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Research Note

Mesoporous ZSM-5 zeolites via alkali treatment for the direct hydroxylation of benzene to phenol with N_2O

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ABSTRACT

An alkali treatment of a commercial ZSM-5 zeolite induces substantial intra crystalline mesoporosity through desilication process. The resulting mesoporous H-ZSM-5 zeolite has been tested for the hydroxylation of benzene and it was found to increase the lifetime of the catalyst by suppressing the catalyst deactivation and enhancing the phenol yield and selectivity with time on stream. The EPR investigations showed that the state of Fe was not altered upon alkali treatment. It is suggested that the improvements in the catalytic performances are due to the presence of mesopores in the crystals, which likely reduce the lengths of remaining micropores and improve the transport of the phenol molecule out of the zeolite crystal.

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1. Introduction

Direct hydroxylation of benzene to phenol with nitrous oxide over zeolite catalysts is an alternative to the conventional cumene process [1–3]. Panov and co-workers were one of the first researchers to propose that iron containing ZSM-5 type zeolites [MFI] to be the most promising catalysts for the direct hydroxylation of benzene to phenol with nitrous oxide [1,2]. There have been several controversial discussions in literature concerning the nature and structure of active sites in zeolites for this reaction. Several reports relate the activity of the zeolite to the presence of Brønsted acid sites [4–6] while others [7–9] to Lewis acid sites. But this seems to be the matter of past discussion. Panov and co-workers found evidences for the extraframework dinuclear iron species in ZSM-5, the so-called alpha sites [10,11], as the active sites. Therefore it is now widely accepted that the presence of iron species is indispensable to catalyze direct hydroxylation of benzene [12–14].

Despite the advantages of this alternative route (e.g., one-step and no acetone co-production), the direct hydroxylation of benzene to phenol is associated with serious problems such as rapid deactivation of the catalyst which results in lower yield and short lifetime of the catalyst [15–19]. The accumulation of phenol inside the ZSM-5 crystal is considered to be a major cause for this rapid catalyst deactivation due to its strong adsorption and hindered diffusion out of the zeolite crystal [16,20]. A suitable catalyst to avoid such rapid deactivation has not been developed yet.

Zeolite crystals that contain mesopores are emerging as a new class of materials with a great potential especially for those catalytic reactions which are affected by diffusion limitations [21,22]. Such mesoporous zeolites can be prepared by special synthesis techniques [23,24] or by post-synthesis modification of zeolites with steam treatment [16,25], acid leaching [26] or alkali leaching [27,28]. Christensen et al. [29] and Groen et al. [30] reported superior catalytic performances for the alkylation of benzene with mesoporous MFI and mordenite crystals, respectively. In both cases, it has been proposed that the improved performances were due to the reduced transport limitations offered by the mesoporosity.

So far, desilicated ZSM-5 catalyst has not been applied to the hydroxylation processes. Our strategy in this work was to take a ZSM-5 zeolite containing just traces of Fe impurities to create mesopores without affecting the state of iron in the zeolite. Thus we compare the catalytic performances of mesoporous MFI zeolite, obtained via desilication through post-synthesis alkali treatment, and a parent zeolite for the direct hydroxylation of benzene to phenol.

2. Experimental

2.1. Catalyst preparation

The parent zeolite catalyst used in this work was a commercial NH_4-ZSM-5 (ALSI PENTA; SM-55) with a nominal SiO_2/Al_2O_3 ratio of 55. The mesoporous zeolite powder was prepared through the post-synthesis alkali treatment. 30 g of parent zeolite (uncalcined) was treated with 1 liter of 0.2 M NaOH aqueous solution for 2 h at 80 °C under stirring conditions. Subsequently the sample

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Table 1
Physico-chemical characteristics of the catalysts.

Catalyst	N_2 adsorption				Chemical analysis				XRD
	S_{BET} (m^2/g)	V_{total} (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	Si/Al[a] (–)	Fe[a] (wt%)	$[Si]_{filtrate}$[b] (mg/L)	$[Al]_{filtrate}$[b] (mg/L)	Q_{Al}
Parent (SM-55)	358	0.19	0.14	0.05	19	<0.02	–	–	0.82
Mesoporous	439	0.47	0.12	0.35	12	<0.02	3985	0.25	0.70

[a] ICP analysis of powder.
[b] ICP analysis of filtrate.

was washed intensively to remove the excess Na^+ ion, and filtered before being dried at 100 °C overnight. The dried sample (about 15 g) was then ion exchanged twice with a 300 ml of 1 M solution of NH_4NO_3 at 70 °C for 24 h. Then the sample was washed, filtered and dried overnight. Both the parent and the alkali treated samples were calcined in air at 550 °C for 3 h in order to get the catalytically active H-form. In this article, the alkali treated zeolite will be named as mesoporous zeolite.

