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Product inhibition in the glycerol oxidation over Au/TiO₂ catalyst quantified by NMR relaxation

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Abstract

Liquid-phase catalytic oxidation of glycerol in aqueous solutions using porous solid catalysts represents a viable strategy for the sustainable production of fine chemicals from renewable resources. Various aspects of this novel type of reactions are still under investigation. Catalyst deactivation is one of those issues that need to be understood and addressed in order to make these processes commercially viable. In a previous study it has been reported that the catalytic activity of Au/TiO_2 catalysts for the oxidation of glycerol with O_2 under basic conditions can be severely inhibited by some reaction intermediates or products. It was suggested that the presence of certain species blocks the active sites of the catalyst, preventing the adsorption of glycerol, which in turn results in a decrease of reaction rate. In this work, we used NMR relaxation time measurements in order to assess surface interactions of glycerol in Au/TiO_2 catalyst pre-treated with aqueous solutions of various oxygenates, including intermediates and products of glycerol oxidation, under basic conditions, in particular evaluating changes in glycerol adsorption properties. The NMR T_1/T_2 ratio of glycerol, which is indicative of the strength of interaction of glycerol with the catalyst surface, traces out well the trend in catalytic activity in the presence of different additives, suggesting that adsorption of glycerol onto the catalyst surface play a crucial role in the reaction, which supports the hypothesis previously made in the literature. This experimental approach and the related results represent a significant advance in the understanding of liquid-phase catalytic reactions occurring over solid surfaces, which can be used to understand and optimise catalytic processes and the effect of intermediate and product inhibition.

Keywords: Glycerol oxidation, catalyst poisoning, NMR relaxation, gold catalysts, adsorption

Introduction

The oxidation of glycerol over gold supported nanoparticles has gained significant attention in the last decade as an alternative, environmentally friendly route for the production of value-added chemicals.[1-6] In order to make these processes commercially viable, catalyst reusability is a key issue that needs to be addressed. In general, gold catalysts are considered to be resistant to deactivation by over-oxidation and strong product adsorption and this is due to the fact that gold surfaces are the most noble among transition metals.[7-9] However, species like carbonates have been shown to deactivate gold catalysts during oxidation reactions.[10-12] In a recent work carried out by Davis and Zope,[13] it has been reported that the catalytic activity of gold nanoparticles supported on titania for the aerobic oxidation of glycerol can be partially or severely inhibited by the presence of several oxygenate compounds, including reaction intermediates and products. In particular, the presence of certain hydroxyl acids, sugar acids and acetone in the initial reaction mixture severely affected the turn over frequency (TOF) of the glycerol oxidation reaction. Methanol, monoacids and diacids were seen to have a less pronounced detrimental effect or no effect at all on the catalytic activity. The authors concluded that compounds with internal −OH groups adsorb strongly on the gold catalysts, blocking the access of glycerol to the active sites, hence inhibiting glycerol adsorption over the surface, which causes the decrease in TOF experimentally observed, relative to the case of additive-free reaction mixture. It was also suggested that under the reaction conditions used addition and condensation products of ketones prevent the adsorption of glycerol.

Recently, we have demonstrated that NMR relaxation time measurements are a non-invasive and fast method to probe and quantify adsorption over metal nanoparticles supported on porous oxides and we have shown that the method is sensitive to the type of solvent used[14-15] for the reaction and it also predicts the behaviour of different catalytic materials used in the oxidation of polyols.[16] More recently we used two-dimensional NMR T_1-T_2 experiments to understand the effect of gold particle size on glycerol adsorption over Au/TiO$_2$ catalysts.[17] It was demonstrated that smaller gold particles act as stronger adsorption sinks for glycerol, which is thought to enhance catalyst oxidation performances. Previous studies suggest that the T_1/T_2 ratio can be linked to an activation energy for surface diffusion,[18] which is intrinsically related to the strength of molecules-surface interactions.

