BIOMASS VALORIZATION

Catalysis makes sweet spirit

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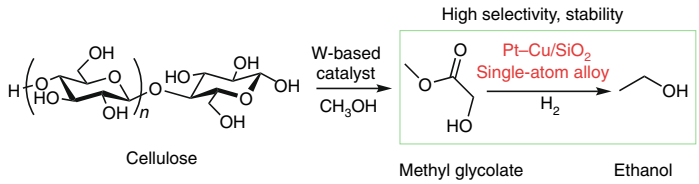

Chemocatalysis holds great promise as a practical alternative to fermentation for the synthesis of cellulosic ethanol. However, the most successful examples are still characterized by limited selectivity, and often the employed catalysts show poor stability, preventing commercial applications. Now, Aiqin Wang, Tao Zhang and co-workers reported a strategy for the conversion of cellulose into ethanol that specifically addresses such issues.

In a previous publication, the group had developed a two-step process relying on a tungsten-based catalyst to transform cellulose into methyl glycolate, followed by a successive hydrogenation to ethanol using Cu/SiO_2 as the catalyst. Nevertheless, methyl glycolate hydrogenation was achieved with only 50% selectivity, affording ethanol in low overall yield. In the present study, the authors alloyed single platinum atoms with copper in order to tune the properties of the hydrogenation catalyst (pictured). A combination of X-ray diffraction techniques and transition electron microscopy analyses revealed that the introduction of very small quantities of platinum — 0.1 to 0.06 wt% — significantly increased copper dispersion, as observed while screening a series of catalysts with increasing platinum content. In addition, platinum promoted the reduction of copper(II) oxide leading to a higher Cu^+/Cu^0 ratio in the material, as confirmed by diffuse-reflectance infrared fourier-transform (DRIFT) spectra of chemisorbed CO as well as XPS spectroscopy. As a consequence, 0.1 wt% $Pt–Cu/SiO_2$ converts methyl glycolate into ethanol with around 80% selectivity, and eightfold higher turnover frequencies compared to Cu/SiO_2.

Moreover, the catalyst also shows a tremendous improvement in lifetime as demonstrated by time on stream experiments run over several days. According to the proposed mechanism, the increased number of Cu^+ sites enhances the cleavage of C–O bonds within methyl glycolate. In addition, platinum, in the form of single atoms, promotes hydrogen activation while minimizing C–C cleavage paths that usually occur on larger nanoparticles. The work showcases how catalyst engineering can significantly improve existing strategies for biomass valorization, and reveals the potential of single-atom alloys within strategies for the production of renewable chemicals.

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