

CrossMark
click for updatesCite this: *Catal. Sci. Technol.*, 2016,
6, 1661

Assessing the effect of reducing agents on the selective catalytic reduction of NO_x over Ag/Al₂O₃ catalysts

Carmine D'Agostino,^{*a} Sarayute Chansai,^b Isabelle Bush,^a Chensong Gao,^a
Mick D. Mantle,^a Christopher Hardacre,^{*b} Stuart L. James^b and Lynn F. Gladden^{*a}

The selective catalytic reduction (SCR) of NO_x in the presence of different reducing agents over Ag/Al₂O₃ prepared by wet impregnation was investigated by probing catalyst activity and using NMR relaxation time analysis to probe the strength of surface interaction of the various reducing agent species and water. The results reveal that the strength of surface interaction of the reducing agent relative to water, the latter present in engine exhausts as a fuel combustion product and, in addition, produced during the SCR reaction, plays an important role in determining catalyst performance. Reducing agents with weak strength of interaction with the catalyst surface, such as hydrocarbons, show poorer catalytic performance than reducing agents with a higher strength of interaction, such as alcohols. This is attributed to the greater ability of oxygenated species to compete with water in terms of surface interaction with the catalyst surface, hence reducing the inhibiting effect of water molecules blocking catalyst sites. The results support the observations of earlier work in that the light off-temperature and maximum NO_x conversion and temperature at which that occurs are sensitive to the reducing agent present during reaction, and the proposal that improved catalyst performance is caused by increased adsorption strength of the reducing agent, relative to water, at the catalyst surface. Importantly, the NMR relaxation time analysis approach to characterising the strength of adsorption more readily describes the trends in catalytic behaviour than does a straightforward consideration of the polarity (*i.e.*, relative permittivity) of the reducing agents studied here. In summary, this paper describes a simple approach to characterising the interaction energy of water and reducing agent so as to aid the selection of reducing agent and catalyst to be used in SCR conversions.

Received 8th September 2015,
Accepted 25th October 2015

DOI: 10.1039/c5cy01508a

www.rsc.org/catalysis

Introduction

The selective catalytic reduction (SCR) of NO_x to N₂ has drawn considerable attention in the past ten years^{1,2} due to its effectiveness in removing NO_x from various exhausts in the presence of excess oxygen, a condition typically found in diesel engine exhausts.³ Metal nanoparticles supported on porous oxides are perhaps the most widely used type of catalysts;² of these, Ag/Al₂O₃ catalysts have shown promising results due to their ability to reduce NO_x in both laboratory and full-scale tests.⁴

One important aspect of the SCR reaction is the choice of the reducing agents and how this affects the catalytic performances. Indeed, the nature of the reducing agent can greatly

affect SCR catalyst activity. Hydrocarbons, like those typically presents in fuel mixtures, are perhaps the most common reducing agents.^{2,3,5} However, the use of other reducing agents such as alcohols, has also been investigated.⁶ Alcohols appear to be better reducing agents, showing much lower light-off temperatures (*i.e.*, the temperature at which 50% of conversion is achieved) relative to hydrocarbons.² This is thought to be due to the greater ability of alcohols relative to hydrocarbons to compete with water for adsorption sites on the catalyst.²

Shimizu⁷ suggested that adsorption properties of the reducing agent affect the rate at which surface acetates, important intermediate species during the SCR reaction, are formed. Therein, the importance of competitive adsorption with water was also highlighted, suggesting that the use of reducing agents with a greater enthalpy of adsorption results in lesser inhibition of reducing agent adsorption by competitive water adsorption, which leads to higher water tolerance and greater reactivity.³

It is, therefore, clear that adsorption properties of reducing agent molecules over the catalyst surface are of

^a Department of Chemical Engineering and Biotechnology, University of Cambridge, Pembroke Street, Cambridge, CB2 3RA, UK.

