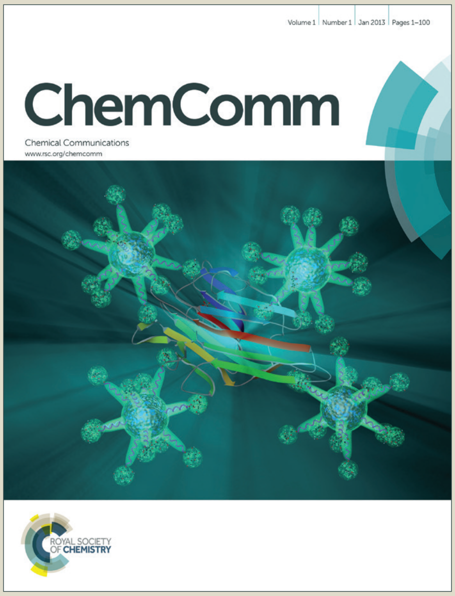
ChemComm

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/chemcomm

Chemical Communications ChemComm

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

COMMUNICATION

Evidence for an H_2 promoting effect in the selective catalytic reduction of NO_x by propene on Au/Al_2O_3

Tesnim Chaieb, [a,b] **Laurent Delannoy,** [a,b] **Sandra Casale,** [a,b] **Catherine Louis,** [a,b] **and Cyril Thomas** [a,b]*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

This work provides the first experimental evidence of an H_2 effect in C_3H_6-SCR over an Au/Al_2O_3 catalyst. This effect could only be observed when the number of Au catalytic sites was decreased. The N_2 turnover rate estimated for the first time for the Au catalytic sites for H_2-C_3H_6-SCR was found to be similar to that estimated for Ag ones supported on Al_2O_3.

Environmental standards on vehicle harmful emissions, such as nitrogen oxides (NO_x = NO + NO_2) and carbon monoxide (CO), have led to the development and the implementation of catalytic converters in the early 1970s.[1] The increased severity of the emission standards requires the development of ever more efficient catalyst formulations and/or improved aftertreatment technologies. In particular, the removal of NO_x from lean exhausts (excess of oxygen), which made the Three-Way Catalysts useless, has become extremely challenging at low temperature and has been the subject of intensive investigations in the last couple of decades.[1,2] Even though aftertreament strategies such as the Selective Catalytic Reduction of NO_x by ammonia (NH_3-SCR) and Lean-NO_x Traps (LNT) made it possible to meet the current NO_x emission standards, these technologies suffer from significant shortcomings.[1,2] As suggested by Burch,[1] the reduction of NO_x by hydrocarbons (Hydrocarbon Selective Catalytic reduction: HC-SCR) could be an elegant alternative to these technologies.

HC-SCR has been intensively studied since it was discovered that NO_x could be selectively reduced to N_2 by hydrocarbons.[3] Later, Miyadera firstly reported on the promising performance of Ag/Al_2O_3 in HC-SCR with various light hydrocarbons.[4] Since this pioneering work, the Ag/Al_2O_3 system has been investigated thoroughly until recently.[5,6] Yet the performance of Ag/Al_2O_3 is still well below that required to meet the NO_x emission standards, in particular at temperatures below 300 °C. A breakthrough in this field was provided by Satokawa and co-workers who discovered that the addition of minute amounts of H_2 in the HC-SCR feed had a dramatic promoting impact on the low temperature performance of Ag/Al_2O_3 with light hydrocarbons.[7] This so-called "hydrogen effect" was then reported in many studies in which various types of hydrocarbons were used.[8]
Although Au belongs to the same column of the periodic table of the elements as Ag, and Au has been the subject of a great number of studies in many catalytic reactions, such as CO and alcohol oxidation[9] and selective hydrogenation[10], supported Au catalysts have been studied in a surprisingly limited number of C_3H_6-SCR investigations.[11-15] In these studies it was shown that Au supported on Al_2O_3 provided the best catalytic performance but at higher temperatures compared to the other supporting oxides investigated.

