

## Preview

## Paired aluminum sites in zeolite catalysts enhance aromatics production

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In this issue of *Chem Catalysis*, Ruiz-Martínez and co-workers investigate the effect of aluminum (Al) proximity and distribution on acid-catalyzed reactions in zeolites. They find that Al enrichment near the external surface results in paired acid sites that exhibit enhanced activity for aromatics formation.

Zeolites have earned widespread recognition as heterogeneous catalysts of exceptional efficacy, capable of driving numerous chemical reactions, including acid-catalyzed conversion processes such as hydrocarbon cracking, isomerization, and alkylation.<sup>1</sup> Their versatility can be attributed to their distinct physico-chemical properties, characterized by a high surface area, tunable acidity, well-defined microporous structures, and uniform pore sizes. These traits facilitate the efficient diffusion of reactant molecules. Furthermore, zeolites exhibit remarkable stability and durability, making them well suited for use under harsh reaction conditions.<sup>2</sup>

In recent years, there has been a growing emphasis on customizing the composition, structure, and morphology of zeolites to optimize their catalytic performance for specific transformations. A notable example is the methanol-to-aromatics process,<sup>3</sup> which is critical for the production of building blocks for fine chemicals and complex organic molecules. This process employs a zeolite catalyst to selectively activate the carbon-hydrogen bonds present in methanol, converting it into higher-value products such as benzene, toluene, and xylene (BTX).<sup>3</sup> The hydrocarbon pool mechanism has been extensively studied and is widely accepted as the primary pathway for the conversion of methanol

to BTX.<sup>4</sup> In this mechanism, a “pool” of reactive hydrocarbon species is formed on the surface of the catalyst, which undergoes a series of complex reactions to produce larger and more complex hydrocarbons, eventually leading to the formation of BTX.<sup>4</sup>

To enhance the efficiency of aromatics formation, previous approaches have employed various strategies, such as introducing low concentrations of aromatic molecules and formaldehyde in the reaction mixture or increasing methanol pressure.<sup>5,6</sup> However, both of these methods have led to unfavorable outcomes, including catalyst coking, dealumination, and irreversible deactivation. A promising alternative and effective approach involves tuning the concentration of Brønsted acid sites present in H-form zeolites to optimize catalyst design and promote the desired reaction.<sup>7</sup> However, precise control of the location and speciation of these sites is critical to prevent the formation of undesired reaction products.

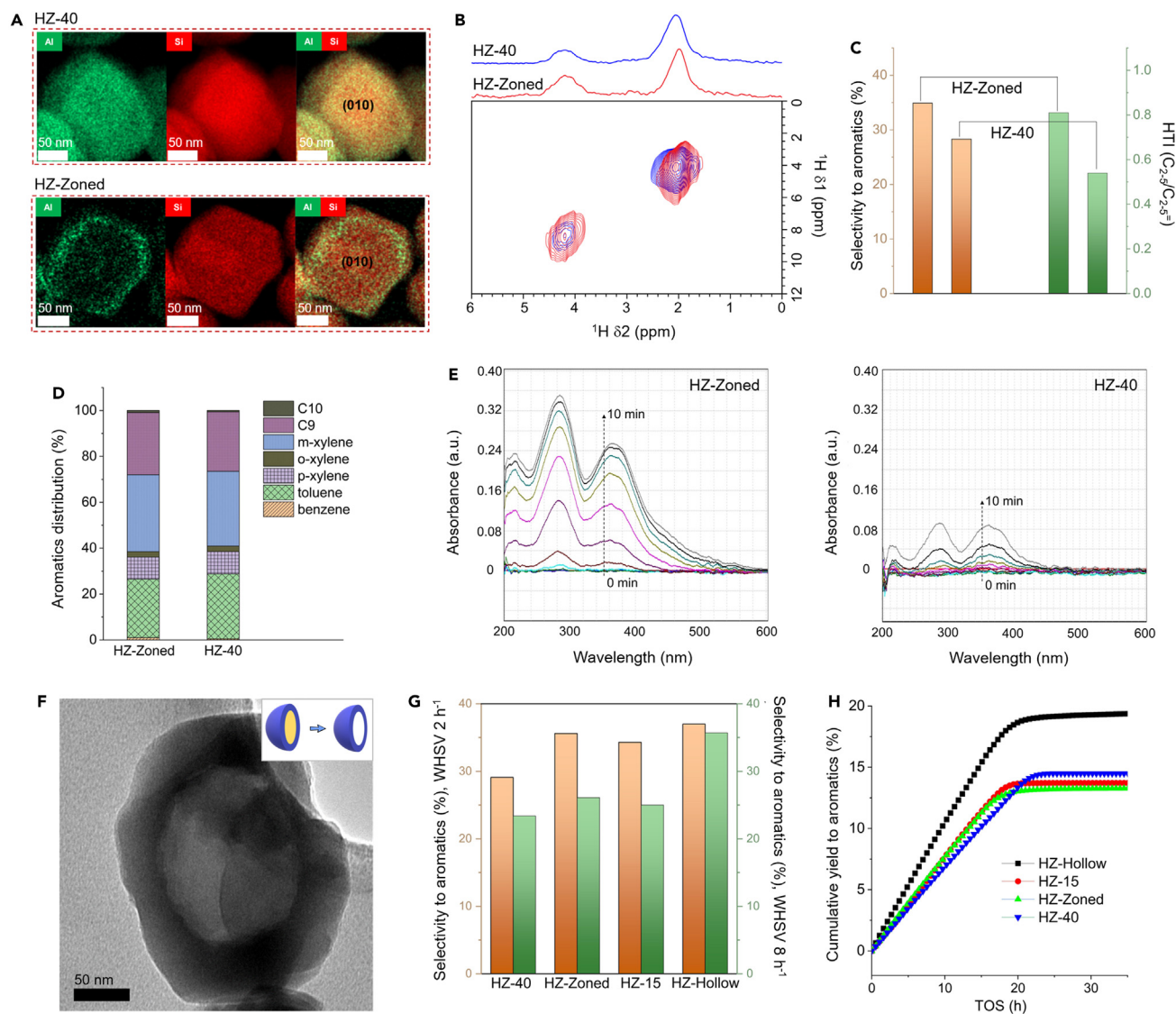
Writing in *Chem Catalysis*, Ruiz-Martínez and colleagues now report a systematic study on the impact of aluminum (Al) distribution on acid-catalyzed reactions at both mesoscopic and microscopic levels.<sup>8</sup> The researchers designed two representative H-ZSM-5 zeolite samples, namely HZ-Zoned and HZ-40, with similar properties—such as surface area,

