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When stronger binding hinders zeolite-catalyzed alcohol dehydration

Zi-Chen Zheng[1,2], **Li-Hua Chen**[3,*]

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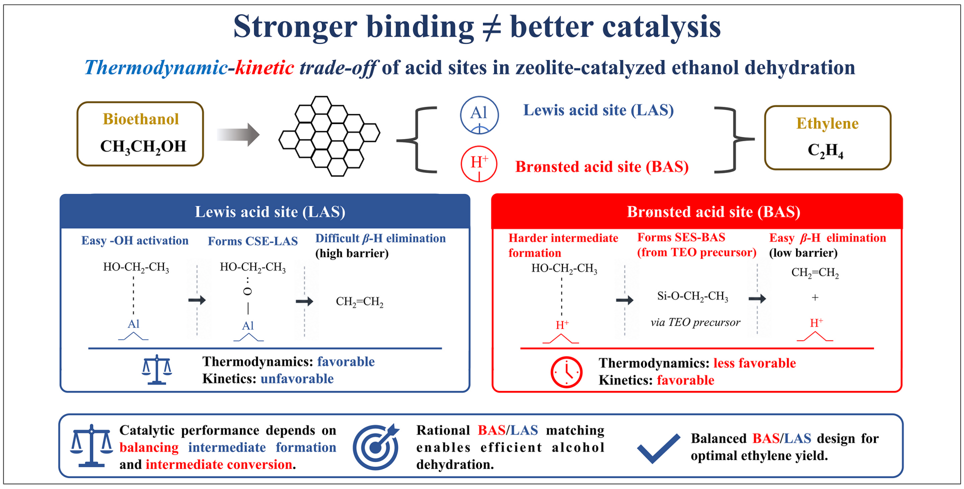

Alcohol dehydration over zeolites is a classic topic in solid acid catalysis, but it has gained fresh relevance as bioethanol is increasingly viewed as a renewable feedstock for light olefins[1]. Among these reactions, ethanol-to-ethylene conversion over ZSM-5 has attracted particular interest because even subtle changes in acid site type and local confinement can strongly affect performance[2]. Still, it has been difficult to clearly separate the roles of Brønsted acid sites (BAS) and Lewis acid sites (LAS) in real catalysts, where multiple sites, short-lived intermediates, and competing pathways exist at the same time. Earlier studies have identified surface ethoxy species as key BAS-bound intermediates in ethanol dehydration[3]. Solid-state nuclear magnetic resonance (NMR) provided another important piece of evidence by directly detecting triethyloxonium ions (TEO) in H-ZSM-5 during the reaction[4]. However, it has remained unclear how BAS and LAS each participate in the individual elementary steps of the same reaction network.

Hu *et al.* help fill this gap by combining solid-state NMR with density functional theory to track site-specific pathways for ethanol dehydration over ZSM-5[5]. They identify two central intermediates, chemisorbed ethanol on LAS (CSE-LAS) and

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[1]Chimie des Interactions Plasma-Surface, University of Mons, Mons 7000, Belgium.
[2]Laboratory of Inorganic Materials Chemistry (CMI), University of Namur, Namur B-5000, Belgium.
[3]State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, Hubei, China.

***Correspondence to:** Prof. Li-Hua Chen, State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, Hubei, China. E-mail: chenlihua@whut.edu.cn