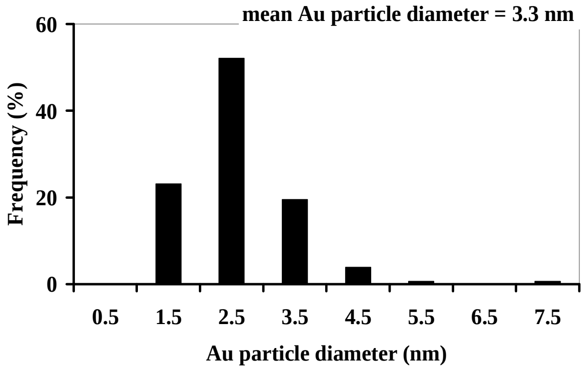


Fig. 1 Au particle-size distribution of the Au(1.6 wt%)/Al_2O_3 sample calcined for 2 h at 550 °C.

It was also shown that the catalytic performance of the Au/Al_2O_3 samples could be promoted to a significant extent with the addition of Mn_2O_3,[12-14] Co_3O_4[14] and CeO_2.[14,15] To our knowledge, the influence of H_2 in the HC-SCR reactions using C_3H_6 and/or *n*-decane (*n*-C_{10}) as reductants was reported only once by Miquel et al. on a Au(1wt%)/Al_2O_3 catalyst.[16] In this study, the H_2 promoting effect was shown for H_2-*n*-C_{10}-SCR but not for H_2-C_3H_6-SCR. This is particularly intriguing as an "H_2 effect" has been reported for both C_3H_6[8] and *n*-C_{10}[17] on Ag/Al_2O_3 samples.

The aim of the present study is to provide further insights into the H_2-assisted HC-SCR reaction on Au/Al_2O_3 and in particular into the reason why the "H_2 effect" has not been observed in C_3H_6-SCR on Au supported on Al_2O_3.[16] The conclusions drawn from the present work may also be impactful for other catalytic reactions involving Au and H_2 in the presence of O_2.

For this purpose, a Au/Al_2O_3 sample with 1.6 wt% Au was prepared by deposition-precipitation with urea of $HAuCl_4$ on a γ-Al_2O_3 support (Procatalyse, 180 m^2/g) according to the experimental procedure described earlier.[18] After calcination under O_2(20 %)/He (100 mL_{NTP}/min) at 550 °C for 2 h, the sample was characterized by TEM on a JEOL 2010 microscope operating at 200 kV equipped with an Orius CCD camera (Gatan). The Au particle-size distribution determined by TEM by measuring ca. 300 particles was found to be rather narrow with a maximum around 2.5 nm (Fig. 1). The mean Au particle size calculated as $\Sigma n_i d_i^3/\Sigma n_i d_i^2$ where n_i and d_i represent the number of Au particles and their corresponding diameter (nm),[19] respectively, was found to be 3.3 nm. Such a particle-size distribution is in good agreement with values reported earlier using the same preparation method.[20]

