzer. To highlight the different structural features directly, Figure S1 provides a comparison of c-In₂O₃ and rh-In₂O₃.

High-purity gases used in the following experiments were provided by Messer-Griesheim. Remaining condensable impurities were further removed by cooling traps set to various temperatures as required by the respective boiling and sublimation points of each gas for the volumetric, impedance and FT-IR experiments. For helium and hydrogen, liquid N₂ at 77 K is used. Oxygen and carbon monoxide were purified by ethanol/liquid N₂ mixtures held at 153 K, CO₂ at 223 K.

2.2. Electrochemical Impedance Spectroscopy (EIS)

A heatable *operando* impedance cell designed for gas treatments up to 1273 K, situated in a tubular furnace (Linn) and controlled by a thermocouple located 5 mm downstream of the sample, together with a Micromega PID temperature controller was used for analysis. Temperature-dependent conductivity (i.e. impedance) measurements were carried out using a IM6e impedance spectrometer (Zahner Elektrik). For all measurements, an excitation frequency of 1 Hz and a stimulation voltage of 20 mV were applied to two circular Pt electrodes (diameter 5 mm) in mechanically enforced contact with the sample (corresponding to a force of 2 N). The latter is a pelletized powder material (several hundred milligrams of the powder are pressed by 2 t into a disk of about 5 mm diameter and about 3-4 mm thickness). Gas treatments are exclusively carried out under flowing conditions (~ 1 mL s⁻¹) up to various temperatures, but not higher than 673 K to eventually avoid triggering phase transformations to a large amount.

2.3. Volumetric Adsorption

All volumetric measurements are carried out in a dedicated quartz glass apparatus, capable of measuring in static or flowing gas mode. Hence, it is used both for temperature-programmed reduction and oxidation experiments under defined static gas conditions and temperature-programmed desorption measurements under flowing conditions. The pressure inside the chamber is measured by a Baratron capacitance manometer (MKS) and the gas flow controlled by mass flow controllers. The powderous samples (several hundred milligrams) are fixed by quartz wool inside the vertical quartz glass tube. Detection of the reactants and reaction products is performed by using a quadrupole mass spectrometer (Balzers) attached to the tube via a capillary leak. For quantification of CO, CO₂ fragmentation is taken into account. Temperature-programmed reduction experiments in either pure hydrogen or carbon monoxide are carried out using defined starting pressures of about 100 mbar. Subsequently, the temperature is ramped standardized with 10 K min⁻¹ up to 673 K, followed by a 10 minute isothermal period and re-cooling the sample in the respective gas mixture back to room temperature. The same procedure is applied for temperature-programmed re-oxidation treatments, necessary for quantification of the oxygen defects introduced by the reduction pre-treatment. These dedicated reduction treatments are usually carried out via exposing the sample to flowing hydrogen at various temperatures (~ 1 mL s⁻¹, highest temperature 618 K), re-cooling it to room temperature and subsequently pumping down the reactor to a base pressure of ~ 1.0x10⁻⁷ mbar. Afterwards, the so-treated sample is heated *in vacuo* with 10 K min⁻¹ up to 823 K to remove adsorbed hydrogen and thus, obtaining information on the bonding strength of hydrogen on different surface sites. Similar thermal desorption treatments are also performed after the respective temperature-programmed reduction treatments.

2.4. Catalytic measurements

All experiments were performed in a Labview-controlled re-circulating batch reactor of about 13 mL volume²⁸. Reactants are detected by a quadrupole mass analyzer attached to the reactor via a capillary leak. The mass-to-charge ratios (m/z) 2 (hydrogen), 15 and 16 (methane), 28 (carbon monoxide), 29 (formaldehyde/methanol fragment), 30 (formaldehyde), 31 (methanol), 40 (argon) and 44 (carbon dioxide) are routinely collected. Fragmentation patterns for carbon dioxide and methanol are considered and the signal intensities converted to partial pressures via external calibration standards. For a typical (inverse) water-gas shift reaction, about 25 mbar CO and 25 mbar water (about 30 mbar CO₂ and 30 mbar H₂) are used. Methanol steam reforming experiments are carried out using ~ 15 mbar methanol and 30 mbar water. To all reaction mixtures, 10 mbar Ar was added to correct for the permanent gas withdrawal through the leak and He added to 1 bar total pressure for temperature equilibration within the reactor and circumvent heat transfer limitations.

