

CrossMark  
click for updatesCite this: *Catal. Sci. Technol.*, 2016,  
6, 7896

# Solvent inhibition in the liquid-phase catalytic oxidation of 1,4-butanediol: understanding the catalyst behaviour from NMR relaxation time measurements†

Carmine D'Agostino,<sup>\*a</sup> Mark R. Feaviour,<sup>b</sup> Gemma L. Brett,<sup>c</sup> Jonathan Mitchell,<sup>d</sup>  
Andrew P. E. York,<sup>b</sup> Graham J. Hutchings,<sup>c</sup> Mick D. Mantle<sup>a</sup> and Lynn F. Gladden<sup>a</sup>

Catalytic reaction studies and nuclear magnetic resonance (NMR) relaxation time measurements have been compared to study the influence of competitive adsorption of reactant and solvent on catalytic conversion. The reaction chosen is the aerobic catalytic oxidation of 1,4-butanediol in methanol over different supported-metal catalysts. From the NMR  $T_1/T_2$  ratio, where  $T_1$  is the longitudinal and  $T_2$  the transverse spin relaxation time, the relative affinity of reactant and solvent for different catalytic surfaces is determined. The catalysts with the lowest activity show a preferential surface affinity for the solvent compared to the reactant. Conversely, the catalyst with the highest activity shows a preferential surface affinity for the reactant compared to the solvent. Significantly, Ru/SiO<sub>2</sub>, which is totally inactive for the oxidation of 1,4-butanediol, exhibited a lower  $T_1/T_2$  ratio (surface affinity) for 1,4-butanediol (reactant) than for a “weakly-interacting” alkane, indicating a very poor surface affinity for the diol functionality. The results provide direct evidence of the importance of the adsorbate-adsorbent interactions on catalyst activity in liquid-phase oxidations and indicate that the competitive adsorption of the solvent plays an important role in these reactions. This work demonstrates that NMR relaxation time analysis is a powerful method for comparing adsorption of liquids in porous catalysts, providing valuable information on the affinity of different chemical species for a catalyst surface. Moreover, the results demonstrate that NMR relaxation time measurements can be used not only to guide selection of solvent for use with a specific catalyst, but also selection of the catalyst itself. The results suggest that this method may be used to predict catalyst behaviour, enabling improved design and optimisation of heterogeneous catalytic processes.

Received 7th July 2016,  
Accepted 29th September 2016

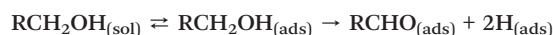
DOI: 10.1039/c6cy01458e

www.rsc.org/catalysis

## Introduction

The adsorption of organic molecules onto catalytic surfaces is a fundamental step in heterogeneous catalysis, and it therefore follows that an experimental probe quantifying the strength of adsorption over solid surfaces should give valuable insights into the design of novel catalysts and catalytic processes. In the liquid-phase oxidation of hydroxyl groups, the adsorption of the reactant from the bulk solution onto

the catalyst surface is widely recognised as the initial step in the oxidation reaction.<sup>1,2</sup> Based on the oxidative dehydrogenation mechanism, the oxidation of the hydroxyl group starts according to:



The adsorption of the reactant in solution onto the catalyst surface occurs at equilibrium. The O–H bond in the alcohol breaks upon adsorption on the surface site, yielding hydrogen and an alkoxide. Adsorbed oxygen is necessary to oxidise the co-produced hydrogen, thus shifting the equilibrium towards the products.

Research into the development of sustainable routes for chemical production has recently focused attention towards the catalytic oxidation of diols and polyols. The use of large amounts of solvent is always necessary in this type of reaction due to the high viscosity of the reactants. Water and methanol tend to be the solvent of choice.<sup>3–7</sup> However, the

<sup>a</sup> Department of Chemical Engineering and Biotechnology, University of Cambridge, Pembroke Street, Cambridge, CB2 3RA, UK.  
E-mail: cd419@cam.ac.uk; Tel: +44 (0)1223 334796

<sup>b</sup> Johnson Matthey Technology Centre, Sonning Common, Reading, RG4 9NH, UK

<sup>c</sup> Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK

<sup>d</sup> Schlumberger Gould Research Centre, High Cross, Madingley Road, Cambridge, CB3 0EL, UK

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6cy01458e



inter-play between adsorption of reactant and solvent can be central to determining the catalytic activity of a certain catalyst for a specific reaction. The choice of an optimum solvent has often been reported to be critical for achieving effective catalytic performance.<sup>8–12</sup> An ideal solvent should not be adsorbed onto the catalyst surface, or at least its adsorption strength should be much lower than that of the reactant.<sup>13</sup> Therefore, a comparison of the adsorption strength of reactants and solvents yields important information and may enable predictions of the catalytic behaviour in a specific chemical reaction.