E-mail: cd419@cam.ac.uk, lfg1@cam.ac.uk; Tel: +44(0)1223 761629, +44(0)1223 334762

^b Centre for the Theory and Application of Catalysis, CenTACat, School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, BT9 5AG, UK. E-mail: C.Hardacre@qub.ac.uk; Tel: +44(0)28 9097 4592



significant importance for SCR reactions. However, it is our understanding that a detailed experimental study of surface interactions between different reducing agents and SCR catalysts, aiming at validating the current hypothesis, has not yet been reported. The issue of characterising competitive adsorption processes is recognised as being of importance in understanding SCR^{2,8} processes, as well as the wider field of heterogeneous catalysis and surface science.^{9,10} It is clear that the nature of the reducing agent has a strong effect on SCR catalytic activity. In the literature it has been reported^{2,3,11–17} that oxygenated molecules, such as alcohols, give improved catalyst performances compared to hydrocarbons, which is thought to originate from competitive adsorption effects between reducing agent molecules and water, the latter being able to inhibit the catalyst sites.^{2,3,18} This is indeed a plausible explanation, although it has to be said that, according to our knowledge, there is little experimental evidence to support it.

NMR relaxation time analysis provides a mean of probing surface interactions between adsorbate/adsorbent by probing changes in molecular dynamics of molecules due to the proximity of a solid surface.^{19,20} In particular, the T_1/T_2 ratio, T_1 being the NMR spin–lattice relaxation time and T_2 the NMR transverse spin relaxation time, is an indicator of the strength of surface interaction.^{19–22} This ratio has been recently used to understand catalytic performances in several heterogeneous catalytic processes^{21,23} and was also used in our previous work to understand the effect of ball milling on the SCR reaction of *n*-octane over Ag/Al₂O₃ catalysts.²⁴ Therein, it was shown that surface modifications due to ball milling of the catalyst may increase the catalytic performance by reducing the competitive adsorption of water relative to the hydrocarbon, which highlighted the importance of competitive adsorption with water during the SCR reaction.

In the current work, we focus on investigating the strength of surface interaction of different reducing agents and see how this reflects on catalytic performances. We have studied the SCR of NO_x in the presence of various reducing agents, namely toluene, *n*-octane and ethanol, over Ag/Al₂O₃ prepared by standard wet impregnation. NMR T_1 and T_2 relaxation measurements, from which T_1/T_2 ratios were also calculated, were used to quantify the strength of surface interaction of the different reducing agents and water on the catalyst in order to understand to what extent this parameter affects the overall catalyst activity. In earlier work²⁵ we have shown that T_1/T_2 gives a characterisation of the strength of a molecule–surface interaction and this value can be related, following appropriate calibration, directly to the adsorption energy as determined by temperature-programmed desorption analysis.

Experimental

Materials and chemicals

Toluene (≥99.5%), ethanol (≥99.5%) and *n*-octane (≥99%) were purchased from Sigma Aldrich and were used without any pre-treatment. Deionised water was obtained from a

laboratory water purification system (ELGA DV 25). The wet impregnated 2% Ag/Al₂O₃ catalyst was prepared using a procedure previously reported.²⁶

Activity tests

The catalytic activity tests were performed as reported elsewhere.²⁷ For completeness, the essential details are also given here. Typically, the catalytic activity tests over Ag/Al₂O₃ catalyst were carried out in a fixed-bed flow reactor system, consisting of a quartz reactor tube. The catalyst was held in place between plugs of quartz wool and a K-type thermocouple was placed in the centre of the catalyst bed. Each of the gases in the feed system was controlled individually by mass flow controllers, while the hydrocarbon and water vapour were introduced to the system by means of separate saturators with Ar as a carrier gas. The hydrocarbon used was supplied using a saturator placed in an ice/water bath. The H₂O saturator temperature was controlled using a thermostatic bath. All the lines following the water saturator were trace-heated to prevent condensation. A feed gas stream consisting of 720 ppm NO; 542 ppm *n*-C₈H₁₈, or 620 ppm C₇H₈, or 2170 ppm CH₃CH₂OH; 4.3% O₂, 7.2% H₂O; 7.2% CO₂; and Ar balance was introduced to the reactor, which was heated from 150 to 600 °C and then back down to 150 °C stepwise at 50 °C intervals dwelling at each temperature for 40 min in order to obtain steady-state conditions. The C₁ concentration of the reducing agent (*i.e.*, concentration as total carbon) was 4340 ppm and the C₁/NO ratio was kept at 6 for all catalytic activity tests. Three reducing agents, *i.e.* *n*-octane, toluene, and ethanol were used. The total gas flow rate was 276 cm³ min⁻¹ over 276 mg of catalyst, which had been sieved to obtain particle sizes in the range 250–450 μm. The space velocity for all catalytic tests was 60 000 cm³ 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 the hydrocarbon was measured online using a Bruker Tensor 27 IR spectrometer, fitted with a gas cell of volume 190 cm³. All the activity data was measured during the decreasing temperature ramp. Using this method, the activity remained constant once the desired temperature had been reached and the conversions were calculated from an average of outlet NO_x readings at each temperature.