2.5. FT-Infrared Spectroscopy (FT-IR)

All FT-IR spectra were recorded with an Agilent Cary 600 and a home-built high-temperature, high-pressure *operando* quartz reactor cell, capable of collecting spectra at temperatures up to 1300 K and pressures up to 1 bar in reactive gases. Its dedicated construction allows the use of ultra-dry conditions with a water partial pressure below 1.0×10^{-7} mbar²⁹. For analysis, the powders (~ 20 mg) are pressed into thin pellets using a hydraulic press at ~ 1-2 t. Treatments under flowing and static conditions are possible.

2.6. X-ray diffraction (XRD)

Two types of X-ray diffractometers are used for analysis. Samples treated via the volumetric and catalytic experiments are analyzed with a Siemens D5000 under ambient conditions using Cu-K α radiation (1.54178 Å) at 300 K in the 2θ range 10 to 70° with a step size of 0.02° in

Bragg-Brentano geometry. Due to the low sample amount, X-ray diffractograms of samples after EIS treatments were collected with a Bruker AXS D8-Advance powder diffractometer also in Bragg-Brentano geometry. The samples were prepared on a rotatable Si single crystal to minimize background signals. The range of measurement was chosen from $2\theta = 20$ to 90° with a step size of 0.02° .

3. Results and Discussion

3.1. Phase stability and reducibility

Hydrogen on rh-In₂O₃

Hydrogen interaction and adsorption is at first measured in the respective temperature-programmed hydrogen reduction experiments as provided in Figure 1. Considerable uptake only sets in above ~ 530 K with a single consumption step up to the highest temperatures of 673 K. In the following isothermal period, further hydrogen uptake points towards still prevailing kinetic limitations. Upon re-cooling to room temperature, the hydrogen remains adsorbed on the surface. Comparing this to c-In₂O₃, the overall features are comparable²⁷, but distinct differences are: (i) the uptake process on rh-In₂O₃ does not proceed via clearly distinguishable steps and (ii) the main consumption occurs only at and above ~ 570 K, in contrast to c-In₂O₃, where this uptake starts at ~ 500 K. A slight hydrogen uptake is, nevertheless, visible starting at ~ 300 K, followed by a plateau region before the uptake drastically increases. This is in fact similar to c-In₂O₃, where it has been assigned to surface-restricted reduction²⁷. The total surface-normalized consumed amount is also comparable at around $10 \mu\text{mol m}^{-2}$. A subsequent thermal desorption spectrum after re-cooling to room temperature (inset in Figure 1) reveals three discernible desorption steps at 540, 650 and 750 K, indicating at least three energetically different binding sites for hydrogen. This again reveals direct differences to c-In₂O₃, which when treated under similar conditions reveals only

two prominent peaks (at 550 and 800 K)²⁷. Note that the X-ray diffractogram taken after performing the TPD after TPR (cf. Figure 3, pink trace), cubic In_2O_3 appears in the pattern, which might explain the peak at 550 K, but the other two are clearly associated with rh- In_2O_3 .

Further information is given by additional temperature-programmed hydrogen desorption experiments. These are exclusively conducted under flowing hydrogen conditions and subsequent hydrogen desorption (cf. Experimental section). Note already at this stage the different conditions with respect to the previously discussed temperature-programmed reduction experiments, which are conducted in a static hydrogen atmosphere. The main difference, hence, is the presence or removal of reactant water, formed by eventual release of oxygen from the lattice, resulting in an oxygen vacancy and gas-phase water.

Figure 1: Temperature-programmed hydrogen uptake measurement (main panel) and subsequent thermal desorption after re-cooling to room temperature (red) alongside the total desorbed amount of hydrogen (blue), shown as inset. Initial starting pressure of hydrogen: 100 mbar, heating and cooling rate: 10 K min^{-1} , isothermal period: 10 minutes at 673 K. The direction of the arrows indicates the heating-cooling cycle.

