POST-SYNTHESIS DESIGN OF HIERARCHICAL ZSM-5 MATERIALS FOR OPTIMAL CATALYTIC PERFORMANCE IN THE CRACKING OF PETROLEUM FEEDSTOCK

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Summary

ZSM-5 zeolites are widely used as catalysts in the oil refining and petrochemical industry due to their outstanding catalytic performance. Despite their undisputed applications, the relative small pore size of ZSM-5 zeolites often imposes intra-crystalline diffusion limitations for reactant molecules, provoking the lower catalyst utilisation. To alleviate such limitations, in this work, an additional network of mesopores has been introduced by the post-synthesis modification. It was found that a hierarchical ZSM-5 material with the large fraction of mesopores (297m^2/g) coupled to the preservation of microporous characteristics (strong Brønsted) can be optimally prepared by base treatment in 0.5M NaOH and subsequent acid washing in 0.5M HCl. The gas phase cracking of cumene, carried out at 250^{o}C as a model reaction to test the spacious properties, revealed that the introduction of mesoporosity enhanced the utilisation of active acid sites mostly located inside the micropores of ZSM-5, consequently the superior cumene cracking activity. Thus, the advantages of ZSM-5 zeolites (strong acidity) and mesostructured materials (high accessibility) can be combined to create advanced hierarchical ZSM-5 catalysts for petroleum processing.

Key words: *Hierarchical ZSM-5, post-synthesis, acidity, catalytic cracking.*

1. Introduction

Zeolites are a unique class of crystalline aluminosilicates which are widely used as catalysts in the oil refining and petrochemical industry. Medium pore zeolite ZSM-5 (Zeolite Socony Mobil-5) belonging to MFI topology, patented by Mobil Oil Company in 1975, is one of the most important zeolites that has been applied in a number of industrial-scale catalysed reactions such as cracking, isomerisation, alkylation, dewaxing or methanol-to-gasoline or methanol-to-olefins (MTG, MTO) etc. [1, 2]. The exceptional performance of ZSM-5 in catalysis primarily results from its strong Brønsted acidity, hydrothermal stability and uniform micropores of molecular dimensions. A typical example among others is the application of ZSM-5 additive in the industrial FCC (fluid catalytic cracking) process. Admixture of a second catalyst containing ZSM-5 to a FCC unit significantly increases the yield of light olefins (propene and butenes) with a gain in gasoline octane number by selective cracking of linear gasoline range olefins [3]. However, ZSM-5 as well as other zeolites to be considered for such applications has a major drawback. As one side effect of their micropores, zeolite catalysts often suffer from diffusion limitations for reactant molecules. The restricted access and slow molecular transport to and from active acid sites inside the micropores provoke lower catalyst utilisation. Obviously this limited mass-transfer negatively impacts on activity, and sometimes on selectivity and lifetime of the zeolite based catalyst [3 - 5].

In order to alleviate the internal diffusion limitations, facilitating the utilisation of the active volume in conventional ZSM-5, much effort has focused on increasing the access to zeolites' active sites by shortening the diffusion path length which leads to the so-called hierarchical zeolites [4, 5]. In such hierarchical zeolites, a large fraction of mesoporosity is introduced in combination with genuine microporosity. More importantly, the various domains of porosity should be interconnected to fulfil a distinct function: the micropores provide a high active surface area, the access to which is enhanced by the newly introduced mesopores [6]. Over the past decades, a wealth of synthesis approaches have been proposed and proved to be effective in introducing additional pores with other dimensions in ZSM-5 and related materials. Top-down routes normally involve the post-synthesis treatment of previously grown zeolites by means of selective leaching of framework atoms, e.g. dealumination by steaming or acid leaching [7] and desilication by base leaching [8], thereby generating the voids inside zeolite crystals. Bottom-up routes can create intercrystalline mesopores by assembling nanosized zeolites or by dispersing them on a porous matrix such as alumina or mesoporous aluminosilicates, etc. [9]. Among them, the introduction of mesoporosity by post-synthesis design is perhaps the most promising route due to the combination of experimental simplicity and efficiency.