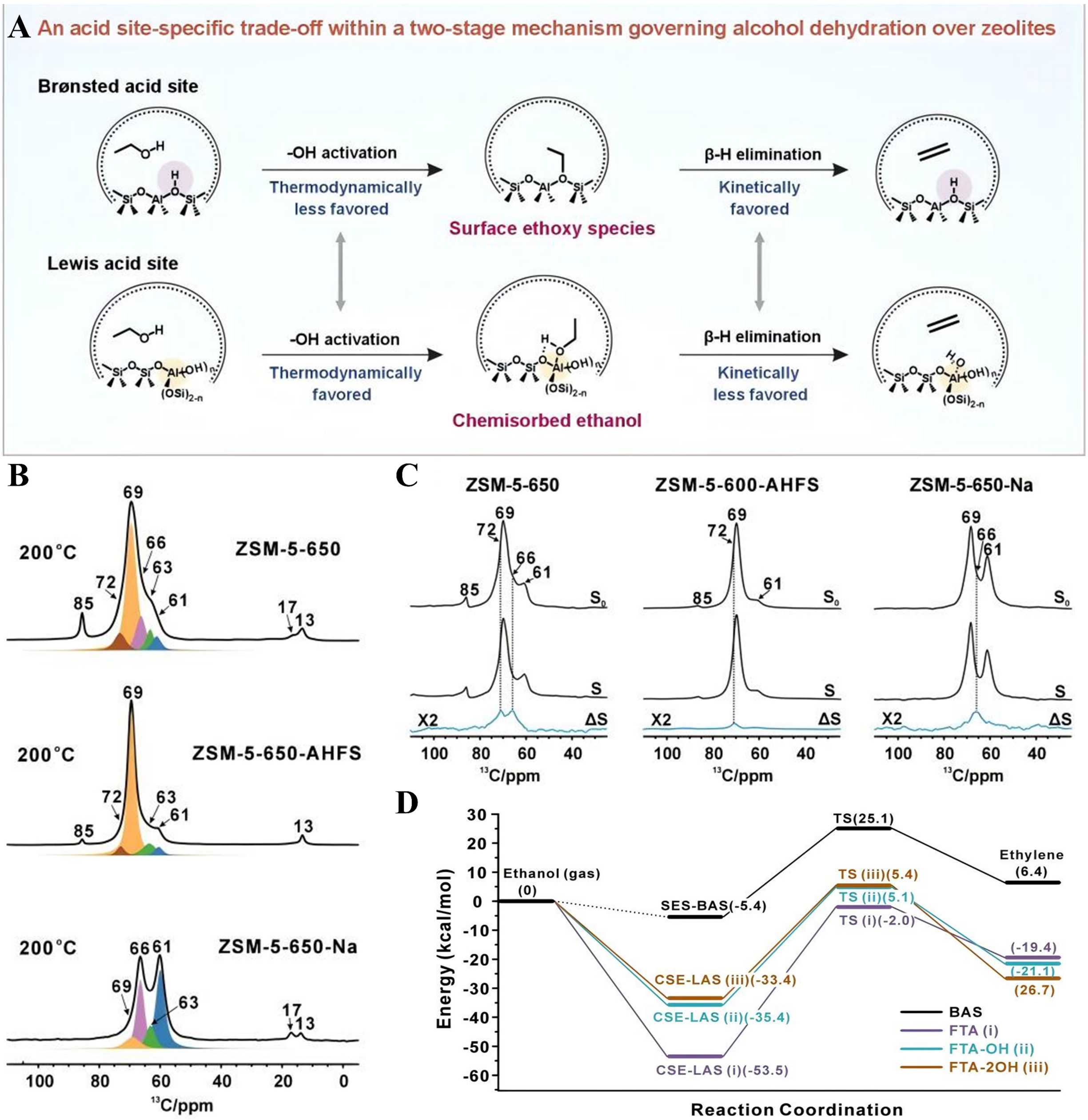

Figure 1. (A) The site-specific division of catalytic labor between BAS and LAS in zeolite-catalyzed alcohol dehydration; (B and C) selected experimental evidence identifying surface species associated with BAS-mediated and LAS-mediated pathways; (D) calculated reaction energy profiles comparing thermodynamic stabilization and kinetic barriers on BAS and LAS. This figure is reproduced with permission from[5], licensed under CC BY-NC-ND 4.0. BAS: Brønsted acid sites; LAS: Lewis acid sites; SES-BAS: surface ethoxy species on Brønsted acid sites; CSE-LAS: chemisorbed ethanol on Lewis acid sites.

surface ethoxy species on BAS (SES-BAS), and they further assign TEO as BAS-related precursors. Importantly, this work brings together several previously disconnected observations into a more coherent mechanistic framework [Figure 1A]. BAS and LAS should therefore not be seen simply as stronger and weaker forms of the same type of site. Rather, they perform distinct functions at different stages of the reaction.

