

Short communication

Reversible deactivation of γ -alumina by steam in the gas-phase dehydration of methanol to dimethyl ether



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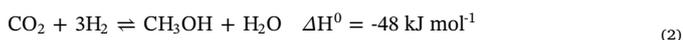
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ABSTRACT

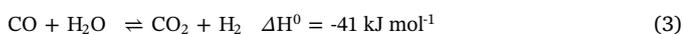
Acidic γ -Al₂O₃ is an active catalyst for the dehydration of methanol to dimethyl ether (DME). However, the produced steam reduces the activity. In this work, the influence of the exposure of γ -Al₂O₃ to steam on the catalytic activity for methanol dehydration has been determined. At 250 °C and increasing stream partial pressure the conversion of γ -Al₂O₃ into γ -AlO(OH) is observed at a p(H₂O) of 13–14 bar. As a consequence, the catalytic activity decreases, reducing the rate of methanol dehydration to around 25%. However, this conversion is reversible and under reaction conditions γ -AlO(OH) converts back to γ -Al₂O₃, recovering its catalytic activity.

1. Introduction

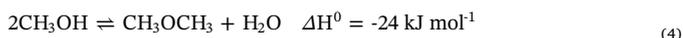
Dimethyl ether (DME) is an ultra-low emissions and nontoxic fuel which can be conveniently handled like conventional LPG. It can serve as an alternative fuel in compression ignition engines, replacing diesel fuel and strongly improving the emissions from combustion. As it can be produced from syngas (CO, CO₂ and H₂) originating from fossil and renewable feedstock alike, it is projected to play an important role in the energy transition [1,2]. The production of DME from syngas proceeds via a number of steps and reactions. First, methanol is produced from syngas:



involving also the water-gas shift (WGS) equilibrium:



as the produced H₂O can react with CO to form CO₂ and H₂. In a last step, DME is produced from methanol through dehydration:



Conventionally, the production of DME proceeds in separate sequential processes, where first methanol is synthesised in a dedicated unit. This twostep approach allows to respond in a flexible way to variations in the methanol and DME market dynamics. An alternative

route is the direct DME synthesis in a single reactor. This option offers a reduction in unit operations and an increased overall DME yield [3]. The direct DME synthesis process is more efficient than the indirect route yet it suffers from the conversion limitation of equilibria in the reactions (1–4) above and the need for separation and recycling remains. In the direct DME synthesis, the O-surplus of the feed ends up in CO₂, and equal molar amounts of DME and CO₂ are produced. Since the reaction is equilibrium limited, downstream separation produces recycle streams of syngas, CO₂, and methanol. Syngas and methanol are recycled back to the DME synthesis reactor, while the CO₂ recycle can be used in synthesis gas generation via dry or tri-reforming in order to improve the carbon efficiency of the process. A novel process route exists, called sorption enhanced DME synthesis (SEDMES). It is based on the use of a solid adsorbent for the in situ removal of steam. The use of a steam sorbent forces the excess oxygen to form steam rather than CO₂, thereby increasing the overall carbon efficiency of the process. According to Le Chatelier's principle, the removal of one of the products will shift the equilibrium-limited conversion to the product side. The process has been analysed theoretically [4] and proven experimentally [5], showing an increased yield of DME, an improved selectivity to DME over methanol, and a strongly reduced CO₂ content in the product. In fact, SEDMES can produce DME directly from a CO₂/H₂ feed mixture, thus allowing for energy and carbon efficiency in CO₂ utilisation. It is currently being developed further in the European Union's Horizon 2020 research project Fledged [6].

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γ -Al₂O₃ as a solid acid remains the catalyst of choice for the industrial production of DME, due to its low cost, high surface area, good thermal and mechanical stability, and high selectivity to DME because its relatively weak Lewis acid sites do not promote side reactions [2]. In fact, the reduced water content in SEDMES will likely promote coking of more acidic catalysts such as zeolites [7,8]. SEDMES uses a typical CuO/ZnO/Al₂O₃ catalyst, catalysing both the methanol synthesis and the methanol dehydration reactions. As SEDMES also requires a water adsorbent, typically an LTA zeolite, it also requires periodic regeneration by a temperature or pressure swing [9]. The catalyst activity for the methanol dehydration reaction can be significantly enhanced by regeneration at relatively high temperatures of 400 °C [9], which has prompted an exploration of the interaction of water with γ -Al₂O₃ and the ensuing activity for the methanol dehydration Reaction (4). The Al₂O₃-H₂O phase diagram has been extensively studied in the liquid phase with the pH as parameter [10]. The phase transformation of γ -Al₂O₃ into boehmite under hydrothermal conditions has been reported by Koichumanova et al. [11], who were able to measure the water induced phase transformation of γ -Al₂O₃ into boehmite. However, remarkably little is known about this system at elevated temperatures.