Recently, we have successfully developed hierarchical ZSM-5 materials by post synthesis modification of commercial ZSM-5 zeolites [11]. The resulting hierarchical ZSM-5 showed significantly enhanced conversion and selectivity toward gasoline-range hydrocarbons and light olefins in the cracking of triglyceride feedstock. In this study, we explored the application of such hierarchical ZSM-5 materials as advanced catalysts for the cracking of petroleum feedstock. The gas phase cracking of cumene was used as a model reaction to evidence the improved performance of the hierarchical ZSM-5 compared to commercial ZSM-5.

2. Experiment

2.1. Catalyst preparation

The post-synthesis design of hierarchical ZSM-5 materials from commercial ZSM-5 (Zeocat PZ-2/25, ZeoChem AG) involved a two-step process, being similar to the previous work [11]. Various samples of the commercial ZSM-5 were first treated in the base solution with increasing NaOH concentrations to generate mesopores by desilication. Then the resulting alkaline treated samples were exposed to a strong acid solution (0.5M HCl) for the complete removal of amorphous debris in order to improve the textural and acidic properties.

In a typical experiment, 3.0g of parent Na-ZSM-5, denoted as ZSM-5-P, was submitted to 100ml of NaOH solutions with different concentrations (0.3, 0.5 and 0.8M) at 65°C under stirring for 30 minutes. In a subsequent acid washing step, 1.0g of the alkaline treated samples was dispersed in 0.5M HCl at 65°C for 2 hours. The resulting sample upon alkaline and subsequent acid treatment is denoted as HZ-xAAT, where AAT means alkaline-acid treatment; HZ and x represent the hierarchical ZSM-5 and the NaOH concentration in the first step, respectively. Prior to characterisation and catalytic study, ZSM-5-P, HZ-xAAT materials were transformed into protonated form by ion-exchanging twice in 0.5M NH_4NO_3 solution at 80°C for 4 hours.

2.2. Catalyst characterisation

The nitrogen physisorption studies were conducted at -196°C with an ASAP 2010 apparatus (Micromeritics). The temperature-programmed desorption of ammonia (NH_3-TPD) measurements was carried out in a home-made set-up using a quartz tube reactor in the range of 100 - 550°C. The Fourier transform infrared spectroscopy measurements for acidity study were performed on a Tensor 27 spectrometer (Bruker) using self-supporting wafers and pyridine as probe molecule (py-IR). The Al and Si contents were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES; 715-ES, Varian) and atomic absorption spectroscopy (AAS; Analyst 300, Perkin Elmer), respectively. More details of these characterisation methods and experiment parameters were described elsewhere [12].

2.3. Catalytic evaluation

The gas phase cracking of cumene was carried out in a fixed-bed down-flow stainless steel reactor (10mm internal diameter) equipped with mass flow controllers for reactant metering (Figure 1).

Typically, a fixed amount of the sieved catalyst (0.2g, particle size 300 - 700µm, diluted with 2.0g of quartz beads of the same size) was placed in the reactor. Prior to the reaction, the sample was activated in N_2 flow at 300°C for 2 hours to remove physically adsorbed water. Liquid cumene was fed at a rate of 0.6g/hour by a liquid flow mass controller (Liquid Flow, Bronkhorst) coupled to a controlled evaporator mixer (CEM, Bronkhorst) using N_2 flow (90ml/minute) as a carrier gas. By this way, the reactant was mixed with N_2 and then evaporated before entering the reactor. The catalytic cracking was conducted at 25°C under atmospheric pressure.

