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Chem Catalysis
Previews

Molecular water provides a channel for communication between Brønsted acid sites in solid catalysts

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Solvent molecules play important mechanistic roles in catalytic reactions, such as the formation of molecular channels and networks to enable communication between spatially isolated active sites. In this issue of *Chem Catalysis*, Resasco and colleagues discuss how molecular water delocalizes proton sites from acidic functional groups grafted on a mesoporous silica support, thus facilitating dual-site elementary steps that lead to increased turnover rates of cyclopentanone condensation.

Chemical reactions commonly involve interactions between reacting species formed at different active sites. In homogeneous catalysis, fluid-phase diffusion mechanisms allow reactive complexes formed at different active sites to interact with each other. By contrast, such interactions in heterogeneous catalytic solids often require surface-diffusion mechanisms to be operative or active sites to be situated in proximity at the reactant length scale. Solvent molecules, however, can form molecular networks and channels that are capable of bridging adjacent active sites to enable inter-site communication. Water molecules can assist chemical reactions through phenomena such as remote bond polarization and H-atom shuttling,[1] and alkanol molecules can form H-bonded clusters and networks to stabilize cationic intermediates and transition states formed at proximal acid sites in zeolites to increase turnover rates of alkanol dehydration reactions.[2] In their prior work, Resasco and co-workers studied cyclopentanone condensation on mesoporous silica-based MCM-41 materials containing sulfonic acid groups at varying site densities, reporting that catalysts with higher acid site density showed turnover rates that followed Langmuir-Hinshelwood (LH) kinetics involving reactions between two adsorbed cyclopentanone molecules on adjacent acid sites, whereas catalysts with lower acid site densities showed turnover rates that followed Eley-Rideal (ER) kinetics involving reactions between one adsorbed cyclopentanone and a second liquid-phase cyclopentanone molecule.[3] Importantly, adding small amounts of water to the cyclohexane solvent increased reaction rates to the greatest extent on the catalyst of lowest acid site density and resulted in a change to its rate expression from one that followed ER kinetics to one that followed LH kinetics instead, leading the authors to hypothesize that an important mechanistic role of water was to bridge distant active sites on the catalyst surface and increase turnover rates.

In this issue of *Chem Catalysis*,[4] Resasco and colleagues further explore this hypothesis of water-assisted inter-site communication through a combination of catalyst synthesis, reaction kinetics, spectroscopy, and computational modeling to provide mechanistic evidence that water acts as a bridge between acid sites by delocalizing protons on the nanometer length scale. Kinetic measurements on MCM-41 samples with widely varying (∼10×) acid site densities revealed the complex dependence of water promotion of reaction rates as a function of the acid site density (Figure 1). This promotional effect of water displays a maximum with respect to acid site density: it is attenuated at the highest site densities (HD) because acid sites are inherently in close proximity and nearly always able to communicate with one another and attenuated at ultra-low site densities (UL) because acid sites are situated too far apart and largely unable to communicate with one another, yet it is prominent at intermediate site densities (LD) because water facilities short-range proton delocalization to facilitate dual-site reaction mechanisms. The presence of water in higher concentrations causes cyclopentanone condensation rates to decrease, however, which is attributed to competitive cyclopentanone and water adsorption at acid sites. Density functional theory and *ab initio* molecular dynamics simulations probed the proton mobility as a function of the extent of water clustering around active sites, finding that sufficiently large clusters (>3 H_2O) delocalize protons up to two water molecules away from associated anionic binding sites, consistent with kinetic observations (Figure 1). These simulations suggest that protons are not delocalized in the absence of water, precluding mechanisms for inter-site communication on catalyst surfaces containing intermediate site densities.

The authors also used solid-state nuclear magnetic resonance (NMR) and *in situ* infrared (IR) spectroscopic measurements to observe the clustering of water molecules in H-bonded networks at hydrophilic SO_3H and Si-OH groups as well as the attenuation of such clustering when hydrophilic Si-OH groups

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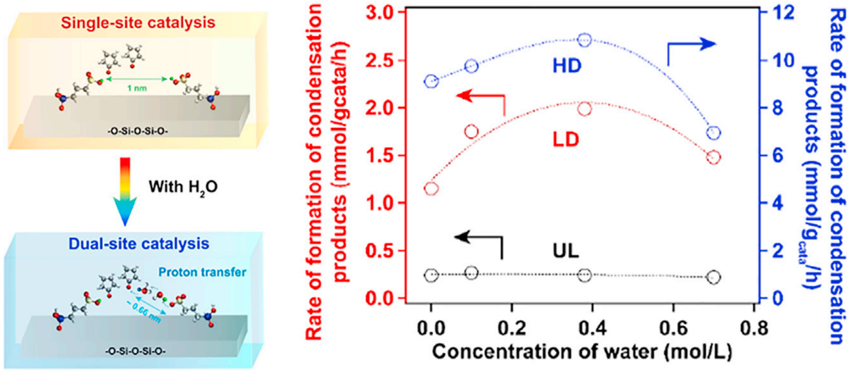

Figure 1. Water-induced enhancements of cyclopentanone condensation rates depend sensitively on the density of acidic SO_3H sites in MCM-41 supports

were replaced with hydrophobic alkyl groups. Water promoted cyclopentanone condensation rates on materials containing C_3 alkyl groups, albeit to a lesser extent than on materials containing a high density of Si-OH groups, suggesting that Si-OH groups assist the formation of H-bonded water networks. Grafting larger (C_8) alkyl groups interfered with water clustering around SO_3H active sites, thus preventing inter-site communication even in the presence of water. Decoupling the effects of solvent polarity and proticity, the authors showed that adding water (polar, protic) in cyclohexane solvent promotes cyclopentanone condensation rates while dimethylsulfoxide (polar, aprotic) does not.