2.2. Characterization

N_2 adsorption/desorption isotherms were measured at 77 K with an ASAP 2010 setup (Micromeritics). The samples were preheated at 300 °C for 2 h in vacuum. SEM analyses were carried out in a scanning electron microscope (Quanta 200, FEI). Inductively coupled plasma optical emission spectroscopy (ICP-OES) analyses were performed on a Plasma 400 (Perkin Elmer) to monitor the concentrations of Si and Al. NH_3-TPD measurements were carried out in an Altamira 100 equipment. Initially, the sample was preheated at 550 °C for 2 h in flowing He. After which NH_3 was adsorbed on the catalyst at 100 °C for 30 min. NH_3 desorption was then carried out from 100 to 800 °C with a ramp of 10 °C. 50 ml/min of He was used as carrier gas during the desorption process. X-ray diffraction measurements were carried out on an X'pert Pro diffractometer (Philips Analytical) using CuK_α radiation. The crystallinity of the parent and the alkali treated catalysts was calculated on the basis of the so-called Q_{Al}-value [31].

Electron paramagnetic resonance (EPR) spectra were recorded in X-band ($\nu \approx 9.5$ GHz) with the cw spectrometer ELEXSYS 500-10/12 (Bruker) at 293 and 77 K. The magnetic field was measured with respect to the standard 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH) at a microwave power of 6.3 mW. A modulation frequency of 100 kHz and amplitude of 0.5 mT were applied.

2.3. Catalytic testing

The activity of the parent and alkali treated zeolites was tested for the direct hydroxylation of benzene reaction in a laboratory microreactor setup. The calcined samples were coated on a stainless steel microreactor channel using a slurry coating technique. 10% Al_2O_3 was used as binder and acetic acid as the peptizing agent. The description of the reactor and the experimental setup is given elsewhere [32].

A 1:1 molar ratio of benzene to N_2O with N_2 as carrier gas was used in the feed. All the experiments were conducted at temperatures ranging from 400 to 480 °C with a 8.5% fraction of benzene and nitrous oxide at a modified residence time of 92 g min/mol (active mass of catalyst per total molar flow rate). The exit gas was analyzed by an online GC equipped with a FID detector. Synthetic air was dosed with a mass flow controller for regeneration of the catalyst. The catalyst was regenerated at 530 °C for one hour to restore the initial activity. The catalytic experiments were focused on comparing the deactivation behavior of the parent and the alkali-treated catalysts, which have been determined through the benzene conversion, phenol yield and selectivity to phenol. For all the experiments, the first measurement was taken 5 min after starting the reaction.

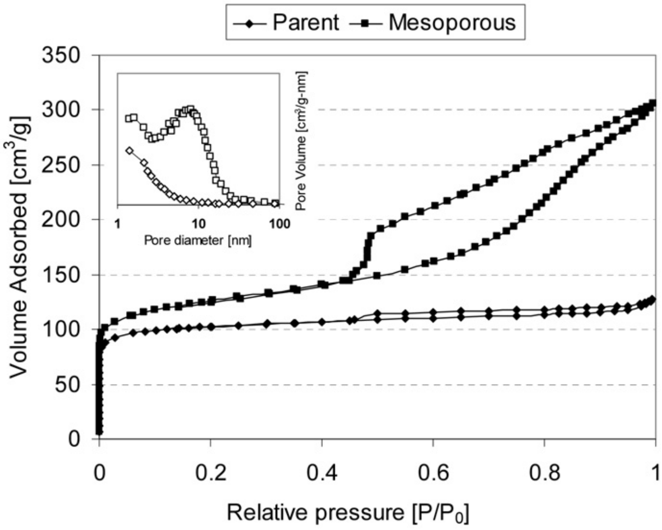
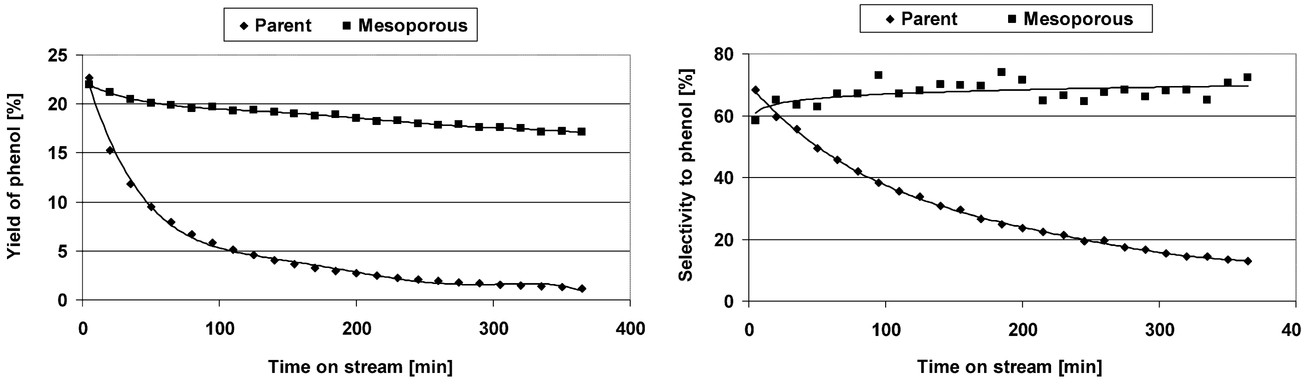


