

Influence of Al₂O₃ support on the activity of Ag/Al₂O₃ catalysts for SCR of NO with decane

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The role of the Al₂O₃ support on the activity of supported Ag catalyst towards the selective catalytic reduction (SCR) of NO with decane is elucidated. A series of Ag/Al₂O₃ catalysts were prepared by impregnation method and characterized by N₂ pore size distribution, XRD, UV–Vis, in-situ FT-IR and acidity measurement by NH₃ and pyridine adsorption. The catalytic activity differences of Ag/Al₂O₃ are correlated with different properties of Al₂O₃ supports and the active Ag species formed. 4wt% Ag supported on sol-gel prepared Al₂O₃ (Ag/Al₂O₃ (SG), showed higher NO_x conversion (65% at 400 °C), compared with the respective catalysts made from commercial Al₂O₃ (Ag/Al₂O₃ (GB), Ag/Al₂O₃ (ALO), (~26 and 7% at 400 °C). The higher surface area, acidity and pore size distribution in sol-gel prepared Al₂O₃ (SG) results in higher NO and hydrocarbon conversion. Based on the UV–vis characterization, the activity of NO reduction is correlated to the presence of Ag_n^{δ+} clusters and acidity of Al₂O₃ support was found to be one of the important parameter in promoting the formation and stabilization of Ag_n^{δ+} clusters. Furthermore from pyridine adsorption results, presence of more number of Bronsted acid sites in Ag/Al₂O₃ (SG) is confirmed, which could also contribute to low temperature hydrocarbon activation and improve NO conversion. *In situ* FT-IR measurements revealed the higher rate of –CN and –NCO intermediate species formation over 4wt% Ag/Al₂O₃ (SG). We conclude that the physico-chemical properties of Al₂O₃ play a crucial role in NO_x conversion over Ag/Al₂O₃ catalysts. Thus, the activity of the Ag/Al₂O₃ catalyst can be tailored by using a proper type of Al₂O₃ support.

KEY WORDS: HC-SCR; Ag/Al₂O₃; acidity; pore size distribution; UV–vis; *in situ* FT-IR.

1. Introduction

The search for effective and durable SCR catalytic system that works with hydrocarbon reductants in oxygen-rich environments is a high-priority issue in NO_x emission control and is the subject of intense research throughout the world. Among the various catalysts proposed for HC–SCR system, Ag/Al₂O₃ was found to be the most active and potential catalytic system, as it reduces the NO_x with hydrocarbons typical of diesel exhaust, and has received considerable attention [1–4]. Extensive studies have been reported on Ag/Al₂O₃ catalysts for SCR of NO using different types of hydrocarbon reductant and the highest catalytic activity was achieved using long-chain paraffin's as reductant, which makes Ag/Al₂O₃ a potential candidate for application in cleaning of diesel engine exhaust [5–7]. Furthermore NO_x can be converted at much lower temperatures, usually encountered in diesel exhaust in presence of hydrogen in the exhaust gas, and several research groups observed such a significant improvement in the activity over Ag/Al₂O₃ catalysts in the low temperature region

[8–14]. However, using a method employing hydrogen to increase the rate of SCR–NO_x could entail considerable problems in storage of hydrogen or its preparation on board in the current NO_x reduction strategies.

Extensive research on characterization and reaction mechanism over Ag/Al₂O₃ catalysts has been carried out to determine the active species responsible for NO reduction activity and the reaction intermediates formed, in order to improve the NO_x reduction activity in general and low temperature activity and catalysts stability in particular. The structure of alumina-supported Ag catalyst for HC-SCR has been well investigated and various types of silver species: isolated Ag⁺ ions, small Ag-aluminate “clusters,” or Ag₂O and small charged metallic Ag_n^{δ+} like clusters have been proposed as the active sites for the HC-SCR reaction [15–19]. However most of the studies were concentrated on the active silver species characterization and a few studies dealt with the support influence on active species formation and NO conversion. Luo et al. [20] used different methods for the preparation of Ag/Al₂O₃ catalysts and tested for NO reduction with propene. It was found that the sol-gel prepared 5wt% Ag/Al₂O₃ showed the improved activity and was ascribed due to suitable surface area and pore size distribution. However the

