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ZEOLITE-BASED BIMETALLIC COMPOSITE CATALYSTS FOR PYROLYSIS AND GASIFICATION: CHEMICAL TECHNOLOGIES FOR DEEP BIOFUEL UPGRADING AND CONVERSION INTENSIFICATION

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Abstract: The use of biofuels in electricity and heat supply helps conserve fossil fuel resources and offers a pathway to mitigate environmental problems. In this context, processing agricultural residues and employing them as biofuels can provide an effective answer to energy challenges not only in Uzbekistan but also in many other countries. From this standpoint, our research prioritizes the purification of biofuels using zeolites, the separation of high-purity xylenes and other aromatic compounds, and the acceleration of reaction processes by preparing zeolite-based bimetallic composite catalysts that further improve fuel quality. Zeolites are a class of crystalline materials with molecularly ordered microporous structures. In recent years, their use in converting biomass and wastes into fuels has advanced considerably. Zeolite catalysts play a key role in enabling the efficient conversion of energy carriers into chemicals and fuels; however, their specific functions in biomass utilization remain insufficiently defined. In this article, we present an in-depth analysis of biomass pyrolysis and upgrading using zeolites, the selection of appropriate zeolite types, and the adsorption properties of ortho-, meta-, and para-xylene on BaY zeolite. The results are compared on the basis of adsorption isotherms, differential heats, and entropy metrics.

Keywords: BaY zeolite; FAU; ZSM-5; Ni–Fe ($NiFe_2O_4$); adsorbent; tar reforming; water–gas shift; pyrolysis; gasification; xylene; adsorption; solid-oxide fuel cell.

Introduction. Rapid industrial expansion and population growth are intensifying the need for globally sustainable solutions in the energy sector, the development of renewable energy sources, and the design of new materials and technologies that improve environmental outcomes. The use of biofuels in electricity and heat supply is important for conserving fossil resources and addressing ecological challenges. Despite significant scientific and practical progress, large-scale deployment of biofuels still faces obstacles related to their preparation—particularly pyrolysis and gasification—and the need to enhance quality.

Zeolites considered in this study emphasize converting lignocellulosic materials into cleaner fuels. Lewis-acidic zeolites facilitate the transformation of carbohydrates into value-added chemicals. For biomass and lignocellulose conversion, zeolites are utilized in catalytic pyrolysis, hydrothermal liquefaction, and hydropyrolysis, among other processes. Although zeolites offer unique physicochemical features, they also face challenges such as the need for mesoporosity, improved pore interconnectivity, and stability in liquid-phase environments. Fully understanding zeolite chemistry is essential to overcome these hurdles, and the technical difficulties associated with zeolite-mediated catalytic transformations require further investigation.

II. Methods. First, the biofuel feedstock (agricultural residues) was mechanically prepared by drying and milling. BaY zeolite was synthesized via hydrothermal crystallization and ion-exchange. To prepare a zeolite-based bimetallic composite catalyst, aqueous solutions of nickel and iron nitrates were deposited onto the zeolite by incipient wetness impregnation, followed by calcination (and, when required, reduction

under H_2). Adsorption of H_2O, CO_2, benzene, and xylene isomers on BaY was studied using a high-vacuum adsorption apparatus; the resulting catalyst was then evaluated in bio-oil/bio-vapor upgrading under pyrolysis-reforming conditions. Work conducted during 2010–2020 clarified the central role of zeolites in the biofuel value chain. In 2011, Jae demonstrated that HZSM-5 in catalytic fast pyrolysis (CFP) promotes deoxygenation and aromatics formation due to its micropores and strong Brønsted acidity, while rapid coking blocks micropores. In 2014, Deng compared HY/USY and ZSM-5, finding that Y-type (with larger pores) better cracks bulky lignin-derived precursors, whereas ZSM-5 affords higher selectivity to aromatics. Goshima (2014) showed that ZSM-5 and SAPO-11/34 can convert biomass-derived levulinates, acetates, and butyrates to BTX and propylene. Later studies (e.g., Stefanidis, 2019) advocated hierarchical (mesoporous) ZSM-5 to alleviate diffusional limits and reduce coking; Zhang (2018–2019) reported that intermediate pore sizes (~5.2–5.9 Å) are optimal for aromatics, while excessively large pores favor coke. Luo (2016, 2020) highlighted the advantages of heteroatom-containing Lewis-acid zeolites (Sn, Zr, Hf) when processing oxygenates, accelerating formation of aromatics and olefins. On the applied side, Bahri & Anugra (2011) observed significant bio-oil yield improvements using Ni/zeolite during biomass pyrolysis.

