Low-Temperature Selective Catalytic Reduction (SCR) of NO$_x$ with *n*-Octane Using Solvent-Free Mechanochemically Prepared Ag/Al$_2$O$_3$ Catalysts

Uraiwan Kamolphop,[†,⊥] Sarah. F. R. Taylor,[†] John P. Breen,*,[†,‡] Robbie Burch,[†] Juan J. Delgado,[§] Sarayute Chansai,[†] Christopher Hardacre,*,[†] Sunantha Hengrasmee,[⊥] and Stuart L. James*,[†]

[†]CenTACat, School of Chemistry and Chemical Engineering, Queen's University, Belfast, BT9 5AG Northern Ireland

[‡]Merck, Sharp & Dohme, Ballydine, Clonmel, County Tipperary, Ireland

[§]Departamento de Ciencia de los Materiales e Ingeniería Metalúrgica y Química Inorgánica, Facultad de Ciencias, Universidad de Cádiz, E-11510 Puerto Real (Cádiz), Spain

[⊥]Department of Chemistry, Faculty of Science, Khon Kaen University, Khon Kaen, 40002 Thailand

Ⓢ *Supporting Information*

ABSTRACT: Low-temperature (<200 °C) hydrocarbon selective catalytic reduction of NO$_x$ has been achieved for the first time in the absence of hydrogen using a solvent-free mechanochemically prepared Ag/Al$_2$O$_3$ catalyst. Catalysts prepared by this ball-milling method show a remarkable increase in activity for the reduction of nitrogen oxides with octane by lowering the light-off temperature by up to 150 °C compared with a state-of-the-art 2 wt % Ag/Al$_2$O$_3$ catalyst prepared by wet impregnation.

The best catalyst prepared from silver oxide showed 50% NO$_x$ conversion at 240 °C and 99% at 302 °C. The increased activity is not due to an increased surface area of the support, but may be associated with a change in the defect structure of the alumina surface, leading to the formation of the small silver clusters necessary for the activation of the octane without leading to total combustion. On the other hand, since one possible role of hydrogen is to remove inhibiting species from the silver, we cannot exclude some change in the chemical properties of the silver as a result of the ball-milling treatment.

KEYWORDS: Ag/Al$_2$O$_3$, NO$_x$, octane, hydrocarbon selective catalytic reduction, ball-milling, mechanochemistry
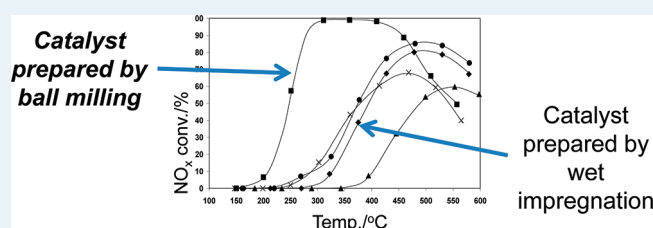
INTRODUCTION

Selective catalytic reduction (SCR) of nitrogen oxides (NO$_x$) by hydrocarbons (HC) has received significant attention over the past two decades.[1] Iwamoto et al.[2] and Held et al.[3] first observed that small concentrations of hydrocarbons in engine exhaust streams was able to reduce NO$_x$ to N$_2$ in the presence of excess oxygen. Although many catalysts have been examined, including ion-exchanged zeolites,[4] supported precious metals,[5] and metal oxide-based catalysts,[6] it is now well established that Ag-based systems supported on Al$_2$O$_3$ are among the most active and selective for the SCR reaction.[1] As well as being highly selective for N$_2$ over N$_2$O compared with platinum-based catalysts,[7] for example, silver-based systems show good activity and have moderate tolerance to water vapor and SO$_2$; however, their lack of activity below 350 °C still remains a problem.

Numerous studies have shown that both the support and the silver loading are critical in producing an active catalyst. Alumina is found to be the support of choice with most studies, demonstrating that 2 wt % silver is optimal for wet-impregnated catalysts. The active Ag phases have been studied in detail, and Ag$^+$ ions,[8] Ag—O—Al species[9] as well as small clusters of ionic Ag$_n^{\delta+}$ [4,10] have been reported to be active for the reaction, although the latter is now favored as the active phase.[11] Large clusters of metallic silver have been shown to be detrimental to the NO$_x$ conversion activity, and this is thought to be the reason that the loading should be limited to 2 wt %, to minimize the silver—silver contacts. In addition, a range of preparation methods for the catalysts have been used and shown to have a significant effect on the HC-SCR activity. Wet impregnation,[8,12] coprecipitation,[9] sol—gel process,[8,13–15] and hydrolysis[16] methods have been reported, with to date, the highest activity catalysts that have been produced via wet impregnation from aqueous solutions using AgNO$_3$ as the Ag precursor.