NMR relaxation time analysis has emerged in recent years as a non-invasive tool for probing surface interactions of liquids in porous media. The strength of surface interaction from NMR relaxation time measurements can be inferred by the  $T_1/T_2$  ratio,<sup>14–17</sup> where  $T_1$  is the longitudinal relaxation time and  $T_2$  is the transverse relaxation time. The  $T_1/T_2$  ratio can also be seen as an equivalent energy of surface interaction, which is related to the residence time of molecules over the surface.<sup>18</sup> This methodology has been successfully used to study interactions of liquids in a variety of porous media<sup>14,16,19,20</sup> and has recently been used to probe surface interactions in supported-metal catalysts;<sup>15</sup> the application of the technique in heterogeneous catalysis is, however, still at an early stage. In our previous work<sup>21</sup> we used NMR relaxation time measurements and NMR diffusometry to study the effect of solvent composition on the oxidation of 1,4-butanediol over Au/TiO<sub>2</sub> catalyst and we concluded that adsorption plays a key role in the oxidation of diols over supported-metal mesoporous catalysts.

The  $T_1/T_2$  ratio is particularly useful in characterising the relative strengths of surface interactions of molecules in different porous materials. In particular,  $T_1$  and  $T_2$  are sensitive to rotational and translational dynamics to different extents. Relative to the bulk, molecules adsorbed onto surfaces exhibit modified rotational dynamics and slower translational diffusion. More precisely,  $1/T_2$  has a spectral density contribution at zero frequency,  $J(0)$ , and one contribution at higher frequencies,  $J(\omega_0)$ , while  $1/T_1$  depends only on spectral densities at higher frequencies,  $J(\omega_0)$ . As a result,  $T_2$  is further affected by changes in molecular dynamics at the surface and is able to probe slow motions. The ratio  $T_1/T_2$  can therefore be linked to the interaction strength of reactants or solvents with the catalyst surface: the higher the  $T_1/T_2$  ratio, the higher the strength of interaction with the surface. We have recently proven that this ratio can be related to an activation energy of desorption, hence it can be used as a non-invasive probe to describe surface interactions of molecules adsorbed over surfaces.<sup>22</sup> In addition, unlike single values of  $T_1$  and  $T_2$ , the ratio of the two relaxation times is independent on pore geometry. Hence, it becomes possible to compare the relative strengths of surface interactions between materials with very different pore sizes, *i.e.*, pores with different surface-to-volume ratio,  $S/V$ . Indeed, the  $T_1/T_2$  ratio can be considered as the equivalent of an activation energy of adsorption<sup>22,23</sup> and this was recently shown and experimentally validated by

combining NMR relaxation time measurements with temperature-programmed desorption (TPD) when studying adsorption of water in several mesoporous materials used as catalysts and supports.<sup>22</sup> Therefore, in principle with appropriate calibration, by knowing this ratio, it is possible to quantify the adsorption strength of liquids in porous catalysts.

In the present work, we consider the same reactant/solvent system as studied in our previous work and demonstrate that NMR relaxation time measurements can be used to guide selection of the catalysts, which gives the highest catalytic conversion. We use NMR relaxation time measurements to study surface interactions of 1,4-butanediol (reactant) and methanol (solvent) species, relevant to the aerobic oxidation of 1,4-butanediol, over a series of heterogeneous supported-metal catalysts. The results are then compared with the activity of each catalyst and a correlation between catalyst activity and the adsorption characteristics of the reactant and solvent is drawn. Although not required to produce the correlation between catalyst activity and the ratio of  $T_1/T_2$  values determined for the reactant and solvent, the  $T_1/T_2$  for cyclohexane is also reported for each catalyst. The absolute values of  $T_1$ ,  $T_2$  and  $T_1/T_2$  for a given solvent interacting with each catalyst will be different. Hence, cyclohexane is used as a reference molecule, chosen because it will not have any specific interaction with the catalyst surface, so that the absolute values of  $T_1/T_2$  can be put in context.

