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Promoting Ag/Al₂O₃ performance in low-temperature H₂-C₃H₆-SCR by thermal pretreatment of γ -alumina in water

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Running title: Promoting Ag/Al₂O₃ performance in H₂-C₃H₆-SCR

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Abstract:

The present work highlights for the first time that a thermal treatment of γ -Al₂O₃ in water at 80 °C for 24 h prior to Ag deposition (Ag/Al₂O₃-OH) leads to a drastic enhancement of H₂-C₃H₆-SCR performance at low temperature. This enhancement is attributed to the higher NO_x coverage on Ag/Al₂O₃-OH compared with that of Ag/Al₂O₃. The higher NO_x adsorption capacity of the sample prepared from the γ -Al₂O₃ thermally-treated in water is proposed to result from the preferential interaction of Ag with newly-created Al₂O₃ anchoring sites (Al(OH)₃ bayerite domains), which were not available on the untreated pristine support.

Key Words: Selective Catalytic Reduction; NO_x-TPD; UV-vis

1. Introduction

Since the implementation of catalytic converters dedicated to the concomitant reduction of nitrogen oxides ($\text{NO}_x = \text{NO} + \text{NO}_2$) and oxidations of carbon monoxide (CO) and unburned hydrocarbons (HCs) in the early 1970s, the environmental challenge has moved to the reduction of NO_x from lean exhausts at low temperatures [1]. Even though the Selective Catalytic Reduction of NO_x by ammonia (NH_3 -SCR) and Lean- NO_x Traps (LNT) remain as the only technologies to comply with the current emission standards, these two technologies exhibit drawbacks [1,2] and many studies have been devoted to seek out for alternative processes such as the reduction of NO_x by hydrocarbons (Hydrocarbon Selective Catalytic Reduction: HC-SCR).

In 1993, Miyadera firstly brought to the attention of the community that $\text{Ag}/\text{Al}_2\text{O}_3$ could be a promising catalyst in HC-SCR with various light hydrocarbons [3]. Few years later, Satokawa and co-workers discovered that the performance of the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst could be improved drastically at low temperatures (below 300 °C) on the addition of small quantities of H_2 in the reacting feed (H_2 -HC-SCR) [4,5]. The $\text{Ag}/\text{Al}_2\text{O}_3$ system has been investigated thoroughly until recently [6-8].

Since these pioneering works, no major improvement of the $\text{Ag}/\text{Al}_2\text{O}_3$ system has been achieved up to the works of Kamolphop et al. [9] and Petitto and Delahay [10] in which superior HC-SCR performance was obtained using long-chain alkanes as reductants and catalysts prepared by ball-milling compared with those synthesized by the conventional impregnation techniques reported to date. Ball-milled prepared $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts were also found to exhibit higher H_2 -HC-SCR activities in comparison with the conventionally prepared samples [11,12]. This was inferred to modifications of the catalyst surface and more specifically to changes in the affinity of the Al_2O_3 surface towards water and decane [11]. In addition, it was found that isocyanates ($-\text{NCO}$), which are supposed to be key intermediates

of HC-SCR reactions [1], were formed quicker and had a higher surface concentration on the ball-milled catalyst compared with the conventionally prepared sample [11,12].

Since it has been proposed that Ag anchored onto the Al₂O₃ support via the interaction with its hydroxyl groups ($\text{Al-OH} + \text{Ag}^+ = \text{Al-O-Ag} + \text{H}^+$) during the impregnation step [13] and that hydroxylation of Al₂O₃ occurs when immersed into water under various experimental conditions (temperature, pressure, pH, time of exposure) [14-16], we found of particular interest to investigate the influence of the hydroxylation of γ -Al₂O₃ prior to Ag deposition on C₃H₆- and H₂-C₃H₆-SCR catalytic performance. To our knowledge, such an approach has never been reported previously for the Ag/Al₂O₃ system, but recently in the case of the Pt/Al₂O₃ system for other catalytic reactions [17].

2. Experimental

2.1. Catalyst synthesis

Hydroxylation of the γ -Al₂O₃ support (Procatalyse, 180 m²/g) was carried out by heating this oxide in distilled water at 80 °C for 24 h under vigorous stirring. After filtering, the solid was dried and kept under vacuum at RT. Ag was deposited following the incipient wetness procedure described in our earlier works [6,8]. Briefly, Ag was deposited via incipient wetness impregnation of an aqueous solution AgNO₃ (Aldrich, >99%) on the hydroxylated Al₂O₃ sample (0.7 cm³/g porous volume) to achieve a silver loading of 1.9 wt%, which was ascertained by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Centre d'Analyse du CNRS, Solaize, France). In parallel, a new batch of Ag/Al₂O₃ sample was prepared from the as-received Al₂O₃ support following the abovementioned Ag deposition procedure. From here on, the samples prepared from hydroxylated Al₂O₃ will be denoted as Al₂O₃-OH and Ag/Al₂O₃-OH and compared with the samples synthesized from the

untreated support denoted as Al_2O_3 and $\text{Ag}/\text{Al}_2\text{O}_3$ (1.8 wt% Ag) either newly-prepared or studied earlier [6,8].

2.2. C_3H_6 -SCR and H_2 - C_3H_6 -SCR runs

The steady state catalytic C_3H_6 -SCR and H_2 - C_3H_6 -SCR experiments were carried out in a U-type quartz reactor (12 mm i.d.). The temperature of the tubular furnace was set by a Eurotherm 2408 temperature controller using a K type thermocouple. Prior to the SCR experiments, the samples (0.18 g of $\text{Ag}/\text{Al}_2\text{O}_3$ or $\text{Ag}/\text{Al}_2\text{O}_3$ -OH diluted in 0.18 g of Al_2O_3 , 125-200 μm) were calcined in situ in O_2 (20 %)-He at 550 $^\circ\text{C}$ (3 $^\circ\text{C}/\text{min}$) for 2 h with a flow rate of 100 $\text{mL}_{\text{NTP}}/\text{min}$. After cooling to 150 $^\circ\text{C}$, the samples were submitted to a C_3H_6 -SCR experiment from 150 to 550 $^\circ\text{C}$ [6]. The samples were subsequently exposed to the H_2 - C_3H_6 -SCR feed at 150 $^\circ\text{C}$. H_2 (2 %/He), NO (4000 ppm/He), C_3H_6 (2000 ppm/He), O_2 (100 %) and He (100 %) were fed from independent cylinders (Air Liquide) without any further purification via mass flow controllers (Brooks 5850TR). Typically, the composition of the SCR feeds was: 0 or 0.21 % H_2 , 385 ppm NO_x (~ 96 % NO), 400 ppm C_3H_6 and 8 % O_2 in He, and the total flow rate was 230 $\text{mL}_{\text{NTP}}/\text{min}$. In both SCR experiments, the temperature was increased stepwise from 150 to 550 $^\circ\text{C}$ with 25 $^\circ\text{C}$ increments and left for about 1 h at each temperature step. Steady state activity was found to be achieved shortly for all reaction temperatures. The reactor outflow was analyzed using a μ -GC (Agilent Technologies, CP4900) equipped with two channels. The first channel, a 5A molecular sieve column (80 $^\circ\text{C}$, 150 kPa He, 200 ms injection time, 30 s backflush time), was used to separate N_2 , O_2 and CO. The second channel, equipped with a poraplot Q column (60 $^\circ\text{C}$, 150 kPa He, 200 ms injection time), was used to separate CO_2 , N_2O , C_3H_6 and H_2O . A chemiluminescence NO_x analyzer (Thermo Environmental Instruments 42C-HT) allowed the simultaneous detection of both NO and NO_2 . NO_x conversion to N_2 and N_2 selectivity were calculated as follows:

$$X_{\text{NO}_x \text{ to N}_2} (\%) = (2 \times [\text{N}_2]) / ([\text{NO}_x]_{\text{inlet}}) \times 100 \quad (\text{Eq. 1})$$

$$S_{\text{N}_2} (\%) = ([\text{N}_2] / [\text{N}_2 + \text{N}_2\text{O}]) \times 100 \quad (\text{Eq. 2})$$

where $[\text{NO}_x]_{\text{inlet}}$, $[\text{N}_2]$ and $[\text{N}_2\text{O}]$ were the concentrations in NO_x measured at the inlet of the reactor and in N_2 and N_2O at the outlet of the reactor. C_3H_6 conversions were calculated on the basis of the CO_x ($\text{CO} + \text{CO}_2$) products formed:

$$X_{\text{C}_3\text{H}_6} (\%) = (([\text{CO}] + [\text{CO}_2]) / ([\text{C}_3\text{H}_6]_{\text{inlet}} \times 3)) \times 100 \quad (\text{Eq. 3})$$

where $[\text{CO}]$, $[\text{CO}_2]$ and $[\text{C}_3\text{H}_6]_{\text{inlet}}$ were the concentrations of CO and CO_2 measured at the outlet of the reactor and that of C_3H_6 measured at the inlet of the reactor, respectively.

2.3. Catalyst characterization

N_2 -sorption measurements were carried out on a Belsorp max instrument (Bel Japan) at 77 K. It was found that the BET surface of the hydroxylated samples both after drying at 120 °C for 12 h in an oven and calcination at 550 °C for 2 h in a muffle furnace ($185 \text{ m}^2/\text{g}$) did not vary to a significant extent from that of the starting Al_2O_3 support ($180 \text{ m}^2/\text{g}$).

XRD measurements were carried out from 10 to 80° by step of 0.01° using a theta-theta D8 Advance (Bruker) powder diffractometer with $\text{Cu-K}\alpha$ radiation (0.154 nm) operated at 30 kV and 30 mA, and equipped with a 1D LynxEye detector set to a 3° opening.

The ultraviolet–visible diffuse reflectance spectra (UV–vis DRS) of $\text{Ag}/\text{Al}_2\text{O}_3$ and $\text{Ag}/\text{Al}_2\text{O}_3\text{-OH}$ were collected on a spectrophotometer (Cary 5000, Varian) equipped with a diffuse reflectance cell at RT in ambient air from 200 to 600 nm after calcination at 550 °C for 2 h and using the corresponding calcined Al_2O_3 supports for the background spectra.

The hydroxylated materials were also characterized by the NO_x -Temperature-Programmed Desorption (NO_x -TPD) method [6,18,19]. Prior to the NO_x -TPD experiments, the samples were calcined in situ under a flow rate of 100 $\text{mL}_{\text{NTP}}/\text{min}$ of 20% O_2 in He at 500 °C (3 °C/min) for 2 h. The samples (about 0.2 g) were firstly contacted with a $\text{NO-O}_2\text{-He}$

(385 ppm–8%–balance, 230 mL_{NTP}/min) mixture at room temperature (RT) until recovery of the inlet NO_x concentration. The samples were then flushed with O₂(8%)–He at RT to remove weakly adsorbed NO_x species until the disappearance of the NO_x species in the stream. The NO_x-TPD experiments were carried out from RT to 550 °C at a heating rate of 3 °C/min under a flow of 230 mL_{NTP}/min of 8% O₂ in He. The reactor outflow was continuously monitored using a chemiluminescence NO_x analyzer (Thermo Environmental Instruments 42C-HT) which allowed for the simultaneous detection of both NO and NO₂.

3. Results

3.1. SCR performance

In the absence of H₂ in the reacting feed (C₃H₆-SCR, Fig. 1), hydroxylation of Al₂O₃ prior to the addition of Ag was found to have little influence on the conversion of NO_x to N₂ (Fig. 1a, black line) although the N₂ selectivity was found to be lowered to a significant extent below 450 °C on the hydroxylated catalyst. Regarding C₃H₆ oxidation (Fig. 1b), it can be seen that the conversion profile of Ag/Al₂O₃ was steeper than that observed on Ag/Al₂O₃-OH.

As expected from the pioneering work of Satokawa [4], the conversions of NO_x to N₂ and C₃H₆ to CO_x occurred at much lower temperatures in the presence of H₂ on both samples (Fig. 2) in comparison with the reaction ran in the absence of H₂ (Fig. 1). The C₃H₆ and H₂ oxidation profiles were found to be shifted to slightly higher temperature on Ag/Al₂O₃-OH compared to Ag/Al₂O₃ (Fig. 2b). Much more interesting are the results obtained regarding the reduction of NO_x to N₂ (Fig. 2a). From 250 to 450 °C, the catalyst prepared from the support thermally-treated in water (Ag/Al₂O₃-OH) remarkably outperformed Ag/Al₂O₃ that had been prepared conventionally, whereas N₂ selectivity remained comparable on both samples (Fig. 2a). The conversion of NO_x to N₂ reached 82 %

at 275 °C on Ag/Al₂O₃-OH, whereas Ag/Al₂O₃ exhibited only 50 % conversion at the same temperature.

One can note that the newly-prepared Ag/Al₂O₃ sample showed reproducible C₃H₆-SCR and H₂-C₃H₆-SCR performance compared to the sample studied earlier (Figs. 1 and 2). Another Ag/Al₂O₃-OH sample was prepared under different pH conditions and its SCR and H₂-SCR catalytic performance (not shown) was found to be close to that reported in Figs. 1 and 2. Considering all the above, the present results highlights for the first time on the beneficial effect of a thermal pretreatment of the pristine γ -Al₂O₃ support in water prior to Ag deposition on H₂-C₃H₆-SCR performance. To gain further insights into the enhanced H₂-C₃H₆-SCR performance of the Ag catalyst prepared from the γ -Al₂O₃ support thermally-pretreated in water compared with that prepared from the as-received Al₂O₃, the samples were characterized by XRD, UV-visible spectroscopy and NO_x-TPD.

3.2. Catalyst characterization

XRD characterization of Al₂O₃, Al₂O₃-OH and calcined Ag/Al₂O₃-OH is shown in Fig. 3. Narrow diffraction peaks appeared at 18.6, 20.3, 27.8, 40.7, 53.1, 57.4, 63.8 and 70.6 ° attesting for the formation of a bayerite phase (Al(OH)₃) when Al₂O₃ was submitted to a thermal treatment in water in agreement with earlier reports [14-16], although the experimental conditions used in the present work differed substantially from those of these earlier studies. The XRD pattern of the dried Ag/Al₂O₃-OH sample (not shown) was found to be identical to that of the parent Al₂O₃-OH shown in Fig. 3. After calcination of Ag/Al₂O₃-OH at 550 °C, the XRD pattern closely resembled that of the parent Al₂O₃ support suggesting that the bayerite phase likely mainly transformed into η -Al₂O₃ [20-21,22], since the XRD patterns of γ -Al₂O₃ and η -Al₂O₃ differ only little from each other [20-22], and probably also transformed back to γ -Al₂O₃ to a limited extent [20,22].