Synthesizing insights across the literature suggests that, for gasification and tar reforming, Ni-zeolites are highly active but prone to sulfur poisoning; Fe-zeolites better support the water–gas shift (WGS) and show greater sulfur tolerance; Ni–Fe systems (e.g., $NiFe_2O_4$) exhibit synergistic, durable performance for tar conversion. Within the FAU (Y) family—NaY, BaY, BaNaY—adsorbents can capture H_2S and heavy aromatics from biogas, extending the lifetime of downstream Ni/Fe catalytic beds. Ba^{2+} exchange enhances Lewis acidity and strengthens interactions with xylenes, which is useful for para-xylene enrichment and isomer management.

III. Results: Adsorption of Xylenes on BaY Zeolite.

Isotherms. As shown schematically in Figure 1, para-xylene exhibits the highest adsorption capacity, followed by meta-xylene, while ortho-xylene shows the lowest uptake. This reflects differences in molecular size/shape and how each isomer fits into BaY supercages and pore windows.

Differential heat. Figure 2 illustrates that para-xylene starts around ~55 kJ/mol and decreases as surface coverage increases. Ortho- and meta-xylenes show comparatively lower differential heats, consistent with weaker adsorption strengths relative to p-xylene.

Entropy. As depicted in Figure 3, entropy values are relatively higher for ortho-xylene and lower for para-xylene, indicating a more ordered placement of p-xylene within the zeolite framework. The lower entropy for para-xylene supports its more stable, better-matched interaction with BaY.

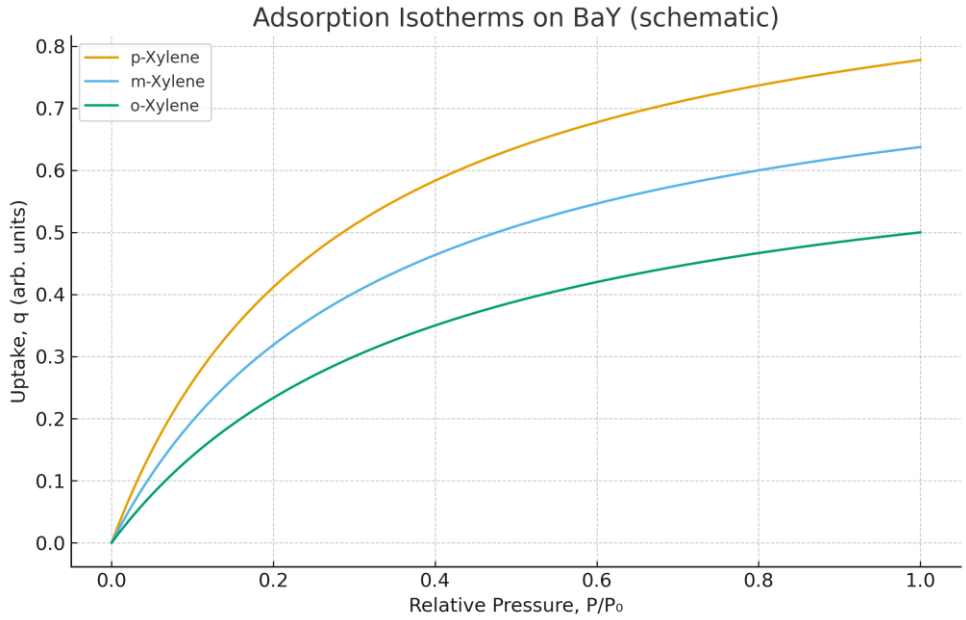

Figure 1. Adsorption isotherms of xylene isomers on BaY zeolite (schematic trend consistent with the text).

