Pd/Ga$_2$O$_3$ methanol steam reforming catalysts:
Part II: Catalytic selectivity

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Abstract

Structure, morphology and composition of two Pd/Ga$_2$O$_3$ methanol steam reforming catalysts were correlated with the associated activity and selectivity changes in the methanol steam reforming reaction and linked to studies on pure Ga$_2$O$_3$ supports. For both systems, that are, a Pd/Ga$_2$O$_3$ thin film model catalyst and a powder-supported Pd catalyst, we identified a temperature range in which the reduction with hydrogen yields a single Pd-Ga bimetallic on a reduced oxide support, which in turn suppresses methanol dehydrogenation and results in a high CO$_2$-selectivity in methanol steam reforming. For the thin film catalyst, this included the Pd$_5$Ga$_2$ bimetallic present after reduction in the temperature range 523-600 K, for the powder-supported catalyst, Pd$_2$Ga, formed after reduction between 523 and 773 K, was found to account for the high CO$_2$-selectivity. In contrast to studies on the corresponding Pd/ZnO catalysts, sintering and metal decoration by reduced GaO$_x$ species will additionally have to be considered for discussions about structure-activity correlations in Pd/Ga$_2$O$_3$ thin film model catalysts. Reduction at 673 K causes catalyst deactivation and loss of CO$_2$-selectivity due to encapsulation of catalytically active bimetallic particles by mobile GaO$_x$ species and hampers oxidative catalyst regeneration. No such behavior has been observed for the powder-supported catalyst. This difference in catalytic activity and selectivity between the two catalysts is interpreted in terms of their different (bi-) metallic - oxide contact area.

Formic acid formation has been observed on pure Ga$_2$O$_3$ supports, which yields additional CO by formic acid decarbonylation. For the CO$_2$-selective methanol steam reforming reaction over a Pd-Ga bimetallic particle, formic acid is not a gas phase species, which indicates a preferential decarboxylation pathway of adsorbed formate species at low temperatures.

Keywords: : Catalysis, CO$_2$ selectivity, methanol dehydrogenation, CO, Ga$_2$O$_3$, reduction, Pd-Ga alloys, Formic Acid

1. Introduction

Bimetallic Pd-Ga systems have attracted recent interest due to their ability to selectively catalyse a range of reactions including methanol synthesis [1,2], methanol steam reforming from CO$_2$ [3] and selective acetylene hydrogenation [4,5]. Concerning steam reforming of methanol, a mixture of Pd$_5$Ga$_2$ and PdGa$_5$ bimetallic phases, obtained after a reduction of an impregnated Pd/Ga$_2$O$_3$ catalyst at 773 K, was reported as the catalytically active and selective phase [3]. A shortcoming of these studies on Pd/Ga$_2$O$_3$ so far - especially in comparison to the corresponding 1:1 PdZn/ZnO-based system - is the lack of differentiation between the potentially active and selective oxide-supported *single* bimetallic phases [3]. The importance of the possible bifunctional synergism of Pd (essentially supplier of atomic hydrogen) and Ga$_2$O$_3$ (stabilizing the reaction intermediates) in methanol synthesis from CO$_2$ and H$_2$, and therefore the importance of the (bi-) metal-support interface in general, has been outlined in detail by Bonivardi et al. [2]. It is tempting to assume a similar synergism also for the methanol steam reforming reaction, but in addition involving a special role of the Pd$_x$Ga$_y$ bimetallic particles. Although ultimately the contribution of the contact area can only be determined by comparing the activity and selectivity of Ga$_2$O$_3$-supported and unsupported (e.g. on an inactive oxide such as SiO$_2$ or Al$_2$O$_3$) bimetallic Pd-Ga particles, major improvements to the present situation can be achieved in two ways, that is, (i) by studying the catalytic activity and selectivity of a Ga$_2$O$_3$-supported bi-

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metallic *single* phase and (ii) by comparing Ga_2O_3-supported Pd systems with different metal-support contact areas.

Since the reproducible preparation and thorough structural characterization of the above-mentioned catalyst systems is a prerequisite to fulfill these tasks, part I of these series was entirely devoted to the structural characterization of different Pd-Ga bimetallic systems [6]. It has been shown that by careful H_2-reduction of two different Pd/Ga_2O_3 systems, (namely a thin film with large metal-support contact area and a Pd/Ga_2O_3 powder catalyst prepared by a standard incipient wetness technique with small metal-support interface) it was possible to obtain GaO_x-supported single Pd_5Ga_2 and Pd_2Ga bimetallic phases, respectively. The formation of Pd_5Ga_2 appears to be essentially driven by the better structural match with the underlying fcc lattice of the Pd particles, i.e. an epitaxial bimetallic growth of Pd_5Ga_2 on Pd has been observed. In contrast, the thermodynamically most stable phase, that is, Pd_2Ga, has been observed to form at somewhat higher temperatures on the Pd/Ga_2O_3 powder catalyst. This difference essentially proves the importance of the metal-support contact area for selective bimetallic formation.

The aim of this paper is to link the results of bimetallic formation, described in Paper I [6], to their catalytic performance in methanol steam reforming. The observed catalytic activity and selectivity changes are correlated with corresponding structural, morphological and compositional changes of metal particles and support. Particular attention will be paid not only to results in the literature and the difference of both Pd/Ga_2O_3 systems, but also to the catalytic activity and selectivity of the clean Ga_2O_3 support.

2. Experimental

The preparation of the catalyst films was outlined in detail in part I [6]. Pd particles were grown by electron-beam deposition on in-situ deposited NaCl films (37 cm² each) at around 623 K and subsequently covered with a film of amorphous Ga_2O_3 by reactive deposition of thermally evaporated β-Ga_2O_3 in 10^{-2} Pa O_2 at either 300 K or 600 K (thickness of the support 25 nm each). All films used for catalytic experiments were subsequently covered by a layer of amorphous SiO_2 (prepared by reactive deposition of SiO in 10^{-2} Pa O_2 at 300 K) to improve the mechanical stability (mean SiO_2 thickness 1000 nm). The films were thoroughly rinsed with distilled water, dried and finally mounted on quartz wool inside the reactor. The Pd/Ga_2O_3 powder samples were prepared following a standard incipient wetness routine followed by calcination in air at 873 K for 1h.