## Experimental methods

### Catalysts and chemicals

2% Pt/SiO<sub>2</sub>, 0.5% Pd/Al<sub>2</sub>O<sub>3</sub> and 1% Ru/SiO<sub>2</sub> were supplied by Johnson Matthey, UK. 2.5% AuPd/SiO<sub>2</sub> (1.25 wt% Au and 1.25 wt% Pd) was prepared by wet impregnation. The detailed procedure for the preparation of the catalyst follows. Palladium chloride (20.83 mg) was dissolved in an aqueous solution of aurochloric acid (2.04 mL of 12.25 mg mL<sup>-1</sup> solution). Silica support (0.975 g) was then added and the mixture was stirred and heated until a paste was formed. The catalyst was then dried (110 °C, 16 h). After this time the catalyst was ground and calcined at 400 °C for 3 hours with a ramp rate of 20 °C min<sup>-1</sup>. The 2.5% Pd/TiO<sub>2</sub>(a) (TiO<sub>2</sub> anatase from Evonik Degussa used as support), 2.5% Pt/TiO<sub>2</sub>(r) (TiO<sub>2</sub> rutile from Evonik Degussa used as support), and 2.5% Pd/ZrO<sub>2</sub> were prepared by an incipient wetness impregnation. All quoted metal loadings are wt% and for simplicity, in the following text, figures and tables the metal loading will be omitted when referring to these catalysts. The incipient wetness method is described as follows. Prior to catalyst preparation, the cold water pick up (CWPU) volumes were measured by carefully adding demineralised water to support (10 g) with a pipette until it appeared wet but no excess water was visible. The pore volume was also measured by BET analysis and a good agreement between the two methods was found. Then a sufficient amount of aqueous palladium nitrate Pd(NO<sub>3</sub>)<sub>2</sub>, or tetraammine platinum hydroxide Pt(NH<sub>2</sub>)<sub>4</sub>(OH)<sub>2</sub>, solution was



diluted with demineralised water and used to saturate the support. The products were dried (105 °C, 20 min) with periodic stirring in an effort to counter the effects of wicking and were then calcined (500 °C, 2 h). Methanol, 1,4-butanediol and cyclohexane were purchased from Sigma Aldrich and were of the highest purity available.

### Catalytic reaction

A 50 mL glass reactor was charged with 1,4-butanediol (0.27 g), sodium methoxide (0.13 g), methanol (10 mL) and catalyst (reactant:metal = 500). The reaction mixture was heated to 40 °C and pressurised to 3 bar of oxygen. Gas chromatographic analysis was carried out using a Varian 3800 chromatograph equipped with a CP 8400 autosampler and CP-wax 52 column. Products were identified by comparison with authentic samples and quantifications were established using an external calibration method. The conversion was calculated according to the following equation:

$$\text{Conversion}(\%) = \frac{n_{\text{start}} - n_{\text{end}}}{n_{\text{start}}} \times 100 \quad (1)$$

where  $n_{\text{start}}$  and  $n_{\text{end}}$  are the moles of 1,4-butanediol at the beginning and after 48 h reaction time, respectively. The main reaction product was  $\gamma$ -butyrolactone for all catalysts.

### NMR measurements

NMR experiments were performed on a Bruker DMX 300 operating at a  $^1\text{H}$  frequency of 300.13 MHz. The  $T_1$  times were measured using the inversion recovery pulse sequence<sup>24</sup> and the transverse  $T_2$  times were measured with the CPMG (Carr Purcell Meiboom Gill) pulse sequence.<sup>24</sup> Samples for NMR measurements were prepared by soaking the catalyst grains in each liquid for at least 24 hours to equilibrate. The grains were then dried on a pre-soaked filter paper in order to remove any excess liquid on the external surface and finally transferred to 5 mm NMR tubes. To ensure a saturated atmosphere in the NMR tube, hence minimising errors due to evaporation of volatile liquids, a small amount of pure liquid was adsorbed onto filter paper, which was then placed under the cap of the NMR tube and sealed with parafilm. The sample was finally placed into the magnet and left for approximately 20 min to achieve thermal equilibrium before the start of the measurements. All measurements were carried out at atmospheric pressure and 20 °C  $\pm$  0.5 °C. The typical relative error on the  $T_1$  and  $T_2$  measurements was 2%, which gives a combined error of approximately 3% on the  $T_1/T_2$  values.