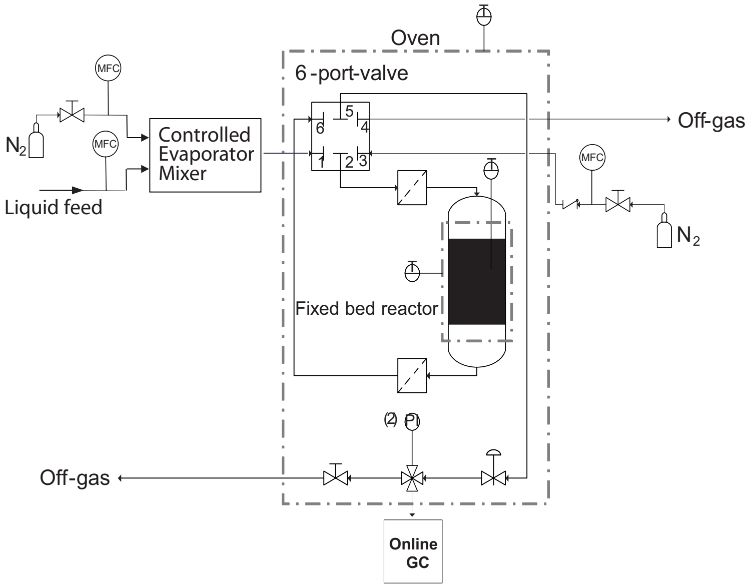


Figure 1. *Experimental setup for catalytic evaluation of ZSM-5-P and HZ-xAAT materials in the gas phase cracking of cumene*

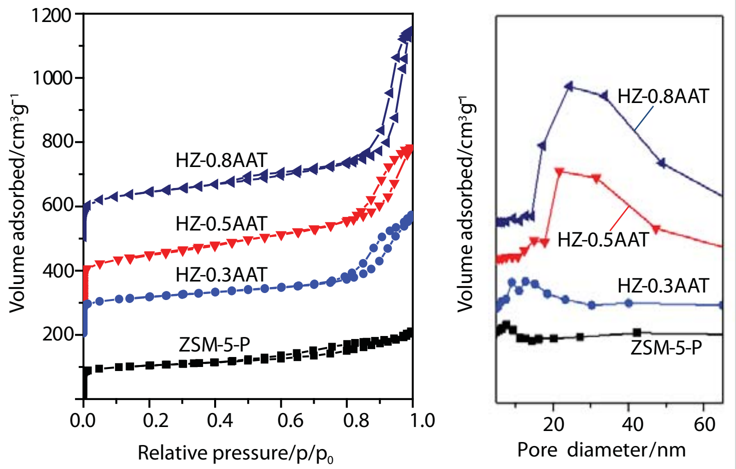
Feed and product samples were analysed with an online gas chromatograph (HP 5890, equipped with a sampling valve, a fused silica capillary column (HP5, 50m x 0.32mm x 0.52µm) and a flame ionisation detector. The temperature of the column was held at 50°C for 2 minutes, then increased to 280°C at a rate of 15K/minute and held for 4 minutes.

3. Results and discussion

3.1. Physico-chemical properties of commercial ZSM-5 (ZSM-5-P) and hierarchical ZSM-5 materials (HZ-xAAT)

As reported previously [11], ZSM-5-P consists of small crystals (ca. 250nm) and their aggregates (ca. 800nm), forming inter-crystalline voids. No intra-crystalline mesopores were evidenced by TEM (not shown) or by analysis of BJH pore size distribution (Figure 2b).

The newly generated mesopores upon base-acid treatment are clearly revealed by N_2-sorption from the transformation of the type I isotherm (ZSM-5-P) into the type I+IV isotherms (HZ-xAAT) with enhanced uptake at high relative pressures (Figure 2a). Moreover, the direct evidence of generated mesopores can also be seen from the corresponding pore size distribution (Figure 2b). The changes in the recovery yield, composition, textural and acidic properties are summarised in Table 1. The post synthesis modification leads to a maximum external surface (S_{meso} = 297m^2/g) which is about 3 times greater than that of ZSM-5-P (S_{meso} = 11m^2/g) at a base concentration of 0.5M and a subsequent acid washing of 0.5M. The severe base treatment (0.8M NaOH) of ZSM-5-P lowers the S_{meso} and V_{micro} of the resulting sample (HZ-0.8AAT) due to the extensive dissolution of the zeolite crystals. Thus, the treatment conditions, i.e. 0.5 NaOH and 0.5 HCl at which the maximum S_{meso} is reached, are defined as "turn point". In addition, the alkaline and subsequent acid treatment decreases the recovery yield and total acidity, but increases the Si/Al ratio (Table 1).



