

## Previews

# *para*-Xylene productivity from syngas over Co<sub>2</sub>C nanoprisms combined with versatile zeolites

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In this issue of *Chem Catalysis*, Wang et al. report high-performance CoMnAl/HZSM-5 bifunctional catalysts for application in the transformation of syngas to aromatics. The versatile HZSM-5@silicalite-1 zeolites, with a hollow nanostructure and a scaly shell, were fabricated to regulate the selective synthesis of aromatic products, especially *para*-xylene.

Aromatics have long been considered important building blocks for highly valuable commodity chemicals.<sup>1</sup> As a result of the rapid depletion of petroleum reserves and the increasing market demand for these types of aromatics, it is highly desirable to develop an alternative process for the production of light aromatics (benzene, toluene, and xylenes [BTX]), especially *para*-xylene (PX), by using non-petroleum carbon resources. Non-petroleum carbon resources can be easily converted into syngas, which can then be converted into methanol or olefins and subsequently aromatics via methanol-to-aromatic (syngas-methanol-aromatic [SMA]) or olefin-to-aromatic (syngas-olefin-aromatic [SOA]) reactions performed over ZSM-5 zeolites.<sup>2</sup>

The SMA process can produce high selectivity toward aromatics (60%–80%) and low CH<sub>4</sub> selectivity (<5%). However, the overall conversion of CO is below 55%, even under harsh reaction conditions (400°C, 5 MPa).<sup>3</sup> For the SOA route, prior studies have mostly focused on the Fe carbide Fischer-Tropsch catalysts combined with HZSM-5 zeolite to produce aromatics.<sup>4</sup> Although a selectivity of >45% toward aromatics can be obtained at a CO conversion higher than 50%, the selectivity toward undesirable

CH<sub>4</sub> is rather high. Additionally, the high working temperature (>300°C) often results in coke deposition and rapid deactivation of both the Fe carbide and zeolite components.<sup>5</sup> Furthermore, the selectivity toward BTX is generally low (<35%) in both routes. Therefore, developing efficient STA catalysts with high catalytic activity, selectivity, and stability remains a great challenge.

In this issue of *Chem Catalysis*, Wang et al. fabricated a range of zeolites and combined them with a high-performance Fischer-Tropsch to olefin (FTO) catalyst consisting of CoMnAl (CMA) composite oxides.<sup>6</sup> The authors evaluated the catalytic activity and product distribution of bifunctional catalysts to transform syngas under mild reaction conditions (280°C, 2 MPa) (Figure 1A). The CMA catalyst was synthesized by a co-precipitation method, and using only the CMA catalyst achieved low CH<sub>4</sub> selectivity (2.7%) and high olefin selectivity (81.1%) at a CO conversion of 38.0%. Combining the CMA catalyst with a range of HZSM-5 zeolites—including Z5-M, Z5-N, and Hol-Z5-N—produced the aromatics differently. For Hol-Z5-N zeolite, because the hollow structure enhances the mass transport of the intermediate and product,<sup>7</sup> a much higher CO conversion could