Catalytic measurements in methanol steam reforming as well as catalyst activation treatments of *all* samples were performed in an NI Labview-automatized recirculating batch reactor of about 8 ml volume [7]. The system allows automated pretreatment cycles (oxidative and reductive) and reaction sequences. As the measurements should in

principle allow assessing the contribution of different oxide-supported Pd-Ga alloys to the activity and selectivity in methanol steam reforming, activation treatments typically used for supported Pd catalysts to induce the formation of the potentially selective Pd-Ga alloy phase(s) were chosen [3]. Standard activation treatments therefore include oxidation in 1 bar O_2 at 673 K followed by reduction in 1 bar H_2 at varying temperature. For thin films, reduction temperatures between 373 K and 773 K were usually applied. Pd/Ga_2O_3 powder samples were treated in hydrogen at temperatures as high as 923 K.

The catalytic measurements were performed using a quadrupole mass spectrometer (Balzers QMG 311) attached to the circulating batch Duran glass reactor via a capillary leak. All methanol steam reforming reactions were conducted with methanol/water mixtures of a 1:9 composition of the liquid phase at room temperature. The gas phase compositions of a variety of different liquid mixtures have been empirically determined by mass spectrometry. On the basis of these measurements we could derive that the volumetric 1:9 mixture corresponds to a gas phase composition of 1:2 = methanol:water at room temperature. All methanol/water mixtures were degassed by repeated freeze-and-thaw cycles. For each catalytic methanol steam reforming experiment, to about 50 mbar methanol/water mixture, 7.5 mbar Ar (to be measured at m/z = 40) was added to account for the decrease of the mass spectrometer signal due to the continuous gas withdrawal through the leak. Finally, He was added to 1 bar total pressure.

The molecular masses m/z =2 (H_2), 16 (CH_4), 18 (H_2O), 28 (CO/N_2), 29 ($CH_3OH/HCOOH$), 30 (CH_2O), 31 (CH_3OH/CH_2O), 32 (CH_3OH/O_2), 40 (Ar) and 44 (CO_2), 45 (HCOOH) and 46 (HCOOH) were routinely collected. All mass spectrometer signals of CH_3OH, CO_2, CO, and H_2 were externally calibrated and corrected for fragmentation in the mass spectrometer. This includes m/z = 28 for both CO_2 and CH_3OH and m/z = 45 for CO_2. The mass m/z = 28 is therefore only influenced by CH_3OH, CO_2, and the formed CO via the reaction itself. In order to account for the partial adsorption of methanol and water on the stainless steel parts of the reaction system, all catalytic measurements include a 15 minute equilibration period in the starting mixture prior to each measurement. For methanol steam reforming, both temperature-programmed conversion and conversion versus time under isothermal conditions were monitored. In each case, the catalyst was exposed to the reaction mixture and the temperature was ramped with 5 K/min to the final value. For the partial pressure change versus time experiments, the product formation was monitored for 1 hour each at fixed reaction temperature. All the catalytic experiments were also corrected for the activity of the catalyst holder containing only quartz wool (almost negligible, at maximum 1 % conversion based on CO_2 formation after 1 h). For data evaluation, the relative intensities of the mass spectrometer signals were converted into partial pressures via external calibration using gas mixtures of defined partial pressures.

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For clarity, all catalytic results are usually plotted as partial pressure change versus temperature or time. An additional experimental difficulty arises from the general inability to provide a reliable quantification method for formic acid, which readily sticks to the reactor pipings. This does not only influence the masses m/z = 45 and 46, but in turn also affects the m/z = 29 trace, which includes fragment contribution from both CH_3OH and HCOOH. As an approximation, the same mass spectrometer sensitivity factor for CH_3OH and HCOOH were used. The partial pressure change for HCOOH therefore gives a rough estimate, but an independently calibrated quantification of HCOOH could not be included for the given reasons. Instead, we point out that the discussion can be completely based on reliable qualitative information.

The usual total conversion versus time information can be extracted from Figure 9 from the sum of the CO_2 and CO partial pressures at a given reaction time and subsequent division of the sum by the initial methanol pressure. The initial slopes of the conversion versus time plots were taken to determine (initial) reaction rates and turnover frequencies (TOF, molecules per site and hour).

3. Results

3.1. General remarks

Since the Pd/Ga₂O₃ thin film model catalysts designed for direct comparison with the TEM samples of part I are grown on a polycrystalline NaCl thin film substrate, their preparation is somehwat different to the ones used for structural characterization - which are prepared on NaCl (001) cleavage faces. Figure 1 highlights a TEM overview image of small Pd particles deposited on a polycrystalline NaCl thin film and subsequently embedded in Ga₂O₃. The reason to choose the particles grown on NaCl(001) cleavage faces for structural studies is essentially based on a more convenient monitoring of the structural alterations if more regular epitaxial Pd particles are used. However, since a larger amount of catalyst is necessary for catalytic measurements, Pd particles grown on extended NaCl thin films are used for these purposes. The structural equality of the catalysts prepared on either template has been verified in a number of publications [8-10]. By comparison of Figure 1 of ref. [6] and Figure 1 of this paper, it is obvious that the overall particle shapes, diameters and particle densities are comparable on both types of thin film model catalysts. Before each catalytic measurement, the "catalytic" thin films were subjected to exactly the same oxidative and reductive treatments as the films supported on gold grids for electron microscopy.