In our previous work on solvent effects, we used NMR relaxation time analysis to assess how solvent type and composition affect the strength of interaction of the reactive species in polyol oxidation reactions over Au/TiO$_2$ catalyst.[14, 19] Thus far, the effect of reaction products, intermediates and other additives, and how these modify the affinity of the catalyst surface for the reactive species, has not been explored. It is therefore of interest to extend this type of studies in order to investigate the presence of such species and assess if such measurements can be associated to the catalyst deactivation behaviour previously observed.[13]

In this work, we have used NMR relaxation time measurements to probe the strength of surface interaction of glycerol over Au/TiO$_2$ catalyst surface in the absence and presence of the same oxygenated species used in the work of Davis and Zope,[13] using the same catalyst (Au/TiO$_2$ supplied by the World Gold Council) and under similar experimental conditions, in order to assess the effect of different species, in particular reaction products, intermediates and other additives that may be present as feedstock impurities, on the adsorption strength of glycerol within the catalyst pores. The spin-lattice, T_1, and transverse spin, T_2, relaxation time constants of glycerol within the Au/TiO$_2$ catalyst are measured and from the T_1/T_2 ratio it is possible to infer the adsorption strength of glycerol over the catalyst treated with different additive solutions. The NMR data collected are then compared with the reaction rates previously observed and the results discussed.

Experimental

Materials and chemicals

All the chemicals were purchased from Sigma-Aldrich and were of the highest purity available. Deionised water was obtained from a laboratory water purification system (PURELAB option, Elga).

The Au/TiO$_2$ catalyst (ca. 1.7% Au by weight) was supplied by the World Gold Council (WGC). Samples were first pre-treated by submerging them in an aqueous solution containing the different additives, with a composition of 5% mole fraction of additive. The catalyst grains were left for at least 24 h within the solution, in order to equilibrate. The catalyst grains saturated with the additive solution were then placed into a basic solution of glycerol/water, 70% wt. of glycerol, with a NaOH : glycerol molar ratio of 1 : 1. The grains were then dried on a filter paper, in order to remove the excess liquid

on the outer surface of the grains, and transferred in 5 mm glass NMR tubes. The measurements were carried out at room temperature and atmospheric pressure. Considering the type of reaction (aerobic oxidation), the preparation method, and the high resistance of gold to over-oxidation[9] it is reasonable to assume that the state of the surface in the NMR measurements will be very similar to that under reaction conditions.[14, 19]

Catalyst characterisation

Transmission electron microscopy (TEM) was performed on a JEOL JEM-2100 operating at 200 kV. Samples were prepared by dispersion in ethanol by sonication and deposited on 300 mesh copper grids coated with holey carbon film. Microscopy was also performed on a Tescan Maia3 field emission gun scanning electron microscope (FEG-SEM) operating between 5-30KV fitted with an Oxford Instruments XMAXN 80 energy dispersive X-ray detector (EDX). Images were acquired using the secondary electron and backscattered electron detectors. Dark field scanning transmission electron images (STEM) were obtained using a STEM holder. Samples were dispersed as a powder onto 300 mesh copper grids coated with Holey carbon film.

NMR experiments

NMR experiments were performed in a Bruker DMX 300 operating at a ^{1}H frequency of 300.13 MHz. The NMR spin-lattice relaxation time, T_1, was measured using the inversion recovery technique [20] and the transverse relaxation time, T_2, was measured with the CPMG (Carr Purcell Meiboom Gill) pulse sequence,[20] using simple exponential functions for fitting the data. The echo time, τ, in the CPMG pulse sequence was set to 250 μs. The 90º and 180º NMR pulses were calibrated for each sample and the average values were about 5.5 μs and 11 μs, respectively. Measurements were repeated several times to check for reproducibility and estimate the relative error on T_1 and T_2 values. Typical experimental measuring times ranged from few to tens of minutes, depending on sample properties and NMR signal-to-noise ratio.

Results and discussion

The Au/TiO2 catalyst supplied by the WGC was characterised by EDX analysis in order to quantify the amount of Au present in the catalyst, which was quantified to be 1.7%