(a)

(b)

Figure 2. *Nitrogen sorption isotherms (a) and the corresponding pore size distribution curves (b) of commercial ZSM-5-P and hierarchical ZSM-5 materials (HZ-xAAT)*

Figure 3a depicts the IR spectra of pyridine adsorbed on the parent and treated ZSM-5 samples after the adsorption procedure and evacuation at 400°C. All samples show two bands responsible for adsorbed pyridine on strong acid sites. The band at ca. 1543cm^{-1} can be attributed to the pyridinium cation and indicates strong Brønsted acid sites (PyH+, BS), while the band at ca. 1455cm^{-1} is characteristic of pyridine coordinated to strong Lewis acid sites (PyL, LS)]. The quantitative estimation of BS and LS was obtained by normalising the integral intensity of the corresponding bands to the BET surface area (Figure 3b). In good agreement with the NH_3-TPD data, the surface density of strong BS and LS undergoes a gradual decline upon the base and subsequent acid treatment. This can be explained by the occurrence of dealumination process during the post-synthesis modifications [13]. Compared to commercial ZSM-5-P, nevertheless, about 74% surface density of strong BS was retained on hierarchical HZ-0.5AAT upon the optimal treatment.

3.2. Gas phase cracking of cumene

The catalytic performance of hierarchical ZSM-5 (HZ-xAAT) compared to commercial ZSM-5 (ZSM-5-P) was evaluated in the gas phase cracking of cumene. Cumene cracking is a well-established test reaction to assess

Table 1. *Physico-chemical properties of commercial ZSM-5 (ZSM-5-P) and hierarchical ZSM-5 materials (HZ-xAAT)*

Sample	**Yield^a (%)**	**Si/Al^b**	**S^c_{meso} (m^2/g)**	**S_{BET} (m^2/g)**	**V^c_{micro} (cm^3/g)**	**V_t (cm^3/g)**	**Total acidity^d (mmol NH_3/g)**
ZSM-5-P	100	11	110	373	0.113	0.22	1.24
HZ-0.3AAT	67	16	124	445	0.144	0.49	0.85
HZ-0.5AAT	62	20	297	456	0.130	0.71	0.71
MZ-0.8AAT	33	38	253	436	0.116	0.82	0.42

^{a}recovery yield (defined as grams of solid received after treatment per gram of parent sample; ^{b}analysed by AAS and ICP; ^{c}t-plot method; ^{d}NH_3-TPD

