Timeless Efficiency of n-hexane Cracking as a Model Reaction for Composite Zeolite Characteriszation

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Significance and Relevance

The n-hexane cracking reaction (α-test) is demonstrated to be and remain a highly effective characterization tool for probing the catalytic properties of porous materials. Initial activity measurements reveal that the USY/ZSM-5 composite exhibits the intrinsic acidic characteristics of both USY and ZSM-5. Moreover, the interaction and proximity between the crystallites of the two structures significantly influence the material's selectivity. Consequently, this hybrid material displays promising catalytic properties, making it suitable for applications in the petroleum industry, fine chemical production, and the conversion of renewable resources.

Preferred and 2nd choice for the topic: ***Green chemistry and biomass transformation, renewable resources conversion***
Preferred presentation: (Oral only / Oral preferred or Short Oral / Poster) **Oral preferred or Short Oral**

Introduction and Motivations

Zeolitic materials are extensively utilized in catalytic and separation-adsorption processes due to their high activity and exceptional selectivity. However, their application is restricted by narrow porosity, which limits their efficiency in the transformation and separation of bulkier molecules. To address this limitation, composite zeolites with hierarchical porosity have been developed. These hybrid materials combine the intrinsic properties of two distinct structures and benefit from enhanced diffusion capabilities provided by hierarchization, making them more versatile catalysts suitable for a broader range of applications. Characterization of such complex materials using conventional physicochemical techniques poses challenges, as these methods often fail to directly assess the reactivity of acid sites and, consequently, their catalytic properties. This gap can be bridged by employing model reactions.
One of the most commonly used catalytic tests is n-hexane cracking, a reaction initially introduced by the Mobil company in the 1960s and still widely applied under the term "α-test." [1] This reaction proceeds via either monomolecular or bimolecular cracking mechanisms. The rate of monomolecular cracking is particularly sensitive to the strength of Brønsted acid sites (BAS).[2] The strength of these sites is closely linked to their local environment, which includes the zeolite's structural and compositional framework, the precise location of acid sites within the framework, and the presence of extra-framework species.[3] Consequently, this catalytic test serves as a powerful tool to probe the acidic properties of composite zeolites. It provides valuable insights into the reactivity of these hybrid materials and reveals potential synergistic, additive, or intimacy effects within the hierarchical structures.

Materials and Methods

The physicochemical properties of the materials were determined as follows: the Si/Al ratio was measured using X-ray fluorescence (XRF), the concentrations of Brønsted and Lewis acid sites (BAS and LAS) were quantified through pyridine adsorption-desorption at 150 °C, assisted by infrared spectroscopy (IRTF), and the morphology was examined using transmission electron microscopy (TEM). The transformation of n-hexane was conducted in a four-parallel fixed-bed reactor system. To ensure an accurate estimation of the reaction rate, the experiment was performed at four different contact times by varying the amounts of the same catalyst. The catalyst, with a particle size of 0.2–0.4 mm, was pre-treated at 540 °C under a nitrogen flow for 12 hours. A diluted n-hexane/nitrogen mixture was then injected into the reactors at 540 °C, maintaining a molar ratio of 11.

Table 1. Main properties of studied catalysts.

Sample	USY/ZSM-5 (wt. %)	Si/Al (mol/mol)	[PyH$^+$] (µmol/g)	[PyL] (µmol/g)
USY/ZSM-5 Composite	41/59	20	148	104

Results and Discussion

The catalytic activities of two series of catalysts USY, with a Si/Al ratio ranging from 2.5 to 40, and HZSM-5, with a Si/Al ratio from 9 to 75, are compared to those of USY/ZSM-5 mixtures (containing 41 % USY and 59 % of ZSM-5) and a composite with a USY/ZSM-5 ratio. The composite consists of hierarchical zeolite Y (41 wt. %) and nano-sized ZSM-5 (59 wt%), produced through partial interzeolite conversion from USY. The key characteristics of this material are presented in Table 1.

The activity is directly proportional to the number of BAS non-exalted by aluminum extraframework (Figure 1A). Accordingly, the turnover frequencies (TOF) of these sites are determined from the slopes of the linear plots of cracking activity versus the concentration of acid sites, measured by pyridine probing at 150 °C. The USY/ZSM-5 composite exhibits the same TOF as the series of mechanical mixtures with similar proportions but different concentrations of BAS (Figure 1A). Therefore, the activity of the composite materials corresponds to an algebraic sum of the activities of pure zeolite Y and ZSM-5. This indicates that the composite retains the distinct acidic properties of its individual components.

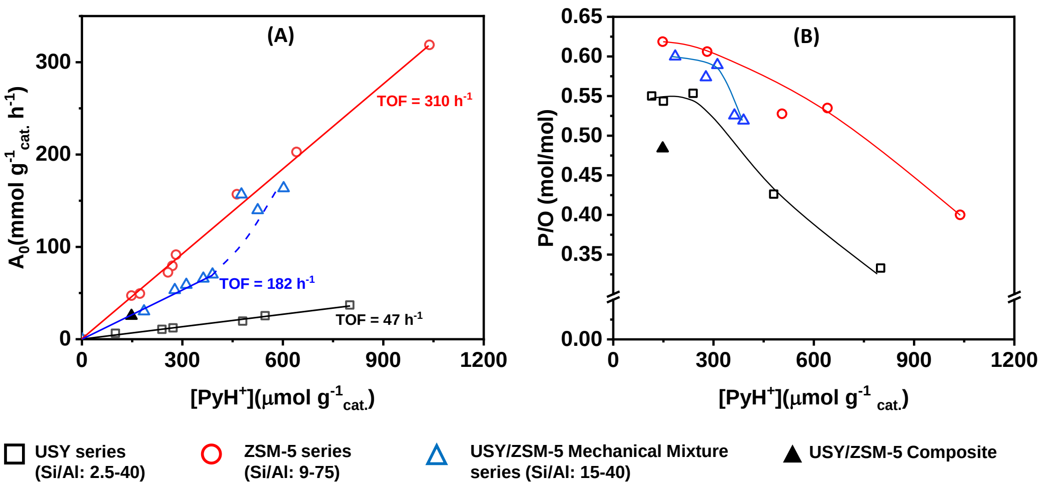

Figure 1. Variation of initial activity (A) and paraffins to olefins ration (B) as function of concentration of BAS probed by pyridine at 150 °C. A_0: initial activity of n-hexane cracking, P/O initial paraffins to olefins ratio.

The paraffins-to-olefins ratio (P/O), calculated from initial reaction rates, is influenced by the zeolite framework but decreases notably with increasing BAS concentrations (Figure 1B) as a result of enhanced secondary cracking. At comparable BAS concentrations, the composite exhibits a significantly lower P/O ratio compared to the mechanical mixture, pure ZSM-5, or pure USY. This difference is likely due to the close interaction between the crystallites of the two zeolitic phases. The texture and intimate contact between these phases (as shown in the TEM image, Figure 1A) influence the balance between primary and secondary cracking, likely by improving the accessibility of acid sites.

References

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