Figure 2 in turn highlights these experiments at three selected reduction temperatures up to ~ 620 K. The maximum TPD temperature has been restricted to 720 K to prevent a considerable transformation into cubic In_2O_3 . After reduction at 553 K and 567 K, a TPD similar to the one obtained after the temperature-programmed reduction is obtained, with two prominent desorption peaks at 600 K and 640 K, and less pronounced shoulders at 520 K, 660 K and ~ 700 K, respectively. Whereas the low-temperature shoulder appears fixed, the maximum of the most prominent peak shifts to lower temperatures with increasing reduction temperature. Consistently, the amount of surface-normalized consumed hydrogen rises from 1.4 to 2.2 $\mu\text{mol m}^{-2}$. The situation is slightly more complex at even higher reduction temperatures of 618 K. One very pronounced peak at ~ 690 K is visible, with a shoulder at ~ 640 K. Most interesting, the total adsorbed hydrogen amount slightly decreases to 2.0 $\mu\text{mol m}^{-2}$ as compared to reduction at 567 K. This appears contradicting at first, but can be related to two helpful observations: (i) the desorbed amount of water is highest after reduction at 618 K (cf. inset in Figure 2; adsorbed hydrogen can be released basically in two competing ways – either by desorption as H_2 or as reactant water by removal of oxygen from the lattice) and (ii) as it follows from the X-ray diffractograms highlighted in Figure 3, reduction at and above 573 K in principle causes partial transformation into the c- In_2O_3 polymorph and at the highest temperatures, also metallic In. Substantial influence of the former (despite being present in the X-ray diffractograms after reduction at 473 and 573 K in amounts of ~ 10 -12 weight-%, according to Rietveld analysis, see Figure 3 and Table 1) can be excluded, as the hydrogen desorption peaks of c- In_2O_3 are observed at different temperatures²⁷. Formation of metallic In is not observed up to reduction temperatures of ~ 600 K, but above, especially at 673 K, 10 weight-% In metal and 90 weight-% c- In_2O_3 are present, while no rh- In_2O_3 is left at all after treatment at the highest reduction temperatures. This, obviously, has to be taken into account when discussing the TPD spectrum obtained after reduction at 618 K in detail, blurring

potential trends in total hydrogen uptake and peak shifts. Similar decreased hydrogen adsorption capabilities after formation of metallic In have also been observed on c-In₂O₃.²⁷

To clarify the stability and the eventually introduced c-In₂O₃ phase and possibly also metallic In, X-ray diffractograms have been recorded after each reduction step and the resulting crystalline phases quantified by Rietveld analysis. Figure 3 and Table 1 summarize these experiments. In fact, rh-In₂O₃ is perfectly stable after performing the static temperature-programmed reduction in hydrogen up to 673 K and even after treating the sample in flowing hydrogen at 473 K (i.e. the TPD experiment at the lowest temperatures). At higher temperatures in flowing hydrogen, slight amounts of c-In₂O₃ are formed (573 K) and at even higher temperatures (673 K), full transformation into c-In₂O₃, as well as further reduction to metallic In, takes place. After the TPD performed subsequent to the TPR experiment, a substantial amount of c-In₂O₃ is observed, but no metallic In. A comparison to c-In₂O₃ reveals that the transformation into metallic In is significantly suppressed on rh-In₂O₃ in comparison to c-In₂O₃. Whereas on the latter clear signals of presence of metallic In are already observed after reduction at ~ 600 K, this is not the case for the polymorph presented here. This certainly rises questions about the influence of the polymorph intertransition on the reduction. Thus, the presented results offer the most probable explanation in terms of a subsequent transformation of rh- into c-In₂O₃, which is then followed by easier reduction of the latter into metallic In. The critical temperature region obviously is the one between 573 and 673 K.

Furthermore, the presented TPD results also allow to estimate the number of oxygen vacancies formed during reduction. The estimation is based on controlled re-oxidation in a defined oxygen partial pressure (~ 200 mbar initial oxygen pressure, heating ramp 10 K min⁻¹). As expected, for the lowest reduction temperatures, the number of introduced oxygen vacancies is smallest and seemingly does not change up to a reduction temperature of 573 K (cf. Table 2). Above, the O₂ consumption increases drastically, indicating that the threshold

temperature for efficient oxygen vacancy formation is found at around 573 K (cf. drastic hydrogen uptake in Figure 1). Together with the data in Figure 2, we might infer at least two different temperature-dependent pathways of hydrogen interaction: hydrogen adsorption at lower reduction temperatures (finally desorbing as hydrogen molecule during TPD) and oxygen vacancy formation (forming reactant water during reduction) at temperatures above 573 K.

