

Chemical layer deposition of porous alumina overcoats increases activity and stability in liquid phase catalytic conversion of biomass-derived chemicals

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Biomass-derived chemicals represent an attractive sustainable alternative to petrochemicals. However, the competitiveness of these processes has been limited by the low stability of metal catalysts under the severe conditions used during biomass upgrading. In order to prevent metal leaching and sintering, we developed a chemical layer deposition (CLD) overcoating technique based on the control over aluminum alkoxide surface reactions kinetics and stoichiometry. After deposition of 30 cycles of an alumina overcoat onto alumina supported copper nanoparticles, imaging using high angle annular dark field scanning transmission electron microscopy (HAADF STEM) revealed a conformal porous overcoat. This porosity was characterized and quantified by nitrogen physisorption. The overcoat suppressed irreversible catalyst deactivation during the liquid-phase hydrogenation of furfural. While a significant loss of activity due to mass transfer limitations and metal coverage by the overcoat was observed by O'Neill *et al.* when using atomic layer deposition (ALD),² most of the surface metal sites remained accessible with CLD as confirmed by chemisorption, illustrating the benefits of overcoats porosity that can be targeted by tuning synthesis parameters. Current work is focused on tuning this porosity for the synthesis of shape selective catalyst overcoats.

[1] Héroguel, F.; Rozmysłowicz, B.; Luterbacher, J. S., *Chim. Int. J. Chem.* **10** (2015), 582-591.

[2] O'Neill, B. J.; Jackson, D. H. K.; Crisci, A. J.; Farberow, C. A.; Shi, F.; Alba-Rubio, A. C.; Lu, J.; Dietrich, P. J.; Gu, X.; Marshall, C. L.; Stair, P. C.; Elam, J. W.; Miller, J. T.; Ribeiro, F. H.; Voyles, P. M.; Greeley, J.; Mavrikakis, M.; Scott, S. L.; Kuech, T. F.; Dumesic, J. A. *Angew. Chem.*, **51** (2013), 14053-14057.