by weight (see Supporting Information). TEM microscopy, Figure 1, revealed a mean particle size of 5.2 nm, which is consistent with the Au/TiO$_2$ catalyst used for the reaction studies on glycerol oxidation.[13] We note that there is a slight difference with the Au particle size given in those reaction studies (reported as 3.5 nm), which might be due to differences in catalyst batches provided by the supplier but also to a different count of particles leading to a slightly different average particle size. We also note that despite such a difference might affect absolute values of relaxation times, it is very reasonable to assume that the relative trend, which is the focus of this work, will remain the same.
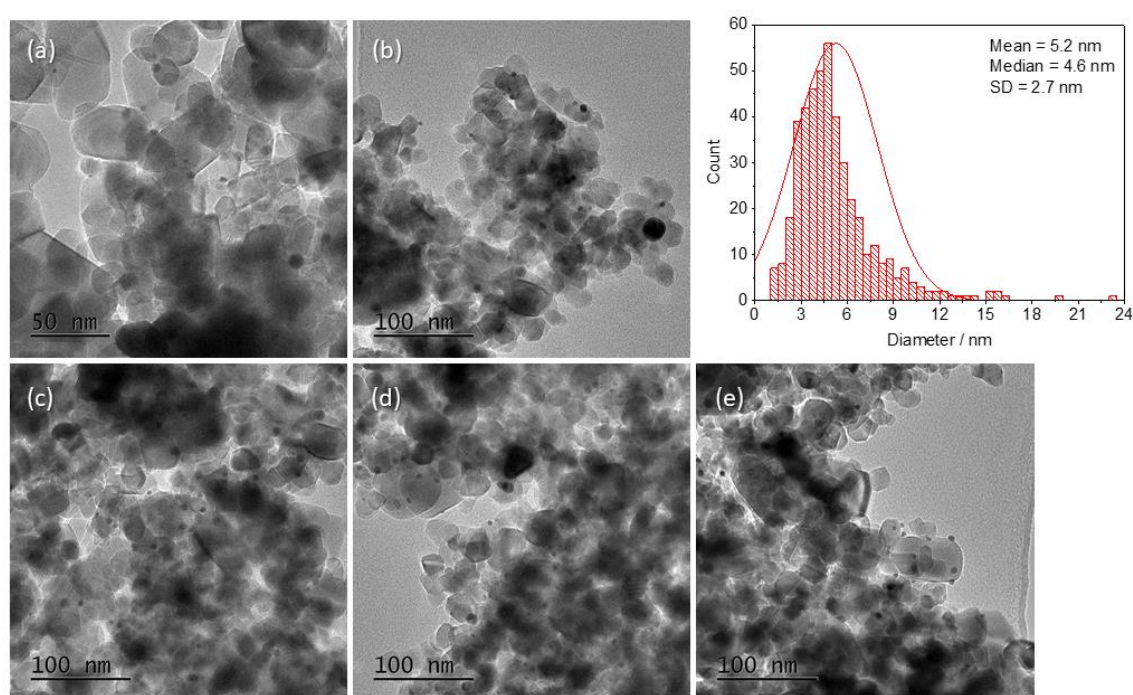

Figure 1. Representative HRTEM micrographs (a-e) and corresponding particle size distribution for the 1.7 wt. % Au/TiO$_2$ WGC catalyst. The particle size distribution (PSD) histogram was constructed based upon 451 nanoparticles using ImageJ software package.

The catalyst was then used for T_1 and T_2 NMR relaxation time measurements. A typical set of data for T_1 inversion recovery and T_2 Carr-Purcell-Meiboom-Gill (CPMG) NMR spectra is shown in Figure 2. Despite the broadening of the NMR lineshapes, it is still possible to distinguish important features of the NMR spectrum. This is not always possible for liquid mixtures in porous catalysts, especially relatively viscous solutions such as aqueous glycerol, as the line broadening can sometimes be quite significant so that different resonances are not distinguishable. However, the Au/TiO$_2$ catalyst used here appears to yield rather well-resolved spectra, which is in agreement with what has