## Results and discussion

The conversion, as defined in eqn (1), of the different solid catalysts for the oxidation of 1,4-butanediol are reported in Fig. 1.

From Fig. 1 it is possible to note that the most active catalyst is the bimetallic AuPd/SiO<sub>2</sub>, with a conversion of approxi-

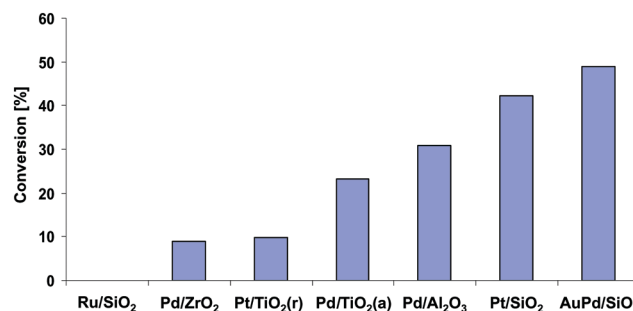


Fig. 1 Conversion of 1,4-butanediol at 48 h reaction time. The main reaction product was  $\gamma$ -butyrolactone in all cases.

mately 50%, whereas Ru/SiO<sub>2</sub> is inactive for the reaction, giving negligible conversion. There is no correlation between the BET surface area of the catalysts and conversion (see ESI† S1). Further, it is observed that the same metal on different supports can have significantly different conversion; for example, Pd/TiO<sub>2</sub>(a) and Pd/ZrO<sub>2</sub> give conversions of ~23% and ~10%, respectively. Likewise, different metals on the same support are also associated with significantly different conversions.

It has previously been suggested that competitive adsorption between solvent and reactant may significantly affect the performances of heterogeneous catalysts in liquid-phase reactions,<sup>10</sup> and this has been confirmed in our earlier work on this reaction.<sup>21</sup> In order to understand the reaction data reported in the current work,  $T_1$  and  $T_2$  relaxation measurements were performed to probe the relative strength of surface interaction of reactant and solvent with the catalyst surface and to explore the extent to which this correlated with catalytic conversion. Typical  $^1\text{H}$  NMR spectra for the samples used in this study are shown in Fig. 2 and in ESI† (S2).

A set of experimental plots of  $T_1$  and  $T_2$  relaxation measurements for some of the catalysts used in this work (Pd/ZrO<sub>2</sub>, AuPd/SiO<sub>2</sub> and Ru/SiO<sub>2</sub>) is reported in Fig. 3, which shows  $T_1$  inversion recovery<sup>24</sup> (Fig. 3a) and  $T_2$  CPMG decays<sup>24</sup> (Fig. 3b) for 1,4-butanediol. Data for the other catalysts samples were of similar quality.

The results of the relaxation time measurements for the different catalysts are summarised in Fig. 4, which shows the  $T_1/T_2$  ratio of methanol (solvent), 1,4-butanediol (reactant) and cyclohexane (reference compound), together with the catalytic conversion. More details on single values of  $T_1$  and  $T_2$  are given in the ESI† (S3). The main oxidation product was  $\gamma$ -butyrolactone in all cases. Note that in Fig. 4, besides values for the reactant (1,4-butanediol) and solvent (methanol), we also report values for cyclohexane, which is not involved in the reaction. As mentioned earlier, the  $T_1/T_2$  of this “weakly-interacting” species is required because the intrinsic  $T_1$ ,  $T_2$  and  $T_1/T_2$  for a given molecular species will differ for any given molecule interacting with different catalyst surfaces. In this work, we compare the relative magnitudes of the  $T_1/T_2$  for the reactant and solvent species for each catalyst and correlate this with catalyst activity. The  $T_1/T_2$  of cyclohexane