While Brønsted acidity of alumina may be inferred from the presence of surface hydroxyl groups, the Lewis acid sites on γ -Al₂O₃ catalyse dehydration reactions of simple alcohols [12,13]. The presence of water formed in the reaction inhibits the catalytically active sites, in two distinctly different ways. Deactivation can be caused by the adsorption of dimers, trimers, or even larger alcohol-water clusters, which is in competition with the desired adsorption of alcohol dimers for the formation of ether [13–15]. (Similar phenomena have been reported in dehydration over H-ZSM-5 [16].) Consequently, prevailing kinetics for methanol dehydration over γ -Al₂O₃ feature a reduction of the rate of reaction by the adsorption of water on the surface [3,17].

$$-r_{\text{MeOH}} = \frac{kK_{\text{MeOH}}^2 \left([\text{MeOH}]^2 - \frac{[\text{H}_2\text{O}][\text{DME}]}{K} \right)}{(1 + 2\sqrt{K_{\text{MeOH}}} [\text{MeOH}] + K_{\text{H}_2\text{O}} [\text{H}_2\text{O}])^4} \quad (5)$$

Conversely, deactivation may also occur due to the irreversible deactivation of γ -Al₂O₃ which has been reported at higher partial pressures of steam [18] has been linked to the formation of (surface) boehmite (aluminium oxide hydroxide, γ -AlO(OH)):



In particular, this may occur in slurry reactors where the rate of water removal might be low [19] and may be particularly relevant in case of the direct synthesis of DME from H₂ and CO₂ [2]. The formation of boehmite under these conditions is not unexpected, since the transition between γ -AlO(OH) and γ -Al₂O₃ also occurs in the range of 300–500 °C [20], but the exact nature of the deactivation of γ -Al₂O₃ and the in situ formation of boehmite and its reversibility have not been reported in literature.

Ideally, the rate of the methanol dehydration reaction is interpreted in terms of the chemical composition of the alumina surface involved in the reaction, being γ -Al₂O₃, γ -AlO(OH), or an intermediate species. Thus, a comprehensive understanding of the interaction of water with γ -Al₂O₃ is required to explain the observed negative reaction order for water in more conventional reaction conditions, as well as understanding of the effect of unconventional reactor conditions (i.e., H₂/CO₂ feed or frequent regeneration) on reversibility of this deactivation. In this work, the transition between boehmite and γ -Al₂O₃ has been studied with the aim to relate the methanol dehydration reaction rate to the state of the alumina catalyst.

This paper presents an investigation of the boehmite to γ -Al₂O₃ phase transition in the range of 250–400 °C and steam partial pressures up to 15 bar. Subsequently, results are reported of methanol dehydration experiments over γ -Al₂O₃ and hydrated γ -Al₂O₃.

2. Experimental

Experiments were performed starting from pure γ -Al₂O₃, purchased as 3 mm pellets (assay > 98%, Riogen NJ, USA) and ground to a 212 to 425 μm sieve fraction. All experiments were performed using the 212–425 μm sieve fraction unless otherwise stated. The surface area was measured on a Thermo Scientific Surfer instrument at 77 K, using vacuum dried samples (200 °C, 3 h). Thermodynamic equilibria under the tested conditions were calculated using HSC Chemistry 5.11. Powder X-ray diffraction (PXRD) patterns were obtained from 5 to 80° 2 θ with a MiniFlex II diffractometer using Ni-filtered Cu-K α radiation, at 30 kV and 15 mA. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a Netzsch Jupiter STA 449F3 instrument in the temperature range 30–700 °C and, using a 1:1 argon/air mixture (20 ml min⁻¹) and a heating rate of 5 K min⁻¹.