In this study, we have prepared for the first time 2 wt % Ag/Al$_2$O$_3$ catalysts using solvent-free mechanochemistry in a ball mill. Mechanochemical treatment by ball-milling and related techniques has a long history in the context of inorganic materials[17–21] and has recently grown in interest for organic[22] and metal—organic synthesis.[23] Although there are few papers on the formation of catalysts using mechanochemistry, actually, a wide range of catalysts has been synthesized, albeit almost exclusively based on bulk oxides: for example Cu/ZnO, CeO$_2$—ZrO$_2$,

vanadium phosphates, perovskites, and supported iron catalysts. Mechanochemically prepared Re—Co/Al$_2$O$_3$ catalysts have been prepared for comparison with similar materials from wet impregnation for CO hydrogenation and conversion of methane to higher hydrocarbons, although different loadings were used.[24] The mechanochemically prepared material was inferior in the former reaction but superior in the second. More recently, highly loaded silver supported on calcium carbonate has been synthesized using ball-milling for propene epoxidation.[25] Although, in some cases, small amounts of solvent are used, ball-milling provides an opportunity for the synthesis step to be solvent-free, therefore circumventing many of the drying and precipitation steps normally involved in preparing such catalysts. Importantly, the technique has also been shown to produce materials that have different activities and selectivities compared with conventionally prepared catalysts. This may arise from the severe mechanical deformation that occurs during the processing, leading to cold welding and fractures so that solid-state and mechanochemical reactions can be induced.[17,26] Herein, the catalytic activity for NO$_x$ reduction over ball-milled Ag catalysts was examined using n-octane as the reducing agent, and the activity of the catalysts has been compared with a 2 wt % Ag/Al$_2$O$_3$ catalyst prepared using standard wet impregnation.

■ EXPERIMENTAL SECTION

Ag/Al$_2$O$_3$ catalysts were prepared by ball-milling using Ag$_2$O, AgNO$_3$, or Ag powders (2—3.5 μm) as the Ag precursor. Accurately weighed powders of the Ag precursors (99.99%, Sigma Aldrich) and 2.00 g of γ-Al$_2$O$_3$ (Grace-Davison, surface area of 261 m^2 g^{-1}) to obtain a silver loading of 2 wt % were well-mixed by hand. The resulting physical mixture was placed into a 500 cm^3 sintered aluminum oxide grinding jar with seven 8-mm-diameter sintered alumina grinding balls. Milling was performed in a Retsch PM100 Planetary Ball Mill at a rotation speed of 150 rpm for 1 h. The resulting powders were calcined at either 550 or 650 °C for 2 h.

Catalysts were also prepared by wet impregnation using both as-received γ-Al$_2$O$_3$ (Grace-Davison, surface area of 261 m^2 g^{-1}) and alumina ball-milled as above in the absence of the silver precursor. For wet impregnation, the support material was sieved to a particle size of <250 μm and mixed with a solution (50 cm^3) containing 0.022 M AgNO$_3$. The catalyst was then dried in an oven overnight at 100 °C, after which the catalyst was calcined at either 550 or 650 °C for 2 h. To test the effect of water on the ball-milled catalyst, the impregnated catalyst was ball-milled, stirred in water (50 cm^3), and then dried in an oven overnight at 100 °C and calcined at 650 °C for 2 h. The Ag content of the catalysts was determined by the direct current plasma method to be approximately 2 wt % for all catalysts.[27]

Typically, the catalytic activity tests over Ag/Al$_2$O$_3$ catalysts were carried out in a fixed-bed flow reactor system consisting of a quartz reactor tube. The catalysts were held in place between plugs of quartz wool, and a K-type thermocouple was placed in the center of the catalyst bed. Each of the gases in the feed system was controlled individually by mass flow controllers, and n-octane and water vapor were introduced to the system by means of separate saturators with Ar as a carrier gas. The n-C$_8$H$_{18}$ saturator was placed in an ice/water bath, and the H$_2$O saturator temperature was controlled using a thermostatic bath. All the lines following the water saturator were heated to prevent condensation.