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previously been observed when studying other reactions in the same type of catalysts.[14, 19] This also suggests that the use of Au/TiO$_2$ catalysts is particularly suitable for NMR studies, especially those that benefit from well-resolved NMR spectra.
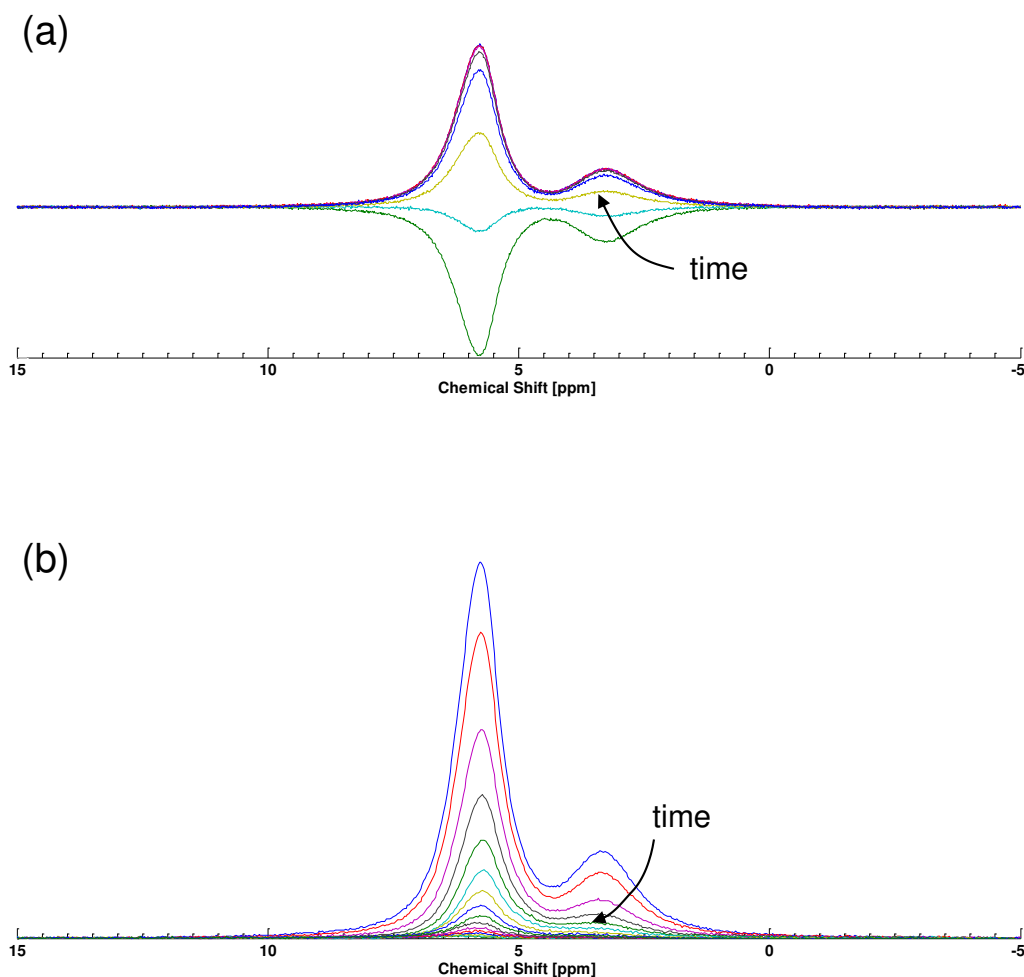
(a)

(b)

Figure 2. NMR spectra during (a) T_1 inversion recovery and (b) T_2 CMPG experiments of glycerol/water in Au/TiO$_2$ catalyst. In each experiment, different spectra are acquired as a function of time delay. The aliphatic region of glycerol at approximately 3.4 ppm can be clearly distinguished.

The peak at approximately 3.4 ppm corresponds to the aliphatic resonance of the glycerol molecules and can therefore be used in order to unambiguously quantify the rate of inversion recovery, Figure 2a, and CPMG decay, Figure 2b, and hence determine T_1 and T_2 relaxation times, respectively, of the glycerol molecules inside the catalyst, similarly to previous studies on diol solutions.[14, 19] The peak at 5.7 ppm, which is a typical chemical shift value for hydroxyl groups, is assigned to the various hydroxyl

moieties present in glycerol, water as well as NaOH. It is noted that, as the catalyst is pre-treated with solutions containing relatively small amount of additives, the total NMR signal will also include such a contribution. However, this will be negligible compared to the signal due to the aqueous glycerol solution.