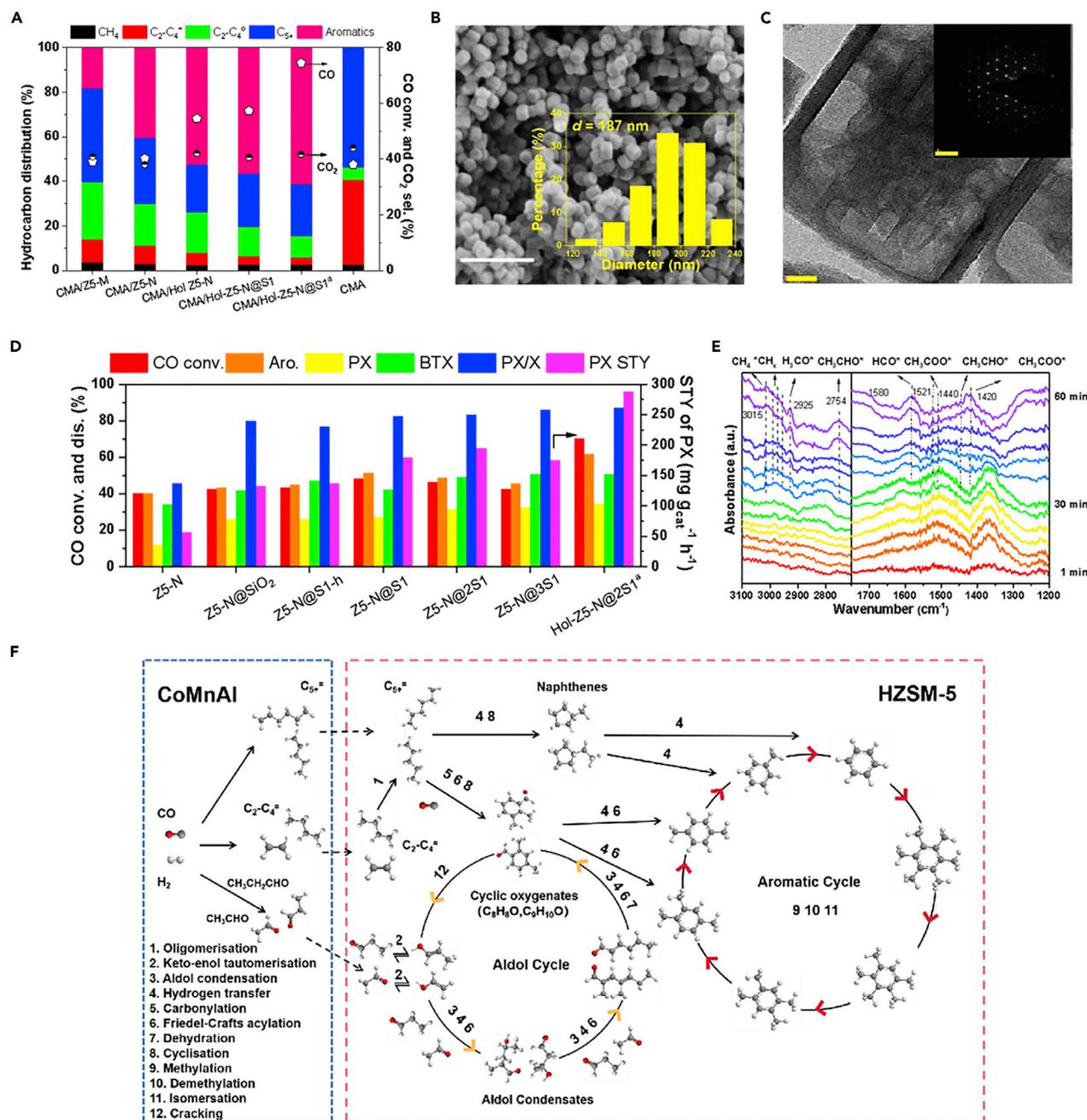
be achieved over CMA/Hol-Z5-N than over CMA/Z5-N and CMA/Z5-M. Interestingly, when the combination of CMA and a versatile Hol-Z5-N@S1 zeolite with a hollow nanostructure and a scaly shell was used, the selectivity toward the aromatics and CO conversion could be further increased and the CH<sub>4</sub> selectivity remained low (2.8%). Under mild reaction conditions, the CMA/Hol-Z5-N@S1 bifunctional catalyst resulted in >63% selectivity toward aromatics and >70% CO conversion.

For the structural characterization part, the authors revealed that the Co<sub>x</sub>Mn<sub>1-x</sub>O species in the reduced CMA are transformed into Co<sub>2</sub>C nanoprisms with (020) and (101) facets during the reaction, leading to high-performance syngas conversion to olefins with very low CH<sub>4</sub> selectivity.<sup>8</sup> Meanwhile, the authors also characterized the structure of different ZSM-5 zeolite catalysts. Scanning electron microscopy (SEM) showed that the hollow nanosized Hol-Z5-N zeolite provides uniform rectangular morphology and a larger average particle than nanosized Z5-N zeolite (Figure 1B). Transmission electron microscopy (TEM) indicated that large voids (about 180 × 270 nm) exist in the interior of Hol-Z5-N with a uniform crystalline shell of 20–30 nm (Figure 1C). Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) experiments combined with the infrared spectroscopy of pyridine adsorption (Py-IR) results suggested that the strong acid sites show a trend similar to that of the Brønsted acid sites. The formation of aromatic products from syngas is

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**Figure 1. Catalytic performance, structural characterization, and reaction mechanism for syngas to aromatics over CMA/HZSM-5 bifunctional catalysts**

(A) CO conversion, CO<sub>2</sub> selectivity, and hydrocarbon distribution over CMA/HZSM-5 bifunctional catalysts. Standard reaction conditions: 280°C, 2.0 MPa, 2,000 mL h<sup>-1</sup> g<sup>-1</sup>, H<sub>2</sub>/CO = 1, mass ratio of CMA/HZSM-5 = 1:2. The C<sub>5</sub><sup>+</sup> hydrocarbon selectivity is exclusive of the aromatics. <sup>a</sup>Optimum reaction conditions: 280°C, 2.0 MPa, 1,000 mL h<sup>-1</sup> g<sup>-1</sup>, H<sub>2</sub>/CO = 1.