Recalling the results of the structural studies outlined in part I [6], we remember that hydrogen treatments at temperatures about 523 K primarily induce bimetallic formation on either of the catalyst samples studied. Epitaxially formed Pd_5Ga_2 and less-ordered Pd_2Ga phases were observed for the thin film and the powder catalyst, respective
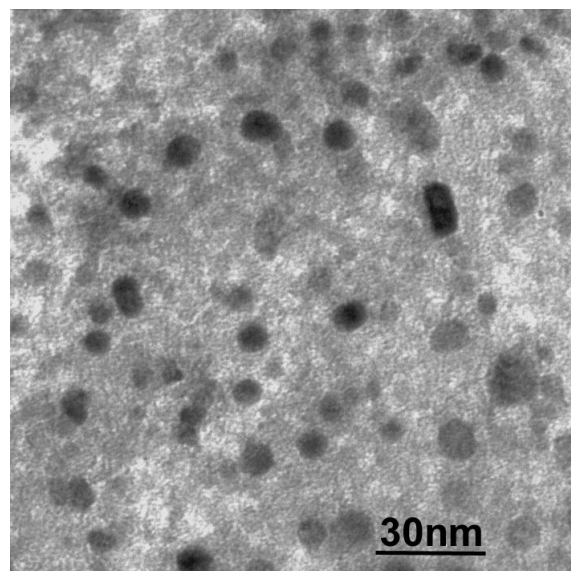

Fig. 1: TEM overview image of the as-grown Pd/Ga₂O₃ thin film sample with the Ga₂O₃ support prepared in 10^{-2} Pa O₂ at 298 K on a NaCl thin film.

ly. On the thin film, this bimetallic formation at higher reduction temperatures (673 K) is accompanied by strong reduction of the oxide support, (bi-) metallic particle sintering and formation of a thin layer of reduced oxide support covering the bimetallic particles. Except from the formation of a Pd-Ga bimetallic, which appears to be crucial for the selectivity and activity of the catalyst in methanol steam reforming [3], none of the above-mentioned phenomena a priori has a beneficial effect on the catalytic properties. It is therefore also tempting to investigate the catalytic activity of the presumably active Pd-Ga bimetallic in view of these phemonena and to detect whether they decrease the catalytic activity/selectivity or if they offer a reaction pathway to a bifunctional synergistic effect between oxide and bimetallic phases.

3.2. Comparison of methanol steam reforming on the Pd/Ga₂O₃ powder and thin film catalysts

3.2.1. Methanol steam reforming on the Pd/Ga₂O₃ powder catalyst

To determine in which temperature regime the catalysts are most active and selective, temperature-programmed experiments have been carried out on both Pd/Ga₂O₃ samples. For each catalytic reaction, 7.5 mbar Ar were mixed with 50 mbar methanol:water mixture (He added to about 1 bar total pressure) in the reactor held at 373 K and subsequently the temperature was ramped with 5 K/min up to 673 K. At this stage we point out that the observed selectivity of the reaction toward CO_2 is always based on competing pathways of methanol dehydrogenation (termed "MDH" in the following; prevails on Pd metal) and methanol steam reforming ("MSR"; prevails on
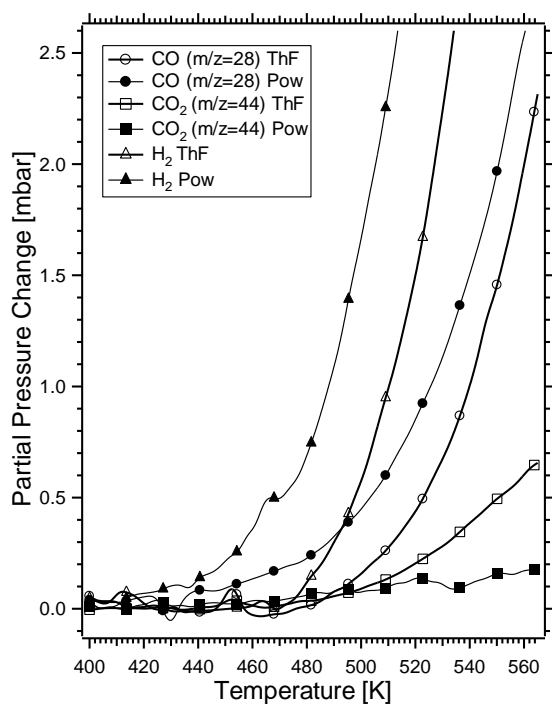
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Fig. 2. Temperature-programmed methanol steam reforming reaction on the Pd/Ga₂O₃ thin film (bold lines) and on the Pd/Ga₂O₃ powder catalyst (fine lines) after an oxidative treatment (1bar O₂, 1 h) at 673 K and 873 K, respectively.

Fig. 3: Temperature-programmed methanol steam reforming reaction on the Pd/Ga₂O₃ powder catalyst after reductive treatments (1bar H₂, 1 h) at 523 K, 593 K and 673 K, respectively. An oxidative treatment (1bar O₂, 1 h) at 673 K was applied in-between each reduction step.

the potentially CO_2-selective bimetallic phases). Figure 2 shows the MSR/MDH reaction as a function of temperature for both catalysts after an oxidation at 673 K, respectively (fine lines with full symbols indicate the powder catalyst, bold lines with open symbols the respective thin film model catalyst). For clarity, the H_2 traces have been plotted within a limited range in Fig. 2, but they further increase according to the stoichiometry of the MSR/MDH reaction. As for the structural experiments, these measurements will in the following serve as the reference state for catalytic activity and selectivity. We remember that by TEM and XRD the states of the Pd/Ga₂O₃ thin film and powder catalysts were characterized as mixtures of PdO/Pd and PdO supported on Ga₂O₃, respectively. As expected, methanol dehydrogenation is the predominant reaction on both catalysts [3]. Reaction starts at around 460 K and the CO signal strongly increases with increasing reaction temperature. According to the CO and CO_2 traces the selectivity towards CO is > 90% on the powder and > 60% on the thin film catalyst at ~ 560 K.