The feed gas stream consisted of 720 ppm NO, 4340 ppm C$_8$H$_{18}$ (as C$_1$), 4.3% O$_2$, 7.2% H$_2$O, and 7.2% CO$_2$, and the He balance. This feed was introduced to the reactor which was heated from 150 to 600 °C stepwise at 50 °C intervals, remaining at each temperature for 40 min to obtain steady state conditions. The total gas flow rate was 276 cm^3 min^{-1} over 276 mg of catalyst, which was sieved to obtain a particle size of 450—250 μm. The space velocity for all catalytic tests was 60 000 cm^3 g^{-1} h^{-1} (calculated using the total gas flow rate divided by the amount of the catalyst used in the activity test). The inlet and outlet NO$_x$ concentrations were determined by a Signal 4000VM series chemiluminescence detector. The oxidation of octane as well as the presence of N$_2$O was measured online using a Bruker Tensor 27 IR spectrometer fitted with a gas cell of volume of 190 cm^3. In all catalytic tests, as found with many other silver catalysts in the absence of hydrogen, the amount of N$_2$O was below the detection limit of the IR spectrometer (<10 ppm). Therefore, no significant conversion of NO$_x$ to N$_2$O was observed, and the NO$_x$ conversion reported is conversion to N$_2$.

All the measurements were taken ramping down the temperature. In this case, no change in conversion was observed once the temperature had been reached. The conversions reported are an average at each temperature. Measurements made on ramping the temperature up showed that steady state was reached after 15—20 min, and the values showed only small variations compared with the ramp down data. The time to reach steady state on increasing the temperature was associated with a dip in the NO$_x$ concentration once the temperature had been reached; however, this is due not to reaction but due to adsorption of the NO$_x$.

Scanning transmission electron microscopy images were recorded on a 200 kV JEOL JEM-2010F instrument using a high-angle annular dark-field detector and an electron beam probe of 0.5 nm. The particle size distribution was obtained by counting up to 350 particles and considering a cubooctahedric morphology. Powder X-ray diffraction (XRD) was performed on a PANalytical X'Pert Pro X-ray diffractrometer using Cu Kα radiation, with a 0.017° step size at room temperature. In-situ ultraviolet—visible diffuse reflectance spectrocopy (UV—vis DRS) measurements were carried out between 210 and 700 nm on a Perkin Elmer UV—vis spectrometer (Lambda 650s) under SCR reaction conditions using a mixture of 720 ppm NO, 4340 ppm C$_8$H$_{18}$ (as C$_1$), 4.3% O$_2$, 1.0% H$_2$O, and Ar balance with a total flow rate of 100 cm^3 min^{-1} to determine the active sites for the SCR activity. MgO was used as a reference material to determine the background spectrum. The UV—vis spectra of Ag catalysts presented here were recorded after 20 min under feed conditions; spectra were derived from the subtraction of bare γ-Al$_2$O$_3$ support under the same conditions.

■ RESULTS AND DISCUSSION

The light-off temperatures for 50% conversion of NO$_x$, (T(50%)), the maximum conversion of NO$_x$, and the temperature at which this occurs is summarized in Table 1, together with the surface area and the pore volume of all the catalysts tested. Figures 1a and 2a compare the HC-SCR NO$_x$ conversions obtained using n-octane for the ball-milled and wet impregnation prepared catalysts under steady state reaction conditions as a function of the reaction temperature. As reported previously,[28,29] Ag/Al$_2$O$_3$ (AgSTD), prepared by conventional wet impregnation, shows initial conversion of NO$_x$ at about 300 °C. Its catalytic

Table 1. Summary of Sample Names, Preparation Procedures, BET Specific Surface Area, Pore Size and Activity Data[a]

sample name	sample preparation	BET surface area/m^2 g^{-1}	pore volume/ cm^3 g^{-1}	T (50%) conv/°C	max NO$_x$ conv/% (temp/°C)
Al$_2$O$_3$	as received	261	0.76		38 (517)
Al$_2$O$_3$	ball-milled	226	0.56		26 (517)
AgSTD	Ag/Al$_2$O$_3$ wet impregnated	258	0.75	390	80 (478)
AgSTD_BM	Ag/Al$_2$O$_3$ wet impregnated then ball-milled	226	0.60	370	86 (480)
Ag$_2$O_BM	Ag$_2$O + Al$_2$O$_3$, ball-milled	235	0.63	240	99 (302)
AgNO$_3$_BM	AgNO$_3$ + Al$_2$O$_3$, ball-milled	225	0.61	298	93 (373)
Ag_BM	Ag + Al$_2$O$_3$, ball-milled	206	0.55	294	88 (360)
Ag/BM_Al$_2$O$_3$	AgNO$_3$ wet impregnated on ball-milled Al$_2$O$_3$	169	0.42	375	68 (468)
AgSTD_BM(aq)	Ag/Al$_2$O$_3$ wet impregnated then ball-milled and washed with water	218	0.56	486	60 (553)

