Structure activity relations in solid base catalysed biodiesel synthesis

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Introduction

Biodiesel is synthesised from plant oils via a liquid base catalysed transesterification of C_{14}-C_{18} triglycerides (TAGs) to their respective fatty acid methyl esters (FAMEs).[1] These soluble catalysts are problematic as their removal necessitates an energy intensive separation to purify biodiesel. To improve process efficiency and eliminate the need for a quenching step we have previously developed a range of tuneable solid bases including Li/CaO, Mg-Al hydrotalcites and Mg/CaO catalysts which exhibit excellent activity for TAG transesterification[2] and can also operate in a continuous reactor. The effects of solid base strength on catalytic activity in biodiesel synthesis however remains poorly understood, hampering material optimisation and commercial exploitation. In order to improve our understanding of factors influencing solid base catalysts for biodiesel synthesis, we have applied a simple spectroscopic method for the quantitative determination of surface basicity which is independent of adsorption probes. Here we report on a systematic study of the relationship between the activity of MgO nanocrystals in biodiesel synthesis and their basicity.

Materials and Methods

A family of nanoparticulate MgO catalysts were prepared from a methoxide precursor which was synthesised by hydrolysis of a 10 wt% solution of magnesium methoxide in methanol in the presence of toluene.[3] The resulting sol was transferred to an autoclave, pressurised to 100 psi N_2, heated to supercritical conditions at 265 °C then vented to leave a dry powder. The resulting white powder was dried in an oven at 120 °C for 2 h and calcined at 300-700 °C under a flow of helium gas. X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) were performed on a Kratos AXIS HSi X-ray photoelectron spectrometer using a monochromatic Al K_α X-ray source.

Results and Discussion

The structural properties of NanoMgO was first analysed by a combination of XRD HRTEM which revealed the parent material consists of small randomly aligned cubic crystallites which appear free of obvious defects and low index (100) terraces. Calcination eliminates results in increasingly large cuboidal crystals. On calcining at 500°C erosion of the cubic structure is observed close to the crystallite boundaries with steps and corner sites becoming visible. Both (111) and (110) planes are present in NanoMgO-500 and NanoMgO-700 as illustrated in **Figure 1a**. The experimentally observed surface terminations for (111) and (110) facets suggest that such restructuring should expose more defective, electron-donating O^{2-} centers, postulated as superbasic sites in solid base catalysis.

Oxygen 1s XP and AES measurements were subsequently used to confirm this hypothesis. Insight into the electronic properties of the surface oxide can be obtained by combining this information into the Auger parameter (α), where α = Kinetic energy (O KLL Auger electron) + Binding energy (O 1s XP electron). An *increase* in α relative to gaseous H_2O (α = 1038.5 eV), and a corresponding *decrease* in the oxide O $KL_{23}L_{23}$ and O KL_1L_{23} Auger separation (DE_k), are indicative of increasing surface polarisability, and thus provide a quantitative measure of Lewis basicity.[4] α and DE_k both predict an increase in MgO surface base strength accompanying crystallite growth and the transformation from regular (100) to stepped (110) facets. The relationship between catalyst structure and performance in TAG transesterification is revealed in **Figure 1b**. Turnover frequencies correlate directly with the surface polarisability parameters DE_k, revealing a striking linear correspondence between the catalytic activity and surface basicity of MgO nanoparticles.[5] This combination of atomic resolution TEM and surface sensitive photoelectron spectroscopies reveals low coordination MgO surfaces as the most active for biodiesel synthesis.

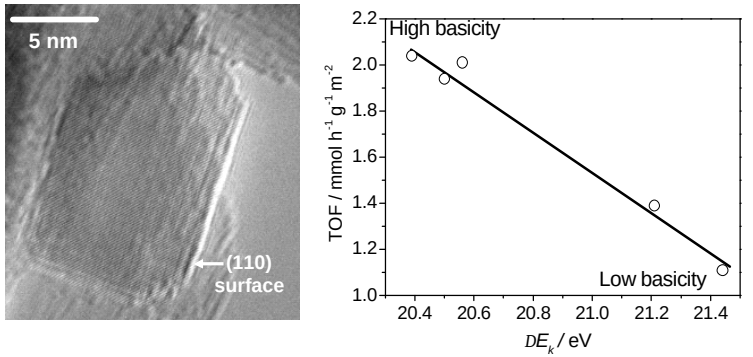

Figure 1. (left) MgO nanocrystal; (right) correlation between Auger parameter determined base strength and TOF in transesterification.

Significance

Auger parameter measurements allow a non-invasive method to quantify surface basicity, and thereby rationalise the catalytic activity of MgO nanoparticles in TAG transesterification, paving the way to rapid screening of new MgO formulations for practical biodiesel synthesis.

References

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