2.1. Boehmite – γ -Al₂O₃ equilibrium

A batch of reference boehmite was prepared by treating 12.0 g of γ -Al₂O₃ pellets in 50 ml of water at 200 °C for 15 h inside a hydrothermal synthesis reactor equipped with a 100 ml Teflon liner. The γ -Al₂O₃ to boehmite phase transition was studied in a batch autoclave. For studying the boehmite to γ -Al₂O₃ interconversion, γ -Al₂O₃ (0.125 g, 1.223 mmol) was transferred to a ceramic crucible which was placed into a 50 ml stainless steel autoclave. Specific volumes of water (see legend in Fig. 2 for details) were added avoiding direct contact with the γ -Al₂O₃. The vessel was sealed and heated to 250 °C under autogenic pressure for a set period of time. After cooling to room temperature the sample was transferred to an oven and dried at 120 °C.

2.2. Catalytic activity of γ -Al₂O₃ for methanol dehydration

The catalytic activity of the sample was tested in a fixed bed flow reactor with a diameter of 20 mm and bed height of 170 mm, equipped with an axially fitted thermocouple. Analysis was performed by a Thermo Scientific TRACE 1300 gas chromatograph equipped with a TCD detector calibrated for CO, CO₂, H₂, O₂, and N₂ and an FID detector calibrated for DME, MeOH, EtOH, ethylene, ethane and methane. The reactor was filled with a homogeneous mixture of 5.26 g 212–425 μm sieve fraction γ -Al₂O₃ and 100.03 g of 600–1180 μm sieve fraction SiC, resulting in a total bed volume of 60 cm³. The reactor was fed with a mixture of 90% N₂ and 10% vapour feed (methanol, steam) at a total gas flow of 889 ml min⁻¹. The liquid feed of methanol (anhydrous 99.8%, Sigma Aldrich) was introduced by a Scientific Systems, Inc. Series 1500 dual piston pump, before controlled evaporative mixing. Both pressure and temperature cycles have been performed. A pressure cycle consists of a 3 h feeding period at a specific pressure with 0.5 h intervals for changing pressure. Consecutive pressures were 40, 35, 25, 15, and 5 bar(a), controlled with a margin of \pm 0.05 bar. The temperature was maintained at 250 \pm 1 °C. A temperature cycle consists of 2 h measurements at a specified temperature with 0.5 h intervals for changing temperature. The temperature range was 250–350–250 °C with intermittent ramping of 25 °C. The pressure would be maintained at 25 bar(a). During any interval where pressure or temperature were changed the liquid feed would be interrupted and the N₂ flow set to 100 ml min⁻¹. The carbon atom balance typically closed within \pm 10%, data with a carbon balance error of more than \pm 20% have been omitted. The carbon selectivity towards DME (S) was calculated according to Eq. (7), the methanol conversion (X) according to Eq. (8), all based on measured outlet concentrations.

$$S = 100 \frac{2[\text{DME}]}{2[\text{DME}] + [\text{MeOH}] + [\text{CO}] + [\text{CO}_2] + [\text{CH}_4] + 2[\text{EtOH}] + 2[\text{C}_2\text{H}_4] + 2[\text{C}_2\text{H}_6]} \quad (7)$$

$$X = 100 \left(1 - \frac{[\text{MeOH}]}{2[\text{DME}] + [\text{MeOH}] + [\text{CO}] + [\text{CO}_2] + [\text{CH}_4] + 2[\text{EtOH}] + 2[\text{C}_2\text{H}_4] + 2[\text{C}_2\text{H}_6]} \right) \quad (8)$$

Typical reproducibility of the measured conversion was within $\pm 3\%$. Overall it was noticed that the $\gamma\text{-Al}_2\text{O}_3$ is highly selective. Throughout the experiments the selectivity towards DME was generally 99.9% and never $< 99.2\%$. After testing catalytic activity, the in situ formation of boehmite was performed by subjecting the material present in the reactor to a $p(\text{H}_2\text{O})$ of 14 bar for 40 h at 250 °C. The reactor was fed with a $\text{N}_2/\text{H}_2\text{O}$ feed with ratio 1:1 at a total gas flow of 400 ml min^{-1} . The total pressure was kept at 28 bar(a). Temperature profile experiments were performed, similar to those for the initial $\gamma\text{-Al}_2\text{O}_3$. Finally, the PXRD pattern of the spent catalysts was recorded using the before mentioned apparatus.