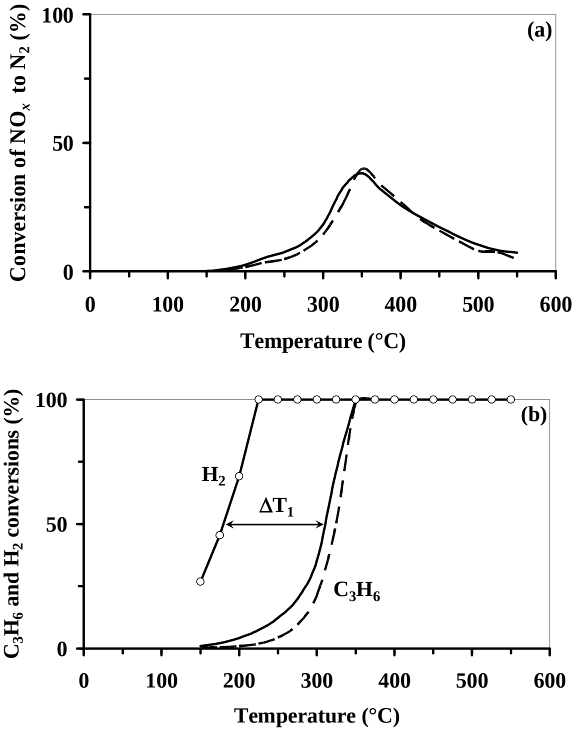


Fig. 2 Conversions of (a) NO$_x$ to N$_2$ in the C_3H_6-SCR (- - -) and H_2-C_3H_6-SCR (—) reactions, and (b) C_3H_6 to CO$_x$ in the C_3H_6-SCR (- - -) and H_2-C_3H_6-SCR (—) reactions and H_2 to H_2O (- -○- -) in the H_2-C_3H_6-SCR reaction in the 150-550 °C range of temperatures for 0.33 g of Au(1.6 wt%)/Al_2O_3. Feed compositions: 0 or 0.21 % H_2, 385 ppm NO$_x$, 400 ppm C_3H_6, 8 % O_2 and He balance with a 230 mL$_{NTP}$/min flow rate.

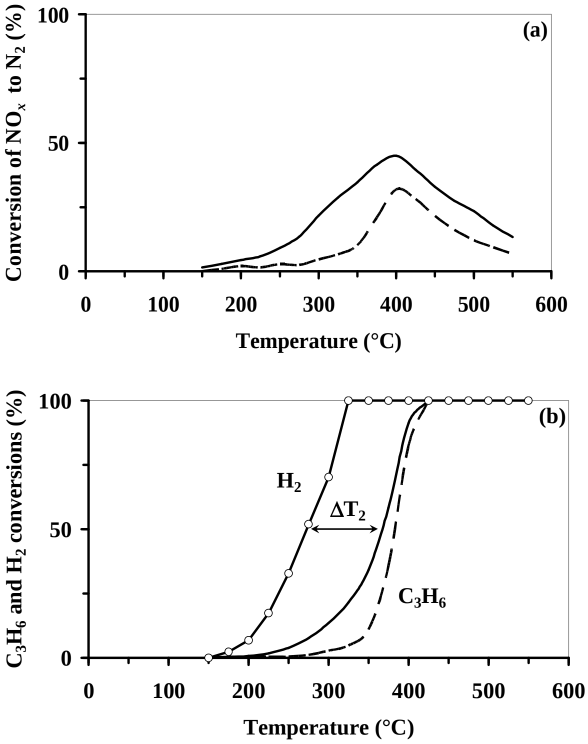


Fig. 3 Conversions of (a) NO$_x$ to N$_2$ in the C_3H_6-SCR (- - -) and H_2-C_3H_6-SCR (—) reactions, and (b) C_3H_6 to CO$_x$ in the C_3H_6-SCR (- - -) and H_2-C_3H_6-SCR (—) reactions and H_2 to H_2O (—○—) in the H_2-C_3H_6-SCR reaction in the 150-550 °C range of temperatures for 0.07 g of Au(1.6 wt%)/Al_2O_3 diluted in 0.30 g of Al_2O_3. Feed compositions: 0 or 0.21 % H_2, 370 ppm NO$_x$, 400 ppm C_3H_6, 8 % O_2 and He balance with a 230 mL$_{NTP}$/min flow rate.

The catalytic C_3H_6-SCR and H_2-C_3H_6-SCR performances of the Au/Al_2O_3 sample were evaluated consecutively in a dynamic fixed-bed micro reactor by stepwise increase of the reaction temperature from 150 to 550 °C, as described in details in our previous studies.[5,8] On 0.33 g of Au/Al_2O_3 under the experimental conditions described in the caption of Fig. 2, the reduction of NO$_x$ to N$_2$ occurred from 200 to 550 °C with a maximum in conversion of about 40 % at 350 °C in C_3H_6-SCR (Fig. 2a, dotted line). The addition of 0.21 % of H_2 into the reacting feed did not affect the conversion of NO$_x$ to N$_2$ to a significant extent, suggesting the absence of hydrogen effect for the Al_2O_3-supported Au catalyst, in agreement with the earlier work of Miquel et al.[16] The conversion of C_3H_6 to carbon oxides (CO$_x$ = CO + CO_2) was found to be slightly promoted to lower temperatures with the addition of H_2 (Fig. 2b). This shift to lower temperature was much less pronounced than that found on Ag/Al_2O_3 catalysts under similar experimental conditions.[8] The conversion of H_2 is also shown in Fig. 2b. It can be observed that H_2 was fully oxidized at 225 °C, thus at temperatures well below those for which significant C_3H_6 oxidation occurred. This differs substantially from what was reported recently on Ag/Al_2O_3 catalysts for which H_2 and C_3H_6 oxidations were found to occur concomitantly.[8]

