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Physico-chemical properties of unusual Ga₂O₃ polymorphs

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Abstract

A comparative structural and spectroscopic study, combined with reactivity tests in (inverse) water-gas shift and methanol steam reforming reaction, has been performed on various Ga₂O₃ polymorphs with special focus on δ -Ga₂O₃ and ϵ -Ga₂O₃ with the aim of highlighting the eventual intrinsic physico-chemical properties of the latter two. Using this comparative approach, the question whether δ -Ga₂O₃ in fact is a nanocrystalline modification of ϵ -Ga₂O₃, a mixture of ϵ -Ga₂O₃ and β -Ga₂O₃ or a single polymorphic form could be answered: especially Raman spectroscopy measurements, alongside reactivity tests, indicate that δ -Ga₂O₃ exhibits lots of properties of ϵ -Ga₂O₃. In fact, particularly in Raman measurements it appears as a mixture of ϵ -Ga₂O₃ and β -Ga₂O₃.

Keywords Catalysis • Material science • Oxides • Nanostructures

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1 **Introduction**

2 Polymorphism is one of the most important features in oxide chemistry. On
3 the one hand, it significantly adds to the complexity of understanding of the
4 fundamental issues of operation, on the other hand – due to the different
5 crystal structures and physico-chemical properties – it opens exciting new
6 possibilities in their use also as technologically relevant materials [1].
7 Furthermore, many of these usually metastable polymorphic modifications
8 can be stabilized even under ambient conditions in their nanostructured
9 forms [1]. In that respect, synthesis of these materials typically is a major
10 challenge and often external modifiers or stabilizers are used. One of the
11 best known example is the ZrO_2 structure, whose metastable cubic or
12 tetragonal polymorphs are usually stabilized by the deliberate incorporation
13 of anions or cations in its crystal lattice [2]. From both a fundamental
14 scientific and more application-oriented viewpoint, the study of oxides with
15 a broad variety of polymorphic modifications is most rewarding. Examples
16 include WO_3 , MoO_3 , Al_2O_3 or HfO_2 , all exhibiting four or more
17 polymorphic structures with different physico-chemical properties [1]. In
18 general, synthesis procedures for almost all structures exist, as in most
19 cases are the stability limits and the transformation temperatures and
20 conditions of the individual modifications. Although in some of the best
21 characterized systems also physico-chemical and even catalytic properties

1 have been examined [1], there appears to be a profound general lack of
2 knowledge of these properties of most of the structures. This is sometimes
3 owing to the difficulty in applying a synthesis routine giving rise to
4 quantitative amounts of materials, especially when no straightforward wet
5 chemical preparation procedures exist and, more importantly, the
6 polymorphic forms cannot be isolated as pure materials [3,4]. One system,
7 which shows most of these difficulties, but appears also very rewarding,
8 regarding its potential use in technology, is the Ga_2O_3 system [4-19]. Its
9 thermodynamically most stable monoclinic β -modification acts as efficient
10 sensor material [20] or exhibits activity in many catalytic reactions (e.g.
11 methanol reforming and synthesis, benzene hydrogenation [21-23] or
12 (inverse) water-gas shift reaction [24]). Although the polymorphic system
13 of Ga_2O_3 has been scrutinized both experimentally and theoretically [4,5,7-
14 9,11-14], there is still some debate about the existence of several structures
15 [4]. It is widely accepted, that cubic α - and γ - Ga_2O_3 modifications exist [4].
16 Reliable synthesis routines to the latter two phases exist [14] and the
17 surface chemistry [5,9,12,19,25] as well as their stability limits and
18 catalytic properties, e.g. in methanol steam reforming [6], propane
19 dehydrogenation [18] or photocatalysis [16] are well-known. They even
20 served as supporting material for small, catalytically CO_2 -selective
21 intermetallic Pd_2Ga particles in methanol steam reforming, giving rise to a

1 catalytic bifunctional oxide-intermetallic synergism [6,26]. In contrast, the
2 physico-chemical properties of most of the remaining polymorphic forms
3 are less clear and even their existence, or at least their synthesis routes,
4 under question [4]. The cubic δ -Ga₂O₃ polymorph is repeatedly reported to
5 be synthesized by prolonged heating of gallium nitrate hydrate at 493 K for
6 several hours [4,14,16,18]. There is some ongoing discussion, whether δ -
7 Ga₂O₃ exhibits a bixbyite structure and hence bears some resemblance to
8 other X₂O₃ oxides like Mn₂O₃ or In₂O₃ crystallizing in the same structure,
9 or if it indeed is only a nanostructured form of another Ga₂O₃ polymorph,
10 namely ϵ -Ga₂O₃ [4]. Nevertheless, propane dehydrogenation activity of δ -
11 Ga₂O₃ has been reported, as are hydrogen uptake measurements [18]. Even
12 more under question is the ϵ -polymorph, which has been reported by Roy
13 et al. almost 50 years ago to be synthesized by simple high-temperature
14 annealing of δ -Ga₂O₃ at temperatures $T > 773$ K [14]. Structural
15 similarities with hexagonal ϵ -Fe₂O₃ have thereby been stressed [14].
16 However, repeated attempts to re-synthesize this phase failed [16], but
17 some authors were finally successful in synthesizing ϵ -Ga₂O₃ [13], also in
18 its nanorod morphology [15]. Recently, the initial X-ray diffractogram of
19 Roy et al. was shown to be in fact a mixture of ϵ -Ga₂O₃ and β -Ga₂O₃, to
20 which ϵ -Ga₂O₃ at high temperatures inevitably transforms [4]. Playford et
21 al. were able to calculate the unit cell of ϵ -Ga₂O₃ from neutron and X-ray

1 diffraction data and hence, the presence of this phase with a hexagonal
2 structure in the Ga-O phase diagram seems to be verified [4]. The latter
3 authors were also able to detect a transient new polymorph, κ -Ga₂O₃, upon
4 oxidation of metallic Ga, but to date, isolation of this phase repeatedly
5 failed [4]. In due course, hardly anything is known about the physico-
6 chemical properties of these materials, which is a particular pity, since
7 correlation of their properties with other Ga₂O₃ polymorphs or isostructural
8 compounds could help in resolving some of the pending questions in this
9 system.

10 As a consequence, the aim of the present study is to provide data on the
11 structure, morphology, surface chemistry, reducibility and electronic and
12 catalytic properties of δ -Ga₂O₃ and ε -Ga₂O₃ to eventually answer the
13 specific questions:

14 (1) Given the contradicting results in literature, can the ε -Ga₂O₃ phase be
15 reproducibly prepared?

16 (2) Are both stable enough to ensure the properties can be studied without
17 unwanted phase transformation?

18 (3) What are the intrinsic physico-chemical properties of the δ -Ga₂O₃ and
19 ε -Ga₂O₃ phase?