To investigate the MSR/MDH reaction over Pd/Ga₂O₃ and especially over Ga₂O₃-supported Pd-Ga bimetallics in more detail, both catalysts were subsequently subjected to H_2 reduction in the temperature range 373 - 673 K. Recalling the structural results of part I [6] for the thin film catalyst, one remembers beginning bimetallic formation on both catalysts at about 523-573 K, resulting in Pd₅Ga₂ and Pd₂Ga particles supported on Ga₂O₃. Both bimetallic phases are structurally stable at least in this temperature range, but considerable sintering has been observed on the thin film model catalyst at 673 K. The pow
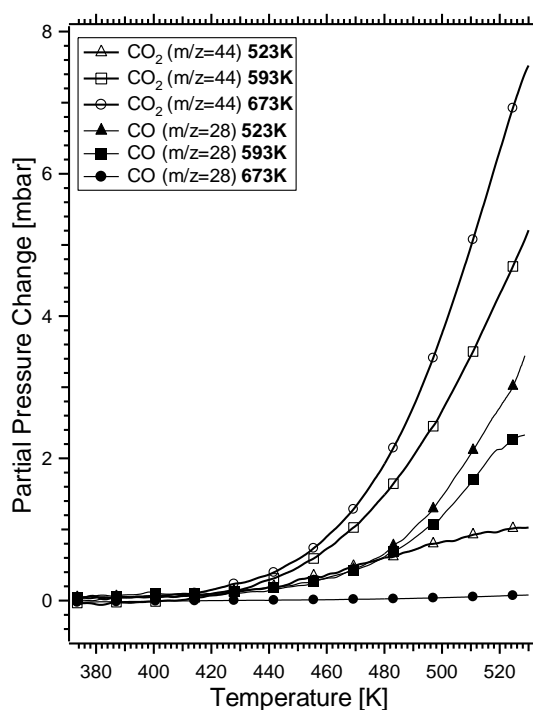
der catalyst is less affected by sintering in this temperature regime [6]. Figure 3 highlights the temperature-programmed MSR/MDH reaction on the Pd/Ga₂O₃ powder catalyst after pre-reduction at 523 K (triangles), 593 K (squares) and 673 K (circles) in 1 bar H_2 for 1 h each. An oxidation step at 673 K (1 bar, 1h) was carried out between each reduction step. According to XRD, this treatment reconverts the Pd₂Ga bimetallic into Pd/PdO supported on Ga₂O₃. The H_2 and CH_3OH traces have been omitted for clarity (their partial pressures again obey the stoichiometry of the MSR/MDH reaction). Since after reduction at 523 K, the formation of the bimetallic phase is less pronounced, the expected result is again preferential methanol dehydrogenation. Figure 3 (triangles) shows that indeed CO is the main product with only little CO_2 formed. If Pd₂Ga bimetallic particles are suspected to selectively catalyze the MSR reaction toward CO_2, first changes in the selectivity pattern are expected after reduction at 573 K (squares). By comparing the CO and CO_2 traces after reduction at 523 K and 573 K, we indeed note a reversal of the selectivity. CO_2 is now the main product, with little CO formed (selectivity towards CO_2 at 530 K reaction temperature about 70 %). It also appears that - in comparison to pre-reduction at 523 K- the overall activity is higher. The CO_2 selectivity is even more pronounced after reduction at 673 K (circles). At 530 K reaction temperature, the selectivity towards CO_2 is > 95 %. Since the CO_2 selectivity does not change with reaction temperature, even if the catalyst is pre-reduced at higher temperatures (773 K), but XRD measurements show an increasing amount of Pd₂Ga if the reduction temperature is
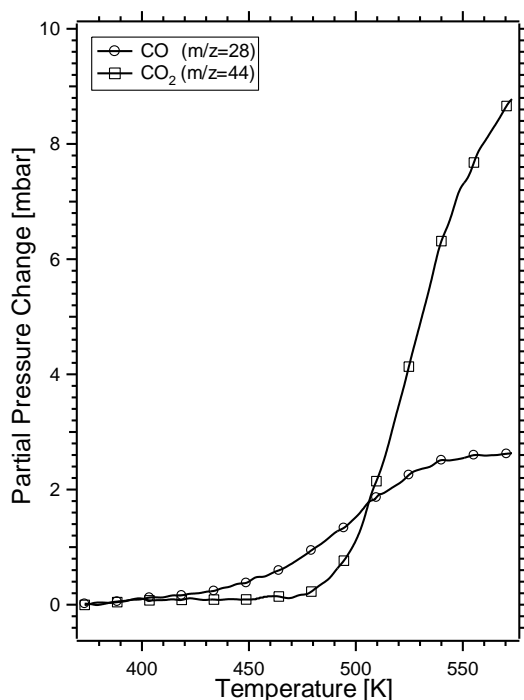
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Fig. 4: Temperature-programmed methanol steam reforming reaction on the Pd/Ga$_2$O$_3$ powder catalyst after a reductive treatment (1bar H$_2$, 1 h) at 923 K

raised from 673 to 773 K, we conclude that - in close correlation to the results of the structural studies [6] - already at 673 K at least the surface-near regions of almost all former Pd particles is converted into a bimetallic state and, for higher reduction temperatures, likely only deeper bulk regions of the particles remain in the pure Pd state. Vice versa, it appears that metallic Pd surface area remains between reduction at 373-573 K and consequently, a certain contribution of methanol dehydrogenation limits the high CO$_2$ selectivity of the pure Pd$_2$Ga bimetallic surface.

As the XRD patterns - at reduction temperatures of as high as 923 K - indicate a full structural conversion of the Pd$_2$Ga into PdGa particles, different surface terminations of the bimetallic phases with respect to Pd and Ga may be assumed [12,13]. Therefore, changes in the catalytic activity and selectivity are also expected. Figure 4 highlights the respective MSR/MDH experiments on a Pd/Ga$_2$O$_3$ catalyst pre-reduced at 923 K. Both the H$_2$ and methanol traces have been omitted (but they in any case obey the stoichiometry of the MSR/MDH reaction). Although the reaction starts at slightly lower temperatures (at about 400 K) as compared to about 440 K for Pd$_2$Ga/Ga$_2$O$_3$, a reversed selectivity and very specific pattern as compared to reduction at lower temperatures (i.e. 773 K, only Pd$_2$Ga present) has been observed between 400 and 500 K reaction temperature. Especially between 400 and 480 K the catalyst is almost 100 % CO-selective, whereas the CO$_2$ signal starts to rise at around 480 K and finally exceeds the CO signal at 500 K. At higher reaction temperatures, a high CO$_2$ selectivity is observed. It is worth to note that the catalyst, after pre-reduction at 923 K, is