(B) SEM image and particle distribution of Hol-Z5-N. Scale bars: 1 μm.

(C) TEM image and electron diffraction patterns of Hol-Z5-N. Scale bars: 20 nm and 2 1/nm (inset).

(D) Catalytic performance of the CMA/HZSM-5 catalysts and BTX and PX distributions for the conversion of syngas to aromatics under standard reaction conditions. <sup>a</sup>Reaction conditions: 280°C, 2.0 MPa, 1,000 mL h<sup>-1</sup> g<sup>-1</sup>, H<sub>2</sub>/CO = 0.5.

(E) *In situ* DRIFTS over CMA/Hol-Z5-N at a reaction temperature of 280°C.

(F) Proposed reaction mechanism for the improved production of aromatics from syngas over the CoMnAl/HZSM-5 bifunctional catalysts.

Adapted from Wang et al.<sup>6</sup>

facilitated by an intermediate strong acid site and the Brønsted acid sites. The infrared spectroscopy of 2,6-ditert-butylpyridine adsorption (DTBPy-IR) results further suggested a remarkable decrease in the concentration of the externally accessible acid sites after the silicalite-1 (S1) coating process, which can tune the distribution of the aromatic products.

To efficiently regulate the aromatic distribution, the authors fabricated SiO<sub>2</sub>- and S1-modified Z5-N zeolites by using different coating strategies. Compared with the Z5-N@S1-h zeolite with a hexagonal shape and thick S1 shell and a silica-coated Z5-N@SiO<sub>2</sub> zeolite, the CMA/Z5-N@S1 zeolite with a scaly S1 shell resulted in much higher selectivity toward aromatic products because the scale-like S1 layer facilitates the transport of the intermediates to a larger extent than the thick and densely wrapped SiO<sub>2</sub> and S1-h shell on the surface of the Z5 core.

Furthermore, when the amount of scaly S1 on the surface of Z5-N increased, both CO conversion and aromatic selectivity decreased gradually. In contrast, the BTX and PX selectivity increased gradually, and the authors obtained a maximum space-time yield (STY) of PX over CMA/Z5-N@2S1 catalysts by applying two coats of silicalite-1 (Figure 1D). On the basis of the above results, using the CMA/Hol-Z5-N@2S1 catalyst, Wang et al. achieved a maximum STY of PX of 286.7 mg g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>, which is higher than that achieved with other reported catalysts under mild reaction conditions, including Fe-based catalysts or oxides and ZSM-5 zeolites. Furthermore, after the hydrophobic CMA modification using the method reported in the literature,<sup>9</sup> the PX fractions of the aromatics produced reached approximately 35%, and the selectivity toward undesired C1 by-products (CO<sub>2</sub> and CH<sub>4</sub>) was suppressed to less than 29%, resulting in an unprecedentedly high STY of PX

331.8 mg g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> over CMA@Si/Hol-Z5-N@2S1. The aromatic selectivity was much higher than that produced via the Fe-based SOA process with significantly lower CH<sub>4</sub> selectivity. The aromatic yield was remarkably higher than that achieved with SMA catalysts under the much milder reaction conditions.

Furthermore, the authors conducted a mechanistic investigation to determine the reaction pathway and the possible intermediates to form aromatic products from syngas. They used different alkenes as the probe molecules to study the aromatization behavior over the different zeolites for the reaction mechanism part of the study. The results suggested that the aromatization process does not proceed smoothly via conversions of C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>, which tend to be converted into long-chain olefins via oligomerization. The conversion of *n*-C<sub>6</sub>H<sub>12</sub> was much higher than that of the lower olefins (C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub>). However, the aromatics obtained were lower than those derived from syngas over the CMA/Hol-Z5-N bifunctional catalysts. Interestingly, the authors also found that CO is involved in coupling olefins, especially long-chain olefins, to produce aromatics over the HZSM-5 zeolite.

