**Defecting metal oxides with light to boost their oxidative capacity**

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Introduction

Defects in ordered materials are often a source of unexpected phenomena which, from a catalytic perspective, can take on the form of catalyst activity and/or product selectivity. Noble or transition-group metals are often utilised as heterogeneous catalysts while defects in metal oxides can also exhibit catalytic properties in some instances, removing the need for these metals. Surface defects in metal oxides can be generated in various ways by using thermal reduction, light treatment or doping. In this work, we employ a combination of reductive and UV light pre-treatments on simple TiO2/SiO2 composites to induce multiple defect sites which work in harmony to promote a catalytic dehydrogenation reaction.

Methods

Flame spray pyrolysis (FSP) was used to prepare a suite of binary TiO2/SiO2 composites with varying Ti:Si ratios. The composites were then reduced in hydrogen at 500°C where, depending on the Ti:Si ratio, they turned a blue colour which was stable. The samples were then treated with UV light (aqueous phase) for 30 min and assessed for their capacity to dehydrogenate formic acid (aqueous phase) under non-illuminated (dark) conditions. Reaction conditions: (i) solution volume = 50mL, (ii) initial fomic acid loading = 1000μmol; (iii) catalyst loading = 1g/L; (iv) solution pH = 3.0±0.05.

Results and Discussion

When reduced and pre-treated with UV light the TiO2/SiO2 exhibited a synergy in terms of dehydrogenation performance, with the greatest benefit delivered for a Ti:Si ratio of 9:1 (Fig. 1)1. The synergy was found to derive from the formation of two adjacent defects, which were different in nature, with each site generated by the two distinct pre-treatments. The hydrogen reduction step served to cleave Ti-O-Si bonds leaving a Ti3+ vacancy next to a silanol (Si-OH) group. UV light pretreatment then served to deprotonate the silanol group to give a non-bridging oxygen hole centre (NBOHC) defect (Si-O•). Combined, these sites were able to dehydrogenate formic acid under ambient, non-illuminated conditions.

**Fig. 1.** 50% mineralisation rate (R50) for formic acid oxidation by binary TiO2-SiO2 catalysts without UV light pre-treatment (grey) and following 30 min UV light pre-treatment (red). Suspension volume = 50mL; catalyst loading = 1g/L; suspension pH = 3±0.05; initial formic acid loading = 1000μmol.

Conclusion

The work demonstrates how light pre-treatment can be used to induce catalytic activity in simple metal oxide systems to produce an inexpensive and abundant catalyst material.

**References**

1. Saputera, W., Tahini, H., Sabsabi, M., Tan, T., Bedford, N., Lovell, E., Cui, Y., Hart, J., Friedmann, D., Smith, S., Amal, R. & Scott, J. (2019). Light-induced synergistic multi-defect sites on TiO2/SiO2 composites for catalytic dehydrogenation, ACS Catal., 9, 2674-2684.