Figure 2: Thermal desorption spectra of hydrogen (main panel) and water (inset) after treatment of rh-In₂O₃ in flowing hydrogen (1 h, 1 mL s⁻¹) at different reduction temperatures. Heating rate: 10 K min⁻¹. Desorption rate shown in red, total desorbed amount of hydrogen in blue.

Figure 3: X-ray diffractograms collected after various flowing and static treatments in hydrogen as indicated. Color code: purple, orange and green denote flowing treatments (1 h, 1 mL s⁻¹) at 473, 573 and 673 K, respectively. Black represents the pattern after the TPR experiments and pink after the subsequent TPD. The calculated peak assignment of the rh-In₂O₃ (black), c-In₂O₃ (red) and In metal (blue) phases is based on PDF cards 22-0336, 06-0416 and 05-0642 (ICDD Powder Diffraction database 4+) and given as solid bars at the bottom of the graph.

Table 1: Rietveld analysis after selected reduction treatments on rh-In₂O₃. Weight-% are rounded to 5 weight-%.

Sample and Treatment/ K	rh-In ₂ O ₃ / weight-%	c-In ₂ O ₃ / weight-%	metallic In/ weight-%
H-473	90	10	-

H-573	85	15	-
H-673	-	90	10
CO-523	90	10	-
CO-673	40	30	30
CO-CO₂-673	25	70	5
CO-H₂O-673	80	20	-

Table 2: Quantification of the temperature-programmed re-oxidation treatment as an estimate of the formed oxygen vacancies during flowing reduction in hydrogen.

Sample and Treatment/ K	O₂ consumption/ $\mu\text{mol g}^{-1}$	O₂ consumption/ $\mu\text{mol m}^{-2}$
H-414	5.9	0.13
H-553	4.6	0.10
H-567	8.1	0.18
H-618	85	1.94

The influence of the reduction on the material's properties of rh-In₂O₃ is further highlighted by temperature-programmed impedance, i.e. conductivity measurements. Previous experiments on the c-In₂O₃ polymorph already indicated the valuable information especially with respect to the formation of metallic In during the reduction process²⁷. Figure 4 shows comparative impedance traces in dry hydrogen in comparison to treatment in CO. While the latter will be discussed in detail in the following section, even the comparative discussion of the behavior in hydrogen reveals interesting features. In contrast to c-In₂O₃, which showed a rapid decrease of the impedance in one single step down to metallic conductivity at around 400 K,²⁷ the corresponding trace on rh-In₂O₃ is significantly different. A continuous decrease of the impedance is observed, starting at around 300 K. At 500 K, where on c-In₂O₃ metallic conductivity is already reached, a distinct temperature-independent plateau in the conductivity of about 50 K range is entered. At higher temperatures, yet another impedance drop finally leads to metallic conductivity, which is preserved up to 673 K and also upon re-cooling to room temperature. Rietveld analysis (important points have been marked in Figure 4) shows

that the plateau is not connected to the formation of metallic In, but must be associated with small structural changes (especially the transformation from rh-In₂O₃ into c-In₂O₃), as from 473 K to 573 K, only 5 weight-% of rh-In₂O₃ are converted into c-In₂O₃. Most interesting, but in accordance with associated experiments on c-In₂O₃,²⁷ metallic conductivity is reached even before metallic In shows up in the X-ray patterns. Relating the conductivity experiments to thermal hydrogen desorption experiments and oxygen vacancy formation, it turns out that up to 573 K (where finally metallic conductivity is reached) oxygen vacancy formation is not a dominant issue. Only at higher temperatures, when the vacancy concentration rises drastically, substantial formation of metallic In takes place and the impedance drops to metallic behavior (low Ω -range). Vice versa, below reduction temperatures of 573 K, the impedance must be associated with adsorbed hydrogen (and water giving rise to a more or less hydroxylated surface) and is therefore most likely a strictly surface-bound conduction phenomenon.

Figure 4: Temperature-programmed *in situ* electrochemical impedance measurements in dry hydrogen (blue) and CO (red). The temperature is ramped from 300 K to 673 K and back, including an isothermal period at 673 K for 10 minutes. Ramp: 10 K min⁻¹. Phase analysis according to Rietveld analysis from the associated X-ray diffractograms at important points has been marked. The direction of the arrows indicates the heating-cooling cycle.