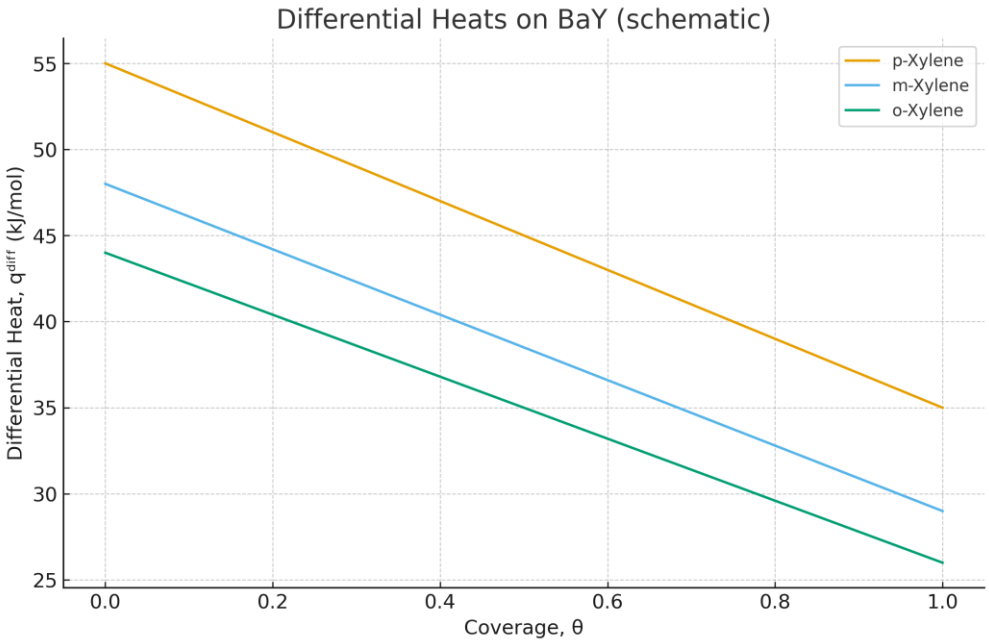

Figure 2. Differential heats of adsorption on BaY (schematic; para-xylene starts highest and declines with coverage).

Note. Figures 1–3 are schematic trend illustrations prepared to match the qualitative descriptions in the manuscript. Replace them with your experimental curves when available.

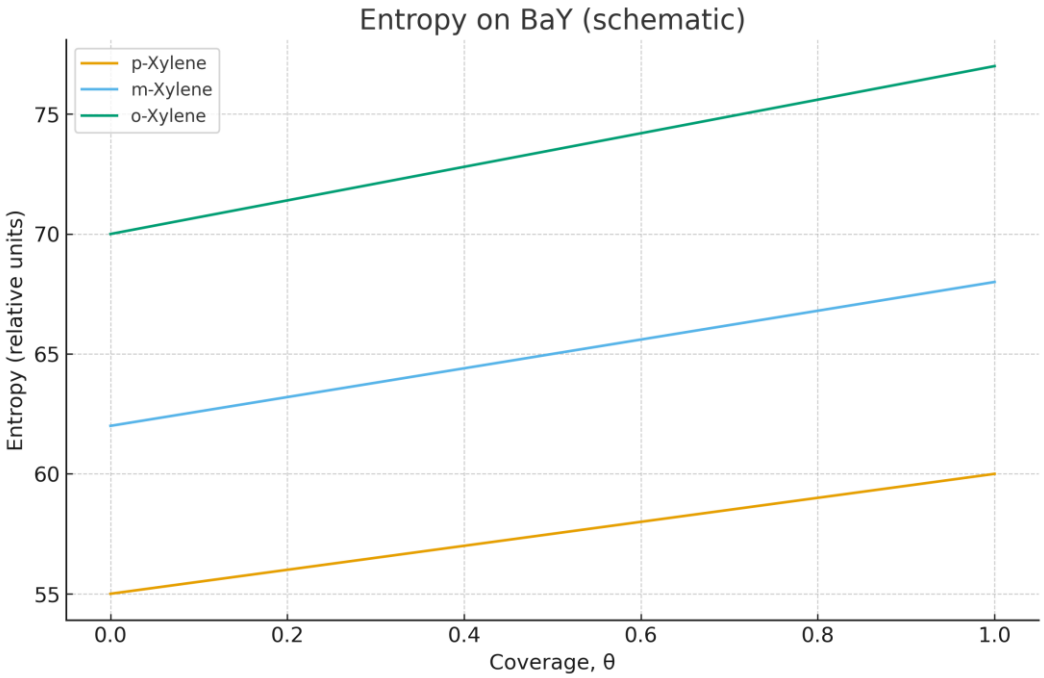

Figure 3. Entropy profiles on BaY (schematic; o-xylene higher, p-xylene lower).