nevertheless almost as active as after pre-reduction at around 673 K. From repeated experiments, that is, re-running the MSR reaction on the same catalyst under identical conditions two times in a row (*without* any oxidation or reduction in-between), we realized that no substantial difference in temperature-dependent activity or product selectivity appears. Therefore we conclude that the reaction profile of Figure 4 is the true catalytic MSR "fingerprint" of the PdGa bimetallic. This behaviour can be interpreted either in terms of a static or dynamic surface activity model of Pd:Ga = 1:1. Concerning the latter, the "dynamic" surface state could be reversibly established up to 500 K by more facile segregation to Pd and Ga$_2$O$_3$ on the Ga-richer PdGa 1:1 surface, which in turn could lead to methanol dehydrogenation and higher selectivity toward CO. Above 500 K, in an reducing environment caused by the H$_2$ formed during the reaction, reduction toward the more CO$_2$-selective bimetallic state could set in reversibly. The assumption on which this model is based is therefore related to a specific reversible dynamic segregation behaviour of PdGa 1:1 as a function of temperature under MSR conditions.

3.2.2. Methanol steam reforming on the Pd/Ga$_2$O$_3$ thin film catalyst

Since some differences in the formation of the potentially selective Pd-Ga bimetallic are noted between thin film and powder catalyst as outlined in section 3.1., we expect them to also have at least some impact on the catalytic selectivity. The preferential dehydrogenation behaviour of the as-prepared Pd/Ga$_2$O$_3$ thin film has already been outlined in Figure 2. More interesting, however, is the evolution of the CO$_2$ selectivity as a function of pre-reduction, as shown in Figure 5. Temperature-programmed experiments were performed after pre-reduction at 523 K, 593 K and 673 K in a similar way as discussed above for the respective powder catalyst (experimental details see above).

By comparing the CO vs. CO$_2$ selectivity measured after pre-reduction at 523 K (panel a) with those on the as-grown thin film catalyst (Figure 2) it appears that increased formation of CO$_2$ prevails above 420 K. At about 560 K, the CO signal then exceeds the CO$_2$ signal. However, activity and selectivity are comparable to the powder catalyst after a pre-reductive treatment at the same temperature. The selectivity pattern of panel a appears reasonable since at 523 K the TEM results suggest a coexistence of bimetallic (i.e. Pd$_5$Ga$_2$) and Pd metal surface accessible to the reactants resulting in competing methanol dehydrogenation and steam reforming pathways at different reaction temperatures. Dehydrogenation on Pd metal starts at T ~ 500 K (see also as-grown catalyst state, Figure 2), whereas MSR sets in already at lower temperatures (T > 460 K). At 593 K pre-reduction temperatures (= more former free Pd metal area converted to bimetallic surface, panel b) the selectivity pattern is the same but with a higher relative fraction of MSR/CO$_2$ formation over the entire range of reaction tem
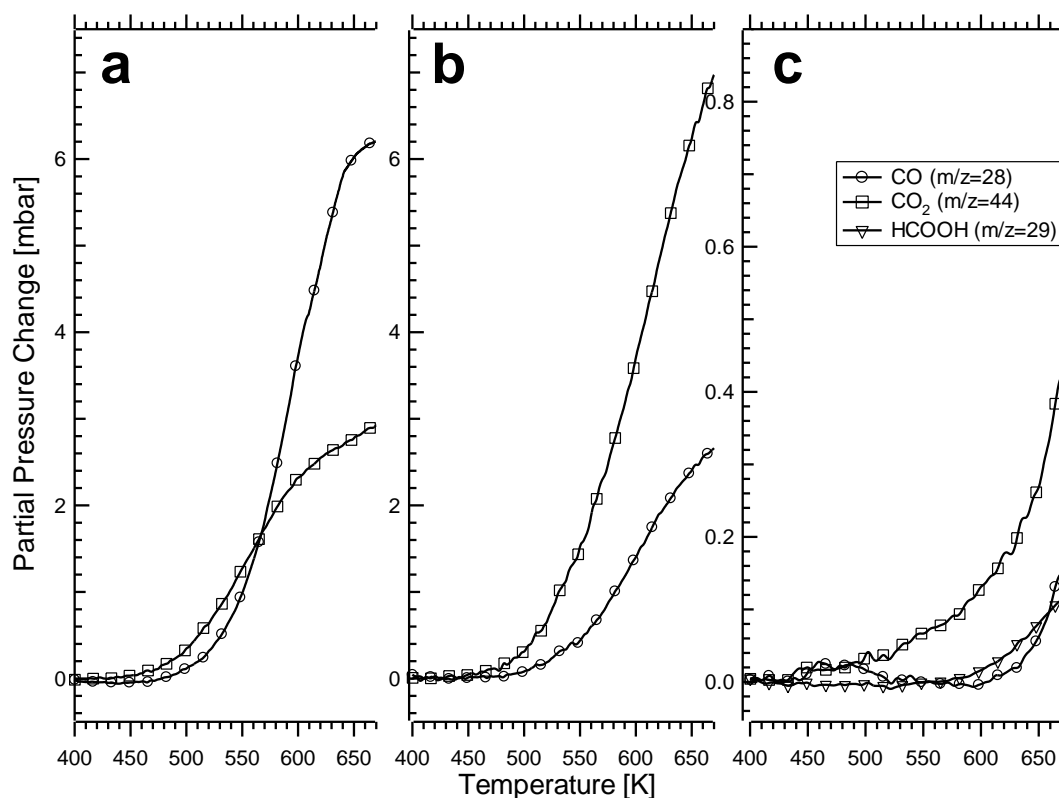
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Fig. 5: Temperature-programmed methanol steam reforming reaction on the Pd/Ga$_2$O$_3$ thin film catalyst after reductive treatments (1bar H$_2$, 1 h) at 523 K (a), 593 K (b) and 673 K (c), respectively. An oxidative treatment (1bar O$_2$, 1 h) at 673 K was applied in-between each reduction step.
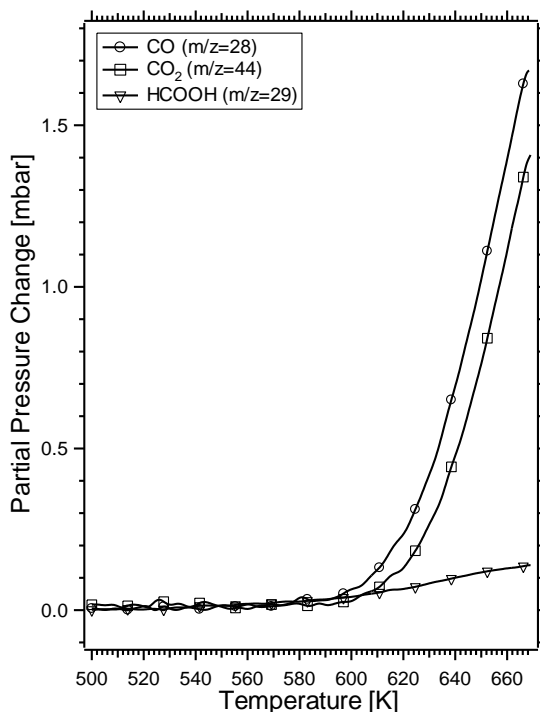