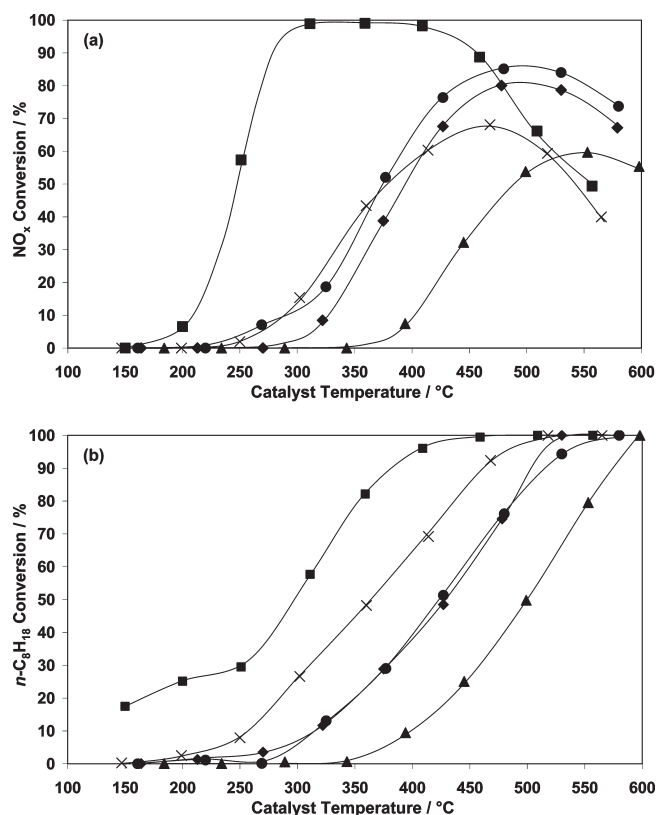[a] All samples calcined at 650 °C except the Al$_2$O$_3$, as received.

Figure 1. (a) NO$_x$ and (b) n-octane conversion as a function of catalyst temperature for the SCR of NO$_x$ reaction with n-octane over Ag catalysts. Feed stream: 720 ppm NO, 4340 ppm (as C1) n-C$_8$H$_{18}$, 4.3% O$_2$, 7.2% CO$_2$, 7.2% H$_2$O, and He balance. Space velocity: 60 000 cm^3 g^{-1} h^{-1}. ■, Ag$_2$O_BM; ♦, AgSTD; ●, AgSTD_BM; ×, Ag/BM_Al$_2$O$_3$; ▲, AgSTD_BM(aq).

Figure 2. (a) NO$_x$ and (b) n-octane conversion as a function of catalyst temperature for the SCR of NO$_x$ reaction with n-octane over Ag catalysts. Feed stream: 720 ppm NO, 4340 ppm (as C1) n-C$_8$H$_{18}$, 4.3% O$_2$, 7.2% CO$_2$, 7.2% H$_2$O, and He balance. Space velocity: 60,000 cm^3 g^{-1} h^{-1}. ■, Ag$_2$O_BM; ♦, AgSTD; □, Ag_BM; ○, AgNO$_3$_BM.