The inversion recovery curves of the T_1 relaxation measurements of aqueous glycerol within the Au/TiO$_2$ are shown in Figure 3 for the case of no additive and catalyst pre-treated with solutions of 2-butanol and acetone as additives. Similar plots are observed for other additives. In all cases, the T_1 curves are very similar for the different additives, which implies that the rotational dynamics of glycerol in solution within the catalyst is not particularly influenced by the type of inhibitor that is still present on the surface.[18] Indeed, whilst generally T_1 depends mainly on rotational and to some extent translational dynamics,[21] for frequencies $\geq$ 300 MHz, such as the case of this work, modulation by rotational dynamics is the dominating relaxation mechanisms.[22]

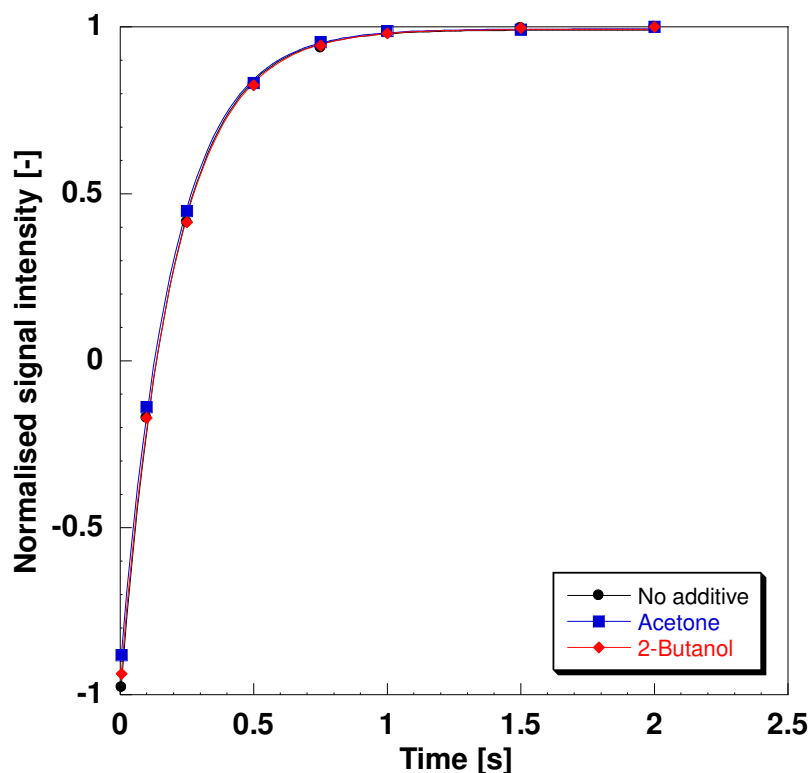**Figure 3.** T_1 inversion recovery plots for glycerol in glycerol/water solutions adsorbed within the Au/TiO$_2$ catalyst without additive and pre-treated with additives.

Conversely, the T_2 CPMG decay curves, shown in Figure 4, show a difference that can be clearly appreciated by looking at the figure. Measurements were repeated showing good reproducibility. At this point it is worth noting that it has been suggested that

whilst T_1 is often considered to be an indicator of the overall pore structure, T_2 reflects local pore geometry and surface chemistry.[23] In addition, it has been suggested that T_2 reflects mainly changes in translational dynamics.[22] In the case under investigation, the overall pore structure is likely to remain similar in all cases (i.e., the same Au/TiO_2 catalyst is used in all experiments) but the pre-treatment with additives will change the local nature of the surface and its adsorption properties; such local changes at the surface may therefore affect translational dynamics of glycerol molecules over the surface, which reflects in the T_2 changes observed in the presence of different additive pre-treatments. This may explain well the data reported here and indicates that these types of measurements are sensitive to small changes in the nature of the surface.
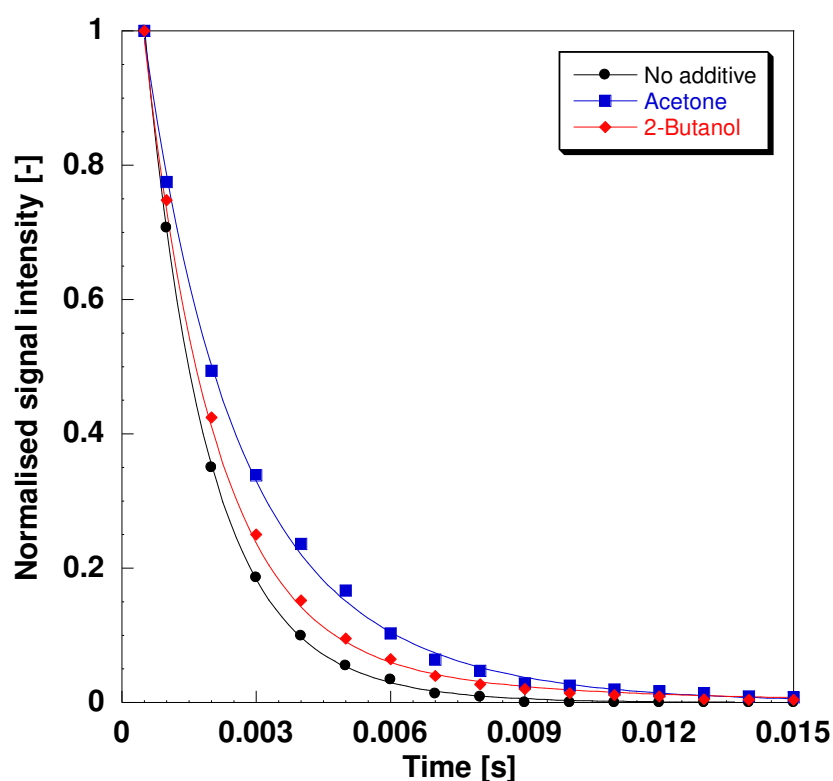