3. Results and discussion

The purchased $\gamma\text{-Al}_2\text{O}_3$ was characterised by PXRD and nitrogen adsorption studies. The PXRD pattern of the catalyst (Fig. 1) showed a well-defined $\gamma\text{-Al}_2\text{O}_3$ structure with characteristic broad Bragg reflections at 46 and 67° 2θ [21], which also contains traces of an amorphous AlO_x phase (broad peak around $2\theta = 38^\circ$) [22]. Nitrogen adsorption showed typical Type II isotherm behaviour according to the Brunauer classification resulting in a Brunauer-Emmett-Teller (BET) specific surface area of 192 m^2g^{-1} with an average pore diameter of 8.98 nm, both of which are well within typical ranges reported for this type of material [23].

3.1. Boehmite – $\gamma\text{-Al}_2\text{O}_3$ equilibrium

The phase transition between boehmite and $\gamma\text{-Al}_2\text{O}_3$ has been monitored using PXRD analysis for the detection of $\gamma\text{-AlO}(\text{OH})$ and TGA/DSC experiments for studying the subsequent decomposition to $\gamma\text{-Al}_2\text{O}_3$. As discussed above, the transition from $\gamma\text{-Al}_2\text{O}_3$ to $\gamma\text{-AlO}(\text{OH})$ by steam is not yet understood. Thus, the initial focus in this work is on the transformation of $\gamma\text{-Al}_2\text{O}_3$ to $\gamma\text{-AlO}(\text{OH})$ in the presence of steam. Section 3.2 discusses the catalytic activity of the steam-exposed sample in comparison to that of the original $\gamma\text{-Al}_2\text{O}_3$.

Two sets of experiments were employed to study the transition of $\gamma\text{-Al}_2\text{O}_3$ to boehmite. The first set (Fig. 1) consisted of exposure to a fixed water concentration for different time spans, while the second set (Fig. 2) consisted of equal times of exposure to different water

concentrations. The main conclusion drawn from the individual steam exposure experiments is that at 250 °C, a steam partial pressure of at least 13 bar is required to convert $\gamma\text{-Al}_2\text{O}_3$ to crystalline $\gamma\text{-AlO}(\text{OH})$ (Fig. 2). Furthermore, the phase transformation of $\gamma\text{-Al}_2\text{O}_3$ to boehmite by steam is unlikely to be complete in < 66 h at 14 bar of H_2O and 250 °C.

From the PXRD studies, $\gamma\text{-Al}_2\text{O}_3$ can easily be identified by the characteristic broad peaks at 46° and 67°, while boehmite can be identified by the sharp peaks at 14.55° and 28.25°. Therefore, the PXRD patterns from the first set of experiments show that the crystalline boehmite phase is already present after 1 h of steam exposure (Fig. 1). However, at this stage the original crystalline $\gamma\text{-Al}_2\text{O}_3$ phase is still present. More boehmite is formed when prolonging the exposure. Even after 66 h of exposure the $\gamma\text{-Al}_2\text{O}_3$ peaks could still be recognized in the PXRD. Furthermore, in the PXRD pattern of the reference boehmite, prepared hydrothermally, the peaks at 46° and 67° corresponding to the $\gamma\text{-Al}_2\text{O}_3$ phase are noticeably smaller compared to the sample exposed for 66 h. We therefore conclude that the steam exposure for 66 h does not fully converted to the $\gamma\text{-Al}_2\text{O}_3$ to boehmite under the employed conditions.

As shown in Fig. 2, after subjecting the $\gamma\text{-Al}_2\text{O}_3$ catalyst to 13–14 bar of steam partial pressure, the characteristic peaks of boehmite are clearly visible in the PXRD, albeit they are less defined than for the sample exposed to 15 bar. Conversely, no boehmite formation was observed after subjecting the material to 12.5 bar and lower partial pressures of steam. Also, for duplications of the experiment at 13 bar steam no significant boehmite formation could be detected by PXRD. Therefore, the required steam pressure to induce the phase transition from $\gamma\text{-Al}_2\text{O}_3$ to $\gamma\text{-AlO}(\text{OH})$ at 250 °C appears to be between 13 and 14 bar.