Carbon Monoxide on rh-In₂O₃

In direct comparison to the reduction experiments in hydrogen, the temperature-programmed reduction experiments in CO (Figure 5A) reveal conversion into CO₂, most probably by removal of and reaction with lattice oxygen, starting efficiently at ~550 K and proceeding also during the 10-minute isothermal period. Upon re-cooling, a small amount is re-formed, also indicated by the respective CO₂ consumption in the same temperature region. The same is also directly visible in the corresponding FT-IR experiments (Figure 5B). Above 573 K, CO₂ appears in the gas phase, in close correlation to the decrease in the CO signal around 550 K in the temperature-programmed reduction experiment.

Figure 5: Panel A: Temperature-programmed carbon monoxide uptake. Initial starting pressure of carbon monoxide: 100 mbar, heating and cooling rate: 10 K min⁻¹, isothermal period at 673 K for 10 minutes. The direction of the arrows indicates the heating-cooling cycle. Panel B: Static temperature-programmed CO FT-IR experiments in direct comparison to the temperature-programmed reduction experiment shown in Figure 6A. Starting CO pressure: 121 mbar, heating and cooling rate: 10 K min⁻¹.

Also the corresponding temperature-dependent conduction behavior as a direct consequence of the different reduction behavior in CO and hydrogen yields valuable information. Re-addressing Figure 4, decrease of the impedance is already observed starting at room temperature until at 420 K a quasi temperature-independent impedance plateau ($\sim 20 \Omega$) is reached. This plateau extends up to ~ 550 K, above which a further drop leads to metallic conductivity. The drop, most interestingly, occurs at almost exactly the same temperature as in hydrogen (also the amount of c-In₂O₃ formed via treatment in H₂ and CO is comparable at lower temperatures), but the distribution between c-In₂O₃, rh-In₂O₃ and metallic In at higher temperatures (above 573 K) is clearly different. In fact, the transformation into c-In₂O₃ using CO as reducing agent is effectively suppressed (40 weight-% rh-In₂O₃ still remaining at 673 K, as compared to 0 weight-% on c-In₂O₃), but at the same time, the amount of metallic In at the same temperature (i.e. 673 K) is three times as large (cf. Figure 4 and 6). This indicates that CO obviously strongly affects the reduction to metallic In, but it appears that this is at least not directly correlated to the intertransformation of the In₂O₃ polymorphs. Further, the X-ray diffractograms in Figure 6 once again corroborate the importance of efficient control of the gas phase chemical reduction potential. While the above discussed mixture of both oxide polymorphs and metallic In is obtained after the flowing CO treatment up to 673 K, after the CO TPR shown in Figure 6, the X-ray diffractogram is essentially unchanged and the phase transformation into c-In₂O₃ is triggered only to a very small extent. Table 1 also reveals that adding CO₂ or H₂O has a huge influence on the transformation behavior. Adding CO₂ (1:1 mixture) to CO suppresses the significant formation of metallic In at 673 K, but encourages the transformation to c-In₂O₃. In contrast, adding H₂O (also a 1:1 mixture), suppresses both transformation into either c-In₂O₃ or metallic In. As both additives have a considerable impact on the defect chemistry on rh-In₂O₃ (and the catalytic behavior in the water-gas shift equilibrium, as shown in section 3.2.), we might assume a partial replenishment of the defects in both CO₂ or H₂O, effectively stabilizing rh-In₂O₃.

Figure 6: X-ray diffractograms collected after various flowing and static treatments in carbon monoxide as indicated. Black represents the pattern after the TPR experiments and red after a flowing treatment in dry CO at 673 K. The calculated peak assignment of the rh-In₂O₃ (black), c-In₂O₃ (red) and In metal (blue) phase is based on PDF cards 22-0336, 06-0416 and 05-0642 (ICDD Powder Diffraction database 4+) and given as solid bars at the bottom of the graph.