NMR experiments

NMR experiments were performed on a Bruker DMX 300 operating at a frequency of 300.13 MHz. The powdered catalyst was pressed into 10 mm tablets before being broken into grains of typically 2–3 mm in dimension. This procedure makes the samples easier to handle and, by reducing the amount of liquid in the inter-particle space, it makes the NMR measurement more sensitive to the liquid–surface interaction (*i.e.*, the amount of signal from bulk liquid is minimised). The catalyst grains were then dried in an oven at



110 °C for 12 h and then immersed in the liquid of interest for at least 24 h. The wet catalyst grains were then removed from the liquid, placed onto a pre-soaked filter paper in order to remove excess external liquid and finally placed into a 5 mm NMR tube. To ensure a saturated atmosphere in the NMR tube, hence minimising errors due to evaporation of volatile liquids, a small piece of adsorbent filter paper was impregnated with the liquid under investigation. This was then placed under the cap of the NMR tube, which was finally sealed with parafilm. All the NMR measurements were performed at atmospheric pressure and room temperature.

NMR data analysis

Proton NMR relaxation times T_1 and T_2 were measured using the standard inversion recovery and CPMG (Carr-Purcell-Meiboom-Gill) techniques,²⁸ respectively, which are schematically shown in Fig. 1. Experimental data were fitted using single exponential functions. The T_1 relaxation time constant was obtained by fitting the experimental data to the equation:

$$S(t) = S_0 \left[1 - 2 \exp\left(-\frac{t}{T_1}\right) \right] \quad (1)$$

The T_2 relaxation time constant was obtained by fitting the experimental data to the equation:

$$S(t) = S_0 \exp\left(-\frac{t}{T_2}\right) \quad (2)$$

In eqn (1) and (2), S represents the NMR signal intensity and t the time. Note that the NMR signal intensity was

calculated by integrating the whole NMR spectrum of the species confined within the catalyst. In this way, the calculated NMR relaxation times are representative of the whole molecular species adsorbed over the catalyst surface.

Results and discussion

SCR catalyst testing

The data for the catalytic activity of NO_x reduction is summarised in Table 1 measured *via* the light-off temperature, $T_{50\%}$, at which 50% of conversion is achieved, and the maximum conversion of NO_x at the temperature at which such conversion is achieved.²⁷ A higher light-off temperature indicates a poorer catalytic performance.

It is clear that both toluene and *n*-octane give $T_{50\%}$ values significantly higher than when ethanol is used as the reducing agent; further, toluene has a higher light-off temperature than *n*-octane. Moreover, this ranking of catalyst performance with reducing agent is furthermore supported on comparing the maximum NO_x conversion and temperature at which it occurs. We also report the $T_{50\%}$ values relative to the reducing agent conversion, which are shown in Table 2. The observed reactivity trend for the reducing agent is similar to that observed for the NO_x, with ethanol showing a significantly higher reactivity, hence a lower $T_{50\%}$ compared to the two other hydrocarbons.

Probing strength of surface interaction

Fig. 2 and 3 show, respectively, the T_1 and the T_2 experimental data acquired for the different reducing agents and water in Ag/Al₂O₃. The quality of the data and the fittings to eqn (1) and (2) for T_1 and T_2 , respectively, are excellent. The T_1 and T_2 values obtained for these data are reported in Table 3.