Similar UV-visible spectra were obtained for calcined Ag/Al₂O₃ and Ag/Al₂O₃-OH (Fig. 4). Three bands were observed at 210, 240 and 350 nm on both samples. Whereas the band at 210 nm has been attributed to Ag⁺ [9,23], the attribution of those at 240 and 350 nm are still the subject of controversy. The band at 240 nm has been assigned to the presence of Ag⁺ [23] and partially charged Ag clusters (Ag_n^{δ+}) [9], whereas that at 350 nm has been attributed to the presence of partially charged Ag clusters (Ag_n^{δ+}) [24] as well as that of small metallic clusters (Ag_n) [9]. Note that the silver plasmon characteristic of Ag metal particles is usually located above 390 nm [23]. From these UV-visible results and the fact that Ag coordination numbers determined earlier by EXAFS were found to remain extremely low under various experimental conditions including those of H₂-HC-SCR [25], it can be assumed that Ag is mainly present in an oxidized state in both samples.

As shown earlier, the characterization of Ag/Al₂O₃ samples by NO_x-TPD provided unique information about the coverage of Al₂O₃ by Ag which could not be obtained by other means [6,8]. The NO_x-TPD profiles obtained for the hydroxylated samples are shown in Fig. 5a. For comparison, those obtained earlier [6] on Al₂O₃ and Ag/Al₂O₃ are displayed in Fig. 5b. Whereas it can be clearly seen that the introduction of Ag on Al₂O₃ led to both a significant decrease in the NO_x uptake (446 μmol NO_x/g for Al₂O₃ compared to 337 μmol NO_x/g_{Al₂O₃} for Ag/Al₂O₃) and a shift of the low temperature desorption peak to higher temperatures (Fig. 5b), this was not observed for the hydroxylated samples. Fig. 5a shows that the NO_x profiles of Ag/Al₂O₃-OH and Al₂O₃-OH are similar in shape, albeit slightly different from those found on Al₂O₃ (Fig. 5b). In addition the NO_x uptakes determined on the hydroxylated samples were found to be similar for Al₂O₃-OH (439 μmol NO_x/g) and Ag/Al₂O₃-OH (442 μmol NO_x/g_{Al₂O₃}) and fairly close to that of Al₂O₃ (446 μmol NO_x/g). Since the transformation of the bayerite domains likely leads to the formation of η-Al₂O₃ [20-22], we found of interest to perform an additional NO_x-TPD experiment on a η-Al₂O₃ support

(SASOL, 314 m²/g) to compare the NO_x adsorption capacity of η-Al₂O₃ to that of γ-Al₂O₃. The NO_x-TPD profile obtained for η-Al₂O₃ (not shown) was found to be similar in shape to that obtained earlier on γ-Al₂O₃ [6], but of higher intensity (761 μmol NO_x/g compared to 446 μmol NO_x/g for γ-Al₂O₃). Taking into account the specific surface areas of 314 m²/g for η-Al₂O₃ and 180 m²/g for γ-Al₂O₃, the amounts of NO_x adsorbed normalized per unit surface area (NO_x surface density) are found to be very close on both polymorphs (2.4 and 2.5 μmol NO_x/m² on η- and γ-alumina, respectively). Zecchina and co-workers [28] also found that the total amounts of NO_x adsorbed from NO₂ on γ- and δ- Al₂O₃ correlated with the specific surface areas of both polymorphs, indicating, in other words, that the NO_x surface density of alumina was unaffected by the nature of its polymorph.

4. Discussion

The treatment of the pristine Al₂O₃ support in water at 80 °C for 24 h prior to Ag deposition led to a drastic improvement of the low-temperature H₂-C₃H₆-SCR (Ag/Al₂O₃-OH) performance compared to the Ag/Al₂O₃ sample prepared on the as-received Al₂O₃ support (Fig. 2a). In contrast, the C₃H₆-SCR performance was found to be comparable on both samples and was thus found not to be influenced to a significant extent by a prior thermal treatment in water of the alumina support (Fig. 1a).

XRD characterization showed that the thermal pretreatment in water led to the hydroxylation of Al₂O₃ with the appearance of reflections attributed to the formation of a bayerite phase (Al(OH)₃, Fig. 3). The fact that the XRD patterns of Al₂O₃-OH and Ag/Al₂O₃-OH in their calcined state closely resembled those of γ-Al₂O₃ and Ag/γ-Al₂O₃ indicates that the bayerite phase likely transformed to η-Al₂O₃ and γ-Al₂O₃ after calcination at 550 °C. The extent of transformation of the bayerite domains to η-Al₂O₃ and γ-Al₂O₃ could not be quantified as the η-Al₂O₃ and γ-Al₂O₃ XRD patterns are only subtly different from each

other [20-22] and that complete conversion of γ -Al₂O₃ to bayerite did not occur (Fig. 3). The UV-visible characterization of calcined Al₂O₃-OH and Ag/Al₂O₃-OH indicated that their Ag speciation was comparable (Fig. 4). Much more interesting is the characterization of the various samples by NO_x-TPD. We reported earlier [6] that the addition of Ag to Al₂O₃ led to a decrease in the NO_x uptake (Fig. 5b) and concluded that Ag occupied some of the Al₂O₃ sites responsible for NO_x adsorption (Scheme 1, Path A). It must be recalled that the NO_x adsorption sites of partly dehydroxylated Al₂O₃ samples have been attributed to Al³⁺ [26,27], O²⁻ [27,28] and OH [27] groups. In the case of the samples prepared from hydroxylated Al₂O₃, the situation is clearly different as the NO_x uptakes of Al₂O₃-OH and Ag/Al₂O₃-OH remained close to that found on Al₂O₃ (Fig. 5a and section 3.2.). The higher NO_x uptake of Ag/Al₂O₃-OH compared to that of Ag/Al₂O₃ (Fig. 5a) cannot be attributed to the likely presence of η -Al₂O₃ domains issued from the transformation of the bayerite ones since it was found that the specific surface area of both samples did not change significantly (section 2.3.) and that the NO_x surface density of η -Al₂O₃ and γ -Al₂O₃ was similar (end of section 3.2.). For Ag/Al₂O₃-OH, it can therefore be concluded that Ag anchored essentially onto sites newly-created by the thermal pretreatment of γ -Al₂O₃ in water, which were not available on the untreated support as illustrated in Scheme 1 (Path B), thus leaving the sites present initially on γ -Al₂O₃ accessible to the adsorption of NO_x. This newly-created sites most likely belong to the bayerite domains formed by thermal pretreatment in water of γ -Al₂O₃ as indicated by XRD (Fig. 3).