20 (4) Does the δ -Ga₂O₃ phase exhibit properties of ε -Ga₂O₃?

A multitude of structural and spectroscopic characterization tools (Raman Spectroscopy, X-ray-Diffraction, Scanning Electron Microscopy), adsorption techniques (volumetric adsorption, surface-area and porosity measurements according to BET and BJH), reactivity tests (influence of water and hydrogen, catalytic testing in methanol steam reforming and water-gas shift reaction) and contact angle measurements will be applied to fulfill these tasks. Particular emphasis will be given to a detailed comparison to other yet well-established Ga_2O_3 polymorphic forms and to bixbyite-type In_2O_3 .

It is be noted at this point, that especially the catalytic profiles could be of particular help in pointing towards the intrinsic properties, since the potentially suspected isostructure of $\delta\text{-Ga}_2\text{O}_3$ and cubic In_2O_3 due to the potentially similar high CO_2 -selectivity in methanol steam reforming (MSR) will be eventually directly revealed. In addition, all Ga_2O_3 profiles in MSR are very characteristic due to the different extent of water-gas shift reactivity and intermediate formic acid formation [6].

Results

Formation of the Phases and Structural Characterization

Figure 1: X-ray diffraction patterns collected after various annealing treatments of the $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ precursor in air and hydrogen. a) 12 h at 493 K (“ δ -Ga₂O₃”), b) subsequent heating (after performing treatment a)) for 14 d at 673 K, c) after performing the temperature-programmed hydrogen treatment at 480 K with the sample prepared via a), d) 30 min at 800 K after 14 days at 673 K and e) 60 h at 800 K after 14 days at 663 K (“ ϵ -Ga₂O₃”). Peaks of “ δ -Ga₂O₃” have been directly assigned [14,18], those of “ ϵ -Ga₂O₃” (and β -Ga₂O₃) indicated as ticks with further assignment in the text (according to [4,27]).

1 Figure 1 reveals the successful preparation of the modifications under
2 question. δ -Ga₂O₃ is represented by its characteristic fingerprint consisting
3 of its broad (222) and (400) peaks at $2\theta=31.3^\circ$ and $2\theta=35.8^\circ$ and (622) at
4 $2\theta=62.5^\circ$ [14,18]. Note that this assignment is essentially based on that
5 reported by Roy et al. [14], which is in fact problematic due to the reasons
6 discussed below. To ensure the validity of the presence of the phase known
7 as δ -Ga₂O₃ and to directly connect to the experiments reported by other
8 authors, e.g. [18], this assignment is kept for the sake of clarity. A typical
9 treatment of prolonged heating in air at 493 K for 12 h was necessary for
10 single phase formation. Preparation of ε -Ga₂O₃ did not prove to be
11 straightforward. More attempts – under however different experimental
12 conditions than previously reported [4,13,15] - were necessary to reproduce
13 the XRD diffractogram that is reportedly assigned to the unequivocal
14 presence of ε -Ga₂O₃. Specifically, only after heating δ -Ga₂O₃ for 60 h at
15 600 K after 14 days at 663 K, characteristic features of ε -Ga₂O₃ all appear
16 in the diffractogram. Note that treatments under conditions, e.g. reported in
17 ref. [4] or [13] (cf. diffractogram b), show the splitting of the group of
18 peaks between 60 and 65°, but not lead to full crystallization of the ε -Ga₂O₃
19 phase. As reported earlier (and will be discussed later on), the ε polymorph
20 is always contaminated with β -Ga₂O₃ and therefore, the measured XRD
21 patterns are always a mixture of both. In that respect (as marked in Figure 1

1 in diffractogram e), the peaks at $2\theta = 35.5^\circ$, 36.9° , 38.4° , 40.8° , 62.2° and
2 64.3° correspond to the (100), (101)/(10-1), (004)/(00-4), (102)/(10-2),
3 (105)/(10-5) and (2-10) reflections of the ϵ -Ga₂O₃ phase ([4] and a
4 theoretically calculated pattern using the Vesta[®] program; Table S1 gives a
5 full overview of the peaks), while the ones at $2\theta = 30.8^\circ$, 31.7° , 33.5° ,
6 48.7° and 57.4° correspond to the most intense reflections (-401), (002), (-
7 111), (510) and (-313) of the β -Ga₂O₃ structure [27].

8
9 **Figure 2:** SEM images of δ -Ga₂O₃ (A) and ϵ -Ga₂O₃ (B) in the as-prepared
10 state.

11

Figure 2A (δ -Ga₂O₃) and 2B (ϵ -Ga₂O₃) show clear differences in the morphologies of both Ga₂O₃ modifications. Whereas the latter shows a distinct and pronounced microporous structure, δ -Ga₂O₃, after the chosen preparation pathway, consists of a network of characteristically randomly oriented elongated grains of 50-100 nm length. No pronounced porous morphology as for ϵ -Ga₂O₃ is observed. It should be noted that effective control of the preparation and synthesis parameters upon dehydration of gallium nitrate induces the formation of a number of different morphologies, including nanorods, for several different polymorphic forms of Ga₂O₃, including e.g. α -Ga₂O₃ and ϵ -Ga₂O₃ [15]. In fact, the morphology differences in the as-prepared states are significant. We note at this stage, that it seems at first contradicting, that the surface area of ϵ -Ga₂O₃, which is prepared by prolonged heating at higher temperatures than used for δ -Ga₂O₃, is actually higher than that of δ -Ga₂O₃. Substantial sintering therefore is not an issue. Rather, the transformation from δ -Ga₂O₃ into ϵ -Ga₂O₃ must be associated with significant recrystallization, leading to the observed morphology in the SEM images, being fully consistent with the BET results.

Spectroscopic Characterization

For further detailed structural analysis, Raman spectra have been collected for δ -Ga₂O₃ and ϵ -Ga₂O₃, as well as for comparison, β -Ga₂O₃ and α -Ga₂O₃.

1 The Raman spectra of the latter are well-known both from the experimental
 2 point of view and theoretical group symmetry analysis and will therefore
 3 serve as reference [16,17,28].

4
 5 **Figure 3:** Raman spectra of different Ga_2O_3 polymorphs. black: $\beta\text{-Ga}_2\text{O}_3$,
 6 red: $\delta\text{-Ga}_2\text{O}_3$, blue: $\varepsilon\text{-Ga}_2\text{O}_3$, magenta: $\alpha\text{-Ga}_2\text{O}_3$. The inset shows a direct
 7 comparison between $\delta\text{-Ga}_2\text{O}_3$ and $\varepsilon\text{-Ga}_2\text{O}_3$.