A typical TGA response of the dehydration of the formed $\gamma\text{-AlO}(\text{OH})$ back to $\gamma\text{-Al}_2\text{O}_3$ is shown in Fig. 3. From 120 °C upwards, a progressive loss of mass is observed, corresponding to the dehydration of the sample. A minimum in differential (DTG) is observed at temperatures in the range of 450–490 °C, depending on the preceding exposure to steam. The observed mass loss relates to the extent to which the sample had been converted to $\gamma\text{-AlO}(\text{OH})$ during steam exposure (note the theoretical maximum weight loss for full conversion according to Eq. (3) equals 15%). Sanchez Escribano et al. [24] have shown that free active hydroxyl groups on the surface of $\gamma\text{-Al}_2\text{O}_3$ gradually disappear with increasing temperatures in the range of 200–400 °C and Krokidis et al. [14] have theoretically shown that several steps and transition states occur in the transformation of $\gamma\text{-AlO}(\text{OH})$ to $\gamma\text{-Al}_2\text{O}_3$, leading to a stepwise dehydration in the temperature range of 320–540 °C. This is very much in line with the TGA data presented here. The observed

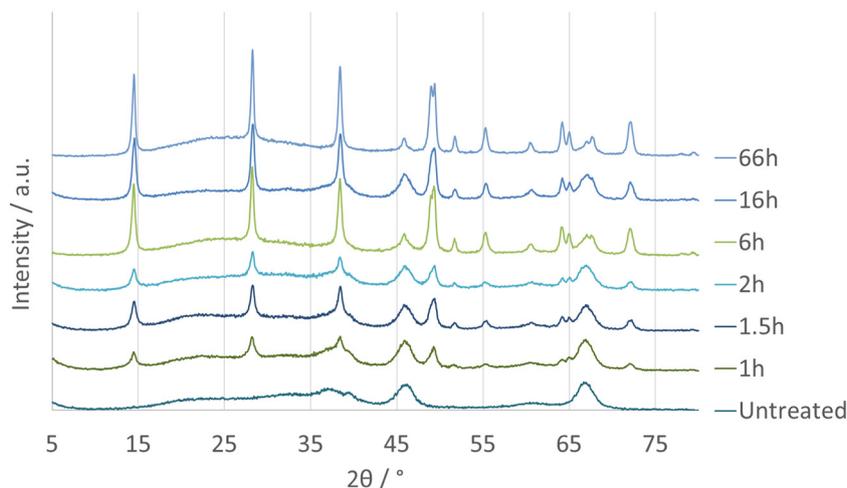


Fig. 1. PXRD measurements of $\gamma\text{-Al}_2\text{O}_3$ after different exposure times to 250 °C, 14 bar H_2O .

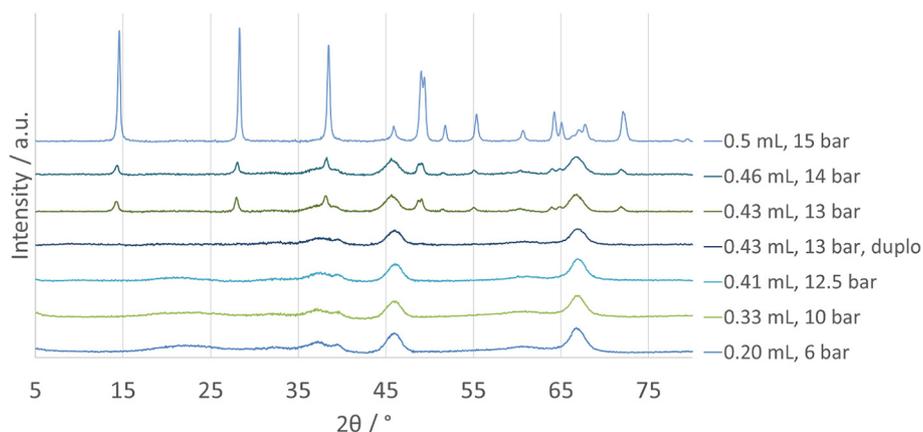


Fig. 2. PXRD measurements of γ -Al₂O₃ after 18.5 h exposure to 250 °C, 6–15 bar H₂O.

weight loss in the range of 120–320 °C may be attributed to the loss of surface adsorbed water and hydroxyl groups, in line with the classical Peri model of the surface of γ -Al₂O₃ [25]. Clearly, the bulk of the material is converted back to γ -Al₂O₃ in the temperature range of 450–490 °C (Table 1), but significant additional dehydration can be observed from 500 °C upwards (Fig. 3). The data shown in Table 1 indicate that the activation energies for the dehydration of boehmite to γ -Al₂O₃ range from ca. 16 to 340 J g⁻¹. However, there is no uniform variation of the activation energies for the conversion of boehmite to γ -Al₂O₃ for the different steam exposure times. This is likely due to several factors involved during the experimental procedures, including the synthetic conditions of boehmite, its structural and morphological properties as well as the steam exposure conditions. Generally, it has been observed that large crystallites lead to large activation energies [26]. Several studies reported that the thermal transformation of boehmite to γ -Al₂O₃ is a complex process involving at least four steps [26–28]. The first step corresponds to the desorption of the physisorbed water, which is a reversible process. The second step involves the desorption of the chemisorbed water, followed by the decomposition of boehmite into transition phase alumina. The last step is the dehydroxylation of the transition phase alumina to γ -Al₂O₃.

