NMR relaxometry studies of adsorbate-catalyst interactions

D Weber, J Mitchell, J McGregor*, Z Huang and LF Gladden
[1]*Univeristy of Cambridge, Department of Chemical Engineering and Biotechnology, Cambridge CB2 3RA (UK)*
**jm405@cam.ac.uk*

Introduction

NMR relaxometry techniques have been applied to the study of the interaction of reactants and solvents with catalyst surfaces. These measurements provide insights into the relative strength of interaction of co-adsorbed species and the geometry occupied by molecules upon adsorption. Understanding such interactions is fundamental in all areas of heterogeneous catalysis, and facilitates the development of new catalysts and catalytic processes. Many and varied techniques have been developed in this area, ranging from computational methods, through surface science to macroscopic engineering approaches [1,2]. In this work we present developments and new applications of NMR relaxometry methods that are capable of providing insight into adsorbate-adsorbent interactions involving real catalytic materials. This is demonstrated through their application to the hydrogenation of methyl-ethyl ketone (MEK), and the reactions of alkenes on supported-metals catalysts.

Materials and Methods

1 wt. % Ru/SiO_2, 1 wt. % $Pd/\theta\text{-}Al_2O_3$, and $\theta\text{-}Al_2O_3$ (Johnson Matthey) were employed as adsorbates. Prior to all experiments, the pellets were soaked in the respective liquid-phase adsorbates for at least 12 h. NMR relaxation time correlation measurements were performed using the experimental procedure outlined elsewhere [3]. All other NMR relaxation time measurements were performed using a standard inversion recovery sequence.

Results and Discussion

The differing strength of interaction of molecules with a catalyst surface, and the changes in this interaction that occur in the presence of a co-adsorbed reactant or solvent, are key in dictating catalytic activity [2]. We have applied two-dimensional T_1-T_2 NMR relaxation time correlation measurements, ^{13}C NMR relaxometry and ^{1}H relaxometry techniques in order to develop a fundamental understanding of such interactions.

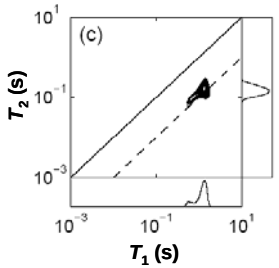

Figure 1. T_1-T_2 correlation plot for MEK in Ru/SiO_2. Solid diagonal line indicates $T_1 = T_2$.

The liquid-phase catalytic hydrogenation of MEK in a mixed H_2O/IPA solvent has previously been shown to be highly dependent on solvent composition [2]. Two-dimensional NMR relaxation time correlation measurements, shown in Figure 1, reveal that the relative strength of interaction of the three adsorbates in this system, with both Pd/Al_2O_3 and Ru/SiO_2, follows the trend H_2O > IPA > MEK. This trend is more pronounced over Pd/Al_2O_3 which, unlike Ru/SiO_2, does not catalyse the production of 2-butanol under the conditions employed. These results are confirmed by displacement measurements acquired by the same technique. This represents the first application of this technique to a catalytically relevant system.

We have also applied ^{1}H and ^{13}C NMR relaxometry techniques to probe adsorbate/adsorbent interactions. The work of Godefroy *et al.* [4], which examined the interaction strength of oil and water in rocks and other minerals, has been extended to catalytic systems such as the hydrogenation of MEK over supported-metal catalysts. ^{1}H NMR techniques however can only probe global relaxation measurements and therefore do not provide information on the interaction of individual atoms within a molecule. This is because magnetic susceptibility differences throughout the sample contribute to significant line broadening of the ^{1}H resonances. ^{13}C resonances however occupy a much greater chemical shift range. As such, atom specific relaxation information can be acquired, indicative of the interaction of individual carbon atoms with the catalyst surface and therefore of the adsorption geometry of the adsorbed species. This is illustrated in Figure 2, which shows the attenuation of T_1 upon adsorption on $\theta\text{-}Al_2O_3$ for each carbon atom within *cis*-2-pentene. These data confirm that upon adsorption the alkene binds in a di-σ fashion, as expected. The conformation of molecules on a surface can significantly influence their catalytic behaviour. This is particularly apparent in the case of bi-functional molecules where one moiety interacts with the surface and undergoes reaction while the other does not. We are extending this technique to such adsorbates including alkenenitriles, the hydrogenation of which has been the focus of recent research.

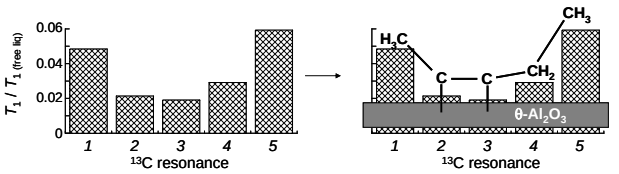

Figure 2. $T_1/T_{1\,(free\ liquid)}$ for *cis*-2-pentene adsorbed on $\theta\text{-}Al_2O_3$. The attenuation of the individual carbon resonances indicate the strength of interaction of each carbon with the adsorbent.

Significance

T_1-T_2 NMR relaxation time correlation measurements have been used to determine the relative interaction strengths between adsorbates and catalysts, with differences observed between different catalysts. Furthermore ^{13}C NMR relaxometry measurements have been shown to be capable of elucidating the adsorption geometry of reactant species. These data provide new insights into the fundamental adsorption processes occurring on the surface of industrial catalysts during reaction. Such understanding allows both for improved predictions of catalyst performance and for a more rational development of new catalytic materials and processes.

References

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