8
 9 In short, the Raman spectra of $\beta\text{-Ga}_2\text{O}_3$ and $\alpha\text{-Ga}_2\text{O}_3$ perfectly agree with
 10 those reported in literature [16,17,28]. The Raman spectrum of $\delta\text{-Ga}_2\text{O}_3$
 11 mainly consists of broad features (found at 245, 530, 635, 718 and 808 cm^{-1})
 12 ¹⁾ (cf. inset of Figure 3). Note that in early publications, $\delta\text{-Ga}_2\text{O}_3$ was

reported to crystallize in the bixbyite structure (space group $Ia\bar{3}$) [4,14].
 Implying that it would occur as a single phase, according to symmetry
 analysis, this should give rise to the following number of Raman-active
 phonon modes:

$$\Gamma = 4A_g + 4^1E_g + 4^2E_g + 14T_g$$

By comparison to the Raman spectrum of ϵ -Ga₂O₃, however, it is obvious
 that some common Raman modes for both structures exist. In fact, all
 modes observed for δ -Ga₂O₃ can be also found for ϵ -Ga₂O₃. The peaks for
 which this can be best seen are marked by asterisks in the main panel of
 Figure 3. Most importantly, the Raman spectrum of ϵ -Ga₂O₃ is essentially a
 superposition of the one observed for β -Ga₂O₃ and the peaks observed for
 δ -Ga₂O₃. The relationship between δ -Ga₂O₃ and ϵ -Ga₂O₃ is best seen in the
 inset of Figure 3, highlighting the direct comparison of Raman spectra.
 This strongly implies – in perfect agreement with previous findings by
 XRD and neutron diffraction [4]– that δ -Ga₂O₃ is in fact a mixture of ϵ -
 Ga₂O₃ and β -Ga₂O₃, and the peaks of δ -Ga₂O₃ are those of the ϵ -Ga₂O₃
 structure.

Thermogravimetric Analysis

To ensure the phase stability of the materials under question, their behavior
 during an annealing cycle from room temperature (298 K) to 873 K was

1 tested by thermogravimetric analysis, coupled with calorimetry and mass
 2 spectrometry measurements. Especially the latter will directly reveal, if and
 3 how δ -Ga₂O₃ and ε -Ga₂O₃ transform to the thermodynamically more stable
 4 β -modification. Coupled with mass spectrometry, also chemical
 5 information on eventual phase transformation can be deduced. Figure 4
 6 shows, that within the temperature regime under scrutiny, both phases do
 7 not show exothermic signals due to phase transformations to β -Ga₂O₃.

Figure 4: Thermogravimetric analysis of (A) δ -Ga₂O₃ and (B) ϵ -Ga₂O₃ during an annealing cycle in He from 298 K and 873 K. black trace: mass loss, red trace: temperature, blue trace: heat flow. Heating Rate: 2 K min⁻¹.

This holds for the annealing, the isothermal and the re-cooling periods. While the mass loss of ϵ -Ga₂O₃ is negligible during the experiment, δ -Ga₂O₃ loses about 0.5 mg total mass. Following the mass loss trace of the latter, several steps can be noticed: the first one, leading to ~ 0.21 mg mass loss, is associated with loss of water, whereas the second (~ 0.22 mg) and the third (~0.05 mg) are connected to removal of CO₂ and CO. This follows from in parallel recorded ATR infrared experiments (Figure S1) and mass spectrometry data (Figure S2), clearly showing peaks in the carbonate region between 1500 and 1000 cm⁻¹. In addition, the ATR spectra also directly reveal the presence of a more or less hydroxylated surface after preparation.

Volumetric Adsorption

To further test the reactivity of both Ga₂O₃ modifications, hydrogen consumption measurements and thermodesorption spectroscopy was performed. This is of particular help in judging the behavior of δ -Ga₂O₃ and

1 ϵ -Ga₂O₃, since especially for β -Ga₂O₃, but also for the other modifications,
 2 a more or less large data set is already available [16,19].
 3 Figure 5A shows the hydrogen uptake curves from room temperature to
 4 773 K. The temperature was restricted generally to below 773 K, to avoid
 5 potential partial phase transformations.

6
 7 **Figure 5:** Volumetric H₂ adsorption uptake (A) and subsequent H₂
 8 thermodesorption (B) on δ -Ga₂O₃ (blue) and ϵ -Ga₂O₃ (green). Heating rate

in both cases: 10 K min^{-1} . Starting pressure in the volumetric experiments: 100 mbar.

Both samples were routinely checked by XRD after use (for $\delta\text{-Ga}_2\text{O}_3$, see Figure 1) and still show the as-prepared structures. Initially, both traces follow almost the same trend and a slight increase in hydrogen uptake is only noticeable starting at 423 K. $\delta\text{-Ga}_2\text{O}_3$ exhibits a second small step in uptake at around 540 K, after which yet another plateau region is reached. Only after 623 K, the hydrogen consumption increases considerably up to 773 K. Also during the 10-minute isothermal period, the uptake still increases, indicating considerable kinetic limitations of hydrogen uptake. Upon cooling, no hydrogen desorption is observed, indicating irreversible hydrogen adsorption. Pronounced hydrogen consumption on $\epsilon\text{-Ga}_2\text{O}_3$ only starts at 573 K, with a small decreased rate compared to $\delta\text{-Ga}_2\text{O}_3$ at around 623 K. Hence, in the temperature region between 523 and 743 K, most differences between the two modifications are noticeable. Also on $\epsilon\text{-Ga}_2\text{O}_3$ hydrogen consumption at the highest temperatures has not yet reached equilibrium and most hydrogen is again irreversibly adsorbed.

The corresponding thermodesorption spectra, taken directly after cooling down the samples to room temperature, in contrast, show qualitatively a very similar behavior (Figure 5B). For both samples, two distinct

desorption peaks have been observed, one at 540 K being present as a broad shoulder, and a second one, more pronounced, at ~ 673 K. For δ -Ga₂O₃, this peak is shifted to slightly smaller temperatures (653 K). In essence, this indicates that hydrogen is bound to two different surface sites, which seem to be very similar on both modifications.

Putting these results into perspective of previous work, the following picture arises: On β -Ga₂O₃, hydrogen consumption starts at much lower temperature (~ 373 K) with a rather steep increase [19]. Qualitatively, the overall feature of hydrogen consumption is pretty similar. Kinetic limitations of irreversible hydrogen uptake still prevail at the highest temperatures. The corresponding TPD spectra taken on β -Ga₂O₃ after performing hydrogen treatments under comparable conditions are also similar [19], both with respect to the number and temperature of the observed desorption peaks and their relative intensity. A pronounced peak at ~ 700 K and a small shoulder at 500 K were also observed on β -Ga₂O₃, indicating similar hydrogen binding sites. The thermodesorption spectra of δ -Ga₂O₃ are also in line with those reported by Zheng et. al. reporting on the dehydrogenation of propane over different Ga₂O₃ polymorphs. In that work, for all modifications small hydrogen adsorption peaks at ~ 473 K were reported, decreasing from α - over β - and γ - to δ -Ga₂O₃. A high-temperature peak at 633 K was interestingly only observed (without

interpretation) on the latter [18]. As for interpretation of these peaks, one may safely assume that the peak at lower temperatures is connected with surface reduction (being obviously qualitatively similar on all modifications) and the high-temperature peak is associated either with reduction of surface-near or bulk regions.

