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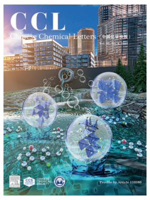

Editorial

Tailoring interatomic active sites for highly selective electrocatalytic biomass conversion reaction

The quest for sustainable energy solutions has intensified the search for alternative feedstocks that can supplement or replace fossil fuels. Obtaining fuels or chemicals through the conversion of renewable biomass is a promising candidate [1,2]. Some noble-metal-based (*e.g.*, Pt, Pd and Rh) catalysts exhibit significant catalytic activity to the conversion reaction of these biomass. The precise conversion of different groups in the biomass is a key issue due to the complexity of the substrates. Lignin, a complex organic polymer found in lignocellulosic biomass, represents an abundant and renewable resource with the potential to serve as a precursor for a variety of chemicals and materials (*e.g.*, coumarin, coniferyl alcohol and ketone-alcohol oil) [3]. However, the efficient conversion of lignin and its derivatives into valuable products is hindered by the cleavage of the pervasive C–O bonds. For example, the etheric C–O(R) bonds (409 kJ/mol) and hydroxylic C–O(H) (466 kJ/mol) bonds have similar bond energies, making it difficult to selectively produce a single product [4]. Developing catalysts capable of selectively activating and breaking these C–O bonds is a critical step towards the valorization of lignin.

Recently, Prof. Buxing Han and his colleagues investigated some representative mesoporous carbon (MC) supported Pt-Co bimetallic electrocatalysts, including Pt nanoparticles (NPs) decorated with Co single atom sites (SASs; $PtCo_1$/MC), physical mixture of Pt NPs and SASs on MC ($Pt + Co_1$/MC) and other reference catalysts ($Pt_1 + Co_1$/MC, PtCo/MC and Pt_1Co/MC) prepared by varying the aggregation states of the Pt and Co metals in the form of NPs and SASs (Fig. 1a) [5]. The intermetallic interactions between Pt and Co species are finely tuned through different aggregation states of these two metals to catalyze the hydrodeoxygenation (HDO) of guaiacol (lignin monomer) through different pathways (Figs. 1b and c). Among these catalysts, the Pt-Pt coordination structure in Pt NP serves as the main aromatic ring hydrogenation site, but has poor selectivity of the cleavage of the C–O bonds, while the Pt/Co SASs show no HDO activity. Electrochemical tests reveal that $PtCo_1$/MC exhibits an efficient hydrogenation of the aromatic ring of guaiacol and affords the desired cleavage of the C–O(H) bond with most of the C–O(CH_3) bond retained, leading to the highest selectivity of methoxycyclohexane of 72.1% at −70 mV versus a reversible hydrogen electrode (RHE) and a maximum methoxycyclohexane yield rate of $19.3\ \text{mmol}\ \text{h}^{-1}\ \text{g}_{\text{cat}}^{-1}$, which was respectively 48.3, 14.5 and 66.6 times higher than those of Pt/MC, $Pt + Co_1$/MC and PtCo/MC catalysts (Fig. 1d). The controlled experiments of different aggregation states catalysts prove that the concrete Pt-Co coordination derived from the decoration of Co SASs on the Pt NPs in the $PtCo_1$/MC catalyst is the critical factor towards high selectivity since this intermetallic interaction helped the Co atoms to afford the capture of electrons by O atoms, which enhances the adsorption capacity for oxygen-containing reactants, especially hydroxyl oxygen. Such a suitable Pt-Co interaction facilitated the adsorption and activation of the C–O(H) bond on the $PtCo_1$ sites, which consequently retained the C–O(CH_3) bond during the HDO process.

Further *in situ* Raman spectroscopy and density functional theory (DFT) calculations demonstrated that the hydrogenation on the OH–C=C or C=C–OCH_3 species of the critical intermediate 2-methoxycyclohex-1-enol is the rate-determining step of the HDO reaction of guaiacol (Fig. 1e). The high selectivity of $PtCo_1$/MC catalyst lies in the fact that the hydroxyl–derived O atom and ethylene-bond-derived C atoms of intermediate coordinated with the Co SAS and its adjacent Pt sites, which enriched the electrons on the Pt sites and spontaneously fed some electrons back to the Co SAS. This electron feedback enhanced the coordination of the positively charged Co SAS with the hydroxyl–derived O atom in the unsaturated OH–C=C–OCH_3 structure, and such electron transfer lengthened the C–O(H) bond and lowered its activation energy, which facilitated the preferential cleavage of the C–O(H) bond over the Pt NP sites (Fig. 1f). Driven by this mechanism, the $PtCo_1$/MC catalyst also exhibits high selectivity for the cleavage of C–O bonds in other biomass-derived substrates with different functional groups.