In order to help the conversions of H_2 and C_3H_6 better coincide, the catalytic H_2-C_3H_6-SCR performance was evaluated on a much smaller amount of Au/Al_2O_3 (0.07 g diluted in 0.30 g of Al_2O_3). In such a case, the size Au particles does not change and thus only the number of Au active sites is decreased. As illustrated in Fig. 3b, the oxidation of H_2 and C_3H_6 were shifted to higher temperatures by 93 and 55 °C, respectively, on the diluted Au/Al_2O_3 sample compared to the experiment carried out on the non-diluted Au/Al_2O_3 sample (Fig. 2b). The narrowing of the temperature domain within which both H_2 and C_3H_6 are oxidized for the diluted sample (ΔT$_2$ = 95 °C, Fig. 3b) compared to the non-diluted catalyst (ΔT$_1$ = 133 °C, Fig. 2b) remarkably influences the conversion of NO$_x$ to N$_2$ (Fig. 3a), and an hydrogen effect can be observed for the first time in C_3H_6-SCR on Au/Al_2O_3. In the presence of H_2 in the C_3H_6-SCR feed indeed, the diluted sample exhibited higher performances and at remarkably lower temperatures (Fig. 3a, solid line) than in the absence of H_2 (Fig. 3a, dotted line). In addition, the overall NO$_x$ conversion to N$_2$ in the 150-550 °C temperature range for the Au/Al_2O_3 diluted sample (Fig. 3a, solid line) was found to be higher than that measured on the non-diluted sample (Fig. 2a) in H_2-C_3H_6-SCR although the amount of Au/Al_2O_3 in the diluted sample was about five times lower. It was verified that the diluted Au/Al_2O_3 sample did not exhibit any NO$_x$ reduction activity in the absence of C_3H_6 in the reacting feed (H_2-SCR), as also reported earlier on Ag/Al_2O_3.[7] Contrary to Ag/Al_2O_3,[5,8] the addition of H_2 to the C_3H_6-SCR feed led to a decrease in the production of N_2O on the Au/Al_2O_3 diluted sample. The selectivity in N_2O (defined as $N_2O/(N_2+N_2O)$ x 100) increased up to 21 % at 550 °C in C_3H_6-SCR, whereas it remained below 7 % in H_2-C_3H_6-SCR (not shown). Finally, one can note the fact that a much lower number of catalytic sites could positively influence the catalytic performance is rather counter-intuitive in the field of catalysis.

Most important, this work thus sheds light on the origin of the absence of "H_2 effect" reported to date in C_3H_6-SCR on Au/Al_2O_3,[16] which we attribute to the too high number of Au catalytic sites in the aliquot of sample tested by Miquel et al.[16] This resulted in the over-oxidation of H_2 by O_2 at temperatures at which C_3H_6 was not yet activated, as clearly illustrated in Fig. 2b. The observation of an "H_2 effect" on a Au/Al_2O_3 sample with *n*-C_{10} as a reductant[16] is thus attributable to the lower activation temperatures of such a higher hydrocarbon[17] compared to C_3H_6,[16] which therefore better coincides with the temperatures of H_2 activation.