To further identify the possible reaction intermediates, Wang et al. performed *in situ* diffuse reflectance infrared Fourier transform spectra (DRIFT) experiments (Figure 1E), which showed that the CH<sub>x</sub>O\* and CH<sub>3</sub>CHO\* species produced on the Co<sub>2</sub>C surface could be converted into unsaturated aldehydes and ketones via an aldol condensation reaction on HZSM-5, which could be further converted into oxygen-containing aromatic compounds via an intramolecular aldol cyclization reaction.<sup>10</sup> The authors also dissolved the spent zeolite in a hydrofluoric acid solution and used gas chromatography-mass spectrometry to detect the carbonaceous compounds. The results indi-

cated that the oxygen-containing aromatic species (mainly 2,4-dimethylbenzaldehyde and *p*-tolualdehyde) were produced by the coupling of CO with olefins or higher-oxygenated species and participated in the aromatic cycle after the hydrogenation and dehydration reactions.

The authors' proposed pathways for forming the aromatics from the conversion of syngas over the CMA/Hol-Z5-N catalyst are based on the above results (Figure 1F). The C<sub>2</sub>-C<sub>4</sub> olefins formed on the CMA surface can diffuse into the zeolite channels and undergo oligomerization to form long-chain (C<sub>5+</sub>) olefins. Furthermore, the higher oxygenates formed over the CMA components can be converted into *p*-tolualdehyde via an aldol-cyclization reaction on HZSM-5 and then into PX at low temperatures. In addition to providing an effective strategy for designing bifunctional catalysts with high catalytic activity, selectivity, and stability, this work proposes a third route of syngas to aromatics through olefin and C<sub>2+</sub> oxygenate intermediates to achieve a more efficient aromatic synthesis under milder conditions than the previously reported SMA and SOA routes over bifunctional catalysts containing metal oxides or iron carbides and zeolites.

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## DECLARATION OF INTERESTS

The authors declare no competing interests.

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## Defect-modulated O-coordination: A new strategy for electronic structure two-tier tuning

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**The creation and precise analysis of novel Fe-N-C atomic architecture with an optimal electronic structure are important for oxygen reduction reaction (ORR) electrocatalysis. In this issue of *Chem Catalysis*, Li's group reports a class of square-pyramidal Fe-N<sub>4</sub> active sites with superior ORR performance derived from two-tier fine-tuning of the electronic structure via well-characterized defect-modulated O-coordination structures.**

Endowed with high intrinsic activity and outstanding selectivity toward the four-electron pathway of the oxygen reduction reaction (ORR), iron- and nitrogen-doped carbon (Fe-N-C) materials are universally agreed to be one of the most promising alternatives to the currently used noble platinum group metal (PGM)-based cathode electrocatalysts in fuel cells. Because Fe-N-C materials are an Earth-abundant resource and have a rather low economic cost, delicately designed architecture, and excellent ORR performance, they are ripe for exploration on both scientific and engineering levels. However,

despite their leading position among non-noble-metal ORR electrocatalysts, many obstacles (such as a lack of catalytic activity, instability of the carbon support under high applied potential, the leaching of Fe atoms, and in particular the lack of a comprehensive understanding and precise characterization of the real active-site structures and reaction mechanism) severely hinder their development and prohibit them from replacing state-of-the-art Pt/Pd-based systems.

The ORR activity and durability of Fe-N-C materials hinge on complicated factors including the nature of the carbon sup-

ports (graphene, graphene oxide, reduced graphene oxide, carbon nanotubes, etc.), defect varieties within the carbon supports, the different coordination environments of the N atoms (graphitic-N, pyridinic-N, and pyrrolic-N), and the d-band center of active Fe atoms.<sup>1</sup> According to the well-known Sabatier principle, a moderate adsorption strength between the active site and oxygenated intermediates is expected for favorable attachment and detachment. Fe-N-C materials (C refers in particular to graphene) situate on the left of the volcano plot.<sup>2</sup> Hence, a proper downshifting of the d-band center serves as a key solution to promote its ORR activity. To downshift the d-band center of active Fe atoms, thus weakening its adsorption with oxygenated reactants, two main tactics are widely conducted: electronic structure tuning and geometric architecture design.

Inducing heteroatoms such as Co,<sup>3</sup> S,<sup>4,5</sup> and Mn<sup>6</sup> to construct dual-atom active sites enables an effective electron-

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