3.2. Catalytic Characterization

(Inverse) water-gas shift reactivity

Together with the MSR reaction profiles, the reactivity in the (inverse) water-gas shift equilibrium is considered to shed most light on the different surface chemistry of the different polymorphs and to eventually explain a different CO₂ selectivity in MSR. Figure 7 A and 7 B show the inverse water-gas shift and water-gas shift reactivity, respectively. The inverse

reaction (Panel A) is characterized by a drop in the CO₂ signal at 630 K with simultaneous increase of CO. Hydrogen is consumed, too, but the consumption starts already at around 470 K, well before the inverse water-gas shift reaction sets in. Above 600-630 K, a further drop in the hydrogen signal indicates the beginning of the stoichiometric inverse water-gas shift reaction. This behavior can be satisfactorily explained by the temperature-programmed reduction and desorption experiments discussed in detail in section 3.1., which showed that hydrogen adsorption (and oxygen vacancy formation) exactly starts in this temperature region, obscuring the inverse water-gas shift reactivity. The water-gas shift direction (Panel B) shows a slightly complexer behavior. Consumption of CO and subsequent formation of CO₂ (starting at around 500 K) is expected based on the results of section 3.1., but a simple oxygen removal mechanism (i.e. Mars-van-Krevelen-type) is excluded, as a rise in the hydrogen signal is also observed (this is not purely stoichiometric because the so-formed H₂ is apparently also re-consumed at these temperatures – see also Panel A). However, the situation is even more complex due to the intermediate appearance of formaldehyde. The latter, as will be reported in the MSR section below, appears also as a key intermediate during the methanol steam reforming reaction. Formaldehyde is obviously formed in parallel to CO₂ and decomposes above 580 K, further increasing the hydrogen yield. Putting these results into the perspective of previous results on c-In₂O₃, it turns out the reaction profile of the latter is distinctly different. In that case, c-In₂O₃ does react with CO yielding CO₂, but not via the water-gas shift reaction, but under strict non-catalytic simple and efficient oxygen removal control. The inverse route by replenishing oxygen vacancies by CO₂ is almost entirely blocked.⁸ In general, the microkinetics of the water-gas shift equilibrium can follow two distinct pathways, depending on the experimental conditions: a regenerative mechanism involving oxygen vacancies (mostly at high reaction temperatures) and an associative mechanism (usually at low reaction temperatures).³⁰ The latter involves the adsorption of both CO and H₂O on the oxide surface, the water activation (i.e. heterolytic water splitting into H

and OH) and finally, the reaction to an intermediate, which further reacts towards the products. The core point of the latter mechanism is the nature of the intermediate, which is up to date controversially discussed.^{30,31} Formates and/or formic acid intermediates have been reported on different catalysts.³¹⁻³⁶ In the present case, the particular question arises if the observed formaldehyde is formed as a key intermediate *en route* from CO and H₂O to CO₂ and H₂ or if it is an intermediate in a parallel reaction to the actual water-gas shift reaction. Scheme 1 highlights in the involved gas-surface reactions

Reaction (1) represents the water-gas shift equilibrium, reaction (2) the reaction of CO and H₂O to formaldehyde and its transformation to H₂ and CO₂ with additional water. Reaction (2) is predominantly found at reaction temperatures above ~ 620 K. From the catalytic data it follows that both reactions at least to certain extent are found as parallel reactions, but not as purely sequential reaction steps. This is derived from the parallel onset of both CO₂ and formaldehyde in the initial stages of the reactions and from the sudden break in the hydrogen signal at around 620 K, where formaldehyde reacts further to yield yet another CO₂ and H₂ molecule. While the intermediate to reaction (1) possibly involves influence both from a regenerative and an associative mechanism (due to the strong interaction of CO with rh-In₂O₃ discussed in the preceding section), the intermediate to reaction (2) is to date unknown, but possibly also involves the participation of oxygen vacancies.

Figure 7: Reaction profile of the (inverse) water-gas shift reaction on rhombohedral In_2O_3 . Panel A): inverse water-gas shift reaction, Panel B): water-gas shift reaction. Reaction conditions: 30 mbar CO_2 , 30 mbar H_2 for Panel A), 26 mbar CO and 26 mbar H_2O Panel B), 10 mbar argon and He added to 1 bar total pressure. Heating ramp: 10 K min^{-1} . Pre-treatment of the samples include oxidation at 673 K for 1 h in flowing oxygen.