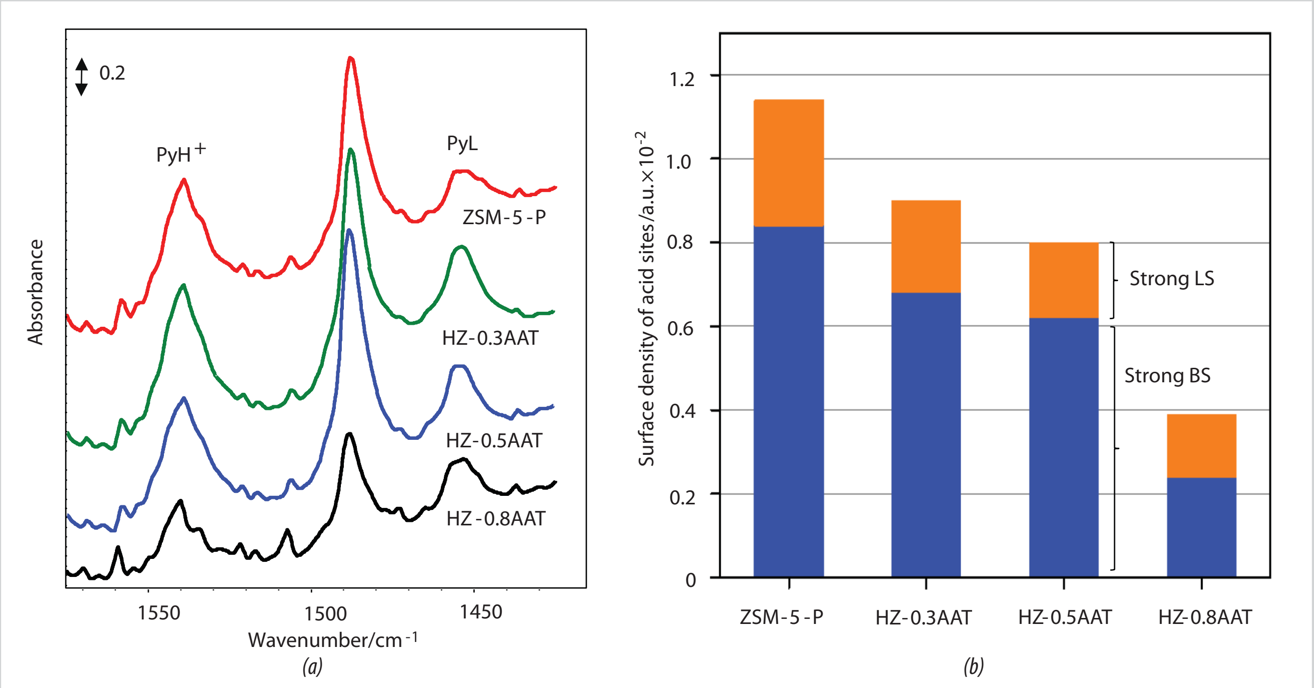


Figure 3. *IR spectra (a) of pyridine adsorbed on the commercial ZSM-5 (ZSM-5-P) and hierarchical ZSM-5 materials (HZ-xAAT) and their corresponding surface density of strong BS (b)*

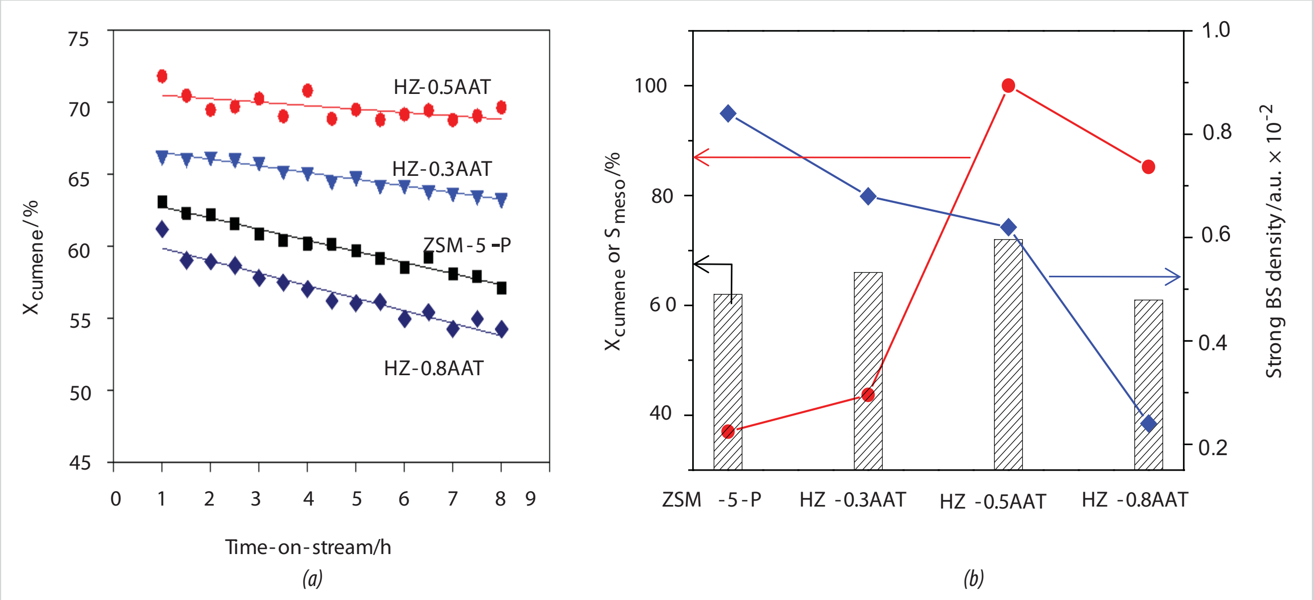


Figure 4. *The cumene conversion (Xcumene) over ZSM-5-P and HZ-xAAT with time-on-stream (a) and Xcumene after 1h on-stream in the relation with the external surface (Smeso) and density of strong BS (b)*