Figure 4. T_2 CPMG decays plots for glycerol in glycerol/water solutions adsorbed within the Au/TiO_2 catalyst without additive and pre-treated with additives.

By visual inspection of Figure 4, it is possible to see that the T_2 plot of glycerol in the absence of additives decays much faster than in the case of additives, such as acetone. It is important to note that whilst single values of T_1 and T_2 can depend on several parameters, such as the degree of pore filling and surface-to-volume (S/V) ratio, the T_1/T_2 is independent of these aspects and hence a more robust indicator of surface interactions. This aspect has been previously discussed in more details.[16, 18]

From the data reported in Figure 3 and Figure 4, it is possible to obtain the T_1/T_2 ratio of glycerol in aqueous solution within the fresh catalyst, without any additive, and the catalyst pre-treated with additive solutions. These values are reported in Table 1.

Table 1. Values of the T_1/T_2 ratio of glycerol within Au/TiO$_2$ catalyst pre-treated with the different additive solutions.

Additive	T_1/T_2 [-]
No additive	129 ± 4
Glycolic acid	118 ± 4
Propionic acid	117 ± 4
Methanol	117 ± 4
Malonic acid	107 ± 3
2-Butanol	100 ± 3
Tartaric acid	89 ± 3
Gluconic acid	85 ± 2
Acetone	80 ± 2

Changes in T_1/T_2 of liquids in porous materials are associated with change in rotational and translational dynamics.[24] In particular, an increase of the T_1/T_2 ratio is associated to an increased barrier for surface diffusion of molecules, which reflects the strength of surface interaction.[18, 25] Such measurements have been successfully used to explain a series of interesting phenomena in heterogeneous catalysis, including solvent effects,[14, 19] mechano-chemical changes of the surface[26] and size of metal nanoparticles deposited over the support surface.[17]

The values of the T_1/T_2 ratios in Table 1 are comparable in order of magnitude to those reported for the same molecule on similar Au/TiO$_2$ catalysts.[17] It is noted that in the

absence of additives, the T_1/T_2 ratio of glycerol is 129, which is higher than when any additive is present. As additives are introduced, the T_1/T_2 ratio of glycerol decreases. Such a decrease is particularly significant when acetone and gluconic acid are used. These results suggest that pre-treatment with additives changes the surface properties and may inhibit the adsorption strength of glycerol compared to the additive-free case. The different additives interact with the catalyst surface and may adsorb or react onto the surface by blocking the accessibility of glycerol molecules to reactive sites. This, in turn, will affect the relaxation times of glycerol, when this is introduced in the catalyst pores. In particular, the higher the inhibition caused by the additives, the lower the strength of surface interaction of glycerol.