activity with octane slowly increases before reaching a maximum NO$_x$ conversion of 80% at 478 °C; the temperature of 50% NO$_x$ conversion is ~390 °C. In comparison with the AgSTD sample, all the catalysts prepared via the ball-milling procedure showed a significant lowering of the light-off temperature. Ball-milling the alumina prior to wet impregnation (Ag/BM_Al$_2$O$_3$) resulted in a decrease in T(50%) to ~375 °C; however, in this case, the maximum NO$_x$ conversion was limited to 68%. A similar decrease in the light-off temperature was observed on ball-milling the AgSTD catalyst (T(50%) ~ 370 °C, maximum 86% NO$_x$ conversion). Both
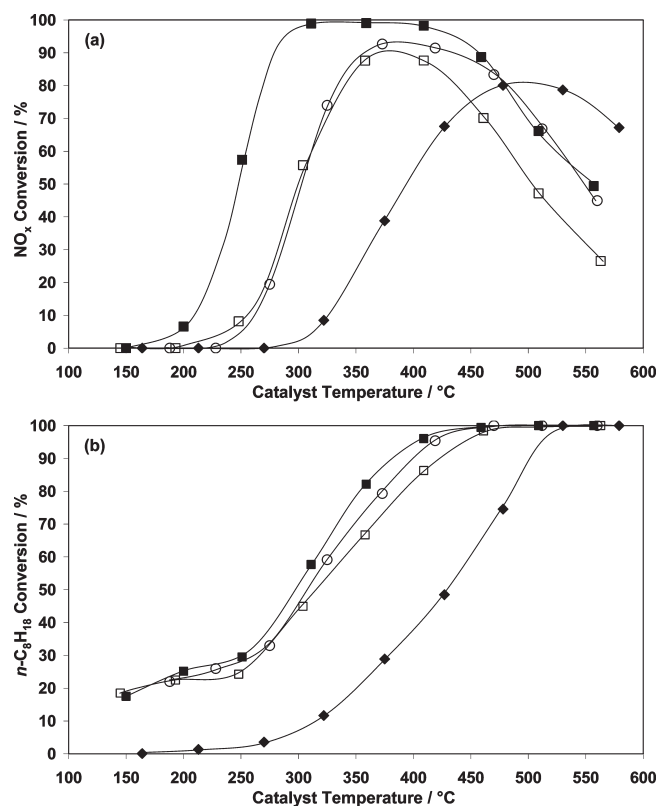
the catalysts prepared from ball-milling silver nitrate or silver metal with alumina showed similar activity with a T(50%) ~ 295 °C; however, the most active catalyst was found by preparing the catalyst by ball-milling silver oxide with alumina, resulting in T(50%) ~ 240 °C. All three of the ball-milled catalysts using silver precursors showed a significant increase in the maximum NO$_x$ conversion compared with AgSTD. Using silver nitrate or silver metal, ~90% conversion was observed at 340 °C, whereas using silver oxide, 99% conversion was found at temperature ranging from ~300 to 400 °C, and initial NO$_x$ activity below 200 °C was observed.
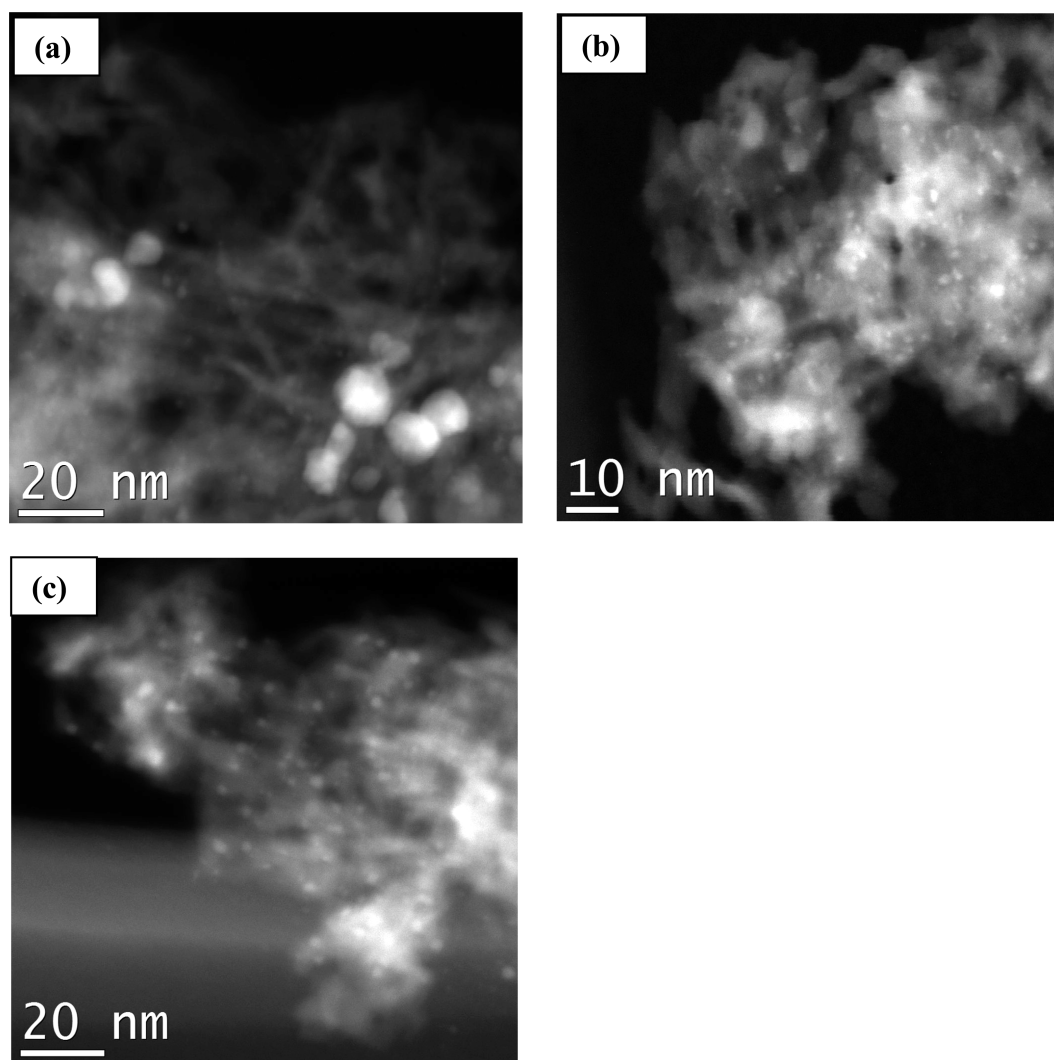
Figure 3. TEM images micrographs of (a) Ag_BM (before calcination), (b) Ag_BM (after calcination at 650 °C), and (c) Ag₂O_BM (after calcination at 650 °C).