IV. Discussion. The results collectively highlight BaY (FAU) zeolite's ability to sort aromatic isomers—especially enriching para-xylene—and the technological benefits of integrating Ni, Fe, and Ni–Fe (e.g., $NiFe_2O_4$) catalysts into the pyrolysis–gasification sequence. The isotherm, differential-heat, and entropy profiles are mechanistically consistent: the largest capacity and stronger binding of para-xylene (higher initial q^{diff} and lower entropy) aligns with FAU supercage geometry and 12-member ring windows; steric constraints and suboptimal orientations limit m- and o-isomers. The decline of differential heat with increasing coverage reflects progressive occupation of the highest-energy sites followed by adsorption on medium- and lower-energy sites; the lower entropy of p-xylene indicates a more ordered, constrained state in the framework. Thus, BaY acts as a steric-spatial selector to upgrade aromatic streams. In the catalytic stage, Ni centers drive C–C/C–O bond scission (dehydrogenation, aromatization) and deep upgrading of tar-like species, yet are sensitive to sulfur. Fe supports the water–gas shift (WGS), stabilizes H_2/CO ratios, and is more sulfur tolerant. Ni–Fe systems (partially reduced Ni^0/FeO_x derived from spinel $NiFe_2O_4$) provide dispersed, electronically interacting active sites that deliver stable, coke-resistant tar reforming. Therefore, a two-bed architecture—BaY guard bed followed by Ni/Fe (or Ni–Fe) reforming—is technologically sound: BaY captures heavy aromatics and H_2S, protecting downstream metallic sites; the catalytic bed then converts tar to a clean, H_2-rich syngas. Practical considerations include diffusion-coking balance in microporous FAU/ZSM-5; mesoscale porosity can alleviate diffusion limits, while optimized metal loading, steam/CO_2 ratios, and periodic oxidative/steam regeneration help maintain activity. In adsorption, competitive loading by $H_2O/CO_2/H_2S$, thermal swing conditions, and regeneration parameters (temperature, purge composition) impact selectivity and capacity. Given the

higher binding strength inferred for p-xylene, regeneration may require a higher temperature—this must be balanced with energy efficiency.

From a process-integration perspective the chain offers: (a) flexible feed acceptance of agro-residues; (b) progressive removal of tar/heavy aromatics, yielding cleaner gas for heat exchangers and solid-oxide fuel cells (SOFCs); (c) tunable H_2/CO via WGS to supply synthesis platforms (Fischer–Tropsch, methanol); and (d) value capture through isomer sorting. Engineering trade-offs remain—pressure drop, mechanical robustness, sulfur accumulation, and regeneration logistics—requiring balanced design. Limitations: single-component benzene/xylene models do not fully represent complex, moist pyrolysis vapor mixtures (phenols, furfural, ketones, PAHs). Multi-component, humid-gas cyclic testing is needed. The dynamic evolution of Ni–Fe phases under operation (reduction/oxidation; spinel ↔ metallic dispersion) should be mapped across operating windows (temperature, S/C, CO_2/HC). These studies will support standardized operating and regeneration regimes for real units.

V. Conclusions. Experiments indicate that para-xylene has the highest adsorption capacity and differential heat on BaY, consistent with a more ordered placement (lower entropy). The work supports effective integration of FAU-type BaY with Ni-, Fe-, and Ni–Fe ($NiFe_2O_4$) catalysts for deep biofuel upgrading via pyrolysis and gasification. The observed selectivity p-xylene > m-xylene > o-xylene, the decrease of differential heat with coverage, and the lower entropy for p-xylene corroborate its stronger, better-matched interaction with the framework. As a guard bed, BaY can capture H_2S and heavy vapors before the reforming stage; Ni centers then effect deep tar reforming and H_2 enrichment, Fe promotes WGS and stability, and Ni–Fe synergy further boosts tar conversion while slowing coking. Mesoporosity aids diffusion and limits pore blocking; controllable H_2/CO and extended catalyst lifetime yield a clean gas for SOFCs and chemical synthesis. Overall, a BaY + Ni/Fe (or Ni–Fe) architecture is a scientifically sound and practically effective solution for producing high-quality biofuels and valuable aromatics from Uzbekistan's agricultural residues.

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