Note, however, that the picture of hydrogen adsorption especially on β - Ga_2O_3 is very complicated due to its dependence on surface area and reduction degree of the surface and bulk regions, as well as the propensity of dissociative hydrogen adsorption, subsequently giving rise to directed Ga-H bonds [19]. The required temperatures are nevertheless hardly accessible on the two Ga_2O_3 modifications under question, due to their inherent structural instability at higher temperatures.

Reactivity Tests

One of the most promising techniques to unravel the properties of the Ga_2O_3 polymorphs under scrutiny is to test their reactivity in C1 chemistry. Particularly useful in this respect are methanol steam reforming and (inverse) water-gas shift reaction experiments, because each polymorph exhibits a characteristic fingerprint in activity and selectivity. This, in turn, provides a reliable basis for disentangling the relationship between δ - Ga_2O_3 , ϵ - Ga_2O_3 and β - Ga_2O_3 .

1 Figure 6 shows the reactivity of both polymorphs in methanol steam
 2 reforming. On δ -Ga₂O₃ (panel A) methanol conversion starts at about 560
 3 K, with a parallel increase of the CO₂ signal.

Figure 6: Temperature-programmed methanol steam reforming reaction on δ -Ga₂O₃ (panel A) and ϵ -Ga₂O₃ (panel B). Sample mass: 50 mg. Temperature ramp: 5 K min⁻¹. Reaction conditions: methanol:water=1:2, 50 mbar total reaction mixture with addition of 10 mbar Ar and He to 1 bar total pressure.

Up to 670 K, the CO₂ selectivity is almost constant at about 40 %. Methanol conversions of ~80 % at the highest reaction temperatures are obtained. Two features are worth noting: at first, a small signal of intermediate formic acid is observed, with a maximum at around 560 K. Secondly, hydrogen desorption is observed prior to actual methanol conversion (at around 520 K), but the hydrogen signal strongly increases at around 560 K, i.e. when the steam reforming reaction starts. After that, the reaction obeys the stoichiometry of the methanol steam reforming reaction. ϵ -Ga₂O₃ (panel B) shows a similar reaction pattern in methanol steam reforming. The onset of reaction is more or less equal (at around 540-560 K), as is the CO₂ selectivity (increasing slightly from about 48 to 55 % during reaction). Intermediate formic acid formation is also observed.

In comparison to the other Ga₂O₃ polymorphs, α -Ga₂O₃ is clearly different, with a much higher CO₂ selectivity. Both δ -Ga₂O₃ and ϵ -Ga₂O₃ bear some similarities to γ -Ga₂O₃ in terms of onset of reaction, intermediate formic acid formation and CO₂ selectivity. Of paramount importance, however,

1 are the correlating experiments to β -Ga₂O₃. This polymorph exhibits a very
2 similar reaction profile as compared to δ -Ga₂O₃ and ε -Ga₂O₃, also with a
3 very comparable onset of reaction and intermediate formic acid formation.
4 Additional hints towards the intrinsic catalytic properties will be given by a
5 direct comparison of reactivities, the extrapolated CO₂-TOF values and
6 apparent activation energies. On the basis of active Ga-O entities [6], the
7 TOF values at 500 K (for better comparison) were calculated as $1.1 \times 10^{-6} \text{ s}^{-1}$
8 and $4.1 \times 10^{-6} \text{ s}^{-1}$, for δ -Ga₂O₃ and ε -Ga₂O₃, respectively. These are in the
9 range of β -Ga₂O₃ ($6.0 \times 10^{-6} \text{ s}^{-1}$), but higher as determined for α -Ga₂O₃ and
10 γ -Ga₂O₃ ($< 1.0 \times 10^{-6} \text{ s}^{-1}$). The corresponding activation energies, on the
11 basis of an Arrhenius rate analysis, were determined as 142 and 134 kJ
12 mol⁻¹, which are also well in the range of those measured for other
13 polymorphs [6].
14 Further corroborating the reactivity similarities of δ -Ga₂O₃ and ε -Ga₂O₃,
15 Figure 7 reveals that the reactivity profile in the reaction $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2$
16 + H₂ is almost identical. Activity starts by CO consumption and in parallel
17 formation of CO₂ at ~ 570 K. As no pronounced inverse water-gas shift
18 activity ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$; insets) is observed, but only a more or
19 less drastic H₂ consumption (at ~ 640 K for both samples) without reaction
20 of CO₂, the reaction of CO in the former case could also be explained by a

1 simple non-catalytic removal of oxygen from the lattice and the subsequent
 2 formation of CO_2 , i.e. a Mars-van-Krevelen – type reaction mechanism.
 3 Finally, we note that both polymorphic forms remain structurally stable
 4 after reaction. All the experiments have been tested on one sample (with re-
 5 oxidation steps at 673 K in between each step). Routinely collected XRD
 6 diffractograms after all reactions still show the initial structures and
 7 especially no signs of re-crystallization or phase transformations (Figure 8).

1 **Figure 7:** Temperature-programmed water-gas shift reaction on δ -Ga₂O₃
2 (panel A) and ϵ -Ga₂O₃ (panel B). Sample mass: 50 mg. Temperature ramp:
3 5 K min⁻¹. Reaction conditions: 25 mbar CO and 25 mbar H₂O (water-gas
4 shift reaction), 50 mbar CO₂ and 50 mbar H₂ (inverse water-gas shift
5 reaction, inset) with addition of 10 mbar Ar and He to 1 bar total pressure.

6
7 **Figure 8:** X-ray diffraction patterns of δ -Ga₂O₃ and ϵ -Ga₂O₃ in their initial
8 states (a and c) and after performing the reactivity tests to ensure structural
9 integrity of the samples (b and d).

10

11 *Surface Chemical Characterization*

1 As the chemical nature of especially oxide systems is of paramount
2 importance for their technological use, e.g. as valuable catalysts,
3 knowledge on the surface chemical properties is imperative. This is even
4 more important in reforming reactions or any reaction which includes water
5 as a reagent. Under normal conditions, the surfaces of most metal oxide
6 materials are hydroxylated. These hydroxyl groups may come in differently
7 bound species, either bridged or isolated. In due course, their thermal
8 stability is different, crucially influencing e.g. the material's reduction or
9 catalytic behavior. Discriminating between the different contributions of
10 the components of the surface free energy will therefore give not only
11 information about e.g. the dispersive or polar nature of the surface, but also
12 about specific bonding affinities to different reactants. Together with
13 reaction profiles discussed above this will lead to a complete picture of the
14 reactivity of the different Ga_2O_3 surfaces and to eventually reveal and
15 explain their intrinsic catalytic properties.