Methanol Steam Reforming

MSR experiments have been conducted on both polymorphic forms under question and are jointly shown in Figure 8. Cubic In_2O_3 (Figure 8 B) shows the anticipated and well-known reaction pattern with very high CO_2 -selectivity. No carbon monoxide can be detected and a total methanol conversion of $\sim 80\%$ is obtained at 673 K. In contrast, rh- In_2O_3 shows a distinctly different behavior. Notable methanol conversion starts at around 520 K with a more or less parallel increase of the hydrogen signal. CO_2 is accordingly also formed at roughly similar temperatures. Most notably, CO is only observed at higher temperatures (above ~ 570 K) and formaldehyde species appear as an intermediate species. In line with this observation, only a diminished CO_2 selectivity between 50 and 60%, depending on the reaction degree, is achieved. A closer look at the hydrogen signal reveals a characteristic maximum at 640 K, followed by a drop at 650 K and yet another increase above that temperature. As deduced from the slowing down of the CO_2 trace and from the inverse water-gas shift reaction profiles discussed in detail in Figure 7, this is the temperature where H_2 and CO_2 back-react to CO (and water) via the inverse water-gas shift reaction. The increase of the hydrogen signal at temperatures above 650 K is then due to the decomposition of the intermediately formed formaldehyde into H_2 and CO. The associated increase in CO is obviously suppressed due to its strong interaction with In_2O_3 (forming e.g. CO_2 via removal of lattice oxygen and the water-gas shift equilibrium), as discussed in the previous section on reducibility. Note that this complex reaction network observed on rh- In_2O_3 is also directly visible in the CO_2 selectivity, finally increasing to its highest value at 673 K (62 %) due to the decomposition of formaldehyde.

Figure 8: Reaction profiles of the methanol steam reforming reaction on rhombohedral (Panel A) and cubic In₂O₃ (B). Reaction conditions: 15 mbar methanol, 30 mbar water, 10 mbar Ar and He added to 1 bar total pressure. Heating ramp: 10 K min⁻¹. Pre-treatment of the samples include oxidation at 673 K for 1 h in flowing oxygen.

Two important questions remain to be answered at this point: the first one concerns the phase stability during the reaction. As directly revealed in Figure S2, X-ray diffractograms taken after the respective MSR (and (inverse) water-gas shift reaction) runs show that rh-In₂O₃ remains structurally stable and no substantial transformation into c-In₂O₃ takes place.

Secondly, the peculiar MSR reaction pattern of rh-In₂O₃ has to be explained in a comparative view to c-In₂O₃ and, most importantly, also with respect to the (inverse) water-gas shift activity. For the sake of clarity, a brief account of previous findings on c-In₂O₃ should be added at this point.^{8,9,27} The latter shows exceptional high CO₂ selectivity in the MSR reaction (close to 99% at 673 K) due its outstanding behavior both in the (inverse) water-gas shift activity and its reactivity towards CO at very low temperatures close to 300 K.^{7,8} This reactivity in due course leads to a very efficient transformation of CO into CO₂ via the water-gas shift reaction, but at the same time, the backward reaction from CO₂ and H₂ to CO (and water) is effectively blocked. This behavior has been explained by the water-gas shift reaction predominantly following a vacancy-mediated mechanism and a very high activation barrier for the replenishment of the so-induced oxygen vacancies by CO₂ (via the inverse reaction).⁸ This behavior (and the associated high CO₂ selectivity in MSR) is typical for oxides with predominant basic surface sites (like c-In₂O₃), enabling both efficient H abstraction from the adsorbed methanol and a very fast onward reaction of the intermediate formaldehyde species to CO₂.³⁷ Therefore, on c-In₂O₃ no formaldehyde is observed as gas-phase intermediate and in fact, dedicated formaldehyde steam reforming reactions revealed similarly high CO₂ selectivities comparable to those observed via MSR.⁸ In contrast, oxides with a corresponding higher number of acidic surface sites (like rh-In₂O₃) tend to form more intermediate oxygenates (such as formic acid-related intermediates) and condensed molecules (such as dimethylether).³⁷ A instructive example in this respect is the Ga₂O₃ polymorphic system: on the β -Ga₂O₃ modification, due its high number of acidic surface sites, formic acid could be detected as intermediate. The more basic α -Ga₂O₃ polymorph in contrast showed CO₂ selectivities up to 70 %.³⁸ From this discussion, we directly infer a corresponding less-pronounced basic character of the surface sites on rh-In₂O₃, in contrast to c-In₂O₃, but at the same time also without a pronounced acidic character, as no formic acid or condensed intermediates are in parallel observed. Most interesting, rh-In₂O₃ seems to exhibit special

adsorption sites stabilizing formaldehyde obviously long enough to detect it as gas-phase intermediate, before final decomposition into H₂ and CO takes place.