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correlation with support properties was not clear as the catalyst/support preparation was similar, derived from sol-gel preparation. Despite vast research work done on NO reduction over Ag/Al₂O₃ catalyst no general consensus was reached on support, active metal species and catalytic correlations. Thus, further fundamental investigations are still required in order to get more insight in to the effectiveness of Ag/Al₂O₃ catalyst and improve its activity, which is still insufficient for real life NO_x abatement from exhaust gases of diesel engines. A systematic revision is therefore undertaken to study various influences of the catalyst properties on NO_x reduction activity. In this article the influence of support surface characteristics on the formation of active Ag species and its activity in NO removal ability is presented. Though alumina is widely used as a support, only a few attempts have been devoted to study the role of Al₂O₃ support properties in the formation of active Ag species and the NO conversion enhancement of Ag/Al₂O₃ catalysts. The present study aims at investigating the influence of physico-chemical properties of sol-gel prepared Al₂O₃ on nature of the Ag species formed and its effect on reduction of NO with decane under lean burn conditions.

2. Experimental

2.1. Catalyst preparation

A series of Ag (4wt%) supported on Al₂O₃ catalysts (Ag/Al₂O₃), from three different sources of Al₂O₃ (i) prepared by sol-gel method (described below) designated as Ag/Al₂O₃ (SG) (ii) GB-45 supplied by Mizusawa Chemical Industries Ag/Al₂O₃ (GB) and (iii) JRC-ALO-7 supplied by Catalysis Society of Japan (Ag/Al₂O₃ (ALO) were prepared by wet impregnation of a calculated amount of aqueous silver nitrate solution. The impregnated samples were dried on a hot plate at 60 °C, followed by drying at 110 °C overnight in air with subsequent calcination in air at 600 °C for 3 h. Al₂O₃(SG) was prepared by sol-gel method by hydrolyzing aluminium tri-sec-butoxide (ASB) by drop wise addition of H₂O (molar ratio H₂O/ASB = 7) at room temperature with continuous stirring. The obtained gel was aged at room temperature for 12 h without agitation, then dried in an oven at 110 °C overnight, followed by calcination at 450 °C for 5 h.

2.2. Catalyst characterization

XRD patterns of the calcined powder samples were recorded using Mac Science M18XHF22 X-ray diffractometer with Cu-K α radiation. The BET surface area of the catalysts was determined by N₂ physisorption at -196 °C using Micromeritics Flowsorb II 2300, after evacuating the samples at 300 °C for 30 min. The Nitrogen adsorption and desorption isotherms were

measured using a Quantachrome Autosorb system after the samples were pretreated at 150 °C overnight in vacuum (below 0.01 mmHg). The data were analyzed by the BJH (Barrett-Joyner-Halenda) method.

The acidity was measured by ammonia adsorption/desorption technique using Quadrupole mass spectrometer unit (BEL JAPAN). Ca. 100 mg of the sample was out gassed at 500 °C for 1 h in a helium flow before ammonia adsorption. Ammonia adsorption was carried out at 100 °C for 1 h and then the sample was flushed with helium for 30 min at 100 °C to remove physically adsorbed ammonia. Ammonia desorption was carried out by rising the temperature to 600 °C with a heating rate of 10 °C/min. Pyridine adsorption was studied in a high vacuum system using infrared (FTIR) technique to determine the type of acid sites on the samples. Prior to pyridine adsorption, the samples were heated to 600 °C at 10 °C/min in vacuum and then cooled down to room temperature. After this pretreatment, they were exposed to saturated pyridine vapor for 10 min and infrared spectra were recorded after out gassing at 150, 250, 350 and 450 °C, respectively.