It is now of interest to compare the relaxation results reported here to the catalytic data reported by Zope and Davis[13] when performing glycerol oxidation in aqueous solutions, with and without the same additives used in this study, within the same Au/TiO$_2$ catalyst. A plot of the T_1/T_2 ratio reported in this work against the TOF of glycerol reported by Zope and Davis[13] with and without additives, is reported in Figure 5.
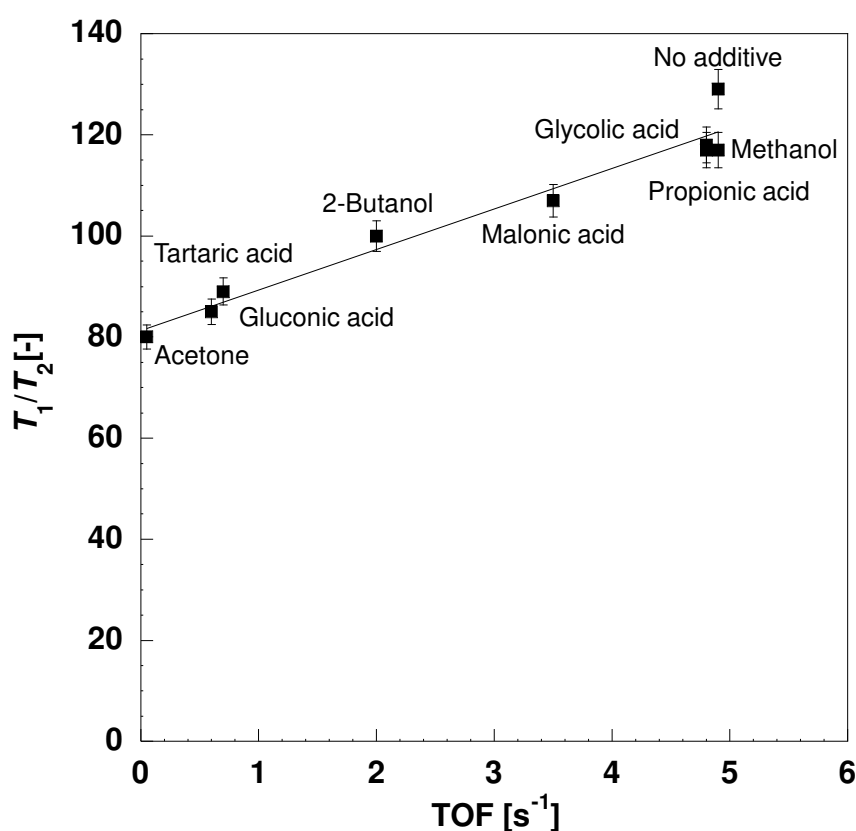

Figure 5. T_1/T_2 ratio of glycerol in the glycerol/water solution adsorbed within the Au/TiO$_2$ catalyst in the absence and presence of additives versus the turn-over frequency (TOF) for glycerol reported by Zope and Davis.[13] The solid line is a linear fit through the data and represents a guide to the eye.

From visual inspection of Figure 5 it is clear that the T_1/T_2 ratio of glycerol traces out the reaction rate with different additives remarkably well, which demonstrates that different additives inhibit the adsorption of glycerol over the gold catalyst surface to a different extent, which in turn affects the reaction rate. The data reported here provide a direct and quantitative experimental evidence of the inhibition of glycerol adsorption, which agrees very well with the data reported by Zope and Davis[13] and suggests that NMR relaxation measurements can be a useful indicator to quantify product inhibition in heterogeneous catalysis in terms of adsorption strength.

Conclusions

NMR relaxation time measurements have been previously used to study the strength of surface interactions of various liquids in porous catalysts. In this work, this methodology was used for the first time to assess product inhibition in liquid-phase catalysis, by investigating relaxation time properties of glycerol in aqueous solutions within a porous Au/TiO$_2$ catalyst, initially pre-treated with various additive solutions (products and intermediates of aerobic liquid-phase catalytic oxidation of glycerol). The results suggest that various additives affect the adsorption strength of glycerol to a different extent, showing that when the glycerol adsorption strength is higher, then a higher reactivity is also observed, and vice-versa. The data highlight the usefulness of NMR relaxation techniques to non-invasively probe the strength of surface interaction of substrates in solutions within catalysts materials. This experimental approach, which exploits the use of NMR relaxation times, can be a useful tool in order to rapidly screen catalysts and rationalise this type of liquid-phase catalytic processes.

Acknowledgements

Supporting Information

Elemental analysis of the Au/TiO$_2$ catalyst used in this work.

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