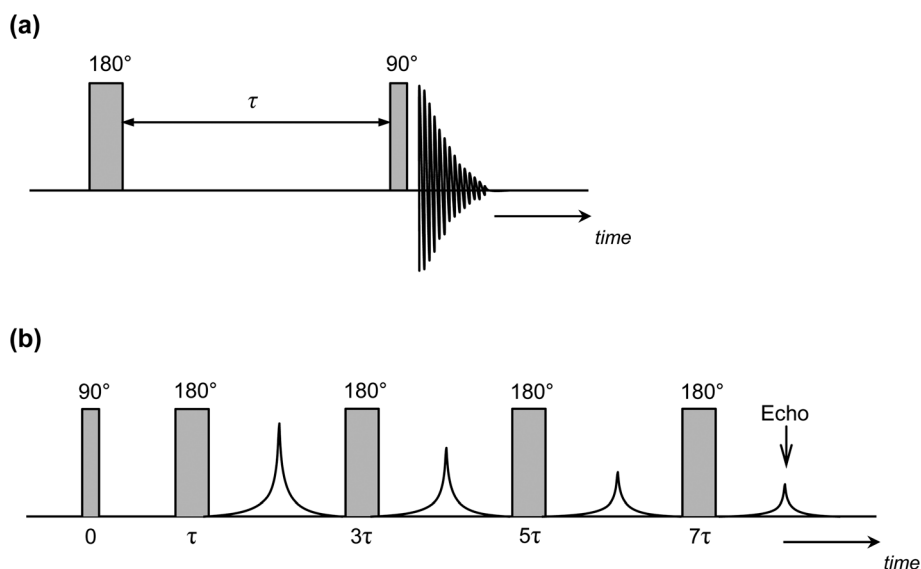


Fig. 1 (a) T_1 inversion recovery and (b) T_2 CPMG pulse sequences used in this work. In the inversion recovery pulse sequence (a) the NMR signal is acquired after a time delay τ for a list of different time delays. In the CPMG pulse sequence (b) the NMR signal is acquired after a series of n echoes, which correspond to a $2 \times \tau \times n$ total time delay for a list of different time delays.



Table 1 Results of catalytic tests for the SCR of NO_x in the presence of different reducing agents over Ag/Al₂O₃.²⁷ $T_{50\%}$ is the light-off temperature (i.e., the temperature at which 50% conversion is achieved) relative to the NO_x conversion in the presence of different reducing agents, whereas T is the temperature at which maximum NO_x conversion is achieved

Compound	$T_{50\%}$ [°C]	Max NO _x conversion [%] (T [°C])
Toluene	520	69 (600)
<i>n</i> -Octane	390	80 (478)
Ethanol	295	98 (354)

Table 2 Results of catalytic tests for the SCR of NO_x in the presence of different reducing agents over Ag/Al₂O₃.²⁷ $T_{50\%}$ is the light-off temperature (i.e., the temperature at which 50% conversion is achieved) relative to the reducing agent conversion, whereas T is the temperature at which maximum reducing agent conversion is achieved

Compound	$T_{50\%}$ [°C]	Max reducing agent conversion [%] (T [°C])
Toluene	435	99 (560)
<i>n</i> -Octane	425	99 (525)
Ethanol	265	99 (400)

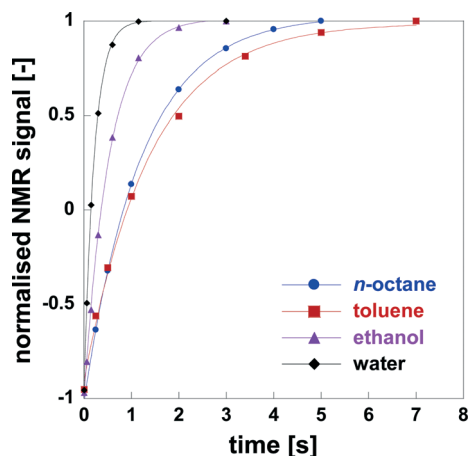


Fig. 2 T_1 plots for different reducing agents and water within Ag/Al₂O₃ catalyst. T_1 is measured using the inversion recovery pulse sequence. Solid lines are fitting to eqn (1).