Fig. 1. N_2 adsorption/desorption isotherms and the BJH pore size distribution (inset) of the parent and the mesoporous zeolites.

3. Results and discussion

The XRD pattern (Fig. S1 in the supplementary material) of the parent and alkali treated zeolites confirm that the MFI structure is preserved in the sample even after the strong alkaline treatment. No additional phases were observed. The minimal loss in the relative crystallinity (Q_{Al}-values [31]) from 0.82 to 0.70 upon alkali treatment might be due to the creation of additional mesopores in the MFI crystals (see Table 1). Fig. 1 shows the N_2 adsorption/desorption isotherms of the parent and the alkali treated zeolites. Their physical characteristics are summarized in Table 1. The course of isotherm of the parent zeolite shows the characteristics of a microporous material without an appreciable contribution of mesoporosity (0.05 cm^3/g) which might be due to the presence of defects in the crystals and an intercrystalline porosity. Upon the alkali treatment in the NaOH solution, development of a distinct mesoporosity in the ZSM-5 was demonstrated by a significant increase in mesopore volume of about 0.30 cm^3/g. The resulting BJH pore-size distribution curves derived from the sorption isotherm confirm the presence of mesopores with an average opening size of ca. 9-10 nm (inset in Fig. 1).

As it can be noted from Table 1, N_2 sorption data show only a slight reduction in the micropore volume from 0.14 to 0.12 cm^3/g after the alkali treatment, which indicates that the micropore system of the zeolite itself remains nearly unchanged. In contrast, the mesopore volume and hence the total porosity increased drastically after the treatment. This bimodal system consists of the micropores with a typical MFI zeolitic pore opening of about 0.5 to 0.6 nm and mesopores with an average pore diameter of 9 to 10 nm which in turn contains pore volumes of about 0.12 and



(a) (b)

Fig. 2. (a) Phenol yield, (b) selectivity to phenol with time on stream for the parent and the mesoporous zeolites ($\tau_{\mathrm{mod}} = 92$ g min/mol, reactor temperature = 440 °C, molar ratio of reactants N_2O:benzene = 1:1).