16 The surface energies and more specifically, the contributions of the
17 dispersive and polar components for all the studied Ga_2O_3 polymorphs are
18 jointly summarized in Table 1. These data were extracted from direct
19 contact angle measurements as outlined in the Experimental section.
20 Although it is known that the surface chemistry of all the Ga_2O_3
21 polymorphs is very variable and ranges from strongly basic surface sites on

α -Ga₂O₃ [5,6] to strongly acidic sites e.g on β -Ga₂O₃ [5], the data do not indicate substantial variations in the resulting surface free energy. Respective energies between 67 and 75 mN m⁻¹ are obtained. In due course, neither the resulting dispersive nor the polar components do vary substantially between the different modifications. However, all of the modifications exhibit a significantly higher dispersive fraction to the free surface energy, implying that the polar contribution is of less importance to the surface chemistry.

Table 1 Dispersive and polar components of the total free surface energy, as deduced from the contact angle measurements, given in mN m⁻¹.

Phase	Dispersive	Polar	Free Surface Energy
α -Ga ₂ O ₃	44.80	27.86	72.67
β -Ga ₂ O ₃	44.10	26.90	71.00
γ -Ga ₂ O ₃	45.80	29.18	74.98
δ -Ga ₂ O ₃	43.39	24.01	67.41
ϵ -Ga ₂ O ₃	45.48	28.97	74.46

Knowing that the catalytic behavior of the polymorphs is indeed different [6], as are the acid-base properties of the individual modifications [6], more

detailed investigations of this particular phenomenon are indicated. This would necessarily include an in-depth study of especially the acid-base properties as well as the electron-donor and –acceptor parameters. The latter are of paramount importance in oxide chemistry, as they also strongly depend on e.g. the hydroxylation degree of the surface, among others.

Discussion

Following the introductory four specific research questions, the discussion is now grouped in three parts, that will provide detailed answers to these questions. For a better correlation of results, the discussion of the physico-chemical properties is merged in one comparative part. As our results in part strongly deviate from what has been outlined in previous literature (and this in fact seems to be an “intrinsic” property of the Ga-O system) especially regarding phase formation and stability, we in the first two sections provide a thorough discussion of the similarities and differences in phase formation and stability and try to establish a reliable basis of understanding.

Formation of the individual phases

The behavior at lower annealing temperatures and generally the transformation of the hydrated gallium nitrate precursor over the δ -Ga₂O₃ phase into ε -Ga₂O₃ is proven to be most interesting. However, in this

respect, most discrepancies arise. While the formation of ϵ -Ga₂O₃ is known for about 50 years now, starting with the initial experiments of Roy et al., the reproduction of this phase proved difficult. Several groups reported the formation of ϵ -Ga₂O₃ under comparable conditions: Playford et al. after heating gallium nonahydrate nitrate at 493 K for 12 h, followed by heating at 673 K for 14 days. The same result was obtained by Nishi et al. [13] after heating at 823 K for 4h (in dry air) or by Roy et al. at 798 K for 30 minutes [14] (in air). In contrast, Zheng et al. [18] and Hou et al. [16], failed to prepare ϵ -Ga₂O₃ under comparable experimental conditions. The reported preparation pathways are in any case preparation procedures in principle following the initial routine of Roy et al. [14]. ϵ -Ga₂O₃ was also prepared in its nanorod morphology by a dedicated microwave-assisted synthesis routine including urea, L-cysteine and EDTA as additives [15]. The poorly crystalline material of ϵ -Ga₂O₃ in our case was only obtained after a final treatment of δ -Ga₂O₃ in air at about 798 K for 60 h. Note that δ -Ga₂O₃ is always the intermediate phase on the way to ϵ -Ga₂O₃ [4,13,14]. The discussion indicates that the formation of the latter phase obviously very much depends on the effective control of the experimental parameters, in particular on the precursor state and heating rate or chemical gas phase environment. We also might infer a considerable influence of the humidity on the phase formation, since as shown in the corresponding ATR spectra,

1 the samples are hydroxylated to a certain extent. However, as the humidity
2 was not controlled and the synthesis routine basically focussed on those in
3 literature [4,14,18], further studies are necessary to fully clarify this
4 specific issue. In any way, as the starting material in almost all cases is a
5 hydrate gallium nitrate precursor, the initial phase occurring after annealing
6 must be a de-nitrated gallia hydroxo-species, which further transforms into
7 the respective Ga_2O_3 polymorphs. So far, no experimental proof of this
8 intermediate phase has been provided. The first species that arises in all
9 experiments is the $\delta\text{-Ga}_2\text{O}_3$ phase as poorly crystalline material. Note that
10 for other polymorphic forms of Ga_2O_3 , such precursors have been already
11 detected: GaOOH for $\alpha\text{-Ga}_2\text{O}_3$ and $\text{Ga}_5\text{O}_7(\text{OH})$ for $\kappa\text{-Ga}_2\text{O}_3$. In the latter
12 case, the $\text{Ga}_5\text{O}_7(\text{OH})$ intermediate was shown to bear significant structural
13 resemblance also to $\varepsilon\text{-Ga}_2\text{O}_3$, which suggests inter-transformation between
14 different polymorphs [14]. It should be noted that this behavior is by no
15 means restricted to the Ga-O system: similar observations have also been
16 made in the Zr-O system, where structural similarities between hydroxy-
17 gels and the tetragonal ZrO_2 polymorph have been held accountable for the
18 favored crystallization of the latter phase upon annealing [29]. In line with
19 these experiments, also for formation of the rhombohedral In_2O_3 phase,
20 structural similarities to InOOH precursors are of paramount importance
21 [30].