As found in all HC-SCR reactions, the NO_x activity goes through a maximum due to the competition between the reactions of octane as a reductant and octane combustion, the latter predominating at higher temperatures. Figures 1b and 2b show the equivalent conversion of octane as a function of catalyst temperature during the SCR reaction on the Ag catalysts examined. It is notable that the rate of octane conversion is highest for the catalyst prepared by ball-milling silver oxide with alumina, showing total conversion of octane at 420 °C. For all other catalysts, similar trends in octane conversion are observed, showing that octane is gradually oxidized between 250 and 500 °C and is completely combusted at temperatures above 500 °C. Clearly, the active site on the ball-milled catalysts can activate the octane sufficiently at low temperature to enable good SCR of NO_x, but it prevents the total combustion of the octane. This may indicate that the concentration of large silver particles is minimized by the ball-milling process followed by calcination at 650 °C, thus reducing the total combustion activity of the catalysts.

The BET surface areas of various catalysts are summarized in Table 1. The results show that for all Ag catalyst samples, the specific surface areas are in the range from 200 to 260 m² g⁻¹. It is notable that no increase in the BET surface area is observed on ball-milling the alumina in the presence or absence of silver. In general, the ball-mill processing results in a decrease in surface area and a corresponding reduction in pore volume. Therefore, it is clear that there is no correlation between the BET surface area and the catalytic activity these Ag catalysts.

The preparation method including the calcination temperature was found to be critical in producing active catalysts for the ball-milled prepared catalysts. For example, ball-milled catalysts prepared using silver oxide showed a $T(50\%)$ of $\sim$380 °C when tested uncalcined or calcined at 550 °C (Figure S1 of the Supporting Information), whereas following calcination at 650 °C, this dropped to $\sim$240 °C. In the case of silver oxide calcined at 450 C, its activity is diminished with the maximum of 41% NO_x conversion at 475 °C. The calcination temperature was found to be less critical for the wet impregnated catalysts (Figure S2 of the Supporting Information). An increase in activity was observed on increasing the calcination temperature, but $T(50\%)$ decreased by only $\sim$40 °C.

Transmission electron microscopy (TEM) images from uncalcined catalysts showed that the ball-milled catalysts prepared using silver had large silver particles (Figure 3a). Similarly, the XRD showed that the catalysts prepared from silver oxide had

large particles before calcination that were found to be a combination of silver oxide and silver metal. Spontaneous reduction of Ag(I) upon ball-milling is well-known.[17] Following calcination, these features gradually disappear with increasing temperature. By 650 °C, the features are not observed in the XRD (Figure S3 of the Supporting Information), and the TEM (Figure 3b) shows well dispersed silver particles on the Al_2O_3 support for both the catalysts prepared from the silver (Ag_BM) and silver oxide (Ag$_2$O_BM) precursors.

There is a narrow size distribution of Ag particles for both catalysts following calcinations at 650 °C of between 1.0 and 2.5 nm, and the mean Ag particle size is ~1.62 nm. Similar XRD diffractograms were observed for all catalysts prepared, irrespective of preparation method after calcinations at 650 °C (Figure S4 of the Supporting Information). This dispersion is well-known for silver. Richter et al. used in situ DRUVS to study the transformation of silver under reduction and oxidation reaction conditions in the temperature range of 250–550 °C.[30] The results indicated that dispersion of silver under oxidizing conditions was facile. This is consistent with EXAFS results during HC-SCR of NO_x using Ag catalysts reported by Breen et al.[31] and TEM/DRUVS studies by Inseesungvorn and co-workers of Ag/Al_2O_3 during the selective catalytic reduction of O_2 with excess H_2 in the presence of C_2H_4.