The central finding of this study is that stronger binding does not necessarily lead to better catalysis. LAS are more effective in the first step, namely -OH activation, whereas BAS perform better in the later β-H elimination step [Figure 1A]. The spectroscopic results make this distinction quite clear. They separate chemisorbed ethanol on LAS from surface ethoxy species and TEO-related intermediates formed under BAS-rich conditions [Figure 1B and C]. The calculated energy profiles further reinforce this point [Figure 1D]. On LAS, ethanol is activated more easily at low temperature, so intermediate formation is thermodynamically favored. But this advantage creates a new problem that the intermediate is bound too strongly, which makes the following β-H elimination step harder. The authors support this interpretation by showing close agreement between experiment and theory. The BAS-rich sample has an apparent activation energy of 31.7 kcal·mol^{-1}, whereas the LAS-rich sample shows 38.5 kcal·mol^{-1}. These values match well with the density functional theory (DFT) barriers for SES-BAS decomposition and CSE-LAS conversion, respectively. BAS show the opposite pattern. Forming the intermediate is less favorable at first, but once BAS-bound species are generated, ethylene release becomes much easier, consistent with the role long assigned to surface ethoxy species on Brønsted sites[3]. In this way, the study shifts the discussion away from the overly simple question of which acid site is stronger. A more meaningful question is which type of site is better suited to a given elementary step. This insight supports the rational design of zeolite catalysts by matching BAS and LAS to their distinct roles in each reaction step, rather than relying solely on acidity strength.

This trade-off also changes how we should think about the coexistence of BAS and LAS in zeolites. They should not be viewed simply as redundant sites or as functions that merely compete with each other. Instead, the results suggest a genuine division of labor along the reaction pathway. Collectively, the data connect the NMR-assigned intermediates, CSE-LAS, SES-BAS, and TEO, with the barrier sequence resolved experimentally and computationally [Figure 1B-D]. In this sense, coexistence is not duplication, but complementarity. Efficient catalysis clearly depends on keeping both intermediate formation and intermediate conversion in balance, rather than maximizing only one of them. This view is also consistent with in situ solid-state NMR studies showing that ethanol conversion over H-ZSM-5 involves several coexisting surface species, whose roles vary with catalyst state and reaction conditions[6].

The implications for catalyst design are quite direct. High ethylene productivity is unlikely to be achieved simply by increasing the total acid site density or enriching only one type of site [Figure 1D]. A more practical approach is to tune the BAS/LAS ratio, their spatial arrangement, and the accessibility of the surrounding microporous environment, so that adsorption, intermediate stabilization, and product-forming turnover can remain properly matched. This perspective suggests that future zeolite design should move beyond acidity maximization and instead focus on matching each acid site with the elementary step it most effectively promotes. In this respect, the work by Xu and co-workers provides a useful mechanistic guideline that goes beyond ethanol dehydration itself. Furthermore, a complementary perspective is emphasized in a recent review, which shows that external surfaces and pore-mouth regions of zeolites can significantly influence reaction pathways, selectivity, and catalyst stability[7]. Taken together with the present BAS/LAS analysis reported by Hu *et al.*[5], this broader view suggests that acid-site identity, site location, and accessibility should be considered in concert in zeolite catalyst design. The authors further note that isopropanol dehydration follows a similar site-dependent kinetic pattern[5], which suggests that the same thermodynamic-kinetic trade-off may apply more broadly in zeolite-catalyzed alcohol dehydration. Overall, this study offers a timely reminder for solid-acid catalysis, while the most effective active site is not always the one that activates the reactant most easily, but the one that preserves the right balance among adsorption strength, intermediate stability, and productive turnover.

DECLARATIONS

Authors' contributions

Made substantial contributions to the conception, writing, and critical revision of the manuscript: Chen, L. H.; Zheng, Z. C.

Availability of data and materials

Not applicable.

AI and AI-assisted tools statement

Not applicable.

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Conflicts of interest

Both authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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