Based on the combined experimental results described above, we can conclude that a reversible conversion between γ -AlO(OH) and γ -Al₂O₃ occurs in the range of 200–500 °C which depends on the partial pressure of steam. In Section 3.2, the state of the alumina will be related to the catalytic activity for the methanol dehydration reaction.

The Lewis acid sites at the surface of γ -Al₂O₃ are due to the

Table 1

TGA results for steam-exposed γ -Al₂O₃.

Entry	Exposure time (h)	Mass loss 120–700 °C (%)	DTG minimum (°C)	DSC area 1 (J g ⁻¹)	DSC area 2 (J g ⁻¹)
1	0	4	–	29.98	–15.9
2	1	7.3	453	75.56	–40.29
3	1.5	8.4	471.8	43.31	–66.19
4	2	7.8	472.6	22.82	–47.71
5	3	10.4	473.6	47.66	–121.6
6	6	11.9	480.2	110	–159.8
7	16	9.6	480.5	67.88	–81.24
8	66	13.5	488.9	132.3	–278.9
10	Hydrothermal	15.7	479.6	80.62	–339.1

coordinatively unsaturated aluminium cations which are formed as a result of dehydroxylation of hydrated oxide surface. A simple dehydroxylation reaction involves two neighbouring hydroxyl groups, leaving coordinatively unsaturated electron-deficient surface aluminium ions without rearrangement of the surface structure. It is known that eliminating > 75% surface hydroxyl groups leads to the rearrangement of oxygen ions and vacancies in the surface layers whilst a removal of > 90% surface hydroxyl groups results in a migration of the ions at the surface [29,30]. Therefore, the mechanism involved in the formation of Lewis acid sites takes into account both the dehydroxylation and deoxygenation reactions at the surface. The generally accepted model is: 2Al-OH → H₂O + AlO⁻ + Al⁺. In this model, Al⁺ is a

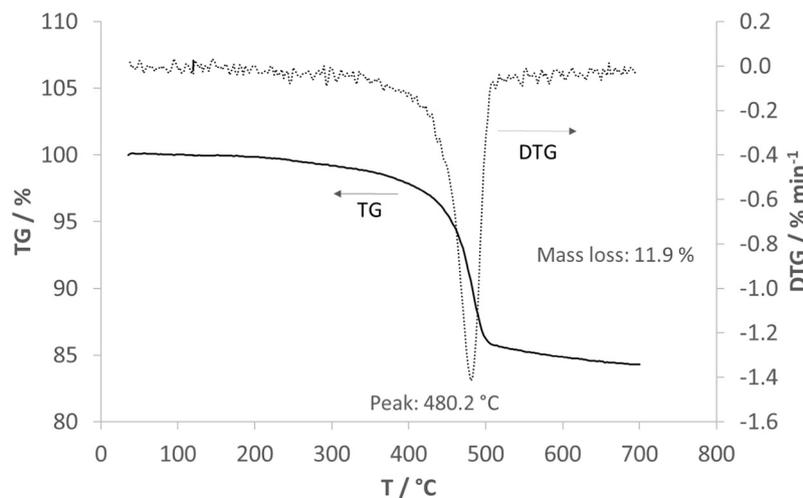


Fig. 3. The TGA curve of the γ -Al₂O₃ sample exposed to steam at 14 bar for 6 h.