From the in situ UV–vis DRS measurements, under SCR reaction conditions at 300 °C, an absorption band at 225 nm was observed for all catalysts (Figure S5a of the Supporting Information). This band can be attributed to the electronic transitions from $4d^{10}$ to $4d^9 5s^1$ of highly dispersed Ag^+ ions on a γ-Al_2O_3 support.[32–34] A shoulder was also observed in the range from 240 to 270 nm that was due to the formation of partially charged silver clusters ($Ag_n^{\delta+}$ with $n \leq 8$).[32–34] It is clear that the spectrum of the Ag$_2$O_BM sample shows that the intensity of the absorption band at 225 and 240 nm is higher than that of AgSTD and Ag$_2$O_BM uncalcined samples, suggesting that both Ag^+ and $Ag_n^{\delta+}$ could be responsible for the HC-SCR reaction on Ag$_2$O_BM catalysts in common with the active sites identified in a number of previous studies.[4,9,10,33,34] As well as the bands at 225 and 240 nm, a broad band above 300 nm was also found that was due to the presence of small metallic silver clusters (Ag_n) in the case of the Ag$_2$O_BM uncalcined sample. In comparison, the in situ UV–vis DRS spectra were also recorded under flowing Ar at 300 °C (Figure S5b of the Supporting Information), and it was found that the broad bands between 300 and 700 nm are noticeable, indicating Ag agglomeration. However, these bands almost disappear under the SCR reaction conditions at 300 °C, demonstrating the increased dispersion of silver under oxidizing versus reducing conditions.

It is clear that the surface state of the alumina is the important factor in producing highly active catalysts for the HC-SCR of NO_x. Ball-milling the alumina followed by standard wet impregnation produced a catalyst (Ag/BM_Al_2O_3) similar to the AgSTD material. In contrast, ball-milling the AgSTD catalyst followed by washing with water (AgSTD_BM(aq)) significantly deactivated the catalyst (Figure 1a and Table 1). It is essential that the silver is mobile on the surface to migrate to the active alumina sites formed during the mechanochemistry. The nature of the alumina surface is being investigated currently, but given that the activity of the AgSTD ball-milled catalyst can be destroyed by the presence of liquid water, this may indicate that a partially dehydrated surface is necessary for the ball-milled catalysts to obtain high silver mobility and, therefore, activity.

Importantly, the water produced during the reaction and in the gas phase is not detrimental to the activity or recyclability of the catalyst during the HC-SCR of NO_x. Moreover, no significant change in the catalyst activity for (Ag$_2$O_BM) was observed on three consecutive temperature cycles between 200 and 600 °C.

CONCLUSIONS

In summary, low-temperature selective catalytic reduction of NO_x with octane has been achieved with activity shown at 200 °C for the first time in the absence of hydrogen using catalysts prepared by solvent-free mechanochemistry using ball-milling. The ball-milled catalysts showed a decrease in the light-off temperature of up to 150 °C, compared with the standard wet impregnated Ag/Al_2O_3 catalysts. The important aspect of the preparation method appears to be the preparation of the alumina surface during the ball-milling process. Coupled with the calcination temperature, this preparation provides a means to form the small silver clusters necessary for the activation of the octane without leading to total combustion.

ASSOCIATED CONTENT

S **Supporting Information.** Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*E-mails : jpbreen@live.com, c.hardacre@qub.ac.uk, s.james@qub.ac.uk.

ACKNOWLEDGMENT

REFERENCES

(1) Burch, R.; Breen, J. P.; Meunier, F. C. *Appl. Catal., B* **2002**, *39*, 283–303 and references therein.

(2) Iwamoto, M.; Yahiro, H.; Shundo, S.; Yu-u, Y.; Mizuno, N. *Shokubai (Catalyst)* **1990**, *32*, 430–433.

(3) Held, W.; König, A.; Richter, T.; Pupper, L. *SAE Paper 900496*, 1990.

(4) Shibata, J.; Shimizu, K.-i.; Takada, Y.; Shichi, A.; Yoshida, H.; Satokawa, S.; Satsuma, A.; Hattori, T. *J. Catal.* **2004**, *227*, 367–374.

(5) Burch, R.; Millington, P. J.; Walker, A. P. *Appl. Catal., B* **1994**, *4*, 65–94.

(6) Bethke, K. A.; Kung, H. H. *J. Catal.* **1997**, *172*, 93–102.

(7) Burch, R.; Millington, P. J. *Catal. Today* **1995**, *26*, 185–206.

(8) Shimizu, K.; Shibata, J.; Yoshida, H.; Satsuma, A.; Hattori, T. *Appl. Catal., B* **2001**, *30*, 151–162.

(9) She, X.; Flytzani-Stephanopoulos, M. *J. Catal.* **2006**, *237*, 79–93.