In situ UV-Vis spectra of the catalysts were recorded by using a UV-Vis (Cary, NIR-5000) spectrometer in a diffuse reflectance mode between 190 and 600 nm range at a step of 0.5 nm with a band width of 2 nm. The catalyst samples were calcined in air at 600 °C for 1 h before measurement. BaSO₄ was used as a reference sample to measure the baseline spectrum. *In situ* FT-IR spectra were taken with a Nicolet Nexus 670 FT-IR spectrometer, accumulating 64 scans at a resolution of 4 cm⁻¹. Prior to each experiment, 25 mg of a catalyst sample was placed in the diffuse reflectance high temperature cell (Spectra Tech) fitted with CaF₂ windows was activated *in situ* by heating in flowing 10% O₂ in He flow at 600 °C, followed by cooling to the desired temperature (300, 350 and 400 °C). The background spectrum of the clean surface was recorded at respective temperatures in inert atmosphere. Then, a gas mixture containing 500 ppm NO, 10% O₂ and 300 ppm *n*-C₁₀H₂₂ in He, at a flow rate of 60 cm³ min⁻¹, was fed to the catalyst and the spectra are recorded after every 5 min, with spectra recorded in He as background.

2.3. Catalytic activity measurement

The catalysts are evaluated for the selective catalytic reduction (SCR) of NO with decane in a fixed bed reactor with a simulated diesel exhaust gas containing 500 ppm NO, 300 ppm *n*-C₁₀H₂₂, 10 vol% O₂, 6 vol% H₂O all diluted in He. The gas mixture was fed to 40 mg of the catalyst at a flow rate of 90 cm³ min⁻¹ (SV = ca.75,000 h⁻¹). The steady-state activity was measured at each reaction temperature by decreasing the temperature in 50 °C steps from 600 to 200 °C. The products were analyzed by gas chromatography (Shimadzu, GC-8A TCD detector) with a Molecular Sieve

5A column to separate N₂ and CO and a Porapak Q column to separate N₂O and CO₂. The concentration of NO was continuously monitored using a NO_x analyzer.

3. Results and discussion

3.1. Activity of Al₂O₃ support

Figure 1 compares the NO reduction and decane oxidation activity of different Al₂O₃ supports as catalysts. Using decane, Al₂O₃ support alone showed significant NO conversion activity above 350 °C. The NO conversion on supports alone is generally observed to occur in the high temperature range [21]. Among the activity of three alumina, Al₂O₃ (SG), Al₂O₃ (GB) and Al₂O₃ (ALO), the sol-gel prepared Al₂O₃ (SG) showed the maximum NO reduction of 55% at 550 °C and the conversion is observed over a considerably wider temperature window of 350–600 °C. No particular trend of HC conversion with NO conversion was observed over Al₂O₃ supports. At high temperatures two competing reactions, NO reduction with HC and HC oxidation to CO₂ take place. However, the decreasing trend of NO_x conversion and >90% decane conversion at high temperatures indicates that the decrease in NO conversion at high temperature is due to complete HC conversion.

The preparation of Al₂O₃ support by sol-gel method results in the formation of large surface area support with relatively broad porosity and higher acidity [22]. Especially the properties such as surface area and active site accessibility are expected to play a major role in the NO conversion with larger hydrocarbons such as decane. Surface area measurement of the three Al₂O₃

supports showed that the Al₂O₃ prepared by sol-gel method (SG) has higher surface area (350 m² g⁻¹) than the two commercial Al₂O₃ supports GB and ALO (140 and 143 m² g⁻¹, respectively). The pore size distributions of the supports are shown in figure 2. Three γ-Al₂O₃ supports show different pore volume, and pore size distribution. The most active Al₂O₃ (SG) showed maximum number of pores in 50–250 Å range compared with Al₂O₃ (GB) (very narrow) and ALO (very broad but relatively less number) pores. The surface area and pore size distribution indicated that the sol-gel prepared Al₂O₃ has higher and easily accessible surface active sites (acid) for large hydrocarbons such as decane and this can have a significant positive influence on NO conversion. Jen [21], and Luo et al. [20] have shown a similar observation of the presence of pores in 20–100 Å range results in higher NO reduction activity with relatively smaller molecule, propene. Furthermore the obvious increase in NO and HC conversion with increase in surface area of the supports indicates that these reactions are occurring on the surface of the support where surface hydroxyl groups (acidity) are expected to play an important role in the formation of reaction intermediates [18].