In a recent investigation, we showed that H₂-C₃H₆-SCR performance unexpectedly decreased as the Ag surface density (Ag/nm²_{Al₂O₃}) increased [8]. The H₂-C₃H₆-SCR kinetic study highlighted the importance of the NO_x coverage in this reaction, based on structure-activity (NO_x uptake-kinetic parameters) correlations. In particular, the increase in the NO reaction order from 0 for C₃H₆-SCR to 0.4 for H₂-C₃H₆-SCR on Ag(0.7 Ag/nm²_{Al₂O₃})/Al₂O₃

was assigned to a depletion in the coverage of NO_x adsorbed species due to a drastic increase in the $\text{H}_2\text{-C}_3\text{H}_6\text{-SCR}$ reaction rate compared to that of $\text{C}_3\text{H}_6\text{-SCR}$ [8]. Likewise, the decrease in $\text{H}_2\text{-C}_3\text{H}_6\text{-SCR}$ catalytic performance observed as the Ag surface density increased was attributed to a decrease in the NO_x coverage due to the anchoring of Ag species onto Al_2O_3 sites also responsible for NO_x adsorption, in agreement with the observed decrease in NO_x uptake [8]. As indicated by the $\text{NO}_x\text{-TPD}$ characterization of the samples studied in the present work (Fig. 5), the NO_x uptake found on $\text{Ag/Al}_2\text{O}_3\text{-OH}$ remained close to that of Al_2O_3 and $\text{Al}_2\text{O}_3\text{-OH}$ but much larger than that of $\text{Ag/Al}_2\text{O}_3$. This suggests that NO_x coverage on $\text{Ag/Al}_2\text{O}_3\text{-OH}$ would be higher than that on $\text{Ag/Al}_2\text{O}_3$ despite the fact that their surface areas were found to be similar for both samples (section 2.3.). The higher NO_x coverage on $\text{Ag/Al}_2\text{O}_3\text{-OH}$ compared with $\text{Ag/Al}_2\text{O}_3$ could thus account for the much higher $\text{H}_2\text{-C}_3\text{H}_6\text{-SCR}$ performance found on $\text{Ag/Al}_2\text{O}_3\text{-OH}$ compared to $\text{Ag/Al}_2\text{O}_3$ (Fig. 2a). In the absence of H_2 in the reacting feed, the similar $\text{C}_3\text{H}_6\text{-SCR}$ performance found on both Ag samples (Fig. 1a) is consistent with the absence of NO partial pressure dependency (0^{th} reaction order with respect to NO for $\text{C}_3\text{H}_6\text{-SCR}$ [8]) and thus with the absence of NO_x coverage dependency for the $\text{C}_3\text{H}_6\text{-SCR}$ reaction. The close $\text{C}_3\text{H}_6\text{-SCR}$ performance obtained on $\text{Ag/Al}_2\text{O}_3\text{-OH}$ and $\text{Ag/Al}_2\text{O}_3$ (Fig. 1a) is also consistent with the fact that the Ag speciation on both samples was found to be similar as indicated by UV-visible characterization (Fig. 4).

Although it is widely acknowledged in the community that the starting supporting oxide/oxyhydroxide is of the utmost importance for the $\text{Ag/Al}_2\text{O}_3$ system, studies in which the SCR performance of $\text{Ag/Al}_2\text{O}_3$ was compared within samples synthesized under identical conditions from various supporting oxide/oxyhydroxides (Al_2O_3 , AlOOH , Al(OH)_3) are rare. To our knowledge, only two studies have been reported to date in which the influence of the starting support was investigated [13,29]. Although calcination of the oxyhydroxides supports eventually leads to Al_2O_3 , from here on the samples studied in these earlier works will be

denoted as Ag/starting oxide/oxyhydroxides for the sake of clarity. Zhang and Kaliaguine reported that Ag/AlOOH exhibited the best C₃H₆-SCR performance compared to Ag/Al₂O₃ and Ag/Al(OH)₃ [13]. Regarding Ag/Al(OH)₃, (i) its very low surface area, leading to a silver density (3.1 Ag/nm²_{Al₂O₃}) well above the optimum Ag density highlighted recently (0.7 Ag/nm²_{Al₂O₃}, [6]) and (ii) the presence of a significant amount of carbonates prevented a fair comparison of its C₃H₆-SCR performance with that of the two other samples. In contrast Ag/Al₂O₃ and Ag/AlOOH exhibited comparable specific surface areas (~ 140 m²/g) and thus we could calculate that their Ag surface densities were similar and close to 0.8 Ag/nm²_{Al₂O₃}. The higher C₃H₆-SCR performance of Ag/AlOOH compared to that of Ag/Al₂O₃ was attributed by Zhang and Kaliaguine to the higher dispersion of Ag on AlOOH due to the greater concentration of OH groups in AlOOH compared to Al₂O₃ [13]. In addition, Zhang and Kaliaguine showed that Ag was present in a more oxidized state on Ag/AlOOH than on Ag/Al₂O₃ [13]. It must be recalled here that oxidized Ag species have been reported to be the active sites of HC-SCR promoted or not by H₂ [1,7,9,24-31]. As indicated by the UV-visible data of the present study (Fig. 4), Ag speciation was found to be comparable for our Ag/Al₂O₃-OH and Ag/Al₂O₃ samples suggesting similar dispersion, so that it is not surprising that both catalysts eventually exhibited close C₃H₆-SCR performance (Fig. 1a).

In a recent study, He and co-workers reported on the superiority of Ag/AlOOH compared to Ag/Al₂O₃ and Ag/Al(OH)₃ in C₂H₅OH-SCR after calcination of the samples at 600 °C [29]. These authors suggested that the C₂H₅OH-SCR activity was correlated to the amount of tetrahedrally-coordinated Al³⁺ cations supposed to be the active sites of the adsorption and activation of the –NCO intermediates [29]. Toops and co-workers initially proposed that atomic hydrogen may be formed on the surface of a Ag/Al₂O₃ catalyst under a C₂H₅OH-SCR feed via the dissociative adsorption of ethanol [32]. The presence of molecular H₂ has been recently detected in the course of methanol-assisted HC-SCR [33] and methanol-

SCR [34,35] reactions. This led these authors [33-35] to the proposal that the high SCR performance found at low-temperature in the presence of alcohols was due, at least partly, to a similar effect as that of H₂ in H₂-HC-SCR [8]. According to the results of the present study, in which it is proposed that the higher H₂-C₃H₆-SCR performance of Ag/Al₂O₃-OH compared to Ag/Al₂O₃ would be attributed to the higher NO_x coverage on Ag/Al₂O₃-OH due to the preferential interaction of Ag with newly created OH groups, the higher C₂H₅OH-SCR performance of Ag/AlOOH compared to Ag/Al₂O₃ reported in [29] could be accounted for by a similar reason. Ag anchoring on AlOOH sites different from those of Al₂O₃ would help preserve a higher NO_x density in the final catalyst as shown in the present work. This explanation, however, cannot stand as the only reason to describe the order of C₂H₅OH-SCR activity found by He and co-workers [29]: Ag/AlOOH > Ag/Al₂O₃ > Ag/Al(OH)₃. Ag/Al(OH)₃ was found to exhibit the lowest C₂H₅OH-SCR performance among the samples investigated indeed, whereas it could have been expected that this particular catalyst should have provided a catalytic performance at least higher than that of Ag/Al₂O₃ on the sole basis of the conclusions drawn in our present work. As highlighted above, the C₂H₅OH-SCR reaction must behave closer to H₂-HC-SCR than to HC-SCR [33-35] and we have reported recently that the performance of Ag/Al₂O₃ catalysts increased as the Ag loading, i.e. Ag surface density, decreased in H₂-C₃H₆-SCR [8]. This is consistent with the fact that Ag/Al₂O₃ samples with Ag contents lower than 2 wt% were found to be more active in C₂H₅OH-SCR than the Ag(2 wt%)/Al₂O₃ sample [36,37]; Ag(2 wt%)/Al₂O₃ has been reported to be the optimum catalyst in HC-SCR [6] but not in H₂-HC-SCR [8] indeed. In the work of He and co-workers, the surface areas of Ag/AlOOH (213.1 m²/g), Ag/Al₂O₃ (197.9 m²/g) and Ag/Al(OH)₃ (168.1 m²/g) were found to be substantially different after calcination at 600 °C [29]. The order of activity reported for these catalysts in C₂H₅OH-SCR (Ag/AlOOH > Ag/Al₂O₃ > Ag/Al(OH)₃) also follows the order expected from the calculated Ag surface