(10) Shibata, J.; Takada, Y.; Shichi, A.; Satokawa, S.; Satsuma, A.; Hattori, T. *J. Catal.* **2004**, *222*, 368–376.

(11) Korhonen, S. T.; Beale, A. M.; Newton, M. A.; Weckhuysen, B. M. *J. Phys. Chem. C* **2011**, *115*, 885–896.

(12) Keshavaraja, A.; She, X.; Flytzani-Stephanopoulos, M. *Appl. Catal., B* **2007**, *27*, L1–L9.

(13) Kannisto, H.; Ingelsten, H. H.; Skoglundh, M. *J. Mol. Catal. A: Chem.* **2009**, *302*, 86–96.

(14) Takagi, K.; Kobayashi, T.; Ohkita, H.; Mizushima, T.; Kakuta, N.; Abe, A.; Yoshida, K. *Catal. Today* **1998**, *45*, 123–127.

(15) Pârvulescu, V. I.; Cojocaru, B.; Pârvulescu, V.; Richards, R.; Li, Z.; Cadigan, C.; Granger, C.; Miquel, P.; Hardacre, C. *J. Catal.* **2010**, *272*, 92–100.

(16) Martínez-Arias, A.; Fernández-García, M.; Iglesias-Juez, A.; Anderson, J. A.; Conesa, J. C.; Soria, J. *Appl. Catal., B* **2000**, *28*, 29–41.

(17) Baláž, P. In *Mechanochemistry in Nanoscience and Minerals Engineering*; Springer-Verlag: Berlin, Heidelberg, 2008.

(18) Ishida, T.; Kinoshita, N.; Okatsu, H.; Akita, T.; Takei, T.; Haruta, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 9265–9268.

(19) Ishida, T.; Nagaoka, N.; Akita, T.; Haruta, M. *Chem.—Eur. J.* **2008**, *14*, 8456–8460.

(20) Huang, J.; Takei, T.; Akita, T.; Ohashi, H.; Haruta, M. *Appl. Catal., B* **2010**, *95*, 430–438.

(21) Huang, J.; Lima, E.; Akita, T.; Guzmán, A.; Qi, C.; Takei, T.; Haruta, M. *J. Catal.* **2011**, *278*, 8–15.

(22) Bruckman, A.; Krebs, A.; Bolm, C. *Green Chem.* **2008**, *10*, 1131–1141.

(23) Lazuen-Garay, A.; Pichon, A.; James, S. L. *Chem. Soc. Rev.* **2007**, *36*, 846–855.

(24) Guczi, L.; Takács, L.; Stefler, G.; Koppány, Z.; Borkó, L. *Catal. Today* **2002**, *77*, 237–243.

(25) Sullivan, D.; Hooks, P.; Mier, M.; van Hal, J. W.; Zhang, X. *Top. Catal.* **2006**, *38*, 303–308.

(26) Castricum, H. L.; Bakker, H.; van der Linden, B.; Poels, E. K. *J. Phys. Chem. B* **2001**, *105*, 7928–7937.

(27) Breen, J. P.; Burch, R.; Hardacre, C.; Hill, C. J.; Krutzsch, B.; Bandl-Konrad, B.; Jobson, E.; Cider, L.; Blakeman, P. G.; Peace, L. J.; Twigg, M. V.; Preis, M.; Gottschling, M. *Appl. Catal., B* **2007**, *70*, 36–44.

(28) Burch, R. *Catal. Rev. — Sci. Eng.* **2004**, *46*, 271–334.

(29) Arve, K.; Backman, H.; Klingstedt, F.; Eränen, K.; Murzin, D. Y. *Appl. Catal., B* **2007**, *70*, 65–72.

(30) Richter, M.; Abramova, A.; Bentrup, U.; Fricke, R. *J. Appl. Spectrosc.* **2004**, *71*, 400–403.

(31) Breen, J. P.; Burch, R.; Hardacre, C.; Hill, C. J. *J. Phys. Chem. B* **2005**, *109*, 4805–4807.

(32) Inceesungvorn, B.; López-Castro, J.; Calvino, J. J.; Bernal, S.; Meunier, F. C.; Hardacre, C.; Griffin, K.; Delgado, J. J. *Appl. Catal., A* **2011**, *391*, 187–193.

(33) Sazama, P.; Čapek, L.; Drobná, H.; Sobalík, Z.; Dědeček, J.; Arve, K.; Wichterlová, B. *J. Catal.* **2005**, *232*, 302–317.

(34) Kim, M. K.; Kim, P. S.; Baik, J. H.; Nam, I.-S.; Cho, B. K.; Oh, S. H. *Appl. Catal., B* **2011**, *105*, 1–14.