Table 3 also reports the T_1/T_2 ratio calculated from the individual T_1 and T_2 values.

As it is seen from Table 3, the oxygenated molecules have significantly higher values of T_1/T_2 ratio, indicating a much stronger interaction with the catalyst surfaces than the *n*-octane and toluene, which is in agreement with the current hypothesis reported in the literature.^{2,7} The stronger interaction of the oxygenated species with the surface is likely to arise from hydrogen bonding with the solid surface, which acts to enhance surface interactions.²⁹

Effect of reducing agent

By inspection of Table 3, it can be observed that the different species have very different relaxation properties. The

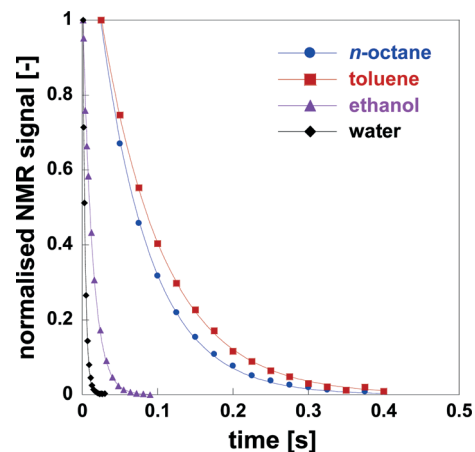


Fig. 3 T_2 plots for different reducing agents and water within Ag/Al₂O₃ catalyst. T_2 is measured using the CPMG pulse sequence. Solid lines are fitting to eqn (2).

reducing agents have higher values of T_1 and T_2 compared to water. In ethanol and particularly water, the decrease of T_2 relative to T_1 is much more significant compared to the two hydrocarbons, resulting in greater values of the T_1/T_2 ratio observed, particularly for water, the latter showing a $T_1/T_2 = 71$, significantly higher than ethanol, $T_1/T_2 = 40$, and substantially higher than *n*-octane, $T_1/T_2 = 18$, and toluene, $T_1/T_2 = 16$. These values can be explained in terms of molecules adsorbed onto the surface and exhibiting modified rotational and translational dynamics at the pore surface.¹⁹ In particular, a decrease of T_2 values relative to T_1 values can be related to a slower translational dynamics over the surface, due to stronger surface interactions.^{19,30} As a result, the T_1/T_2 ratio increases. Such a ratio can be considered to be an analogous of a surface interaction energy³¹ as we have recently demonstrated.²⁵ It has to be noted that paramagnetic species may also affect the values or NMR relaxation times but this is not relevant to our current work for reasons previously explained in detail elsewhere.^{24,25}

In summary, from the NMR relaxation time results it can be inferred that water shows the greatest strength of surface interaction, significantly greater than that of all the reducing agents, as it can be inferred by the large values of its T_1/T_2 ratio, which are also plotted in Fig. 4 for clarity. As for the

Table 3 Experimental values from T_1 and T_2 relaxation measurements of different molecular species in Ag/Al₂O₃. The typical relative error on T_1 , T_2 and T_1/T_2 was estimated to be in the range 2–3%^a

Compound	T_1 [ms]	T_2 [ms]	T_1/T_2 [-]
Toluene	1390	85	16
<i>n</i> -Octane	1204	66	18
Ethanol	522	13	40
Water	212	3	71

^a For the pure bulk liquids, $T_1 \sim T_2$ with the following values: 4240 ms for toluene, 2500 ms for *n*-octane, 2630 ms for ethanol, 2700 ms for water.