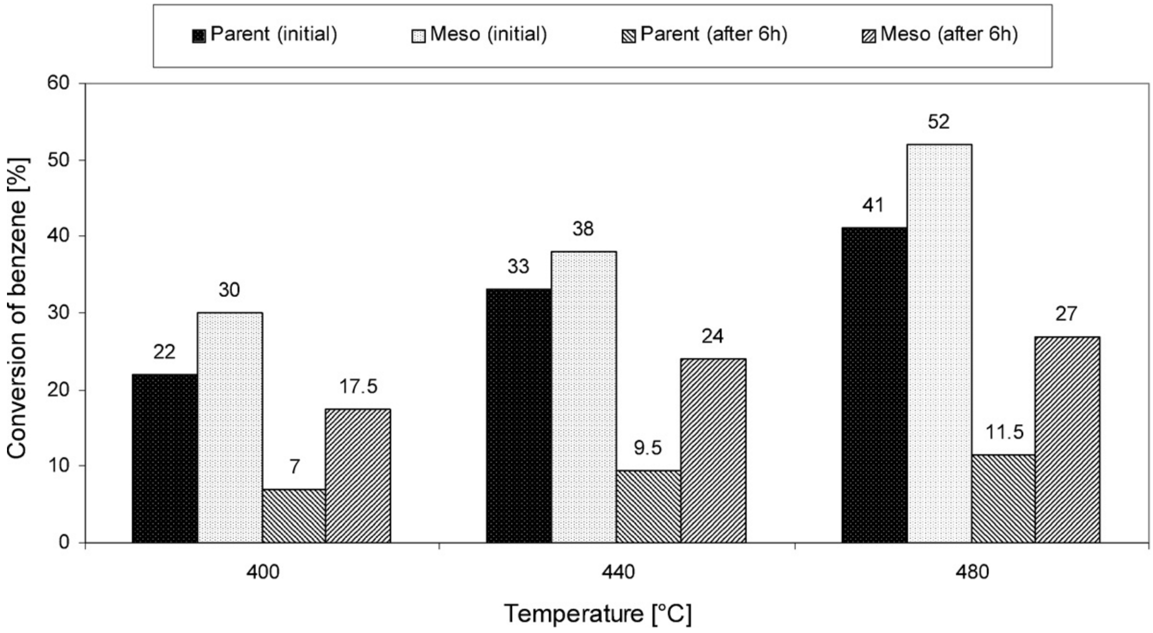


Fig. 3. Conversion of benzene with parent and mesoporous zeolites after 5 min (initial) and 6 h time on stream at different temperatures ($\tau_{\mathrm{mod}} = 92$ g min/mol, molar ratio of reactants N_2O:benzene = 1:1).

0.35 cm^3/g, respectively. In addition, the comparison of SEM micrographs parent and alkali treated zeolite (Fig. S2 in the supplementary material) revealed that neither the crystal size (∼4.5 µm) nor the morphology was affected by the aforementioned treatment.

The Si/Al ratio of the mesoporous zeolite obtained via the ICP-OES analysis was found to be lower than that of the parent catalyst. This can be explained by the partial removal of Si from the framework of the zeolite (desilication) during the alkali treatment. The absence of measurable amounts of Al in the filtrate indicates that aluminum was not leached from the framework.

The catalytic results are summarized in Figs. 2 and 3. The dependency of the phenol yield for both parent and mesoporous zeolites up to 6 h time on stream (TOS) is shown in Fig. 2a. The initial yield of the parent and the mesoporous zeolite was nearly identical with about 22%. However, after 6 h time on stream, the phenol yield of the parent zeolite was reduced to only 1% whereas the phenol yield of the mesoporous zeolite was still around 17%. The corresponding selectivity towards phenol based on benzene for the parent and mesoporous zeolites (Fig. 2b) exhibits a well pronounced difference between these two catalysts. As the reaction proceeded, the selectivity to phenol was observed to reduce for the parent zeolite from 70 to 13% whereas it was found to be constant at about 70% for the mesoporous zeolite.

A similar catalytic behavior was observed for the reactions conducted at temperatures 400 and 480 °C. Fig. 3 shows a comparison of the conversion of benzene between the parent and the mesoporous catalysts after 5 min (initial) and 6 h time on stream. At all temperatures, we observe a higher benzene conversion with the mesoporous zeolite compared to the parent one and the benzene conversion was always found to increase with an increase in the temperature. However, the relative deactivation calculated as the ratio of the difference between the initial and the final conversion to the initial conversion, was higher for the parent zeolite. Thus, at 400 °C, the initial conversion of the mesoporous zeolite was about 30% which is 8% higher than that of the parent zeolite. After 6 h TOS the parent catalyst and the mesoporous catalyst exhibit a conversion of 7 and 17.5% which amounts to relative deactivations of 69% and mere 42%, respectively. A further increase in the temperature did not affect the relative deactivation. At all instances the deactivation of the mesoporous zeolite catalyst was about 2 times less than that of the parent catalyst indicating a better long term stability of the catalyst.