densities of the corresponding samples ($\text{Ag}/\text{AlOOH} : 0.5 \text{ Ag}/\text{nm}^2_{\text{Al}_2\text{O}_3} < \text{Ag}/\text{Al}_2\text{O}_3 : 0.6 \text{ Ag}/\text{nm}^2_{\text{Al}_2\text{O}_3} < \text{Ag}/\text{Al}(\text{OH})_3 : 0.7 \text{ Ag}/\text{nm}^2_{\text{Al}_2\text{O}_3}$). To summarize, in addition to the potential involvement of tetrahedrally-coordinated Al^{3+} cations in $\text{C}_2\text{H}_5\text{OH-SCR}$ [29], the superiority of the Ag/AlOOH catalyst compared to $\text{Ag}/\text{Al}_2\text{O}_3$ and $\text{Ag}/\text{Al}(\text{OH})_3$ in $\text{C}_2\text{H}_5\text{OH-SCR}$ reported in [29] may also result from differences in the NO_x coverage on the corresponding samples influenced by (i) the preferential interaction of Ag with AlOOH anchoring sites different from those found on Al_2O_3 , as highlighted in the present work, and/or (ii) the Ag surface density of the samples [8].

5. Conclusion

This work highlights for the first time that a thermal treatment in water of $\gamma\text{-Al}_2\text{O}_3$ prior to Ag deposition leads to a drastic enhancement of $\text{H}_2\text{-C}_3\text{H}_6\text{-SCR}$ performance at low temperature. Based on an earlier $\text{H}_2\text{-C}_3\text{H}_6\text{-SCR}$ kinetic investigation [8] and on the NO_x uptake data, this improvement is attributed to the higher NO_x coverage on $\text{Ag}/\text{Al}_2\text{O}_3\text{-OH}$ compared with $\text{Ag}/\text{Al}_2\text{O}_3$. The higher NO_x adsorption capacity of $\text{Ag}/\text{Al}_2\text{O}_3$ prepared from the $\gamma\text{-Al}_2\text{O}_3$ support thermally-pretreated in water is proposed to result from the preferential interaction of Ag with newly-created Al_2O_3 anchoring sites ($\text{Al}(\text{OH})_3$ bayerite domains), which were not available on the untreated pristine support. The identification of the latter sites is currently being investigated. The present work may also provide arguments on the fact that boehmite (AlOOH) is known to be a preferred starting Al_2O_3 precursor for the preparation of $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts in the HC-SCR field, as however scarcely discussed in the corresponding literature.

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Figure Captions

Fig. 1. (a) Conversion of NO_x to N_2 (solid lines) and selectivity to N_2 (dashed lines), and (b) conversion of C_3H_6 to CO_x in the C_3H_6 -SCR reaction on $\text{Ag}/\text{Al}_2\text{O}_3$ (grey) and $\text{Ag}/\text{Al}_2\text{O}_3\text{-OH}$ (black). For comparison, the data obtained previously on a different batch of $\text{Ag}/\text{Al}_2\text{O}_3$ sample [6] are also reported (\bullet, \circ). 0.18 g of $\text{Ag}/\text{Al}_2\text{O}_3$ in 0.18 g of Al_2O_3 . Feed composition: 385 ppm NO_x , 400 ppm C_3H_6 , 8% O_2 and He balance with a 230 $\text{mL}_{\text{NTP}}/\text{min}$ flow rate.

Fig. 2. (a) Conversion of NO_x to N_2 (solid lines) and selectivity to N_2 (dashed lines), and (b) conversions of C_3H_6 to CO_x (solid lines), and H_2 (dotted lines) in the H_2 - C_3H_6 -SCR reaction on $\text{Ag}/\text{Al}_2\text{O}_3$ (grey) and $\text{Ag}/\text{Al}_2\text{O}_3\text{-OH}$ (black). For comparison, the data obtained previously on a different batch of $\text{Ag}/\text{Al}_2\text{O}_3$ sample [8] are also reported (\bullet, \circ). 0.18 g of $\text{Ag}/\text{Al}_2\text{O}_3$ in 0.18 g of Al_2O_3 . Feed composition: 0.21 % H_2 , 385 ppm NO_x , 400 ppm C_3H_6 , 8% O_2 and He balance with a 230 $\text{mL}_{\text{NTP}}/\text{min}$ flow rate.

Fig. 3. XRD patterns of Al_2O_3 calcined for 2 h at 550 °C, $\text{Al}_2\text{O}_3\text{-OH}$ dried at 120 °C for 12 h and $\text{Ag}/\text{Al}_2\text{O}_3\text{-OH}$ dried at 120 °C for 12 h and calcined for 2 h at 550 °C. Al_2O_3 (JCPDS 79-1558), Bayerite (JCPDS 20-11).

Fig. 4. UV-vis spectra of $\text{Ag}/\text{Al}_2\text{O}_3\text{-OH}$ (black) and $\text{Ag}/\text{Al}_2\text{O}_3$ (grey) after calcination at 550 °C for 2 h.

Fig. 5. NO_x-TPD profiles on (a) Al₂O₃-OH (-○-) and Ag/Al₂O₃-OH and (b) Al₂O₃ (-○-) and Ag/Al₂O₃ [6] after exposure of 0.18 g of sample to 385 ppm NO_x and 8% O₂ in He (230 mL_{NTP}/min flow rate) at RT for about 4 h.

Scheme 1. Simplified representation of the influence of the hydroxylation process of Al₂O₃ on the deposition of Ag species (●), and the distribution of the NO_x species adsorbed on thermally-treated (Δ) Al₂O₃ surfaces starting from the as-received Al₂O₃ (path (A)) and Al₂O₃-OH (path (B)).