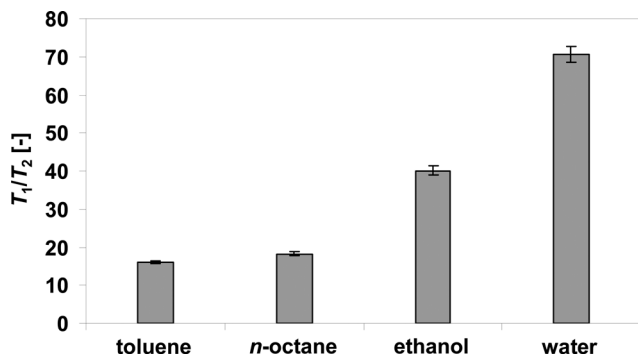


Fig. 4 T_1/T_2 values for water and reducing agents within Ag/Al₂O₃ catalyst. Errors bars are also reported.

reducing agents, toluene shows the lowest strength of surface interaction (*i.e.*, lowest T_1/T_2 value), followed closely by *n*-octane, which shows slightly higher values; ethanol shows considerably higher strength of surface interaction compared to toluene and *n*-octane and its T_1/T_2 values are significantly closer to water compared to those measured for the two hydrocarbons. The results clearly suggest that, compared to toluene and *n*-octane, ethanol has a greater ability to compete with water for adsorption when compared to toluene and *n*-octane. This has been speculated in the literature^{2,18} and the current results give a clear experimental evidence of this effect.

The current results seem to explain well the catalytic performances reported in the literature in terms of type of reducing agent.^{2,32} It is now of interest to compare the results gathered from NMR relaxation measurements to the catalytic performance of these samples, in order to see to what extent surface interactions and catalyst activity are inter-related.

Catalyst activity and strength of surface interaction

There is a general agreement in the literature^{2-4,7,33-36} that the SCR of NO with hydrocarbons reaction begins with the oxidation of NO by O₂ to adsorbed NO_x species and with the oxidation of reductant to form partially oxidized hydrocarbon species over the catalyst surface, which have been reported to reduce adsorbed NO_x species *via* organo-nitro and/or organo-nitrito adsorbed species to yield gaseous N₂.

Comparing the SCR catalytic tests, summarised in Tables 1 and 2, and the results from NMR relaxation time measurements, summarised in Table 3 and Fig. 4, it is clear that the reactivity trend reflects well, at least qualitatively, the trend in surface interactions obtained from NMR relaxometry measurements of T_1/T_2 . A reducing agent of higher strength of surface interaction, such as ethanol, will have greater ability to reach the surface and react, hence enhancing the catalyst performances. This is consistent with several catalytic studies previously reported on SCR reactions in the presence of oxygenated reducing agents.^{2,6,37,38} The large variation in catalytic performances observed in this work by changing the reducing agent strongly suggests that its adsorption strength

is important for the overall catalytic process. The use of reducing agents of higher adsorption strength can indeed have several implications that will ultimately affect the whole SCR process, as this will reduce the competitive adsorption of water, improving the surface coverage of the reducing agent molecules, as previously suggested.²⁴ In addition, a higher strength of surface interaction of the reducing agent, associated with its higher surface concentration, would increase its ease of partial oxidation, which is important in order to form partially oxidized organic species over the catalyst surface that reduce adsorbed NO_x species *via* organo-nitro and/or organo-nitrito adsorbed species and ultimately yield N₂.

It is interesting to note that the trend in T_1/T_2 matches qualitatively the trend in both $T_{50\%}$ for NO_x and reducing agent. In particular, it can be observed a much closer correlation between T_1/T_2 of reducing agents (see Table 3) and $T_{50\%}$ of reducing agents (see Table 2). Indeed, the difference in T_1/T_2 values between *n*-octane and toluene is not as large as that observed between these two hydrocarbons and ethanol. The trend in $T_{50\%}$ of reducing agent leads to the same conclusion. This strengthens the hypothesis that reducing agents with higher strength of surface interactions increase its ease of partial oxidation, which is important in order to reduce adsorbed NO_x species.²⁴

In general, for the species studied in this work, we observe that the trend of T_1/T_2 in Table 3 reflects to some extent the polarity of the molecules. The trend for relative permittivity is $\epsilon_{\text{water}} = 80.4 > \epsilon_{\text{ethanol}} = 24.5 > \epsilon_{\text{toluene}} = 2.38 \sim \epsilon_{\text{n-octane}} = 2$, which is similar to the trend in T_1/T_2 . However, based solely on polarity, one might expect toluene to give slightly better SCR catalytic performances than *n*-octane, which is not the case. The T_1/T_2 values reveal that, despite its slightly greater polarity compared to *n*-octane, toluene has a slightly lower strength of surface interaction with the catalyst surface, which agrees qualitatively with the reaction data.