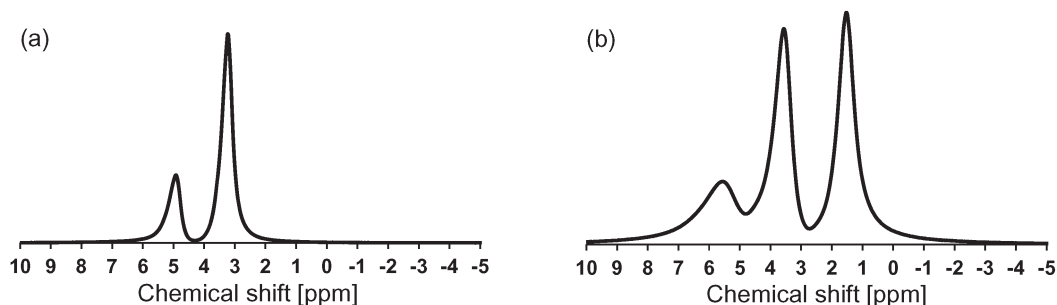


Fig. 2  $^1\text{H}$  NMR spectra of (a) methanol and (b) 1,4-butanediol in Pd/TiO<sub>2</sub>(a) catalyst.

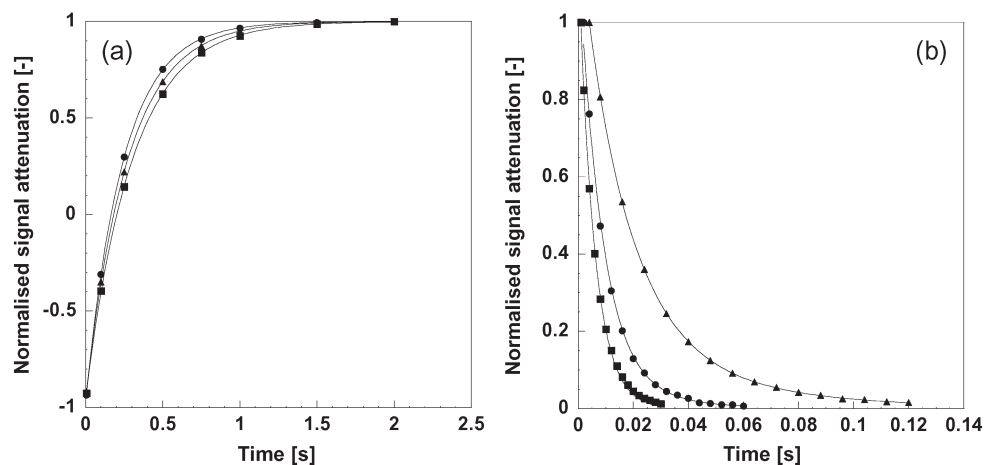


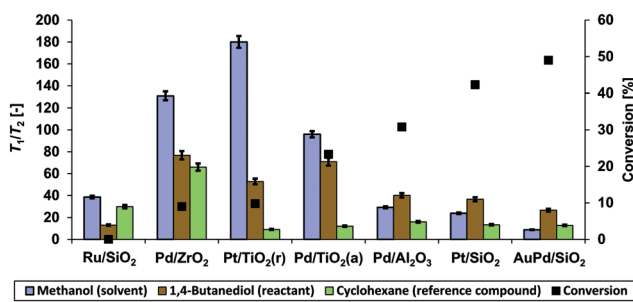
Fig. 3 (a)  $T_1$  inversion recovery and (b)  $T_2$  CPMG relaxation data of 1,4-butanediol in different catalysts: (■) Pd/ZrO<sub>2</sub>; (●) AuPd/SiO<sub>2</sub>; (▲) Ru/SiO<sub>2</sub>. The values of the relaxation times are:  $T_1 = 301$  ms and  $T_2 = 6$  ms for Pd/ZrO<sub>2</sub>;  $T_1 = 242$  ms and  $T_2 = 9$  ms for AuPd/SiO<sub>2</sub>;  $T_1 = 272$  ms and  $T_2 = 21$  ms for Ru/SiO<sub>2</sub>. The solid lines are fits to the data using the theoretical expressions to (a) inversion recovery<sup>24</sup> and (b) CPMG decay.<sup>24</sup>

provides a useful reference against which to benchmark the effective strength of surface interaction for a given molecular species across different catalytic systems because it does not have any specific functionality or molecular configuration, which promotes strong interaction with the solid surface. In this context, we note the work of Lanin *et al.*,<sup>25</sup> who used gas chromatography to study the adsorption of several

classes of organic compounds over titanium dioxide and showed that alkanes exhibit lower adsorption energies compared to molecules with specific functionality such as alkenes and oxygenated polar molecules. We also note that since alkanes are hydrophobic, the  $T_1/T_2$  ratio of alkanes is expected to increase with increasing hydrophobicity of the solid surface.<sup>26</sup>