1 *Stability of the individual phases*

2 Most notably, both structures proved to be very stable, both in hydrogen up
3 to about 773 K and in helium up to 873 K. No substantial transformation
4 into β -Ga₂O₃ has been observed. This is insofar remarkable, as – according
5 to previous works – these temperatures are in principle high enough to
6 induce the corresponding phase transformation. Playford et al., for
7 example, reported transformation of ϵ -Ga₂O₃ into β -Ga₂O₃ at temperatures
8 $T > 773$ K [14]. Nishi et al. observed full transformation into β -Ga₂O₃ at
9 923 K (4 h) [13]. Most importantly – in line with the argumentation
10 outlined in the preceding section - Roy et al. reportedly observed
11 significant differences in the phase stability upon treatment under dry and
12 moist conditions. In fact, the stability of δ -Ga₂O₃ under wet conditions
13 directly produced β -Ga₂O₃ at $T > 573$ K. Under dry conditions, ϵ -Ga₂O₃ is
14 formed above $T > 773$ K, whereby final β -Ga₂O₃ formation is observed at
15 temperatures higher than 1143 K. Note that a very sharp transformation
16 temperature of 773 K for ϵ -Ga₂O₃ has been observed, but no transformation
17 was observed at slightly lower temperatures, even when held for a week
18 [14]. Two conclusions can be immediately drawn from these two
19 experiments: Firstly, the hydroxylation degree is obviously of paramount
20 importance also for the observed phase transformations and not only for
21 phase formation. Secondly, it appears that the phase transformation itself

1 seems to be dominated by kinetic effects, as a crucial temperature has to be
2 overcome to induce the structural changes. Unfortunately – although some
3 structural key features between the associated hydrated species and the
4 resulting structure of the Ga_2O_3 polymorphs are known [4] – the detailed
5 mechanism of the phase transformation remains unclear up to now. This
6 would also explain why seemingly similar experimental procedures lead to
7 varying results in extent of phase transformation. Careful and reproducible
8 control of the experimental parameters would be necessary for reliable
9 phase preparation. Again, cross-correlation to results on the phase
10 transformation in the Zr-O system helps in getting a clearer picture: In this
11 specific system, the transformation between the metastable tetragonal and
12 thermodynamically more stable monoclinic ZrO_2 phase is extremely
13 dependent on grain size, defectivity of the structure, heating rate and
14 chemical potential of the gas phase during annealing. The amount of
15 monoclinic ZrO_2 could e.g. be steered between 0 and 80 % by controlling
16 the annealing temperature between 673 K and 1273 K and the gas phase
17 environment. Oxygen-rich conditions are reported to induce the formation
18 of a higher amount of monoclinic ZrO_2 , whereby annealing in vacuum (i.e.
19 more reducing conditions) lead to stabilization of the associated tetragonal
20 phase. Hence, the extent of phase transformation is strongly connected with
21 the defectivity of the material [29]. Note that due to the high purity of the

materials (99.99%), a substantial influence of external stabilizers can be excluded. In due course, similar behavior is expected in the Ga-O system and this is strongly backed by the outlined results and previous studies. In the Ga-O system, the picture is further complicated by the still existing discrepancies whether some polymorphs (especially δ -Ga₂O₃) are true modifications or just nano-crystalline variants of the same structure.

Physico-chemical properties of the δ -Ga₂O₃ and ε -Ga₂O₃ phase

Revisiting the initially introduced questions about the physico-chemical properties of the δ -Ga₂O₃ and ε -Ga₂O₃ as to whether especially the former is an individual polymorph in the Ga-O system, the following picture arises: Especially Raman measurements and volumetric adsorption give clear indications, that δ -Ga₂O₃ in fact exhibits many features of ε -Ga₂O₃. This is in line with previous XRD and neutron diffraction experiments, which strongly indicate that δ -Ga₂O₃ is in fact a nanocrystalline variant of ε -Ga₂O₃. [4] Furthermore, the Raman spectra of ε -Ga₂O₃ support the assumption that ε -Ga₂O₃ is always contaminated with the thermodynamically more stable β -Ga₂O₃ modification (as it also follows from XRD). As has been discussed in the catalytic section, the reactivity in the water-gas shift equilibrium and CO₂-selectivity in methanol steam reforming is clearly different for the different modifications [6]. α -Ga₂O₃, for example, is a strongly basic oxide yielding high amounts of CO₂ in the

reactant feed [6]. In contrast, β -Ga₂O₃, due to the presence of acidic and basic surface sites, is also highly reactive in the inverse water-gas shift reaction, therefore yielding only decreased CO₂-selectivity [24]. The presence of formic acid during methanol steam reforming indicates also the presence of strong acidic surface sites. This correlation of surface chemistry and product selectivity in methanol synthesis and steam reforming is highlighted in a concept recently introduced by Tatibouet [31] and is therefore also valid for δ -Ga₂O₃ and ε -Ga₂O₃: The acidic character of the surface is much more pronounced than its associated basic character. The CO₂ selectivity in MSR is therefore not very pronounced.

Conclusion

Exemplarily shown for the Ga₂O₃ polymorphic system, the advantages of a concerted methodological approach in resolving pending questions of phase stability, structure and physico-chemical properties are highlighted. In the present case, some of the most crucial structural information is derived indirectly from characterization of the physico-chemical properties, including catalytic reactivity profiles. In line with the four questions raised in the introductory chapter, we are now able to give detailed answers:

(1) ε -Ga₂O₃ can be reproducibly prepared, but the details of preparation (e.g. reaction temperature and time, gas atmosphere, etc.) are different from

those in literature and very much depend on the specific reaction conditions. In that respect, ϵ -Ga₂O₃ in the present case needs experimental conditions, where other authors already observed beginning phase transformation. The mechanism of stabilization is unclear up to now, but given the high surface area, particle size effects, a common phenomenon in oxide phase stabilization, cannot be excluded.

(2) Both polymorphs are stable enough to ensure that the properties can be studied without unwanted phase further transformations, although, as reported earlier, the final phase of both samples is always β -Ga₂O₃. This in particular refers to stability in methanol steam reforming and (inverse) water-gas shift reaction mixtures.

(3) Surface properties of ϵ -Ga₂O₃ phase are similar to other polymorphic forms, which is also true for reaction profiles in methanol steam reforming and (inverse) water-gas shift reaction. In this respect, our physico-chemical characterization results corroborate previous suggestions that ϵ -Ga₂O₃ is always contaminated with β -Ga₂O₃. This is especially derived from Raman measurements.

(4) Our results strongly indicate that δ -Ga₂O₃ phase exhibits properties of ϵ -Ga₂O₃. Apart from Raman measurements, especially the steam reforming experiments do not show the characteristic high CO₂ selectivity being

typical for bixbyite-type basic oxides like In_2O_3 . On the contrary, the catalytic profile is very similar to $\epsilon\text{-Ga}_2\text{O}_3$.