Figure 3 shows the acidity of the different Al₂O₃ supports measured by NH₃-TPD. The total acidity of sol-gel prepared Al₂O₃ (SG) is much higher than the commercial Al₂O₃ supports (GB and ALO). Though acidity seems to be important in determining the catalytic activity, the differences in acidity are not proportionally reflected on the NO_x conversion. One main reason for this is different pore size distribution of alumina. It can be expected that the higher acidity and large number of pores in sol-gel prepared Al₂O₃ leads to higher rate of hydrocarbon adsorption, and the uniformity of the pores may help in confining the adsorption and formation of reactive oxygenated hydrocarbon species. The differences NO_x conversion over Al₂O₃

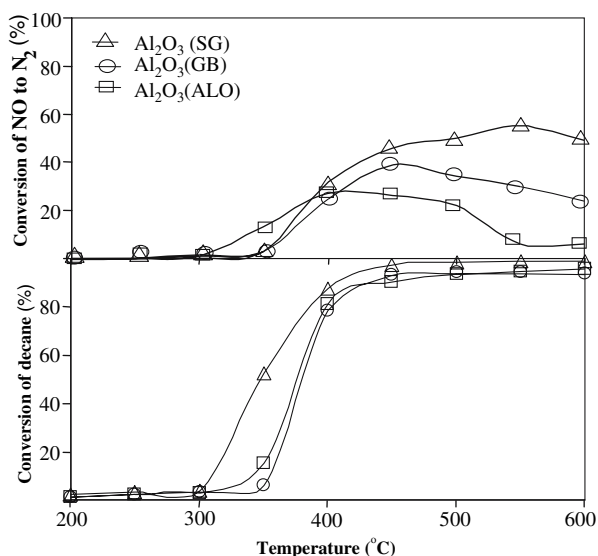


Figure 1. NO and decane conversion at different reaction temperatures during NO SCR with decane over different Al₂O₃ supports. Reaction conditions: 500 ppm NO, 300 ppm *n*-C₁₀H₂₂, 10 vol% O₂ and 6 vol% H₂O all diluted in He, SV -75,000 h⁻¹.

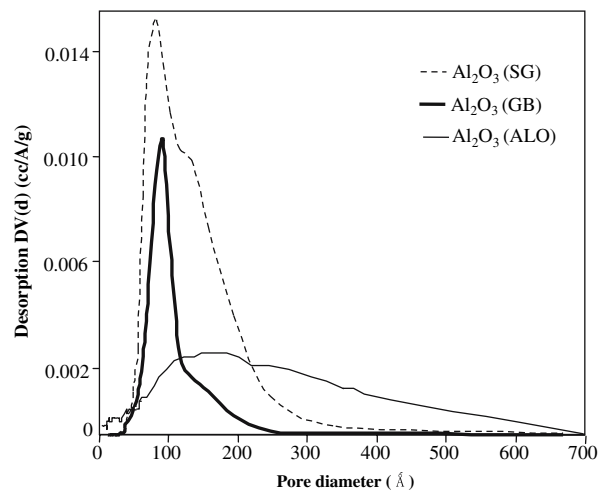


Figure 2. Pore size distribution of different Al₂O₃ supports.

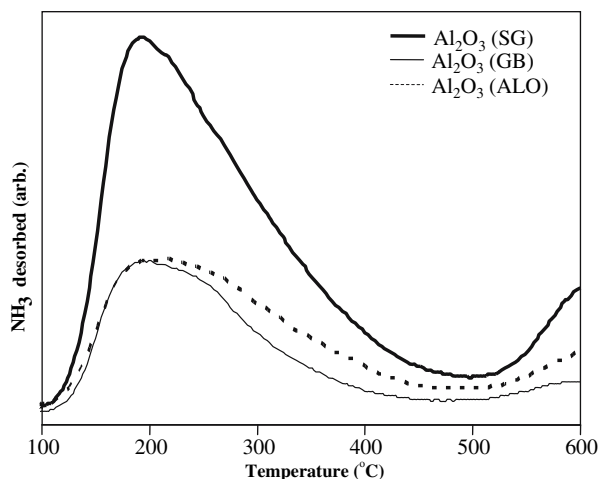


Figure 3. NH₃-TPD profiles of different Al₂O₃ supports.

catalysts having similar acidity could be explained by the differences in pore size distribution. One interesting observation that can be made from the NO conversion trends (figure 1) is that the activity is not shifted to significantly lower temperatures with different support surface area/accessibility, but only increased at respective temperatures among different supports. This indicates that the NO_x conversion is occurring on similar active sites on all the support only the population of these sites are increasing.