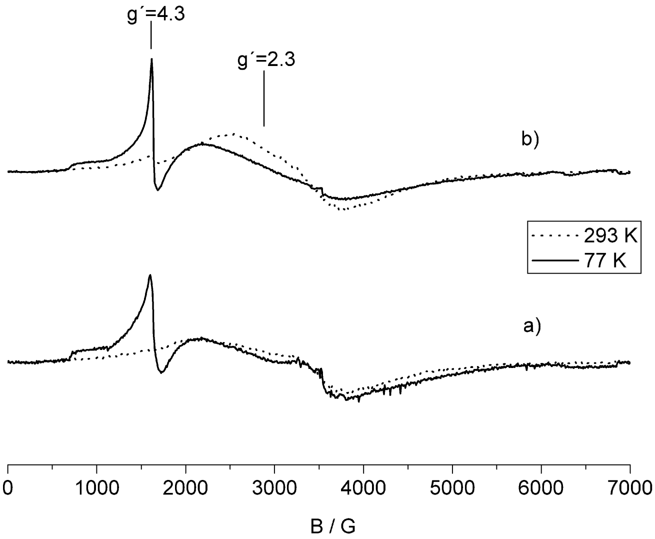


Fig. 4. EPR spectra: (a) parent, (b) mesoporous zeolite.

The suppressed deactivation and enhanced selectivity of the mesoporous zeolites could be explained through two possible reasons: (i) changes in the active site speciation upon alkali treatment and/or (ii) creation of mesopores upon alkali treatment in the MFI crystals. Since iron sites are considered to be inevitable for the benzene to phenol hydroxylation [12–14], ICP-OES and EPR analyses were employed to determine the amount of Fe present in the samples and its corresponding state. The ICP-OES analyses showed that the studied H-ZSM-5 samples of both the parent and mesoporous (alkali treated) catalysts contained a very low amount of iron (<0.02 wt%, below the detection limits of the used setup). However, EPR measurements revealed that traces of iron are present in both the zeolites. The traces of iron might be caused by the impurities present in the raw materials used for the synthesis of the commercial product.

Fig. 4 shows the comparison of the EPR spectra of the parent (H-form) and the mesoporous zeolites (H-form) measured at 293 and 77 K. The assignment of EPR signals were made according to Pérez-Ramírez et al. [33]. It can be observed that both the parent and mesoporous catalysts contained Fe in the form of isolated Fe^{3+} species (signal at around 1500 G, $g' = 4.3$) as well as in the form of anti ferromagnetic Fe_2O_3 cluster (broader signal at around 3000 G, $g' = 2.3$). As far as the Fe^{3+} species are concerned, both the samples show the same behavior. At 77 K, both the zeolites showed a sharp signal at $g' = 4.3$ (isolated Fe^{3+} species) where as the intensities of these signals reduced with an increase in temperature (at 293 K). The mesoporous catalysts seemed to contain slightly higher amounts Fe_2O_3 species which is considered to be inactive during the benzene hydroxylation reaction. This observation suggests that the alkali treatment did not considerably alter the state of the iron. Though Fe is present in trace amounts, the amount and the state of Fe are similar in both the parent and the mesoporous catalysts. These results prove that the improvements in the catalytic performances might not be due to the changes in the iron state upon the alkali treatment.

In contrast, the observed changes in the pore system upon the alkali treatment are quite obvious. The removal of about 40% of the Si atoms from the framework leads to mesoporous ZSM-5 crystal with a mesopore volume of about 0.35 cm^3/g. A nearly random distribution of the mesopores inside the crystal might result in shorter pore lengths which reduce the necessary diffusion path lengths for the produced phenol molecule out of the crystal. Hence, the suppressed deactivation, enhanced activity as well as selectivity of the mesoporous catalyst can be attributed to the improved transport of the product molecule (phenol) in the shortened micropores of alkali treated samples. In [16], an improved catalytic performance of steam treated catalyst on benzene hydroxylation has been speculated to the presence of mesopores. However, the accompanied changes in the state of Fe after steam treatment could not be avoided.

In summary, a commercial parent MFI type zeolite and its alkali-treated mesoporous counterpart were tested for the direct hydroxylation of benzene to phenol. We have shown that (i) a commercial MFI zeolite containing traces of iron is active in the benzene to phenol hydroxylation and (ii) the oxidation state of the iron is nearly unaffected after the alkali treatment. The activity and the long term stability obtained with the mesoporous catalyst were found to be always higher than that of the parent catalyst. Improvements in these quantities could be attributed to the presence of mesopores, as there were no changes in the state of iron upon alkali treatment. These results prove that the introduction of mesopores in the parent zeolite has a positive effect in the investigated reaction, as it has been thought to favor the intracrystalline diffusion steps. The results indicate that the mesoporous zeolite with the bimodal pore structure could be a suitable catalyst in order to increase lifetime of the catalyst for the investigated reaction. Further experiments are underway in order to find the optimal mesopore to micropore ratio and understand its influence in the phenol yield and selectivity.

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Supplementary material

The online version of this article contains additional supplementary material.

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