From the data presented in Fig. 4 it is clear that the catalysts demonstrating lower conversion are characterised by a  $T_1/T_2$  of the methanol solvent significantly greater than the  $T_1/T_2$  of the 1,4-butanediol reactant. As conversion increases, the value of  $T_1/T_2$  associated with the solvent reduces relative to that of the reactant. The AuPd/SiO<sub>2</sub> catalyst has the highest activity, followed closely by Pt/SiO<sub>2</sub> and then Pd/Al<sub>2</sub>O<sub>3</sub>. The activity of Pd/ZrO<sub>2</sub> and Pt/TiO<sub>2</sub>(r) is relatively poor, whereas the Ru/SiO<sub>2</sub> exhibited negligible activity for the oxidation of 1,4-butanediol.

For a more complete analysis, we now consider the strength of surface interaction inferred from the relaxation time ratio of 1,4-butanediol (reactant)  $[T_1/T_2]_R$ , methanol (solvent)  $[T_1/T_2]_S$ , and cyclohexane (reference compound)  $[T_1/T_2]_{ref}$  within the different catalysts and see how these values relate to the catalyst activity. It is also clear from Fig. 4 that for the catalysts showing higher activity, *i.e.*, AuPd/SiO<sub>2</sub>, Pt/



<sup>a</sup> (a) indicates TiO<sub>2</sub> anatase and (r) indicates TiO<sub>2</sub> rutile

Fig. 4 Conversion and  $T_1/T_2$  ratio values of methanol (solvent), 1,4-butanediol (reactant) and cyclohexane (reference compound) in different catalysts. The relative error in the  $T_1/T_2$  ratio is approximately 3%. The  $T_1/T_2$  value for each of the bulk liquids (methanol, 1,4-butanediol and cyclohexane) is equal to one.



SiO<sub>2</sub>, and Pd/Al<sub>2</sub>O<sub>3</sub>,  $[T_1/T_2]_R > [T_1/T_2]_S$ . We interpret this comparison of relaxation time ratios as a greater strength of surface interaction for the 1,4-butanediol reactant than the methanol solvent. For Pd/TiO<sub>2</sub>(a), which shows an intermediate activity compared with the other catalysts,  $[T_1/T_2]_R \sim [T_1/T_2]_S$  (similar strength of surface interaction for reactant and solvent). Conversely, for the catalysts showing poor activity the situation is reversed and  $[T_1/T_2]_R < [T_1/T_2]_S$  (*i.e.*, the solvent has a preferential interaction with the surface). In summary, the  $T_1/T_2$  ratio provides a measure of the competitive adsorption of the reactant and solvent with the limiting cases

$$\begin{aligned} [T_1/T_2]_R > [T_1/T_2]_S & \text{ Adsorption of reactant favoured over solvent} \\ [T_1/T_2]_R < [T_1/T_2]_S & \text{ Adsorption of solvent favoured over reactant} \end{aligned}$$

The combination of NMR relaxation time ratios with catalytic activity data suggests that competitive adsorption of the solvent is an important factor in determining the catalyst activity for the reaction studied here. Preferential adsorption of the solvent molecules on the catalytic surface limits access of the reactant to active surface sites and hence reduces the catalytic activity.