In summary, the encouraging work by Prof. Buxing Han and colleagues has successfully demonstrated the feasibility of producing ether chemicals from renewable lignocellulosic biomass feedstock through the selective cleavage of C–O bonds. This study demonstrates the potential of optimizing reaction selectivity by regulating intermetallic interactions. Such a relationship between the catalyst

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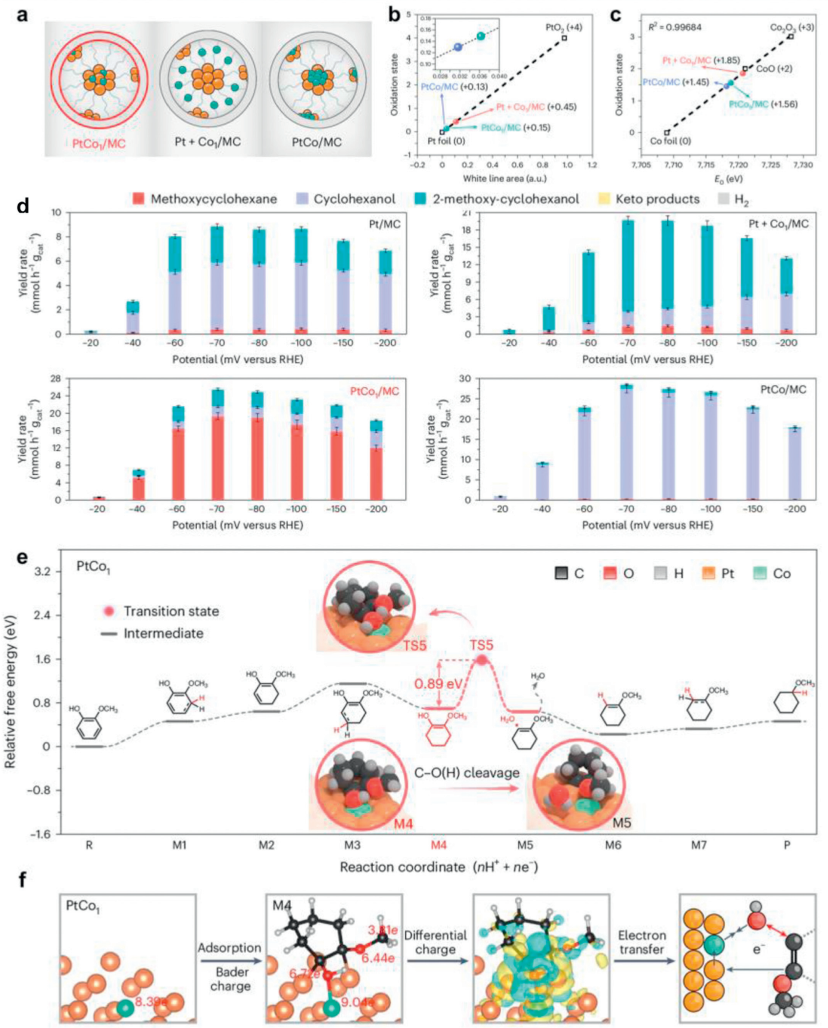

Fig. 1. (a) Schematic of prepared catalysts. (b) Calculated Pt valence states from the difference in X-ray absorption near-edge structure spectra of the Pt + Co_1/MC, $PtCo_1$/MC and PtCo/MC catalysts in (c) The fitted average oxidation states of Co species in the Pt + Co_1/MC, $PtCo_1$/MC and PtCo/MC catalysts. (d) The yield rate of products on Pt/MC, Pt + Co_1/MC, $PtCo_1$/MC and PtCo/MC catalysts under different current densities. (e) DFT calculations of the HDO pathway for the reaction of guaiacol on $PtCo_1$ catalyst. (f) Bader charge and differential charge density analyses for the adsorption of the OH−C=C−OCH_3 structure on $PtCo_1$ catalyst, and the proposed electron flow in the coordination environment of the (C)=C-$PtCo_1$−O(H)-C configuration. Yellow and cyan isosurfaces show the accumulation and depletion of electron densities, respectively. Reprinted with permission [5]. Copyright 2024, Springer Nature.

structure and reaction performance should be further explored, especially for catalysts with other structures (*e.g.*, high entropy alloys and intermetallic alloys), to regulate the catalytic selectivity towards different functional groups and enable the green and efficient synthesis of a broader range of chemicals.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Xuan Liu: Writing – original draft. **Qing Li:** Writing – review & editing, Writing – original draft, Supervision.

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