Solvent Effects in the Hydrogenation of Citral: On the role of intrinsic environment of the active site at the molecular level

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Introduction
An understanding of the environment, at the molecular level, of the catalyst active site during reaction is critical in the development of new catalysts and green chemical processes. This includes the surface adsorption/desorption of molecules on the active site and the support, which can interfere with the mechanistic analysis of events to control reaction rates and product selectivity. Recently, using in situ operando techniques we have been able to explain structure-activity relationships in liquid phase reactions. We have shown solvents are not just spectators but important design parameters by investigating the selective hydrogenation of 2-butane, ketosiphorone and cinnamaldehyde [1-2]. The selective hydrogenation of α,β-unsaturated aldehydes is an important reaction in the food, fragrance and pharmaceutical industries; however the presence of multiple functionalities results in complex reaction networks. Herein, the liquid phase hydrogenation of citral was studied and significant enhancement in reaction rate and selectivity to unsaturated alcohols was achieved using 5 wt% Pt/SiO2 catalyst in mixed solvents. We have further shown for the first time the importance of the STOS-ATR-IR spectroscopy technique in the liquid phase combined with neutron scattering analysis and reaction data to develop selective and green chemical process in water/2-propanol as solvent to achieve enhanced rates and high selectivity to α,β-unsaturated alcohols. To the best of our knowledge, there has been no complete study on the role of the structure of mixed solvents, catalyst active site, mode of adsorption geometry and strength to control reaction rate and selectivity to particular products.

Materials and Methods
Hydrogenations were carried out in a 100 cm³ Autoclave Engineers pressure reactor and liquid samples were analysed using a GC. ATR-IR spectra were collected over Pt/SiO2 catalyst films using a PIKE accessory within a Bruker Tensor 27 spectrometer. Neutron scattering data were collected using SANDALS at the ISIS pulsed neutron source at the Rutherford Appleton Laboratory, UK.

Results and Discussion
In the hydrogenation of citral using 5wt% Pt/SiO2, the observed rate and selectivity to unsaturated alcohols (geraniol and nerol) increased with water mole fraction (xH2O) in water/solvent mixtures. A significant jump in the intrinsic reaction rate and selectivity (98% to geraniol and nerol) was observed for high water fractions (x ≈ 0.9) indicating that solvent structure was playing a key role in the reaction mechanism (Fig. 1a). The structural analysis of the 2-propanol/water mixtures performed with neutron scattering showed that extent of the degree of hydrogen bonding varied with the composition of the mixture. A mixed 2-propanol/water mixture is more structured than either of the components individually, with the highest degree of structuring occurring at x ≈ 0.90 water. EPSR analysis indicates that there are there are ~1.38 hydrogen bonds per 2-propanol molecule bonded to 2-propanol and water molecules at x ≈ 0.9 which is slightly higher than pure 2-propanol. In this study, we have shown a good correlation between the enhanced structure of solvent mixtures and extent of hydrogen bonding at the molecular level with an increased reaction rate and selectivity in the liquid phase hydrogenation of citral. In a set of separate experiments, hydrogenation of citral was performed by spiking the reaction mixture with citronellal. Citronellal competitively adsorbed on the catalyst surface, as verified by adsorption isotherms, and enhanced the rate and selectivity to C=O hydrogenation. STOS-ATR-IR spectra probing the perturbation in citral adsorption following pre-adsorption of citronellal showed that there is the loss of the band at 1394 cm⁻¹ (aldehyde C-H rock). The absence of the band associated with the aldehydic C-H suggests that the C=O group is adsorbing. Comparing the STOS-ATR-IR spectra of citral adsorption 81 s and 4 min after introducing citral/2-propanol to the Pt/SiO2 catalyst it is evident that adsorbed citronellal alters the interaction of citral by enhancing equilibrium citral amount adsorbed and changing the mode of adsorption. This is consistent with the higher selectivity to geraniol/nerol observed in the reaction spiked with citronellal.

![Figure 1](https://via.placeholder.com/150)

**Figure 1.** (a) the initial reaction rate of citral hydrogenation with respect to varying mole fraction of water, (b) the site-site oxygen oxygen partial radial distributions, for 30 mol% 2-propanol/water (dashed lines) and 90 mol% 2-propanol/water (solid lines) (c) STOS-ATR-IR spectra of 0.1 M citral in 2-propanol over Pt/SiO2 (grey spectra) and CO-Pt/SiO2 (black spectra) after (a) 81 s for Pt/SiO2 and 108 s exposure for CO-Pt/SiO2 and (b) 4 min exposure. ◎ bands due to citral adsorbed on support and * bands due to citral adsorbed on Pt.

Significance
By considering the structure and degree of hydrogen bonding of the solvent mixtures, it is possible to design a green process with significantly enhanced reaction rates and selectivity to the desired products. It was possible to switch the hydrogenation between C=O bond and C=C double bond by modifying the catalyst surface by spiking with citronellal or citronellol at the start of the reaction through modification of the mode of adsorption of citral.

References