3.2. Activity of Ag/Al₂O₃ catalyst

Addition of Ag to Al₂O₃ increased the NO conversion and shifted the temperature range of both NO reduction and hydrocarbon conversion significantly to lower temperature region, from 350–600 °C to 250–450 °C range (figure 4). Furthermore high NO conversion is observed compared with the Al₂O₃ supports alone. Among the catalysts 4 wt% Ag supported on Al₂O₃ (SG) showed maximum NO_x conversion 65% at 400°C and significant NO conversion in a wider temperature window (250–450 °C) compared with the catalysts made from commercial γ -Al₂O₃ (~26 and 7% at 400°C) as supports. NO conversion decreased over all the catalysts above 400 °C due to complete HC conversion. The decane conversion to CO_x (CO + CO₂) over Ag/Al₂O₃ (SG) was also found to be much higher especially, in the low temperature region (250–350°C) compared to Ag/Al₂O₃ catalysts prepared from commercial Al₂O₃. Unlike Al₂O₃ supports as catalysts, over Ag/Al₂O₃ catalysts the HC conversion followed the trend of NO conversion.

3.3. Active sites of Ag/Al₂O₃ catalysts

UV–vis spectra of 4wt% Ag supported on three different Al₂O₃ samples after subtracting the respective Al₂O₃ spectrum are shown in figure 5. The bands obtained upon deconvolution are shown below each

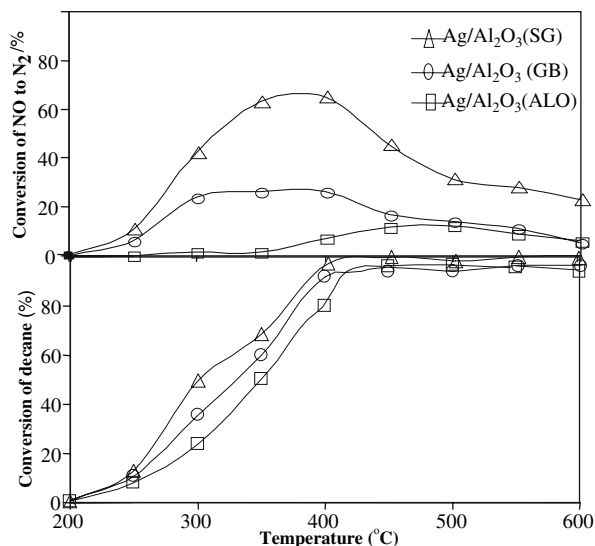


Figure 4. NO and decane conversion at different reaction temperatures during NO SCR with decane over different 4 wt% Ag/Al₂O₃ supports. Reaction conditions : 500 ppm NO, 300 ppm *n*-C₁₀H₂₂, 10 vol% O₂ and 6 vol% H₂O all diluted in He, SV –75,000 h⁻¹.

respective spectra. The UV–Vis spectra are deconvoluted and, the bands at 250–290 nm and 330–385 nm are attributed to Ag_{*n*1} small clusters, and Ag_{*n*2} larger clusters, respectively. The band at 220 nm is assigned to the electronic transition from 4d¹⁰ to 4d⁹5s¹ of highly dispersed Ag⁺ species. It is clear from the deconvoluted spectra that Ag/Al₂O₃ (ALO) has relatively more number of larger Ag clusters. The area under 220 nm