As this work provides the first experimental evidence of an "H_2 effect" in C_3H_6-SCR on Au/Al_2O_3, it appeared relevant to compare the production of N_2 on Au sites to that found on Ag sites under similar experimental conditions[8] on a turnover rate (TOR) basis. N_2 TOR represents the rate of N_2 formation per metal (M: Au or Ag) surface atom. In the case of Au/Al_2O_3, the number of Au surface atoms was estimated from the mean Au particle size determined by TEM (Fig. 1) and the associated dispersion.[19] Regarding the Ag(0.88 wt%)/Al_2O_3 catalyst, it was assumed that the Ag atoms were all accessible (Ag dispersion of 100 %) as earlier characterization of Ag/Al_2O_3 samples with Ag loadings as high as 2 wt% by EXAFS concluded to the presence of Ag as clusters of 3-8 Ag atoms.[21] The N_2 turnover rates were estimated at 250 °C, as we reported previously that the contribution of the bare Al_2O_3 support was negligible for temperatures lower than or equal to 250 °C.[8] Table 1 lists the conversions of NO_x, C_3H_6 and H_2 together with the corresponding data required for the estimation of the N_2 turnover rates for the Au/Al_2O_3 sample investigated in the present work and for a Ag/Al_2O_3 sample studied previously.[8] It can be seen that the N_2 turnover rates are close to each other, differing by less than one order of magnitude, on Au and Ag sites supported on Al_2O_3. Note that the higher dispersion and the lower H_2 oxidation capacity of Ag compared to those of Au on Al_2O_3 allow for a better coincidence of the C_3H_6 and H_2 oxidation reactions in the H_2-assisted C_3H_6-SCR reaction and for the introduction of a much higher number of Ag sites than Au sites into the catalytic bed.

Table 1 Comparison of the N_2 turnover rates (N_2 TOR) at 250 °C in H_2-C_3H_6-SCR on Au(1.6 wt%)/Al_2O_3 and Ag(0.9 wt%)/Al_2O_3. Feed composition: 0.21 % H_2, 378±8 ppm NO_x, 400 ppm C_3H_6, 8 % O_2 and He balance with a 230 mL_{NTP}/min flow rate.

		Au/Al_2O_3	Ag/Al_2O_3
	Metal loading (M, wt%)	1.59	0.88
	M/Al_2O_3 sample weight (g)	0.07	0.38
	Al_2O_3 sample weight (g)	0.30	0.00
Conversions (%)	NO_x to N_2	8.8	30.5
	C_3H_6 to CO_x	3.9	22.3
	H_2 to H_2O	32.8	17.4
	N_2 rate (μmol/s $g_{cat.}$)	381	258
	M dispersion (%)	35.2[(a)]	100.0[(b)]
	Number of surface M atoms (μmol/gcat.)	35.7	81.6
	N_2 TOR (s^{-1})	13.4	3.2

[(a)] estimated from the mean particle diameter of 3.3 nm determined by TEM, (b) deduced from earlier EXAFS characterization of Ag/Al_2O_3 samples which showed that Ag was present as clusters of 3-8 Ag atoms.[21]

Conclusions

This work provides the first experimental evidence of an "H_2 effect" in H_2-C_3H_6-SCR over a Au/Al_2O_3 catalyst. This effect could only be observed when the number of Au catalytic sites was decreased. In that case, C_3H_6 and H_2 oxidations occurred in a closer range of temperatures, which resulted in an improved conversion of NO_x to N_2. The N_2 turnover rate estimated for the first time for the Au catalytic sites for H_2-C_3H_6-SCR was found to be of the same order of magnitude as that estimated for Ag supported on Al_2O_3. Yet the higher metal dispersion and the better temperature coincidence between the C_3H_6 and H_2 oxidation reactions in H_2-C_3H_6-SCR on Ag compared to that on Au on Al_2O_3 allow for the introduction of a much higher number of Ag sites into the catalytic bed and therefore for better catalytic H_2-C_3H_6-SCR performance for Ag/Al_2O_3 compared to Au/Al_2O_3.

Acknowledgements

TC gratefully acknowledges UPMC for financial support (PhD Grant 322/2012).