Fig. 6: Temperature-programmed methanol steam reforming reaction on the Pd/Ga$_2$O$_3$ thin film catalyst after a reductive treatment (1bar H$_2$, 1 h) at 673 K, followed by oxidation at 673 K and re-reduction at 600 K.
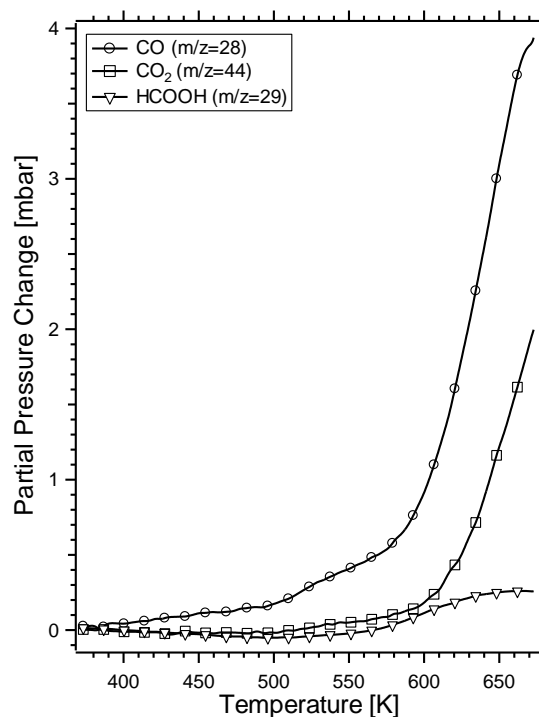
Fig. 7: Temperature-programmed methanol steam reforming reaction on the as-grown Pd/Ga$_2$O$_3$ thin film catalyst with the Ga$_2$O$_3$ support prepared in 10^{-2} Pa O$_2$ at 600 K on a NaCl thin film.

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peratures. Up to 593 K pre-reduction temperature, no substantial differences between thin film and powder catalysts could be noted, which is reasonable since also the TEM investigations on both samples do not suggest a considerable structural or morphological change (except of increased bimetallic formation).

TEM studies nevertheless indicate structural changes at reduction temperatures of 673 K, which basically refers to an increased Ga and Pd mobility to result in a considerable increase in bimetallic particle size. Panel c reveals that this is accompanied by corresponding changes in the catalytic properties. The overall activity is drastically decreased, but we also observe that the onset temperature of catalytic activity is shifted upwards by almost 100 K to about 500 K and that the high CO_2 selectivity is lost. Equally important, we observe that the corrected methanol trace m/z = 29 (i.e. m/z = 29 - m/z = 32) is not a flat line, as for all experiments discussed before, but starts to increase at 550 K. This strongly suggests that a second species is present, which additively contributes to the mass m/z = 29 signal. From the discussion of Figure 8 (see below) it is clear that this second species is formic acid. It is worth to note, that this activity and selectivity pattern with intermediate formic acid formation does not resemble the catalytic properties of either the free Pd metal area (as-grown state; methanol dehydrogenation) or the Pd_5Ga_2 bimetallic (reduction between 523-600 K; CO_2-selective methanol steam reforming), which *never* showed any trace of formic acid. In fact, as will be outlined in section 3.2, the formic acid intermediate is a characteristic of the clean Ga_2O_3 support. The 673 K deactivation and selectivity shift effect can be interpreted in terms of mobile GaO_x species largely covering the active bimetallic surface area. Hence, Ga_2O_3 in part acts like a quasi-"SMSI" oxide [14], which is also supported by the TEM studies showing increased Ga mobility at 673 K [6].