The mechanistic implications of this work regarding active-site solvation and inter-site communication provide numerous opportunities for future research directions in the catalysis community. Sulfonic acid groups were assumed to be distributed homogeneously on the catalyst surface in this work, motivating research into synthetic methods to position active site functions more precisely on catalyst surfaces at desired relative proximity. Characterization methods to identify and quantify active sites separated by various distances on the catalyst surface, including titrations with appropriate probe molecules and kinetic measurements using suitable catalytic probe reactions, would augment the experimental toolkit available to characterize solid catalysts and provide new structural descriptors that can be correlated to catalytic reactivity. Changes to the chemical structure of the acid site functional group would influence their deprotonation energies, which should impact the delocalization and stability of the acid site in the presence of a solvent as has been shown in liquid-phase homogeneous systems,[5] and this could alter the length scale over which inter-site communication occurs. Computational modeling of free energy landscapes with increasing levels of chemical accuracy would provide additional insights into the various mechanisms of solvent-assisted elementary steps. These insights would allow harnessing solvent interactions to control reactivity in solid acids through inter-site communication, beyond their well-documented effects to (1) assist in forming clusters and extended networks that influence reactivity by altering the solvation environment and stabilities of protons, reactive intermediates, and transition states[6] and (2) influence the ionic strength of cation-anion pairs formed between hydrated protons and conjugate base anions in zeolitic voids to influence the rates of acid-catalyzed reactions by altering the energetics of uncharged reactants relative to charged transition states.[7]

In broader contexts, the inter-site communication mechanisms described in this work, wherein proton active sites are solvated into molecular complexes, are reminiscent of metal-zeolite systems wherein solvation by molecules (e.g., H_2O, NH_3) and mobilization of metal cation sites enable catalytic reactions to occur via reversible, dynamic interactions between nominally isolated metal sites.[8] Similar principles of solvent-induced inter-site communication can be extended to connect two active sites of different identity (e.g., acid and base sites) in bifunctional reaction pathways. The report by Resasco and co-colleagues in this issue of *Chem Catalysis* provides another example of a broader theme in heterogeneous catalysis research regarding how solvents provide molecular shuttles to influence intramolecular and intermolecular reactions, including those catalyzed by metal clusters;[9,10] such mechanisms can cause reaction rates to depend on both the density of surface active sites and the solvent environment, thus providing opportunities to influence reactivity and selectivity by modifying catalyst and solvent properties.

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DECLARATION OF INTERESTS

The authors declare no competing interests.

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Electron polarization induced by alloying changes mechanism of NH_3 synthesis from NO_3^- electroreduction

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Understanding the influence of intermediates to catalytic performance is critical for electrochemical conversion of nitrate to ammonia. In this issue of *Chem Catalysis*, Peng and co-workers report that electron polarization induced by alloying effect can lead to the change of adsorption sites and affect the formation of intermediates, thus paving a new mechanism for ammonia synthesis from nitrate reduction reaction.

Ammonia (NH_3) is an important chemical feedstock and hydrogen storage material. At present, ammonia is mainly produced by a conventional Haber-Bosch process using N_2 and H_2 as raw materials.[1] However, the splitting of the stable triple bond in the nitrogen molecule requires a heavy energy consumption, and the utilization of H_2 can result in a large amount of CO_2 emissions.[2] Therefore, it is imperative to develop economical and environmentally friendly ammonia synthesis methods. Due to its low energy consumption and strong controllability, electrochemical methods have shown great potential in the field of synthetic ammonia. Nitrate (NO_3^-) can be used as alternative N source to reduce energy consumption due to the lower dissociation energy of N=O relative to the N≡N bond cleavage energy.[3] Meanwhile, a nitrate-reduction reaction can reduce the harmful pollutants in water bodies and alleviate environmental contamination.[4] Several catalysts have been developed recently, but the complex eight-electron reaction and the competitive hydrogen-evolution reaction still largely suppress the selectivity of electrocatalytic nitrate-reduction reaction (NITRR).[5]

Revealing the relationship between structure and activity can guide the design of catalysts with high performances. Alloying is an efficient strategy for tuning the geometric and electronic structure and then modifying the adsorption energy of intermediates of catalysts.[6] In this issue of *Chem Catalysis*, Peng and co-workers report that electron polarization induced by alloy effect can tune the adsorption energy of intermediates during nitrate electroreduction to ammonia.[7] The authors obtain a PdCu alloy highly dispersed on an ultrathin Cu_2O shell via solution-processed impregnation-reduction method with Cu_2O and $PdCl_4^{2-}$. The existence of Pd^0, Cu^0, and Pd-Cu bonds indicates the presence of PdCu alloys. X-ray photoelectron spectroscopy and X-ray adsorption fine structure

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