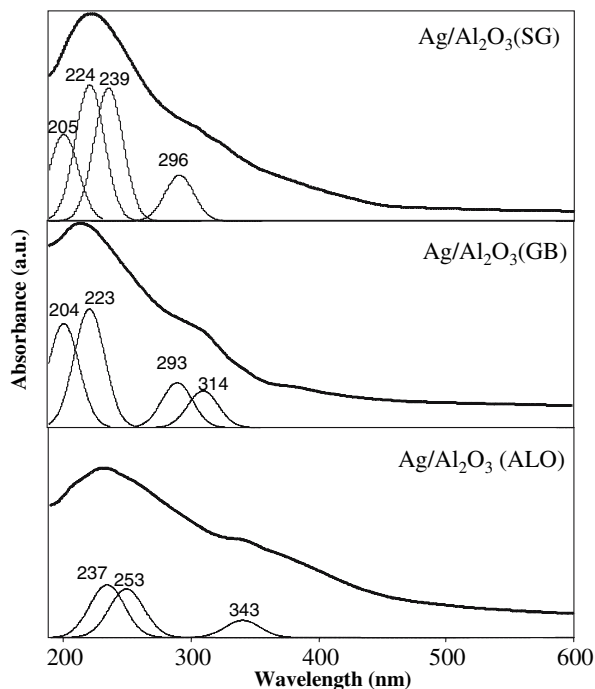


Figure 5. Diffuse reflectance UV–Vis spectra of 4 wt% Ag/Al₂O₃ catalysts. The deconvoluted bands are shown below each respective spectrum.

deconvoluted curve for Ag/Al₂O₃ (SG), Ag/Al₂O₃ (GB) and Ag/Al₂O₃ (ALO) are 16, 10 and 5 (arb. units), respectively. Among the three spectra, the Ag/Al₂O₃ (SG) which is the most active catalyst showed an intense absorption band around 220 nm compared to Ag/Al₂O₃ (GB) and Ag/Al₂O₃ (ALO), corresponding to small Ag_n^{δ+} clusters which are reported to be the catalytically active species for NO reduction with decane [15, 23]. It can also be noted that relatively large Ag_n^{δ+}/Ag⁰ species (bands above 300 nm) can be observed over Ag/Al₂O₃ (ALO). Despite the fact that the surface area and acidity of Al₂O₃ (GB-45) and Al₂O₃ (ALO) are similar, these two supports have shown entirely different population of silver species. One reason for the observed large silver species over Ag/Al₂O₃ (ALO) can be derived from its pore size data shown in figure 2. Al₂O₃ (ALO) has relatively broad (above 10 nm) pore size distribution and the small silver clusters initially formed during the impregnation can be more easily prone to agglomeration over Al₂O₃ (ALO). Therefore increase in surface area of the support is expected to increase the population of Ag_n^{δ+} species. Furthermore the increased number of hydroxyl groups will also stabilize such silver species compared with low surface area commercial supports. Although the silver species were not quantified by UV-Vis spectroscopy, the deconvolution of the spectra clearly shows a qualitative relationship between Ag_n^{δ+} species giving a band around 220 nm and NO_x conversion. The Ag/Al₂O₃ (ALO) catalyst which has relatively larger Ag_n^{δ+} clusters and metallic Ag⁰ clusters (340 nm) has shown lower NO conversion compared with Ag/Al₂O₃ (GB) and Ag/Al₂O₃ (SG) catalysts which have small dispersed Ag_n^{δ+} clusters. Though the acidity is similar for Ag/Al₂O₃(GB) and Ag/Al₂O₃ (ALO), deconvoluted UV-Vis spectra clearly showed that, the distribution of silver species over both the compared

aluminas are very different, which may be arising due to differences in pore size distribution which is again reflected over NO_x conversion. It can be expected that over larger silver clusters or metallic silver clusters hydrocarbon can be easily oxidized, at high temperatures, whereas these are mostly inactive at low temperatures. Furthermore due to lower number of silver species that can form intermediate nitrate species, necessary for the conversion to N₂, are decreased leading to lower NO conversion over Ag/Al₂O₃(ALO). The high performance of Ag/Al₂O₃(SG) catalyst in general can be correlated to Ag_n^{δ+} species (220 nm) as seen in UV spectrum of Ag/Al₂O₃ (SG) (figure 5).