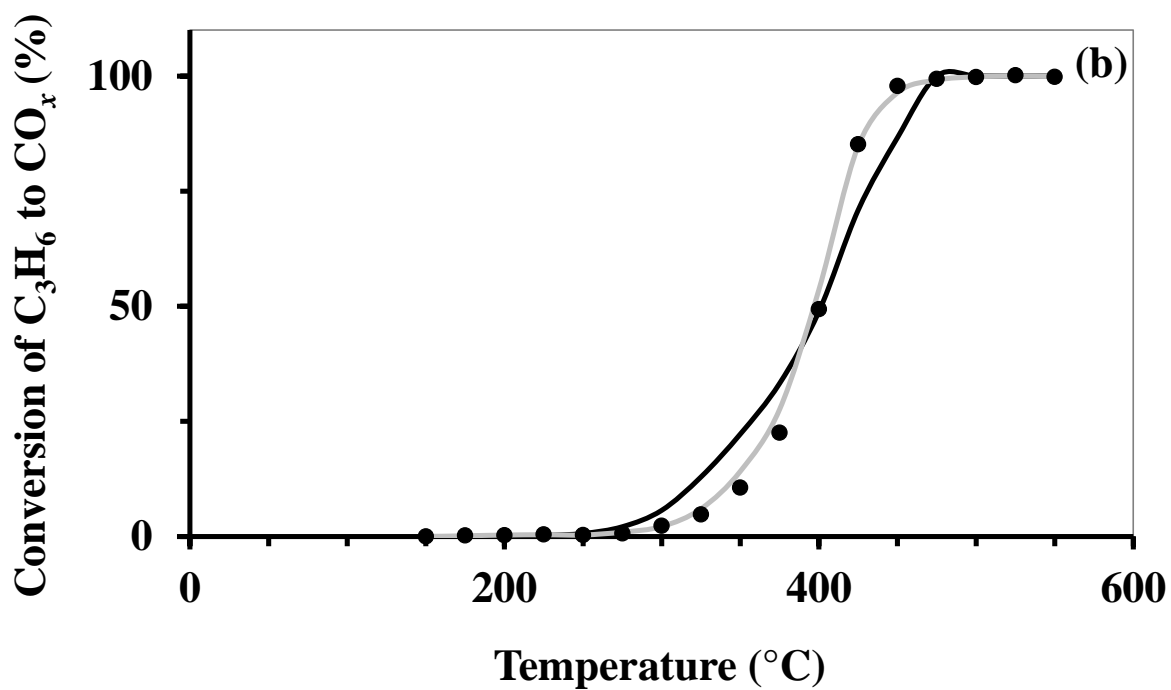
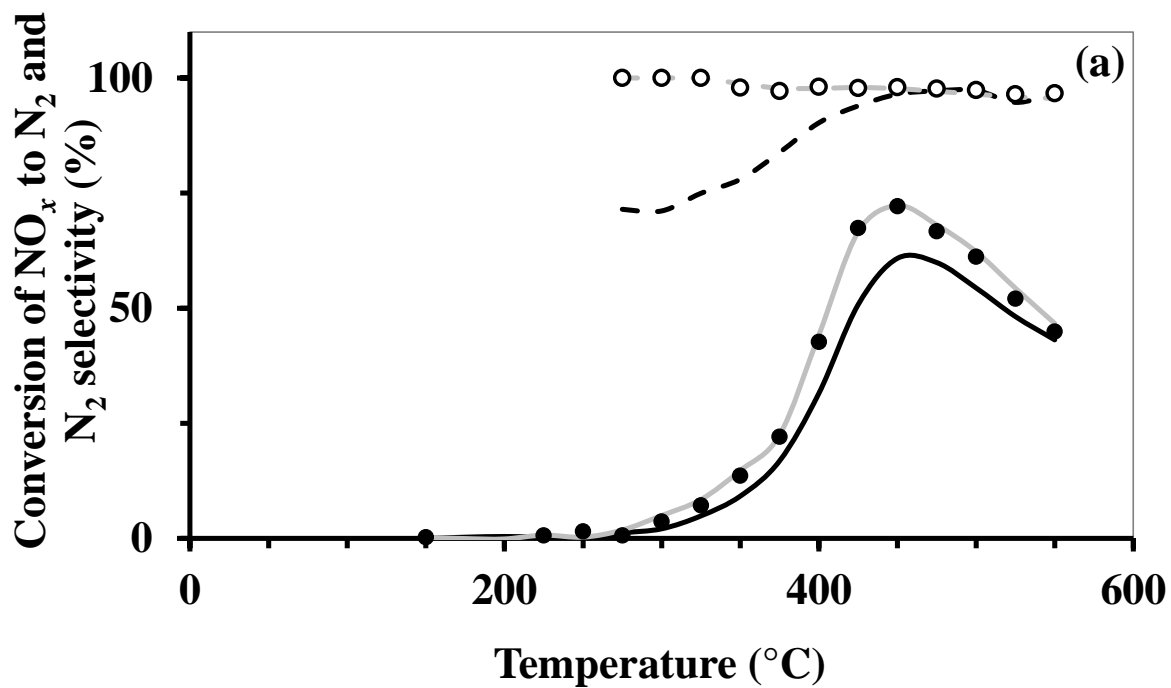


Fig. 1

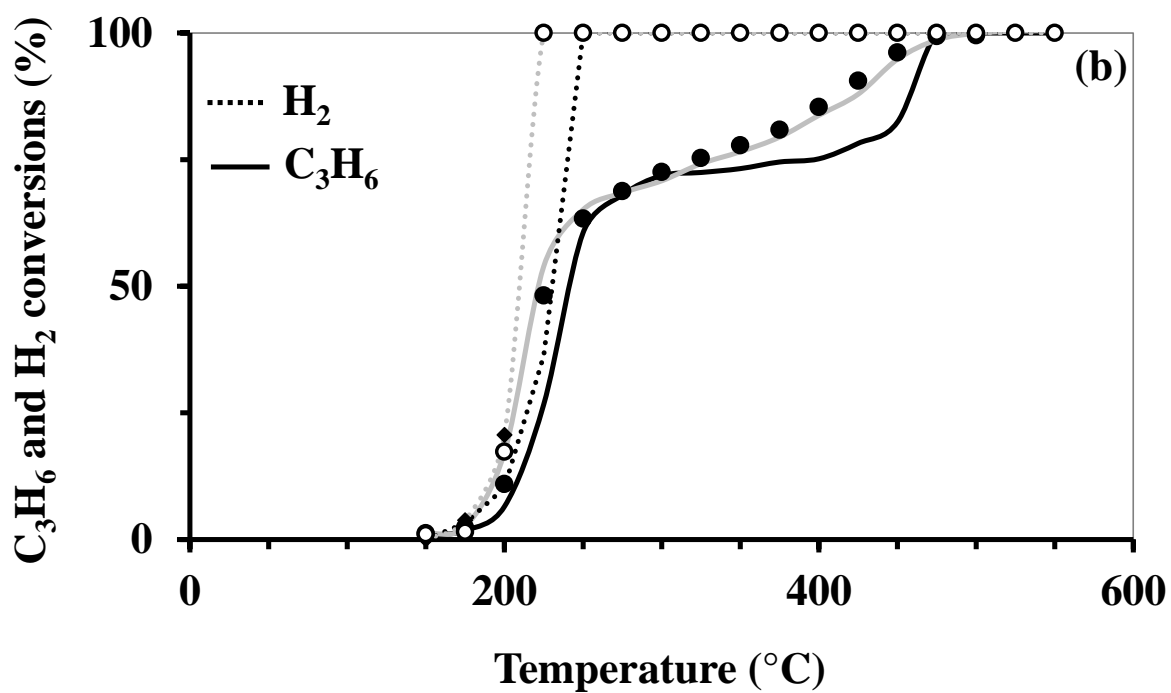
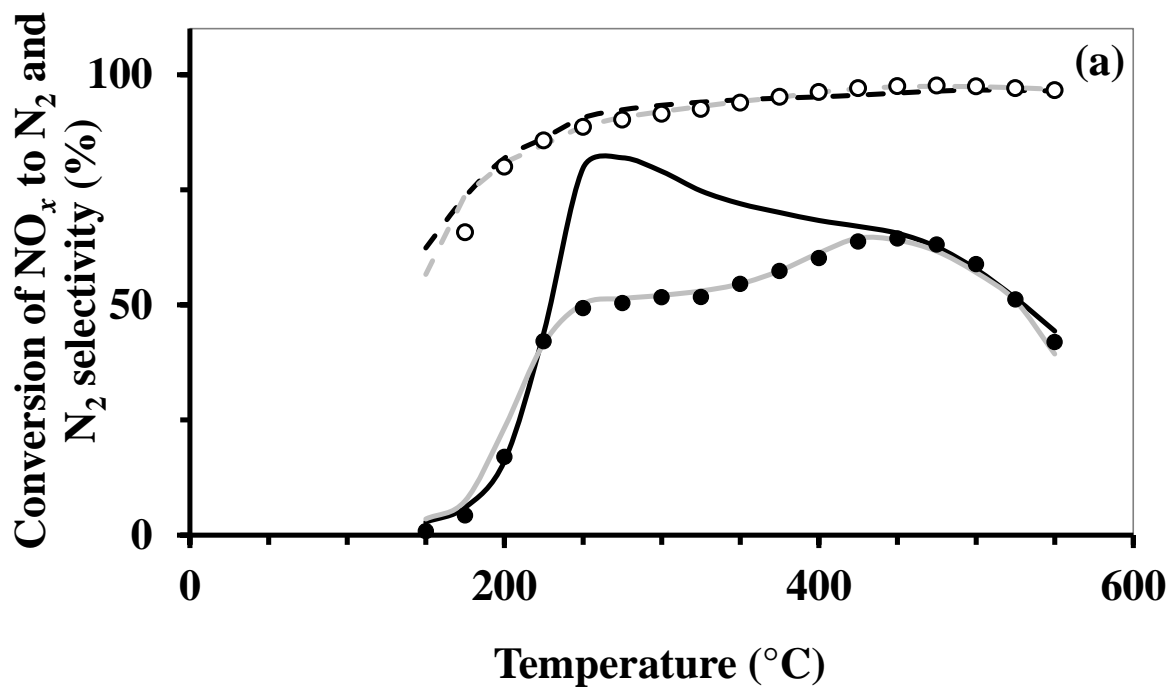