porosity, crystal size, acid number, and strength—but varying Al distribution (Figure 1A) and number of acid pairs. In particular, while the crystal of HZ-Zoned shows an uneven distribution of Al with the shell displaying higher content than the core, the crystal of HZ-40 had a homogeneous Al distribution. As a result, the researchers were able to evaluate the effects of Al pairs and Al zoning in acid catalysis. The authors employed multiple characterization techniques, including advanced solid-state nuclear magnetic resonance (NMR), to uncover the nature, location, and distance of Al atoms and proved from the pronounced autocorrelation NMR peak for the HZ-Zoned the higher content of Al pairs (Figure 1B). Controlled catalytic experiments revealed that the enrichment of Al at positions closer to the external surface leads to an enhanced formation of aromatics (Figure 1C) without altering their product distribution (Figure 1D). This result was confirmed by time-resolved ultraviolet-visible (UV-vis) spectroscopy, proving faster kinetics on HZ-Zoned (Figure 1E). Theoretical calculations were employed to prove that paired acid sites exhibited greater reactivity than isolated acid sites at a molecular level. It was shown that this heightened activity stemmed not only from the enhanced ability of paired acid sites to protonate and activate the reactants but also from their increased capacity to stabilize the corresponding dimerization/cyclization intermediates. Moreover, Al zoning facilitated the creation of additional acid sites in closer proximity and at more readily accessible positions for the reactants. As a consequence, cascade reactions leading to the formation of aromatics proceeded with greater efficiency.

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**Figure 1. Collection of experimental data showing the role of active-site proximity in zeolites on Brønsted acid-catalyzed reactions**

(A) Energy-dispersive X-ray (EDX) mapping for the HZ-40 and HZ-Zoned catalysts reported in the work by Ruiz-Martínez and colleagues, evidencing the Al distribution in the samples.

(B) Solid-state  $^1\text{H}$ - $^1\text{H}$  double-quantum/single-quantum (DQ/SQ) magic angle spinning (MAS) NMR spectra of the dehydrated HZSM-5 zeolites.

(C) Catalytic performance for the methanol-to-aromatics reaction, showing selectivity to aromatics and the hydrogen transfer index (HTI) after 12 h on stream at  $T = 400^\circ\text{C}$  and  $\text{WHSV} = 2\text{ h}^{-1}$ .

(D) Distribution of aromatic species in the products in the same experimental conditions.

(E) *In situ* UV-vis spectra recorded during the methanol conversion over the two zeolite catalysts at  $T = 325^\circ\text{C}$  and  $\text{WHSV} = 6\text{ h}^{-1}$ .

(F) Transmission electron microscopy (TEM) image of a crystal of hollow zeolite crystals (HZ-Hollow) by desilication of Al-zoned crystals, with an inset schematically showing the process of desilication in Al-zoned crystals.

(G) Selectivity to aromatics over 5 h time-on-stream at  $\text{WHSV} = 2\text{ h}^{-1}$  and  $\text{WHSV} = 8\text{ h}^{-1}$ .

(H) Cumulative yield of aromatics with time-on-stream (TOS) over different zeolite samples at  $\text{WHSV} = 8\text{ h}^{-1}$ .

Reproduced from Ruiz-Martínez and co-workers.<sup>8</sup>

Building upon the importance of olefins as critical raw materials in the formation of aromatics from aliphatic alcohols, the scientists further extrapolated their findings to investigate the aromatization of

long-chain aliphatic olefins that have a tendency to form aromatics. Finally, the authors prepared an extra sample through desilication, which also showed improved selectivity to aromatics (Figures 1F–1H).

Overall, this study provides valuable insights for researchers in the fields of chemistry, materials science, and chemical engineering, shedding light on the optimal design of zeolite

catalysts for acid-catalyzed reactions. By emphasizing the role of non-uniform Al distribution, this work demonstrates how the engineering of heterogeneous catalysts can lead to improved catalytic activity, ultimately enabling the development of more sustainable and efficient industrial processes.

### DECLARATION OF INTERESTS

The author declares no competing interests.

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