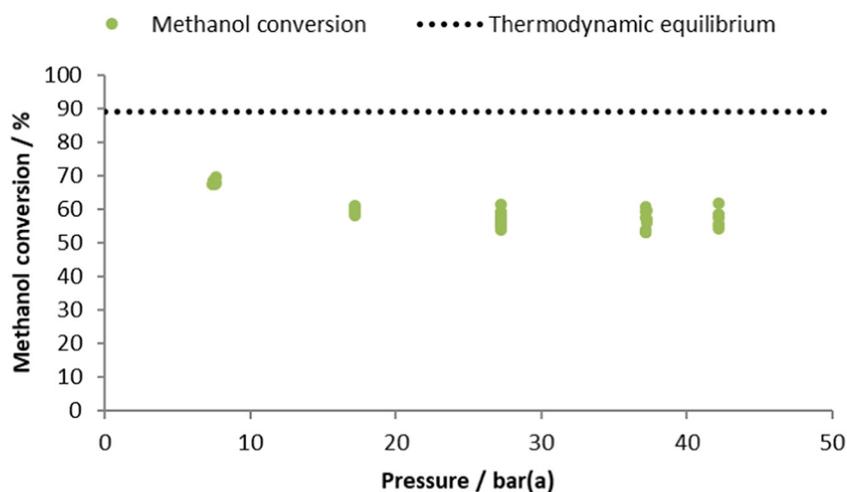


Fig. 4. Methanol conversion over 5.26 γ -Al₂O₃ at 250 °C, 7–42 bar(a), 10% methanol in nitrogen, feed flow rate 889 ml_n min⁻¹.

surface oxygen vacancy creating a low-coordinated Lewis acid site. Considering that the transition of γ -Al₂O₃ to boehmite results in a higher concentration of surface hydroxyl groups, this scenario implies that the surface acidity of restored γ -Al₂O₃ is highly dependent on its exposure on stream. Consequently, the acidity of restored alumina is expected to increase with the time exposed to steam.

3.2. Catalytic activity of γ -alumina for methanol dehydration

To investigate the implications of the observed reversible transition between γ -Al₂O₃ and γ -AlO(OH) for the catalytic activity for methanol dehydration, several catalyst tests have been performed. Initially, the methanol conversion was measured as a function of the reactor pressure as shown in Fig. 4. Under these conditions, based on Eq. (5), the surface adsorption of the produced steam is expected to have a negative impact on the observed methanol conversion as determined by the work of Berčič and Levec [17]. The reaction rate has a negative order dependence on the steam partial pressure and a positive (less than first) order in methanol partial pressure, which has been widely reported in literature for this and similar alcohol dehydration reactions over γ -Al₂O₃ [13,15,17,31]. Indeed, this is reflected in the experimental results (Fig. 4). Note that the steam adsorption is clearly reversible as the experiments were performed in the order of decreasing reactor pressure. Under these conditions, the maximum applied steam partial pressure is about 2.4 bar which cannot induce the formation of γ -AlO(OH), as shown above in Section 3.1. In conclusion, the surface adsorption of water is reversible under these conditions.

The second experimental campaign involved high steam pressures,

which were applied in between catalytic tests. Fig. 5 shows the methanol conversion as a function of time at 250 °C. (Data at higher temperatures have been omitted for clarity.) Three tests can be discerned: (i) the initial test with γ -Al₂O₃ for the first 120 min, (ii) testing after exposure to 14 bar of steam at 250 °C for 40 h, and (iii) testing of the sample after a temperature programme to 350 °C.

As discussed above, the exposure to 14 bar steam is expected to convert the γ -Al₂O₃ catalyst into γ -AlO(OH), not only on the surface but also in the bulk of the material. The high surface coverage by adsorbed water and hydroxyl groups is expected to have a strong impact on the catalytic activity of the sample by preventing the adsorption of methanol [32]. Indeed, the catalytic activity appears to be strongly affected as the measured methanol conversion starts significantly lower (at around 446 min on stream). This can be attributed the conversion of γ -Al₂O₃ to γ -AlO(OH) which has been discussed above. Takagi et al. [33] have shown that the concentration of weak Lewis acids sites, that catalyse the methanol dehydration reaction, increases by more than a factor 4 when γ -AlO(OH) is calcined to γ -Al₂O₃. A similar restoration can be observed in the following data points, which show an in situ restoration, i.e. in the presence of produced steam, as the activity for methanol dehydration reaches a constant 45% conversion after 485 min on stream. The temperature of 250 °C is too low to completely restore the γ -Al₂O₃ phase as shown in Section 3.1, yet sufficient to largely restore the Lewis acid surface sites and hence the catalytic activity of the surface. In addition, the temperature programme to 350 °C further restores the activity to the range of the original catalytic activity of the γ -Al₂O₃ sample. At this temperature, a significant part of the sample will remain as γ -AlO(OH), as observed in the XRD pattern of the spent