We now use the data in Fig. 4 to calculate the ratio,  $\beta$ , of the  $T_1/T_2$  values obtained for the reactant relative to the solvent;  $\beta$  therefore indicates the strength of adsorption of the reactant (1,4-butanediol) relative to the solvent (methanol):

$$\beta = [T_1/T_2]_R [T_2/T_1]_S \quad (2)$$

This parameter enables a straightforward comparison between the surface interactions of the reactant and solvent in different catalytic materials; hence, it provides a way to quantify competitive adsorption between reactant and solvent. A plot of  $\beta$  against conversion is shown in Fig. 5. In general, a good correlation (dotted line) is obtained between the catalyst activity and the relative adsorption strength of the reactant. This correlation provides further evidence that competi-

tive adsorption plays an important role in determining the catalytic activity. We note that the only catalyst that provides a significant deviation from this correlation is the bimetallic AuPd/SiO<sub>2</sub>. We suggest that the presence of two metal species provides an additional influence in the reaction, such as O<sub>2</sub> uptake, resulting in less conversion than expected based solely on the preferential adsorption of the reactant compared to the solvent. Notwithstanding, the qualitative nature of our correlation is retained: the catalyst with the highest affinity for the reactant also provides the greatest conversion, which suggests that competitive adsorption does indeed play a crucial role in determining catalytic conversions for this reaction.

It is interesting to compare the behaviour of Pt/SiO<sub>2</sub>, being the most active catalyst that obeys our empirical correlation, with Ru/SiO<sub>2</sub> which is the least active. For Pt/SiO<sub>2</sub> the  $T_1/T_2$  ratio of the solvent is lower than that of the reactant, implying that the adsorption of 1,4-butanediol is highly favoured compared to that of the methanol solvent.

The results presented in Fig. 5 suggest that NMR relaxation time analysis of reactant and solvent interacting with the catalyst surface can explain catalyst conversion on the basis of competitive adsorption of reactant and solvent species. This approach may be useful in understanding the behaviour of other systems. For example, Bianchi and co-workers<sup>3</sup> studied the liquid-phase catalytic oxidation of ethylene glycol in water (solvent) and reported that the type of support is important for determining catalytic performance. They also suggested that the presence of the solvent can markedly modify the reaction pathway through interaction with the solid surface of the catalyst. Ongoing work is exploring the extent to which NMR relaxometry can yield insight into catalyst selectivity.

## Conclusions

The liquid-phase oxidation of 1,4-butanediol by molecular oxygen in methanol as solvent has been studied over a series of supported-metal catalysts. Catalytic conversion has been compared with the adsorption characteristics of reactant and solvent, inferred by NMR relaxation time ratios. The competitive adsorption of reactant and solvent on the catalyst surface is characterised and seen to correlate with conversion. A higher interaction strength of the reactant with the surface, compared to the solvent, is associated with increased conversion. Conversely, when the solvent interaction with the surface is stronger than that of the reactant, conversion decreases, most likely due to solvent molecules blocking access of reactant molecules to the surface. Whilst we have shown aspects of this effect previously,<sup>21</sup> this work demonstrates that the NMR relaxation time analysis approach can be applied to evaluate competitive adsorption processes across a range of catalytic materials for the same chemical conversion. This NMR method is particularly useful because it provides an *in situ* measurement of molecular adsorption strengths and therefore has the potential to become a useful tool for

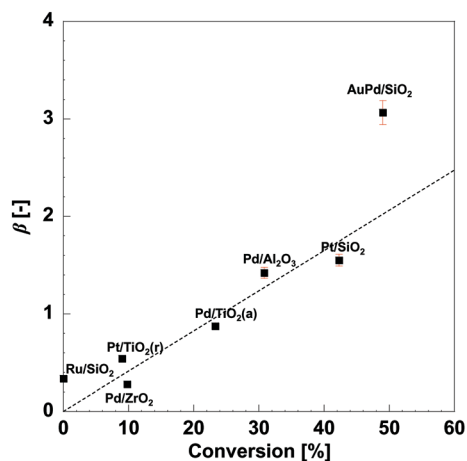


Fig. 5 Plot of  $\beta$ , as defined in eqn (2) against catalytic conversion. Note that (a) indicates TiO<sub>2</sub> anatase and (r) indicates TiO<sub>2</sub> rutile. The dotted line is a guide to the eye.



both solvent and catalyst selection for a particular conversion.

## Acknowledgements

We would like to thank Johnson Matthey and Evonik-Degussa, for supplying the catalyst supports used in this work and the Technology Strategy Board for funding, Grant No. TP/7/ZEE/6/1/N0262B. The Technology Strategy Board is a government body, which promotes and supports the development and exploitation of technology and innovation for the benefit of UK business, in order to increase economic prosperity and improve quality of life. We also wish to thank the EPSRC and the CASTech consortium for supporting this work (EP/G011397/1). Carmine D'Agostino would also like to acknowledge Wolfson College, Cambridge, for supporting his research activities.