Fig. 2

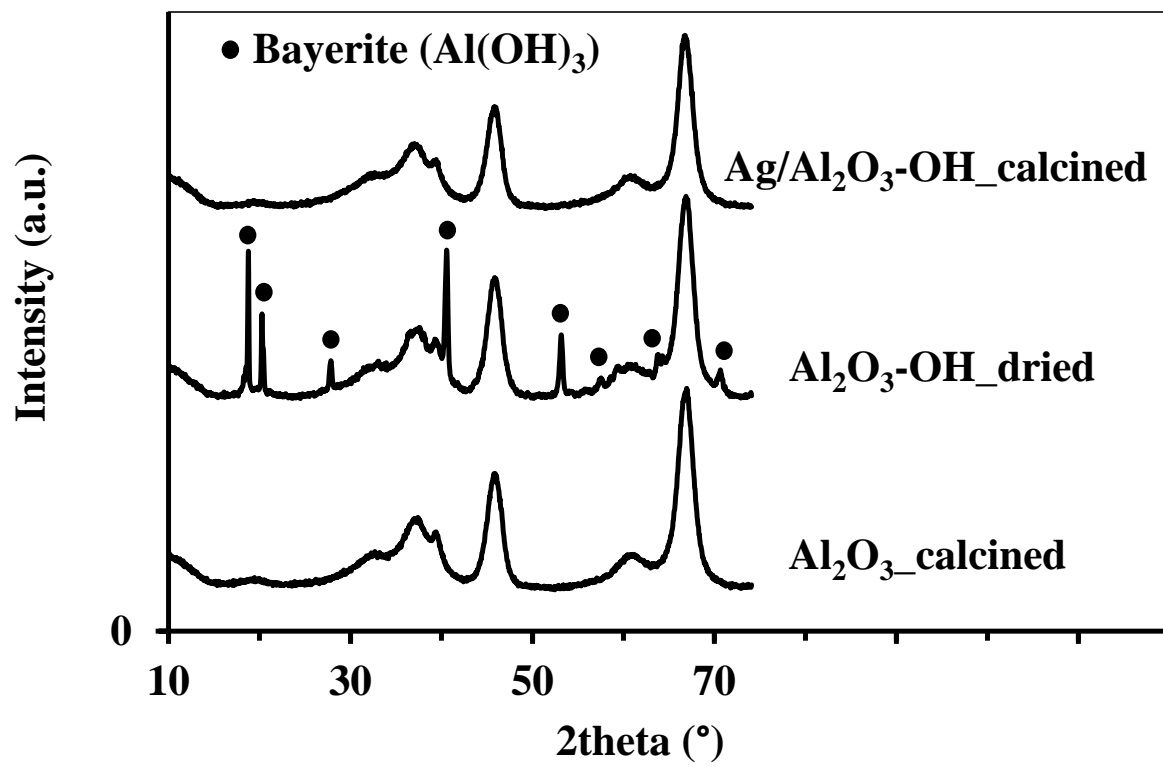


Fig. 3

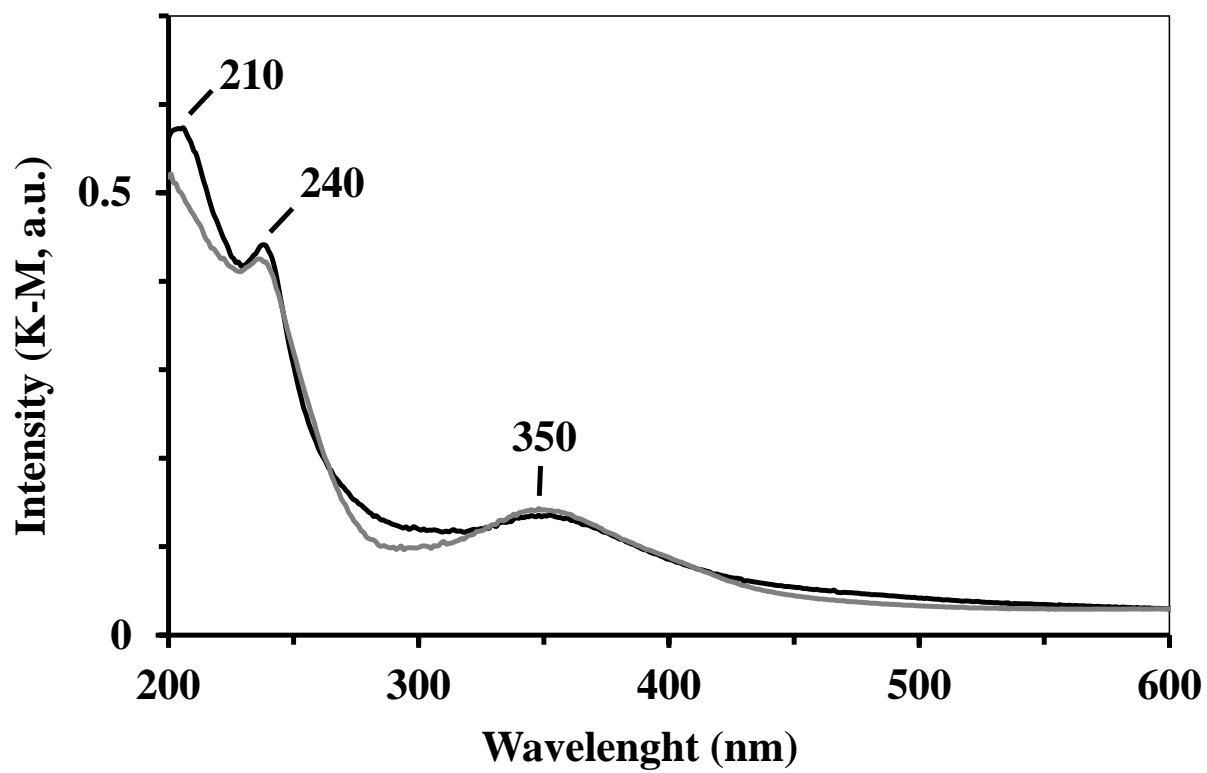


Fig. 4

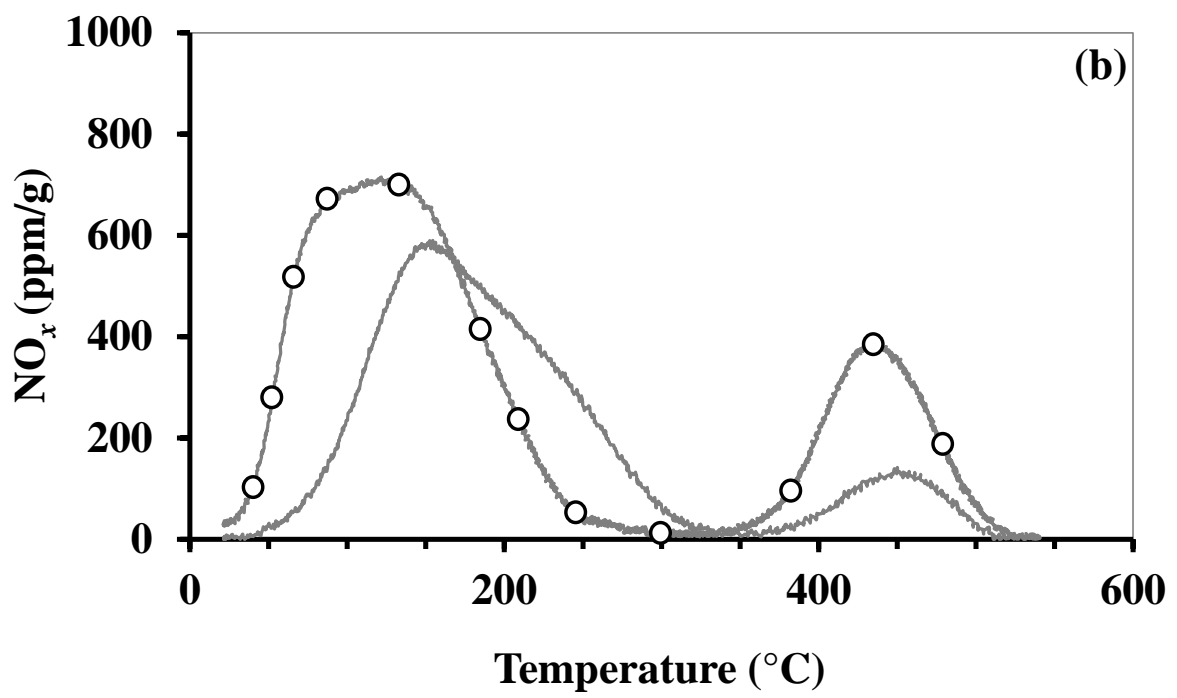