3.4. Role of acid sites in SCR of NO with decane

Figure 3 shows the acidity of the different Al₂O₃ supports measured by NH₃-TPD. The total acidity of sol-gel prepared Al₂O₃ (SG) is much higher than the commercial Al₂O₃ supports (GB and ALO). Therefore, it can be presumed that the Ag species will more efficiently interact and stabilized with the acidic Al₂O₃ (SG) having large number of surface hydroxyl groups than the less acidic commercial alumina supports. This leads to the formation of more stable active silver species. Over such supports it is also possible to load relatively high amounts of silver which can improve the low temperature NO_x conversion desirable for diesel exhaust treatment. Scarce number of studies has been reported concerning the correlation between the acidic properties of supported Ag/Al₂O₃ catalyst and their de-NO_x activity, even though these surface properties are of crucial importance for the choice of a catalyst.

FTIR spectra of pyridine adsorbed on different Al₂O₃ and Ag/Al₂O₃ are shown in (figure 6). The interaction of silver species with surface hydroxyl groups is further

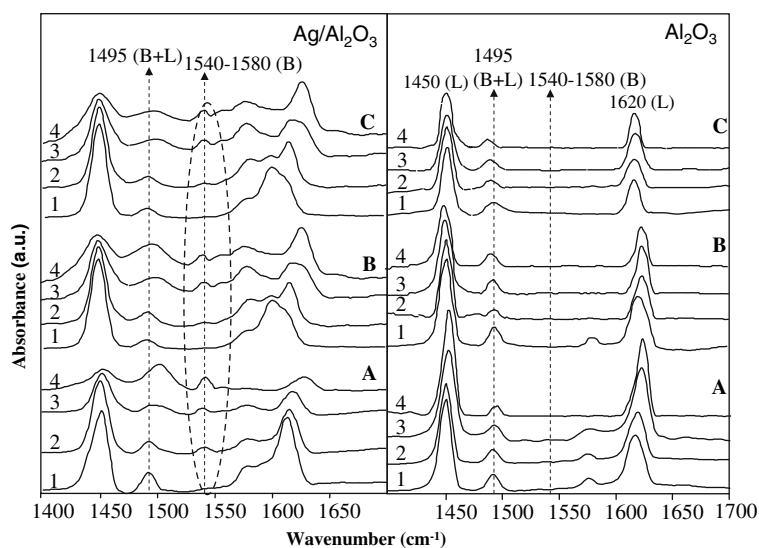


Figure 6. Infrared spectra of pyridine desorbed on Al₂O₃ and 4 wt% Ag/Al₂O₃ catalysts. A) SG, B) GB and C) ALO at 1) 150 °C 2) 250 °C 3) 350 °C and 4) 450 °C.

evident from the IR spectra of pyridine adsorbed catalysts. The bands corresponding to Bronsted (1540 cm⁻¹), Lewis (1450 cm⁻¹ and 1590–1620 cm⁻¹) and Bronsted/Lewis (1490 cm⁻¹) sites are observed in both the materials. Over Al₂O₃, pyridine is strongly adsorbed on Lewis sites as indicated by the unchanged intensity of band at 1450–1590 cm⁻¹. Whereas over Ag/Al₂O₃ catalysts, the Lewis acid site intensity is much lower especially, at 450 °C indicating the occupation of alumina Lewis acid sites with silver species, which weakly adsorbs pyridine. It is therefore concluded that acid sites (hydroxyl groups) of Al₂O₃ support plays an important role in the formation of Ag_n^{δ+} cluster formation and their dispersion [14]. Furthermore the Bronsted acid sites increased in Ag/Al₂O₃ catalysts as seen from the relative intensity of 1490–1500 cm⁻¹ band. This result is in accordance with earlier report by Wang et al [18] who has shown by using different adsorption techniques that the Ag ions on impregnation are preferably deposited on the –OH groups (Lewis acid sites) and creates Bronsted acid sites on the surface of alumina and forms a dominant Ag⁺ species. Increase in Bronsted acid sites was found to be higher in Ag/Al₂O₃ (SG) compared to Ag/Al₂O₃(GB) and Ag/Al₂O₃ (ALO). The presence of Bronsted acid sites in Ag/Al₂O₃ catalysts are further likely to contribute for enhanced hydrocarbon activation and may also act as active centers for NO adsorption [24–26].