## References

- 1 T. Mallat and A. Baiker, *Chem. Rev.*, 2004, **104**, 3037–3058.
- 2 M. Besson and P. Gallezot, *Catal. Today*, 2000, **57**, 127–141.
- 3 C. Bianchi, F. Porta, L. Prati and M. Rossi, *Top. Catal.*, 2000, **13**, 231–236.
- 4 C. L. Bianchi, P. Canton, N. Dimitratos, F. Porta and L. Prati, *Catal. Today*, 2005, **102**, 203–212.
- 5 N. Dimitratos, J. A. Lopez-Sanchez, S. Meenakshisundaram, J. M. Anthonykutty, G. Brett, A. F. Carley, S. H. Taylor, D. W. Knight and G. J. Hutchings, *Green Chem.*, 2009, **11**, 1209–1216.
- 6 I. S. Nielsen, E. Taarning, K. Egeblad, R. Madsen and C. H. Christensen, *Catal. Lett.*, 2007, **116**, 35–40.
- 7 E. Taarning, A. T. Madsen, J. M. Marchetti, K. Egeblad and C. H. Christensen, *Green Chem.*, 2008, **10**, 408–414.
- 8 S. Mukherjee and M. A. Vannice, *J. Catal.*, 2006, **243**, 108–130.
- 9 P. Lignier, S. Mangematin, F. Morfin, J. L. Rousset and V. Caps, *Catal. Today*, 2008, **138**, 50–54.
- 10 H. Takagi, T. Isoda, K. Kusakabe and S. Morooka, *Energy Fuels*, 1999, **13**, 1191–1196.
- 11 N. M. Bertero, A. F. Trasarti, C. R. Apesteguia and A. J. Marchi, *Appl. Catal., A*, 2011, **394**, 228–238.
- 12 B. S. Akpa, C. D'Agostino, L. F. Gladden, K. Hindle, H. Manyar, J. McGregor, R. Li, M. Neurock, N. Sinha, E. H. Stitt, D. Weber, J. A. Zeitler and D. W. Rooney, *J. Catal.*, 2012, **289**, 30–41.
- 13 E. G. Derouanne, *A molecular view of heterogeneous catalysis*, De Boeck Université, Brussels, 1996.
- 14 L. F. Gladden and J. Mitchell, *New J. Phys.*, 2011, **13**, 46.
- 15 D. Weber, J. Mitchell, J. McGregor and L. F. Gladden, *J. Phys. Chem. C*, 2009, **113**, 6610–6615.
- 16 P. J. McDonald, J. Mitchell, M. Mulheron, P. S. Aptaker, J. P. Korb and L. Monteilhet, *Cem. Concr. Res.*, 2007, **37**, 303–309.
- 17 C. D'Agostino, S. Chansai, I. Bush, C. Gao, M. D. Mantle, C. Hardacre, S. L. James and L. F. Gladden, *Catal. Sci. Technol.*, 2016, **6**, 1661–1666.
- 18 S. Godefroy, M. Fleury, F. Deflandre and J. P. Korb, *J. Phys. Chem. B*, 2002, **106**, 11183–11190.
- 19 J. P. Korb, *New J. Phys.*, 2011, **13**, 26.
- 20 P. J. McDonald, J. P. Korb, J. Mitchell and L. Monteilhet, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2005, **72**, 9.
- 21 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.
- 22 C. D'Agostino, J. Mitchell, M. D. Mantle and L. F. Gladden, *Chem. – Eur. J.*, 2014, **20**, 13009–13015.
- 23 S. Godefroy, J. P. Korb, M. Fleury and R. G. Bryant, *Phys. Rev. E: Stat., Nonlinear, Soft Matter Phys.*, 2001, **64**, 13.
- 24 E. Fukushima and S. W. Roeder, *Experimental pulse NMR*, Addison-Wesley, Reading, US, 1981.
- 25 S. N. Lanin, E. V. Vlasenko, N. V. Kovaleva and F. M. Zung, *Russ. J. Phys. Chem. A*, 2008, **82**, 2152–2155.
- 26 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.