The difference in the reactivities is also reflected upon consideration of the CO₂-related turnover frequency numbers (TOF's) and the calculation of the apparent activation energies. The estimation is based on the sample mass (70 mg rh-In₂O₃, 60 mg c-In₂O₃), the densities of the oxide structures, their molar mass (277.6 g mol⁻¹) and their specific surface areas (43.5 m² g⁻¹ for rh-In₂O₃, 0.74 m² g⁻¹ for c-In₂O₃) as well as the definition of one In-O entity as catalytic active site. This yields 3.80x10¹⁹ In-O sites for rh-In₂O₃ and 5.54x10¹⁷ sites for c-In₂O₃. Based on these numbers, the TOF's can be estimated and are summarized in Table 3.

Table 3: Overview of the CO₂-related catalytic turnover frequency numbers in methanol steam reforming, as obtained on rh- and c-In₂O₃.

Sample	CO ₂ TOF/ s ⁻¹ In-O site ⁻¹	CO ₂ TOF/ h ⁻¹ In-O site ⁻¹
rh-In₂O₃		
593 K	6.68x10 ⁻⁵	0.24
613 K	1.05x10 ⁻⁴	0.38
623 K	9.68x10 ⁻⁵	0.35
653 K	3.26x10 ⁻⁵	0.12
c-In₂O₃		
593 K	2.18x10 ⁻³	7.8
623 K	6.25x10 ⁻³	22.5
643 K	7.73x10 ⁻³	27.8
653 K	7.34x10 ⁻³	26.4

As can be clearly seen, the maximum turnover frequency obtained at the highest reaction temperatures on c-In₂O₃ exceeds that of rh-In₂O₃ by a factor of 200, although the methanol conversion is almost equal at about 80 %. The higher reactivity is also derived from the lower apparent energy of 121 kJ mol⁻¹ for c-In₂O₃, in comparison to 137 kJ mol⁻¹ for rh-In₂O₃, as derived from an Arrhenius analysis of the initial reaction rates.

As a concluding remark, we note that the X-ray diffractograms (shown in Figure S2) reveal that none of the treatments reported in this section causes substantial transformation of rh- into c-In₂O₃, an obvious pre-requisite for catalytic characterization.

4. Conclusions

In conclusion, we were successful in providing an in-depth physico-chemical and catalytic characterization of the corundum-type rhombohedral-type In₂O₃ phase. In due course, gas-phase dependent stability limits with respect to the transformation to the cubic polymorphs as well as to metallic In after reduction in hydrogen and carbon monoxide were established. Summarizing, treatment in either of the reduction agents caused distinctly different changes in the crystal structure of initial rh-In₂O₃ and thereby, the relative amounts of still persisting rh-In₂O₃ and newly formed cubic In₂O₃ and metallic In. As for behavior in the (inverse) water-gas shift reaction and methanol steam reforming, rh-In₂O₃ behaves distinctly different from its cubic counterpart, as it effectively catalyses the inverse water-gas shift reaction route. As a consequence, the CO₂ selectivity in methanol steam reforming is at ~60% much lower than observed on cubic In₂O₃. On the latter, the inverse water-gas shift route is almost entirely blocked, giving rise to almost 100% CO₂ selectivity in methanol steam reforming. This obviously is due to the different reactivity of the lattice oxygen in both In₂O₃ modifications and the associated reactivity of the reduction-created oxygen vacancies. As an obvious prerequisite to monitor the catalytic behavior of rh-In₂O₃, the latter proved especially stable in water-gas shift and methanol steam reforming mixtures. Finally, we deem the studies a first step to a better understanding of the chemistry of the In-O system and its various modifications, and anticipate that the ideas can be directly transferred to other even less-common In₂O₃ polymorphs.

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Supporting Information Available

Structure models; Additional X-ray diffractograms

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