Notes and references

[a] *Sorbonne Universités, UPMC Univ Paris 06, UMR 7197, Laboratoire de Réactivité de Surface, 4 Place Jussieu, Case 178, F-75252, Paris, France, E-mail: cyril.thomas@upmc.fr*

[b] *CNRS, UMR 7197, Laboratoire de Réactivité de Surface, 4 Place Jussieu, Case 178, F-75252, Paris, France*

1 R. Burch, *Catal. Rev. Sci. Eng.*, 2004, **46**, 271.
2 B. Epling, C. Peden, I. Nova, *Catal. Today*, 2014, **231**, 1.
3 W. Held, T. Konig, T. Richter, L. Puppe, *SAE Tech. Paper Ser.*, 1990, **900496**, 13; M. Iwamoto, H. Hamada, Held, *Catal. Today*, 1991, **10**, 57.
4 T. Miyadera, *Appl. Catal. B: Environ.*, 1993, **2**, 199.
5 T. Chaieb, L. Delannoy, C. Louis, C. Thomas, *Appl. Catal. B: Environ.*, 2013, **142-143**, 780.
6 F. Liu, Y. Yu, H. He, *Chem. Commun.*, 2014, **50**, 8445.
7 S. Satokawa, *Chem. Lett.*, 2000, **29**, 294; S. Satokawa, J. Shibata, K-I. Shimizu, A. Satsuma, T. Hattori, *Appl. Catal. B: Environ.*, 2003, **42**, 179.
8 T. Chaieb, L. Delannoy, G. Costentin, C. Louis, S. Casale, R.L. Chantry, Z.Y. Li, C. Thomas, *Appl. Catal. B: Environ.*, 2014, **156-157**, 192.
9 T. Takei, T. Akita, I. Nakamura, T. Fujitani, M. Okumura, K. Okazaki, J. H. Huang, T. Ishida, M. Haruta, *Adv. Catal.*, 2012, **55**, 1.
10 L. McEwan, M. Julius, S. Roberts, J.C.Q. Fletcher, *Gold Bull.*, 2010, **43**, 298; F. Cardenas-Lizana, M.A. Keane, *J. Mater. Sci.*, 2013, **48**, 543.
11 A. Ueda, T. Oshima, M. Haruta, *Appl. Catal. B: Environ.*, 1997, **12**, 81, M.C. Kung, K.A. Bethke, J. Yan, J.-H. Lee, H.H. Kung, 1997, **121/122**, 261, E. Seker, E. Gulari, *Appl. Catal. A: Gen.*, 2002, **232**, 203, L.Q. Nguyen, C. Salim, H. Hinode, *Appl. Catal. A: Gen.*, 2008, **94**, 203.
12 A. Ueda, M. Haruta, *Appl. Catal. B: Environ.*, 1998, **18**, 115.
13 A. Ueda, M. Haruta, *Gold Bull.*, 1999, **32**, 3.
14 D. Niakolas, Ch. Andronikou, Ch. Papadopoulou, H. Matralis, *Catal. Today*, 2006, **112**, 184.
15 X. Wang, A. Wang, X. Wang, X. Yang, T. Zhang, *Gold Bull.*, 2006, **40**, 52.
16 P. Miquel, P. Granger, N. Jagtap, M. Dongare, C. Dujardin, *J. Mol. Catal. A: Chem.*, 2010, **322**, 90.
17 P. Sazama, L. Čapek, H. Drobná, Z. Sobalík, J. Dědeček, K. Arve, B. Wichterlová, *J. Catal.*, 2005, **232**, 302.
18 R. Zanella, L. Delannoy, C. Louis, *Appl. Catal. A: Gen.*, 2005, **291**, 62.
19 G. Bergeret, P. Gallezot, in *Handbook of Heterogeneous Catalysis*, ed. G. Ertl, H. Knözinger and J. Weitkamp, Wiley-VCH, Weinheim, 1st edn., 1997, vol. 2, ch. 3, pp. 439-464.
20 L. Delannoy, R. L. Chantry, S. Casale, Z. Y. Li, Y. Borensztein, C. Louis, *Phys. Chem. Chem. Phys.*, 2013, **15**, 3473.
21 J.P. Breen, R. Burch, C. Hardacre, C.J. Hill, *J. Phys. Chem. B*, 2005, **109**, 4805; K-I. Shimizu, M. Tsuzuki, K. Kato, S. Yokota, K. Okumara, A. Satsuma, *J. Phys. Chem. C*, 2007, **111**, 950.