Experimental

Preparation of materials

Preparation of the materials was done using standard routines outlined in recent literature [4,13,14]. Starting material in all cases was $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (99.99% Alfa Aesar). A muffle furnace operated under ambient conditions was used to decompose $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ and to subsequently form the desired Ga_2O_3 modifications. $\delta\text{-Ga}_2\text{O}_3$ was prepared by annealing $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ for 12 h at 493 K. The XRD diffractogram of the resulting white powder (cf. Figure 1) coincides well with those reported for “ $\delta\text{-Ga}_2\text{O}_3$ ” in literature [4,13,14,18]. Preparation of the corresponding “ $\epsilon\text{-Ga}_2\text{O}_3$ ” phase proved more demanding, since a simple annealing treatment of $\delta\text{-Ga}_2\text{O}_3$ for 14 d at 673 K, as reported earlier [4,14], did not lead to reproducible crystallization of $\epsilon\text{-Ga}_2\text{O}_3$. Only after a prolonged treatment (60 h) at 800 K, the XRD fingerprint of $\epsilon\text{-Ga}_2\text{O}_3$ was finally obtained (cf. Figure 1) [13,15]. A detailed discussion of this issue is provided in section 3.1. BET areas were measured using a Quantachrome 2000 Pore Size Analyzer and yielded 17 and 54 $\text{m}^2 \text{g}^{-1}$ for $\delta\text{-Ga}_2\text{O}_3$ and $\epsilon\text{-Ga}_2\text{O}_3$, respectively. Further details of N_2 sorption analysis (pore size diameter and volume) are given jointly in Table 2.

Table 2 N₂-Physisorption data for δ -Ga₂O₃ and ε -Ga₂O₃

	Surface area-BET / Pore volume /		Pore radius/
Sample	m² g⁻¹	cm³ g⁻¹	nm
δ-Ga₂O₃	17	0.022	2
ε-Ga₂O₃	54	0.121	2

Summarizing, the experimental conditions to obtain the Ga₂O₃ modifications discussed in here, are as follows:

(i) δ -Ga₂O₃: annealing Ga(NO₃)₃·xH₂O for 12 h at 493 K in air under ambient conditions,

(ii) ε -Ga₂O₃: as δ -Ga₂O₃, but subsequently, the sample was treated at additional 14 days at 663 K followed by 60 h at 800 K,

(iii) α - and γ -Ga₂O₃ were synthesized according to recipes further described in [6], and

(iv) β -Ga₂O₃ is a commercial sample (Alfa Aesar 99.999%).

Table 3 gives an overview of the structural parameters of the polymorphs under question

- 1 **Table 3** Overview of the known polymorphic forms of Ga₂O₃. ^aNote the
 2 discussion of the structure in the Results and Discussion sections.

		Lattice	
Sample	Space group	parameters/Å	Remark
α -Ga ₂ O ₃	R $\bar{3}c$	a=4.98	Ref [6]
		c=13.43	
β -Ga ₂ O ₃	C2/m	a=12.23	Ref [27]
		b=3.04	
		c=5.80	
γ -Ga ₂ O ₃	Fd $\bar{3}m$	a=8.24	Ref [4]
δ -Ga ₂ O ₃	Ia $\bar{3}$	a=9.99	Ref [14] ^a
ϵ -Ga ₂ O ₃	P6 ₃ mc	a=2.903	Ref [4]
		c=9.255	

- 3
 4 The chemical homogeneity of the samples has been checked by EDXRFA
 5 measurements (Spectro-XEPOS) and revealed a 99.99% purity of the
 6 synthesized materials (cf. Table S2).

- 7
 8 *Structural and Morphological Characterization*

X-ray diffraction experiments were performed ex-situ under ambient conditions using a Siemens D5000 Spectrometer and Cu-K α radiation (1.54178 Å) at 300 K in the 2 θ range 10 to 70° with a step size of 0.02°.

For SEM experiments, an SM 982 GEMINI ZEISS field emission scanning electron microscope was used. Prior to SEM imaging, the samples were coated with 10 nm Au/Pd to improve its conductance and fixed with conducting carbon paste.

Spectroscopic Characterization

Confocal Raman spectra in the range of 50 – 3800 cm⁻¹ were recorded with a Horiba Jobin Yvon Labram-HR 800 Raman micro spectrometer. The samples were excited using the 532 nm (2.33 eV) emission line of a frequency-doubled 25 mW Nd:YAG laser under an Olympus 100x objective lens with a numerical aperture of 0.9. The size of the laser spot on the surface was approximately 1 µm in diameter. The scattered light was dispersed by an optical grating with 1800 lines mm⁻¹ and collected by a 1024 x 256 open-electrode CCD detector. The spectral resolution, determined by measuring the Rayleigh line, was better than 2 cm⁻¹. The spectra were recorded in unpolarized mode at ambient conditions. To determine the accuracy of wavelength measurement, a calibration using a Si-Wafer (522 cm⁻¹) was performed.

1 *Thermogravimetric Analysis*

2 The DTA experiment was performed on a Setaram SetsysEvolution 2400
3 instrument, using a TGA-DTA1600 transducer, equipped with Pt/Pt-Rh S-
4 type thermocouples. The instrument is coupled with an OmniStar QMS200,
5 Pfeifer Vacuum quadrupol mass spectrometer. Several mg of the powdered
6 samples were filled in a 100 μL Al_2O_3 crucible. Subsequently, after a
7 routine pre-run including evacuation and flooding the sample chamber with
8 He, the DTA experiment was carried out by heating with a rate 2 K min^{-1} to
9 a maximum temperature of 873 K in He atmosphere and simultaneous
10 recording of selected masses ($m/z = 16, 17, 18, 28$ and 44 corresponding to
11 H_2O , CO , CO_2 and OH-fragments).

12 *Reactivity Tests*

13 Tests in methanol steam reforming and (inverse) water-gas shift reaction
14 were performed in a NI Labview-automatized re-circulating batch reactor
15 of about 13 ml volume [6]. A quadrupole mass spectrometer (Balzers QMG
16 311) attached to the circulating batch quartz glass reactor via a capillary
17 leak was used for analysis. Details of the basic catalytic setup have been
18 outlined elsewhere [6]. For the specific reaction details, we refer to the
19 respective Figure Captions. Note that for all experiments, about 10 mbar Ar
20 was added to account for the decrease of the mass spectrometer signal due
21 to the continuous gas withdrawal through the leak and for correction of

thermally induced expansion. Finally, He was added to 1 bar total pressure. All mass spectrometer signals were externally calibrated and corrected for fragmentation in the mass spectrometer. In order to account for the partial adsorption of some reactants, all catalytic measurements include a 30 minute equilibration period in the starting mixture prior to each measurement. In each case, the catalyst was exposed to the reaction mixture and the temperature was ramped with 5 K min^{-1} to the final value of 673 K. Blind reactivity was corrected by the activity of the catalyst holder containing only quartz wool resulting in an almost negligible, at maximum 1 % conversion based on CO_2 formation after 1 h (for methanol steam reforming). 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.