3.5. In situ IR studies of SCR of NO by decane

Formation of various reaction intermediates is reflected in IR bands characteristic for adsorbed nitrite –NO²⁻ or bridging bidentate nitrite (1230 cm⁻¹) [17], monodentate (1300 and 1550 cm⁻¹) and bidentate –NO³⁻ (1580 cm⁻¹) [5], acetate (1460 cm⁻¹) and bands corresponding to C–H stretching vibration mode (2800–

3000 cm⁻¹) [27]. In 4wt% Ag/Al₂O₃ (SG), the intensity of nitrites, nitrates and CH_x–O containing reaction intermediates decreased, while the intensity of –NCO (2230 cm⁻¹) and –CN (2150 cm⁻¹) bands increased with increase in reaction temperature. The result indicates that the reaction between nitrites, nitrates and surface oxygenates is leading to the formation of –NCO and –CN which is in accordance with our earlier reports [15, 17]. On the other hand, in Ag/Al₂O₃ (GB-45) and Ag/Al₂O₃ (ALO) catalysts the intensity of peak corresponding to –NCO species did not significantly change and –NO³⁻ and –CH_x–O peaks did not decrease with increase in reaction temperature which can be explained by the presence of scarce number of active Ag species responsible for the formation of –NCO species. It is generally established that the adsorption of hydrocarbon and the intermediate –CN and –NCO species formation during SCR of NO with decane is responsible for NO conversion to N₂. *In situ* FT-IR measurement (figure 7) clearly shows the higher rate of –CN and –NCO intermediate formation evident from the evolution of bands at 2150 cm⁻¹ and 2230 cm⁻¹, respectively, over Ag/Al₂O₃ (SG) catalysts. These intermediates are furthermore observed over a broad temperature window under the reaction conditions in insitu IR experiments, which explains the observed increase in NO conversion over a broad temperature window over sol-gel prepared Ag/Al₂O₃ (SG) catalysts.

4. Conclusions

In conclusion it may be stated that:

1. The Ag/Al₂O₃, prepared by sol-gel method, exhibits the highest NO_x conversion in a broad temperature window compared with traditional alumina supports.

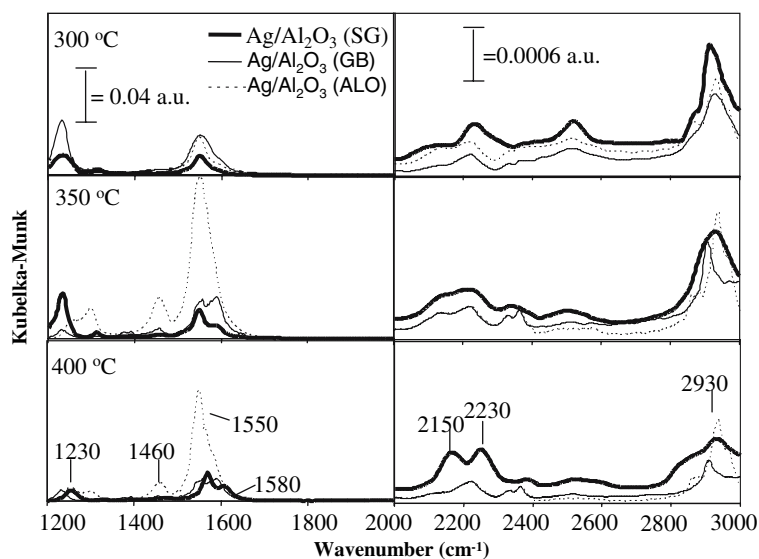


Figure 7. FTIR spectra of adsorbed species on different 4 wt% Ag/Al₂O₃ catalysts in flowing gas mixture of NO (500 ppm), *n*-C₁₀H₂₂ (300 ppm) and O₂ (10 vol%) at temperatures as indicated.

2. The characterization and conversion differences in the Ag supported on different types of Al₂O₃ indicated that these differences are arising from the differences in surface area, pore size distribution and acidity of the support. Acidity and pore size distribution can significantly influence the formation of active Ag_n^{δ+} clusters and their stabilization on Al₂O₃ support by strong metal support interaction as indicated by UV–Vis and FTIR spectroscopy.
3. Thus, we can conclude, that the NO reduction with higher hydrocarbons over Ag/Al₂O₃ catalyst can be significantly improved by tuning acidity and pore size distribution of the alumina support.

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