The question now arises if this effect can be reversed by subsequent oxidation, i.e. if the prior catalyst activities and selectivities can be regenerated. To answer this question, one has to consider the TEM results [6], which clearly indicated the formation of a Ga_2O_3 skin after oxidation at 673 K if the catalyst has been previously pre-reduced at 673 K. Subsequent reduction at 523-600 K (in short: pre-reduction at 673 K followed by re-oxidation at 673 K and subsequent pre-reduction at 523-600 K) indicated removal of the most part of the Ga_2O_3 skin. However, as obvious from Figure 6 showing the MSR reaction over a thin film catalyst subjected to the above-mentioned treatment cycle, the most active and selective state of the catalyst (after pre-reduction at 600 K) can not be restored. Instead, the catalytic fingerprint again suggests reaction on the Ga_2O_3 support. We therefore conclude that even after a final reduction at 600 K a thin Ga_2O_3 skin persists, which is not visible in the TEM images. The formation of a Ga_2O_3 skin is further corroborated from experiments on the preparation of Pd/Ga_2O_3 catalysts where Ga_2O_3 was deposited at 600 K in 10^{-2} Pa O_2 (not at 298 K as usual). In part I [6] a very similar core-shell particle structure has been observed in TEM
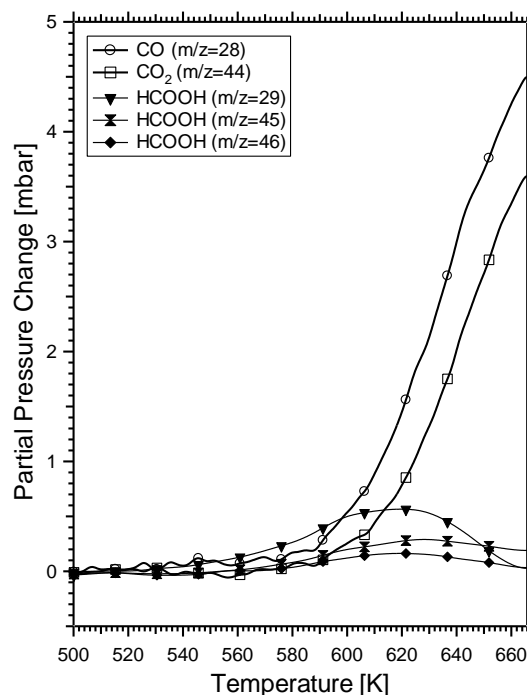

Fig. 8: Temperature-programmed methanol steam reforming reaction on clean Ga_2O_3 powder support. The sample has been subjected to oxidation at 673 K in 1 bar O_2 for 1 h followed by reduction at 523 K in 1 bar H_2 for 1 h.

images in the as-grown state of this catalyst, Figure 7 highlights that again essentially the activity/selectivity of pure Ga_2O_3 is measured on this catalyst, although a minor increase in the CO_2 signal is already obtained at 500 K. Hence, this catalyst consists of Pd particles mostly encapsulated in Ga_2O_3 and no catalytic contribution of Pd or Pd_xGa_y is detectable.

3.2. Methanol steam reforming on clean Ga_2O_3 thin film and powder catalysts

The reason to include the catalytic characterization of the clean Ga_2O_3 supports is obviously on the one hand driven by the need to understand the differences between the activity/selectivity patterns obtained on Pd/Ga_2O_3 after different pre-reduction steps, on the other hand these experiments will link the Ga_2O_3 results to those obtained on clean In_2O_3 samples [8], where a CO_2-selectivity similar to that obtained on Pd_xGa_y bimetallic particles has been observed. This ultimately should lead to the understanding of the reaction mechanism of MSR on both Ga_2O_3 and Pd/Ga_2O_3, but also In_2O_3/ Pd-In_2O_3.

The structural characterization of Ga_2O_3 thin films and powders is outlined in ref [15]. Figure 8 shows the temperature-programmed MSR/MDH reaction over clean Ga_2O_3 powder after an oxidation/reduction cycle at 673 K and 523 K, respectively (the Ga_2O_3 thin film shows qualitatively a similar behaviour, not shown here). CO, CO_2, m/z = 29 after subtraction of the CH_3OH m/z = 29 fragment

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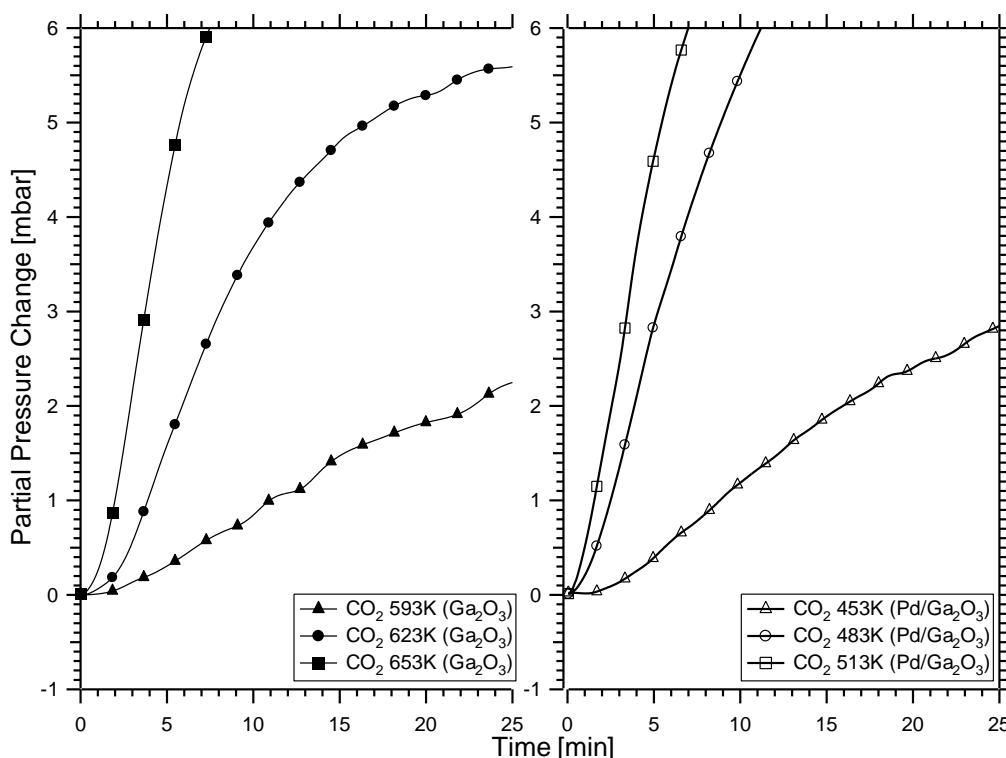
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Fig. 9: Pressure change (CO_2 traces) versus time plots measured in the methanol steam reforming reaction on clean Ga_2O_3 powder (left panel; reaction temperatures: 593 K, 623 K, 653 K) and on the corresponding Pd/Ga_2O_3 powder catalyst (right panel; reaction temperatures: 453 K, 483 K, 513 K).