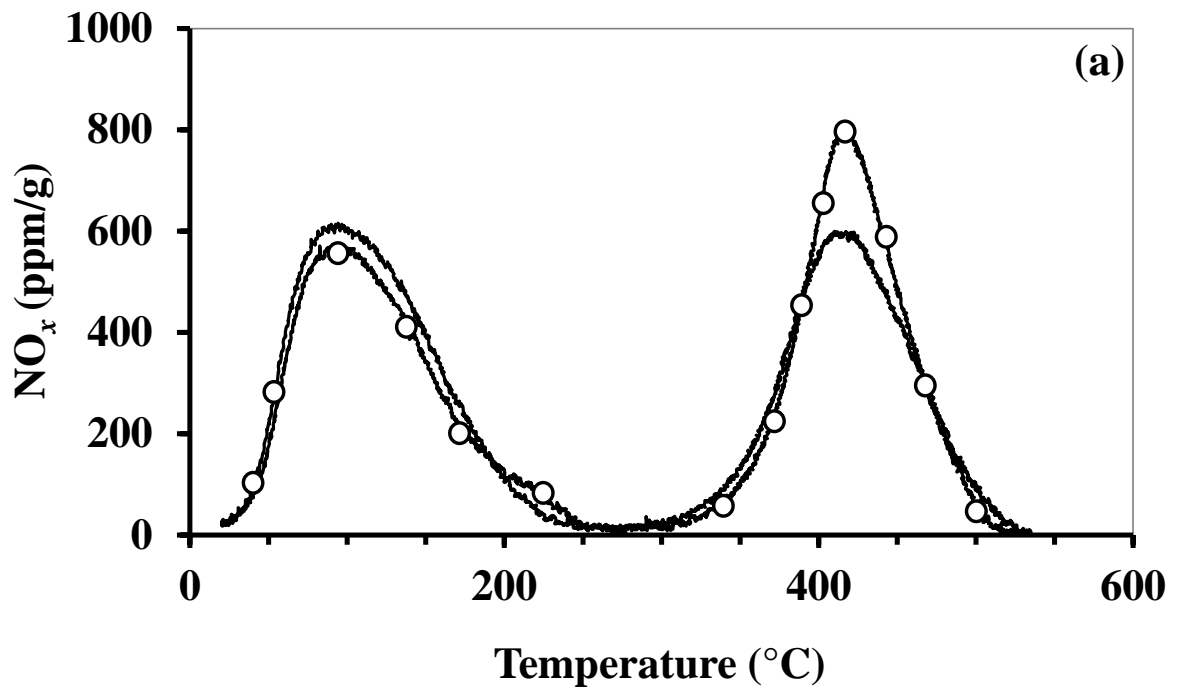
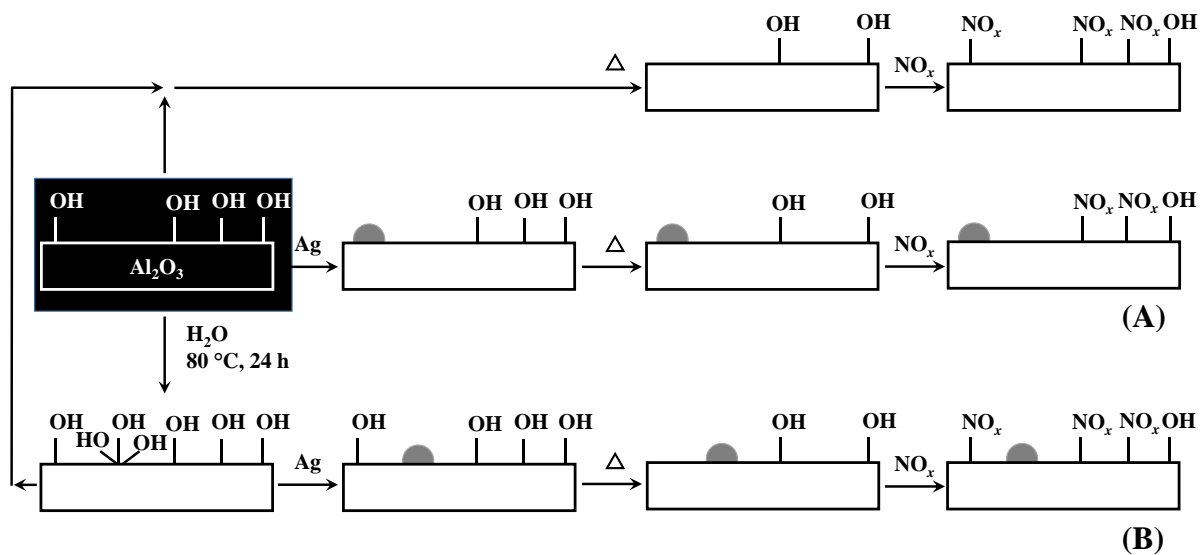


Fig. 5



Scheme 1.

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