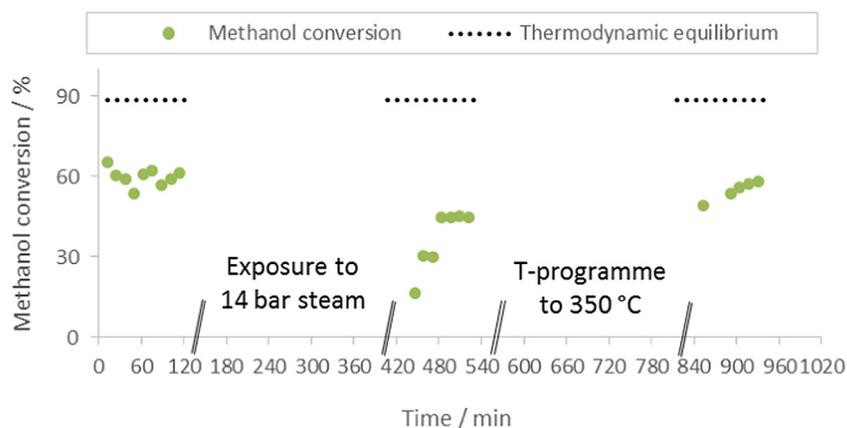


Fig. 5. Methanol conversion over 5.26 γ -Al₂O₃ at 250 °C, 25 bar(a), 10% methanol in nitrogen, feed flow rate 889 ml_n min⁻¹.

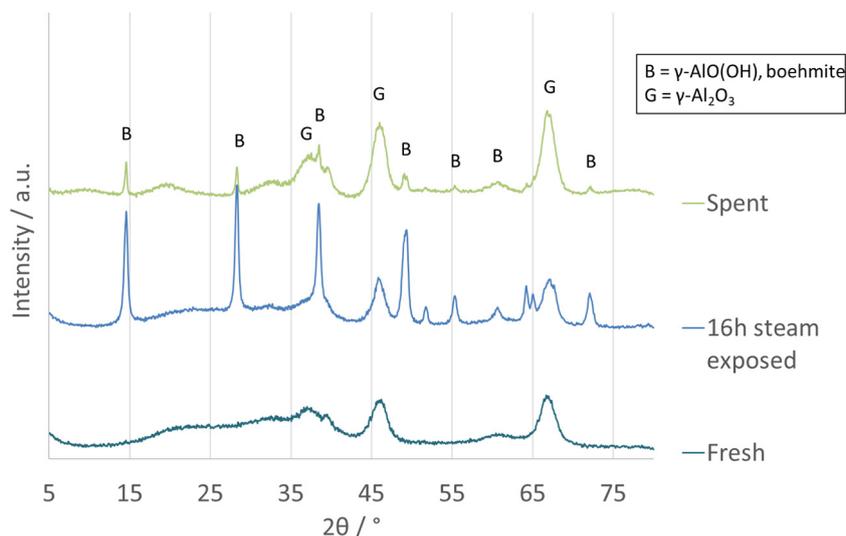


Fig. 6. PXRD patterns for the spent catalyst, steam-exposed γ - Al_2O_3 (14 bar steam, 250 °C, 40 h), and fresh γ - Al_2O_3 .

catalyst (Fig. 6). It can be concluded that, whereas γ - $\text{AlO}(\text{OH})$ remains after testing at 350 °C, this does not affect the catalytic activity for methanol dehydration and the deactivation by formation of γ - $\text{AlO}(\text{OH})$ is reversible in practice.

4. Conclusions

In the framework of developing a direct, sorption-enhanced dimethyl ether (DME) synthesis process (SEDMES), the activity and stability of γ - Al_2O_3 for the methanol dehydration reaction has been investigated. It was found that γ - Al_2O_3 has a high activity and selectivity for the production of DME from methanol at 250 °C. Adsorbed steam, however, reduces the catalytic activity of γ - Al_2O_3 . At 250 °C and steam partial pressures of 14 bar and higher, the conversion to crystalline boehmite has been confirmed through PXRD measurements. While crystalline boehmite remained present after testing methanol dehydration at 350 °C, it was shown that the activity for methanol dehydration restores in situ at 250 °C. This confirms that the deactivation by steam is reversible under DME synthesis conditions.

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