(CH_3OH/HCOOH), m/z = 45 and 46 (HCOOH) are plotted as partial pressure change versus temperature, with the calibration restrictions outlined in section 2. The analogous selectivity pattern of Figure 8 and Figures 6 or 7 is obvious. The reaction starts at around 520-540 K with an increase in the formic acid signals. Both CO and CO_2 start to rise at around 560 K, but no pronounced selectivity is observed. The formic acid signals start to decrease slightly at 630 K, indicating further reaction to CO and/or CO_2. The question now arises how to interpret the origin of the formic acid. The product selectivity of Ga_2O_3 and other oxides in the MSR reaction can be at least in part rationalized from a concept of Tatibouet [16] based on the strength of acidic and basic oxide surface sites, originally applied to selective methanol conversion. According to this concept, the methanol conversion over Ga_2O_3 as an amphoteric but also redox-active oxide without pronounced acidic or basic character should represent a compromise between partially oxidized species such as CO, formic acid (or possibly) formic acid methyl ester (not detected) and full oxidation toward CO_2. This sets Ga_2O_3 apart from its more basic and more easily reducible In_2O_3 counterpart, which steers the MSR reaction predominantly towards CO_2.

3.3. Determination of activation energies over Pd/Ga_2O_3 and Ga_2O_3 powder catalysts

A rough estimation of binding sites on the clean Ga_2O_3 surface and the Pd/Ga_2O_3 catalyst and thus, the turnover frequencies as well as the apparent activation energy via an Arrhenius plot, can also be obtained. For clean Ga_2O_3, the number of "catalytic sites" (i.e. Ga-O surface units; a specific surface area of 4 m^2g^{-1} and a sample mass of 6.2 $\times 10^{-2}$ g were considered) was determined to be 5.8 µmol [17]. Figure 9 highlights the time-resolved CO_2 traces on clean Ga_2O_3 (left panel) and Pd/Ga_2O_3 (right panel) at different reaction temperatures (593, 623 and 653 K for clean Ga_2O_3; 453, 483 and 513 K for Pd/Ga_2O_3). Both samples were subjected to identical pre-treatments in O_2 (1 bar 673 K, 1h) and H_2 (1 bar, 673 K, 1h), respectively. From the initial CO_2 slopes of the left panel and the number of "catalytic" Ga-O sites the turnover frequencies based on CO_2 formation were determined to be 2.9 h^{-1} (593 K), 8.6 h^{-1} (623 K) and 34.1 h^{-1} (653 K). An Arrhenius plot ln (TOF) versus reciprocal reaction temperature yields an apparent activation energy of ~ 130 kJ mol^{-1}. This is somewhat higher to clean In_2O_3, where an apparent activation energy of ~ 100 kJ mol^{-1} has been obtained [8]. For Pd/Ga_2O_3, the number of active catalytic sites was estimated in the following way: from a sample mass of 0.023 g the mass of Pd was determined to be 0.00275 g (12% Pd/Ga_2O_3). Considering a mean Pd particle diameter from TEM of 7.5 $\times 10^{-9}$

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m (this refers to the as-grown particles) and assuming hemispherical particles, the number of Pd particles (on the basis of the Pd mass) was determined to be 2.1×10^{15}. The entire Pd surface of the catalyst is thus given by 0.182 m^2. The total number of metal surface sites finally results in 3.44 μmol (the space required for one Pd atom was determined to be 8.8×10^{-20} m^2 assuming an isotropic contribution from (111), (100) and (110) facets). Again, from the initial CO$_2$ slopes of the right panel and the number of active sites the turnover frequencies based on CO$_2$ formation were determined to be 5.7 h^{-1} (453 K), 7.8 h^{-1} (483 K) and 36.6 h^{-1} (513 K). An Arrhenius plot ln (TOF) versus reciprocal reaction temperature yields an apparent activation energy of ~ 61 kJ mol^{-1}, which is comparable to different oxide-supported Cu catalysts [18], but considerably less than for clean Ga$_2$O$_3$.

4. Conclusions

The concluding remarks are best summarized by recalling the MSR reaction pathways on Ga$_2$O$_3$ and Pd/Ga$_2$O$_3$. Both pathways will have to include possible surface-adsorbed species (both on metal and oxide) and species that are detected in the gas phase. For clean Ga$_2$O$_3$ this includes H$_2$O and CH$_3$OH (MSR reactants), CO, H$_2$, CO$_2$ and HCOOH (MSR products). Typically, formate species, H$_{ads}$ and OH$_{ads}$ are the most important surface-bound species on Ga$_2$O$_3$ [17]. We do not consider species limited to the surface such as methoxy or formyl. At 500-550 K, decomposition of the Ga$_2$O$_3$-adsorbed formate species is feasible via either decarbonylation (to CO and OH$_{ads}$) or decarboxylation (to CO$_2$ and H$_{ads}$) as outlined in detail in ref [17]. Some of the formate species may react with H$_{ads}$ to form HCOOH which desorbs.

A different situation is present if a Pd$_x$Ga$_y$ particle is supported on Ga$_2$O$_3$. As long as free Pd metal is present at low temperatures, dehydrogenation of methanol starting at 400 K is the dominant reaction on the metal surface. Formaldehyde was never observed, suggesting fast oxidation of this species. For the CO$_2$-selective MSR reaction over a Pd-Ga bimetallic particle on Ga$_2$O$_3$, HCOOH is not observed in the gas phase. It is well-known that formate species readily decompose on noble metal surfaces via a preferential decarboxylation pathway at low temperatures (e.g. 280 K on Pd(111) [19]). Hence, for the present case, on the Pd-Ga bimetallic particles we suggest an additional pathway of HCOOH decarboxylation to CO$_2$ and H$_{ads}$ (and finally desorption as H$_2$) at lower temperatures either via reverse formate spillover from the Ga$_2$O$_3$ support to the Pd-Ga bimetallic or by direct gas phase interaction. This adds to the CO$_2$-selectivity of Ga$_2$O$_3$-supported Pd-Ga bimetallic catalyst particles, since these are also expected to be less active in HCHO dehydrogenation toward CO, in analogy to the related PdZn systems [20].

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