In summary, the current results show that the adsorption strength of the reducing agent plays an important role in determining the catalyst activity in the SCR reaction. NMR relaxation time measurements allow us to quantify this by means of T_1/T_2 values, hence offering a tool to optimise and rationalise the selection of different reducing agents.

Conclusions

The SCR reaction of NO_x in the presence of toluene, *n*-octane and ethanol over a wet impregnated Ag/Al₂O₃ catalyst has been investigated by assessing the catalyst activity, using reaction studies, and adsorption phenomena, using NMR relaxation time analysis. The trend in strength of surface interaction, obtained by NMR relaxation measurements, explains the reactivity trend. Reducing agents with weaker strength of surface interaction relative to water, such as hydrocarbons, show poorer activity compared to reducing agents with stronger strength of interaction, such as ethanol. This is likely to be due to the greater ability of the reducing



agents with higher interaction strength to reduce the inhibitory effect of water molecules blocking the catalytic sites, hence improving the conditions for the surface formation of partially oxidized organic species needed for the SCR reaction to proceed further. The results serve, therefore, as an experimental validation of the hypothesis on competitive adsorption previously speculated in the literature. In summary, the adsorption strength of the reducing agent over the catalyst surface is a very important parameter to take into account when investigating SCR reaction and NMR relaxation can be used as a valid tool to probe such adsorption phenomena, hence rationalising the choice of catalysts and reducing agents.

Acknowledgements

We gratefully acknowledge funding for this work from the EPSRC CASTech grant (EP/G012156/1). Carmine D'Agostino would like to acknowledge Wolfson College, Cambridge, for supporting his research activities. The authors would also like to thank Dr Jonathan Mitchell for useful discussions.