hydrocarbon cracking activities of zeolite catalysts [14]. With its molecular cross-section of 0.5nm, cumene can penetrate the micropores of ZSM-5 (pore opening size of 0.52 - 0.54nm) wherein most active strong BS are located. However, even when cumene molecules have readily entered ZSM-5 crystals, the pore diffusion might be relatively slow, which reduces the catalyst utilisation, and thereby consequent catalytic activity [15, 16]. Thus, in this study, the cumene cracking over ZSM-5-P and HZ-xAAT catalysts was run at 250°C to evaluate the influence of both the acidic properties and porosity on their catalytic performance because the overall cracking reaction rate of cracking is likely to be determined by the diffusion rate at such low temperature [15]. The effect of thermal cracking was checked with an inert material (glass beads). No cumene conversion was detected with glass beads under the investigated reaction conditions. With the presence of the catalysts, cumene was mostly dealkylated on BS to form benzene and propylene as main products, suggesting that BS are at play in this reaction [14].

Figure 4a presents the cumene conversion over the various catalysts with time-on-stream. As expected, hierarchical HZ-xAAT catalysts show higher cracking activities than commercial parent ZSM-5-P, except HZ-0.8AAT. Remarkably, HZ-0.5AAT displays the highest cumene conversion which looks almost stable within the initial 8 hours on-stream. Figure 4b shows the cumene conversion over ZSM-5-P and MZ-xAAT after 1 hour on-stream with respect to their strong BS density and S_{meso}. No reasonable relationship between the cumene conversion and the strong BS density can be found, suggesting that there are diffusional transport constraints affecting cumene reactivity under the tested conditions. On the other hand, a good correlation between the cumene conversion and external surface (S_{meso}) has been established. These results agree well with the work of Zhao et al. [17] who found that the diffusion rate of cumene in mesoporous ZSM-5 is by 2 - 3 orders of magnitude faster than that in conventional ZSM-5, which doubled the cumene conversion over mesoporous ZSM-5 despite its lower Brønsted acidity. Al-Khattaf et al. [18] reported that under the diffusion-controlled regime, the larger the external surface, the higher the catalyst effectiveness and consequently the catalytic activity. Taking these findings into account, the improved cumene conversion over the hierarchical ZSM-5 samples in this work can be attributed to the enhanced acid site utilisation due to the increased accessibility and physical transport provided by substantial mesoporosity. For MZ-0.8AAT, the cumene conversion drops though the considerable fraction of mesopores are already available. The lower activity of MZ-0.8AAT can be explained by a sharp decrease in its surface density of strong BS in this sample as confirmed by the py-IR data. Hence, the introduction of mesoporosity combined with the preservation of microporous characteristics, i.e. strong BS plays a key role for the superior catalytic activity in a strong acid catalysed reaction like cumene cracking.

4. Conclusions

We evidenced that one can improve the catalytic performance of commercially available ZSM-5 zeolites in the cracking of petroleum feedstock by simple, post synthesis modification involving alkaline and subsequent acid treatment. The key is to optimise the synthetic parameter, i.e. the NaOH concentration to maximise the generation of mesoporosity (S_{meso}) without the significant loss of intrinsic zeolite characteristics (strong Brønsted acidity). A subsequent acid washing step is of crucial importance to completely remove aluminium debris for uncovering the micro-/mesoporous network. Most notably, the alkaline treatment of commercial Al-rich ZSM-5 in 0.5 NaOH, followed by the strong acid washing in 0.5M HCl, was found to be optimal for the preparation of hierarchical ZSM-5 (HZ-0.5AAT) containing the substantial mesoporosity (S_{meso} = 297m^2/g) with the preserved intrinsic zeolite features (74% surface density of strong Brønsted acid sites). The gas phase cracking of cumene revealed that the introduction of mesoporosity indeed increases the reactivity of commercial ZSM-5 zeolites when the surface density of strong Brønsted sites is mainly retained. In fact, the cumene conversion upon 1 hour on-stream over HZ-0.5AAT (72%) was noticeably higher than that over commercial ZSM-5 (63%) even though the latter samples possessed a higher surface density of strong Brønsted acid sites. These findings might stimulate future works on the preparation and application of hierarchical ZSM-5 materials as advanced catalysts for the oil refining and petrochemical industry.

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