Volumetric Adsorption

The volumetric adsorption measurements were conducted in an all-quartz apparatus equipped with metal bellow valves (Witeg), a Baratron pressure transducer (MKS), mass flow controllers (MKS), and a Balzers QMA125 quadrupole mass analyzer. The furnace was a Linn model operating up to 1473 K. Before each experiment and to ensure identical starting conditions, the samples were fully oxidized by heating for 1 h in 1 bar of dry flowing O_2 to 733 K. The samples were cooled to 298 K in dry flowing O_2 followed

1 by evacuating the cell to about 5×10^{-7} mbar. The temperature-programmed
2 reduction experiments in hydrogen involved heating from 298 K up to the
3 final temperature of 733 K at a linear rate of 10 K min^{-1} in a defined
4 amount of ~ 100 mbar H_2 , maintaining the maximum temperature for 10
5 minutes, and then re-cooling to 298 K at a similar rate. For better
6 comparison also to literature-reported data, all mass spectrometer data (in
7 mbar) – except H_2 - were converted into μmol based on the ideal gas
8 equation, with subsequent normalization to sample mass and surface area.
9 Hydrogen in the the TPR experiments was quantified via the overall system
10 pressure in the cell.

11 The temperature-programmed experiments were concluded by a
12 subsequent thermodesorption measurement, where the amount of hydrogen
13 being irreversibly adsorbed after the experiments was deliberately
14 desorbed. This included heating the sample at a linear rate of 10 K min^{-1} in
15 the evacuated cell up to 753 K. After these experiments, the structural
16 integrity of the samples was ensured by XRD measurements (cf. Figure 1).

17 *Surface Chemical Characterization*

18 Contact angle measurements were performed with a Drop Shape Analyzer
19 DSA 25E (Krüss) applying the sessile drop method with double distilled
20 water and diiodomethane at ambient conditions. To achieve perfect smooth
21 surfaces, 10-70 mg powder were compressed with the hydraulic press PW

10 (Paul Weber) using flat-faced punches (8 mm diameter) and a maximum pressing force of 25 kN. To calculate the surface free energy the OWRK-Model (Owens-Wendt-Rabel and Kaelble) provided by the Software Advance 1.2 (Krüss) is used.

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Figure Captions

Figure 1: X-ray diffraction patterns collected after various annealing
treatments of the $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ precursor in air and hydrogen. a) 12 h at
493 K (“ δ - Ga_2O_3 ”), b) subsequent heating (after performing treatment a))
for 14 d at 673 K, c) after performing the temperature-programmed
hydrogen treatment at 480 K with the sample prepared via a), d) 30 min at
800 K after 14 days at 673 K and e) 60 h at 800 K after 14 days at 663 K
 (“ ϵ - Ga_2O_3 ”). Peaks of “ δ - Ga_2O_3 ” have been directly assigned [14,18], those
of “ ϵ - Ga_2O_3 ” (and β - Ga_2O_3) indicated as ticks with further assignment in
the text (according to [4,27]).

Figure 2: SEM images of δ - Ga_2O_3 (A) and ϵ - Ga_2O_3 (B) in the as-prepared
state.

Figure 3: Raman spectra of different Ga_2O_3 polymorphs. black: $\beta\text{-Ga}_2\text{O}_3$, red: $\delta\text{-Ga}_2\text{O}_3$, blue: $\epsilon\text{-Ga}_2\text{O}_3$, magenta: $\alpha\text{-Ga}_2\text{O}_3$. The inset shows a direct comparison between $\delta\text{-Ga}_2\text{O}_3$ and $\epsilon\text{-Ga}_2\text{O}_3$.

Figure 4: Thermogravimetric analysis of (A) $\delta\text{-Ga}_2\text{O}_3$ and (B) $\epsilon\text{-Ga}_2\text{O}_3$ during an annealing cycle in He from 298 K and 873 K. black trace: mass loss, red trace: temperature, blue trace: heat flow. Heating Rate: 2 K min^{-1} .

Figure 5: Volumetric H_2 adsorption uptake (A) and subsequent H_2 thermodesorption (B) on $\delta\text{-Ga}_2\text{O}_3$ (blue) and $\epsilon\text{-Ga}_2\text{O}_3$ (green). Heating rate in both cases: 10 K min^{-1} . Starting pressure in the volumetric experiments: 100 mbar.

Figure 6: Temperature-programmed methanol steam reforming reaction on $\delta\text{-Ga}_2\text{O}_3$ (panel A) and $\epsilon\text{-Ga}_2\text{O}_3$ (panel B). Sample mass: 50 mg. Temperature ramp: 5 K min^{-1} . Reaction conditions: methanol:water=1:2, 50 mbar total reaction mixture with addition of 10 mbar Ar and He to 1 bar total pressure.

Figure 7: Temperature-programmed water-gas shift reaction on $\delta\text{-Ga}_2\text{O}_3$ (panel A) and $\epsilon\text{-Ga}_2\text{O}_3$ (panel B). Sample mass: 50 mg. Temperature ramp: 5 K min^{-1} . Reaction conditions: 25 mbar CO and 25 mbar H_2O (water-gas shift reaction), 50 mbar CO_2 and 50 mbar H_2 (inverse water-gas shift reaction, inset) with addition of 10 mbar Ar and He to 1 bar total pressure.

Figure 8: X-ray diffraction patterns of δ -Ga₂O₃ and ϵ -Ga₂O₃ in their initial states (a and c) and after performing the reactivity tests to ensure structural integrity of the samples (b and d).

Table 1 Dispersive and polar components of the total free surface energy, as deduced from the contact angle measurements, given in mN m⁻¹.

Phase	Dispersive	Polar	Free Surface Energy
α -Ga ₂ O ₃	44.80	27.86	72.67
β -Ga ₂ O ₃	44.10	26.90	71.00
γ -Ga ₂ O ₃	45.80	29.18	74.98
δ -Ga ₂ O ₃	43.39	24.01	67.41
ϵ -Ga ₂ O ₃	45.48	28.97	74.46

Table 2 N₂-Physisorption data for δ -Ga₂O₃ and ϵ -Ga₂O₃

Sample	Pore radius		
	Surface area-BET /	Pore volume /	/
	m ² g ⁻¹	cm ³ g ⁻¹	nm
δ -Ga ₂ O ₃	17	0.022	2
ϵ -Ga ₂ O ₃	54	0.121	2

1 **Table 3** Overview of the known polymorphic forms of Ga₂O₃. ^aNote the
2 discussion of the structure in the Results and Discussion sections.

		Lattice	
Sample	Space group	parameters/Å	Remark
α -Ga ₂ O ₃	R $\bar{3}c$	a=4.98	[6]
		c=13.43	
β -Ga ₂ O ₃	C2/m	a=12.23	[27]
		b=3.04	
		c=5.80	
γ -Ga ₂ O ₃	Fd $\bar{3}m$	a=8.24	Ref [4]
δ -Ga ₂ O ₃	Ia $\bar{3}$	a=9.99	Ref [14] ^a
ϵ -Ga ₂ O ₃	P ₆ 3mc	a=2.903	Ref [4]
		c=9.255	

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Figure 1

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4 **Figure 2**

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

1 Graphical abstract

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