References

- J. P. Breen and R. Burch, *Top. Catal.*, 2006, **39**, 53–58.
- R. Burch, J. P. Breen and F. C. Meunier, *Appl. Catal., B*, 2002, **39**, 283–303.
- K. Shimizu, A. Satsuma and T. Hattori, *Appl. Catal., B*, 2000, **25**, 239–247.
- K. Eranen, F. Klingstedt, K. Arve, L. E. Lindfors and D. Y. Murzin, *J. Catal.*, 2004, **227**, 328–343.
- Y. Kintaichi, H. Hamada, M. Tabata, M. Sasaki and T. Ito, *Catal. Lett.*, 1990, **6**, 239–244.
- H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and T. Yoshinari, *Appl. Catal., A*, 1992, **88**, L1–L7.
- K. Shimizu, J. Shibata, A. Satsuma and T. Hattori, *Phys. Chem. Chem. Phys.*, 2001, **3**, 880–884.
- Y. H. Hu, K. Griffiths and P. R. Norton, *Surf. Sci.*, 2009, **603**, 1740–1750.
- A. Ruban, B. Hammer, P. Stoltze, H. L. Skriver and J. K. Nørskov, *J. Mol. Catal. A: Chem.*, 1997, **115**, 421–429.
- C. H. Christensen and J. K. Nørskov, *J. Chem. Phys.*, 2008, **128**, 8.
- T. Miyadera, *Appl. Catal., B*, 1993, **2**, 199–205.
- T. Miyadera and K. Yoshida, *Chem. Lett.*, 1993, 1483–1486.
- S. Kameoka, Y. Ukisu and T. Miyadera, *Phys. Chem. Chem. Phys.*, 2000, **2**, 367–372.
- J. H. Lee, S. J. Schmiege and S. H. Oh, *Appl. Catal., A*, 2008, **342**, 78–86.
- H. Dong, S. Shuai, R. Li, H. Wang, X. Shi and H. He, *Chem. Eng. J.*, 2008, **135**, 195–201.
- C. Zhang, H. He, S. Shuai and J. Wang, *Environ. Pollut.*, 2007, **147**, 415–421.
- K. Arve, K. Eranen, M. Snare, F. Klingstedt and D. Y. Murzin, *Top. Catal.*, 2007, **42–43**, 399–403.
- K. Shimizu and A. Satsuma, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2677–2695.
- J. Mitchell, L. M. Broche, T. C. Chandrasekera, D. J. Lurie and L. F. Gladden, *J. Phys. Chem. C*, 2013, **117**, 17699–17706.
- D. Weber, J. Mitchell, J. McGregor and L. F. Gladden, *J. Phys. Chem. C*, 2009, **113**, 6610–6615.
- C. D'Agostino, G. L. Brett, P. J. Miedziak, D. W. Knight, G. J. Hutchings, L. F. Gladden and M. D. Mantle, *Chem. – Eur. J.*, 2012, **18**, 14426–14433.
- P. J. McDonald, J. Mitchell, M. Mulheron, P. S. Aptaker, J. P. Korb and L. Monteilhet, *Cem. Concr. Res.*, 2007, **37**, 303–309.
- C. D'Agostino, T. Kotionova, J. Mitchell, P. J. Miedziak, D. W. Knight, S. H. Taylor, G. J. Hutchings, L. F. Gladden and M. D. Mantle, *Chem. – Eur. J.*, 2013, **19**, 11725–11732.
- K. Ralphs, C. D'Agostino, R. Burch, S. Chansai, L. F. Gladden, C. Hardacre, S. L. James, J. Mitchell and S. F. R. Taylor, *Catal. Sci. Technol.*, 2014, **4**, 531–539.
- C. D'Agostino, J. Mitchell, M. D. Mantle and L. F. Gladden, *Chem. – Eur. J.*, 2014, **20**, 13009–13015.
- U. Kamolphop, S. F. R. Taylor, J. P. Breen, R. Burch, J. J. Delgado, S. Chansai, C. Hardacre, S. Hengrasme and S. L. James, *ACS Catal.*, 2011, **1**, 1257–1262.
- K. L. Ralphs, S. Chansai, C. Hardacre, R. Burch, S. Taylor and S. L. James, *Catal. Today*, 2014, **246**, 198–206.
- E. Fukushima and S. W. Roeder, *Experimental pulse NMR*, Addison-Wesley, Reading, US, 1981.
- A. Ignatchenko, D. G. Nealon, R. Dushane and K. Humphries, *J. Mol. Catal. A: Chem.*, 2006, **256**, 57–74.
- P. J. McDonald, J. P. Korb, J. Mitchell and L. Monteilhet, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2005, **72**, 9.
- S. Godefroy, M. Fleury, F. Deflandre and J. P. Korb, *J. Phys. Chem. B*, 2002, **106**, 11183–11190.
- H. He, Y. B. Yu, Y. Li, Q. Wu, X. L. Zhang, C. B. Zhang, X. Y. Shi and X. P. Song, *Chin. J. Catal.*, 2010, **31**, 491–501.
- J. P. Breen, R. Burch, C. Hardacre, C. J. Hill and C. Rioche, *J. Catal.*, 2007, **246**, 1–9.
- P. Sazama, L. Capek, H. Drobna, Z. Sobalik, J. Dedecek, K. Arve and B. Wichterlova, *J. Catal.*, 2005, **232**, 302–317.
- F. C. Meunier, J. P. Breen, V. Zuzaniuk, M. Olsson and J. R. H. Ross, *J. Catal.*, 1999, **187**, 493–505.
- F. C. Meunier, V. Zuzaniuk, J. P. Breen, M. Olsson and J. R. H. Ross, *Catal. Today*, 2000, **59**, 287–304.
- M. Tatsuo, *Appl. Catal., B*, 1993, **2**, 199–205.
- M. Tabata, H. Tsuchida, K. Miyamoto, T. Yoshinari, H. Yamazaki, H. Hamada, Y. Kintaichi, M. Sasaki and T. Ito, *Appl. Catal., B*, 1995, **6**, 169–183.

