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Catalytic Performance of Phosphorus Modified H-IM-5@meso-\$iO2^{9/C9NJ02440A} **Composite in Alkylation of Toluene with Methanol**

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ABSTRACT

A core-shell H-IM-5@meso-SiO₂ hybrid material was synthesized via a method of reversing the external surface of IM-5 crystals to positively charged by PDDA, which could induce an oriented self-assembly formation of meso-SiO2 shell. The as-synthesized H-IM-5@meso-SiO2 composite was thereafter modified with phosphorus species to further enhance the selectivity of target product. The sample morphology and structure were analyzed by electron microscopy technology, XRD, XPS and N₂ adsorption-desorption. The effects of meso-SiO₂ shell and phosphorus species on sample acidity were investigated by NH3-TPD, FT-IR and solid-state NMR measurement. The catalytic properties and characterization results revealed that the meso-SiO₂ shell could passivate the external surface acids of H-IM-5 crystals. The phosphorus modification could adjust the surface acidity as well as the size of pores and pore-opening simultaneously. The TPD of xylene analysis showed that the sample surface acidity and geometric factors play important roles in the diffusion process of the diffusing molecules.

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Keywords: H-IM-5; meso-SiO₂; phosphorus; toluene; alkylation; diffusion activation²/^{C9NJ02440A} energy

1. Introduction

P-xylene is the main raw material for the production of terephthalic acid (PTA) and dimethyl terephthalate (DMT), which are used in the synthesis of polyesters such as polyethylene terephthalate (PET) and polybutylene terephthalate (PBT).¹ The selectivity synthesis of p-xylene by methylation of toluene using zeolite catalysts has been developed.^{2,3} As an important commercial zeolite for industrial catalysis, ZSM-5 has been proved to be very appropriate for the selective production of aromatics with para-alkyl groups since its pore dimension approximates the size of these aromatic moleculars.⁴ However, the external surface acid sites of the catalyst exhibit different catalytic behaviors and reduce the selectivity of target product. In the methylation reaction of toluene, the xylene isomerization which is favorable to produce m-xylene was roughly correlated with the external surface of the catalyst particles.^{5,6} Hence, surface passivation and pore size control have been proposed in order to improve the selectivity, such as silicon modification by methods of chemical vapor/liquid deposition (CVD/CLD)⁷⁻¹² and impregnation with P, Mg or B et al.¹³⁻¹⁷ Although these modification techniques could increase para-selectivity, they are also accompanied by pore blockage, which reduce the catalytic activity significantly.¹⁸ In recent years, core-shell composites with excellent special functions have broadened the application areas of these materials from electrode¹⁹ and biomaterial²⁰ to catalysis²¹ and separation.²² A number of core-shell zeolites have been synthesized, among which

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MFI@MFI composites with excellent para-selectivity have been synthesized through heterogeneous nucleation methods.²³⁻²⁵ In addition, core-shell composites with an active zeolite core and an inactive mesoporous silica shell were also synthesized for selective catalytic reactions.²⁶⁻²⁸

As a new zeolite reported by Benazzi et al.,^{29,30} IM-5 zeolite consists of an unusual 2D 10-MR channel system with large internal 3D cavities,³¹ which is different from the MFI zeolites. IM-5 zeolite is considered as a promising catalyst alternative to ZSM-5 zeolite due to its strong acidity, excellent hydrothermal stability and catalytic cracking activity.³²⁻³⁴ As described by He et al.,³⁴ the excellent physico-chemical properties of IM-5 zeolite may be related to its numerous high acidic Al, H-sites. Previous studies have investigated the catalytic properties of IM-5 zeolite by reactions of aromatization,³⁵ selective reduction^{36,37} and alkylation.^{38,39}

In the present study, a novel H-IM-5@meso-SiO₂ composite with hierarchical pores was prepared to passivate the external acid sites of the core H-IM-5 zeolite. Thereafter, the phosphorus species were incorporated into the composite to adjust the surface acidity as well as the size of pores and pore-opening simultaneously, and enhance the selectivity of target product eventually. The texture and acid properties were analyzed by N₂ adsorption-desorption, NH₃-TPD and Py/Coll-IR. The Al and P species were tested by solid-state NMR measurement. The catalytic performance of modified samples were studied by alkylation of toluene with methanol under different reaction conditions. Moreover, the diffusion activation energies of p/m-xylene on the samples were determined by the TPD technique.

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2. Experimental

2.1. Reagents

ZSM-5 zeolite (SiO₂/Al₂O₃ = 50) was obtained from Nankai University Catalyst Co., Ltd. Tetraethylorthosilicate (TEOS, 28 wt% SiO₂, Greagent), sodium hydroxide (NaOH, 98 wt%, Greagent), aluminum nitrate nonahydrate (Al(NO₃)₃·9H₂O, 99 wt%, cetyltrimethylammonium bromide (CTAB, 99 wt%, Greagent), Adamas). poly(diallyldimethylammonium chloride) (PDDA, 20 wt% in water, Aldrich), ammonium chloride (NH4Cl, 99.5 wt%, Greagent), phosphorus acid (H3PO4, 85 wt% in water, Greagent), ammonium aqueous solution (NH3·H2O, 28 wt%, Greagent), 2,4,6-collidine (C₈H₁₁N, 99 wt%, Adamas), pyridine (C₅H₅N, 99 wt%, Adamas), toluene (C7H8, 99.5 wt%, Greagent), methanol (CH3OH, 99.8 wt%, Greagent) and ethanol (C2H5OH, 99.7%, Greagent) were purchased from Shanghai Titan Scientific Co., Ltd. The structure-directing agent was supplied by Guangzhou Dayou Fine Chemical Plant. The silica sol (40 wt% in water) was supplied by Qingdao Haiyang Chemical Co., Ltd.

2.2. Synthesis of H-IM-5@meso-SiO2 Core-shell Composite

Firstly, the raw Na-IM-5 zeolite was synthesized according the procedure reported in the literature⁴⁰ with a precursor mixture of 30SiO₂:11Na₂O:0.6Al₂O₃:3 (1,5-MPPBr₂):1200 H₂O. The synthesized Na-IM-5 was calcined at 550 °C for 5 h to eliminate the organic template. And then the calcined sample was ion-exchanged with 1.0 mol/L NH₄Cl solution at 80 °C three times and dried at 110 °C overnight. The white powder named NH₄-IM-5 was obtained. The H-IM-5 zeolite was obtain by the

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calcination of NH4-IM-5 at 500 °C for 5 h. Secondly, the external surface of NH₄-IM-5 crystals was functionalized to positively charged by an aqueous solution of polycation agent (PDDA). The modification procedure was as follows: NH4-IM-5 mixed with a 2 g/L aqueous solution of PDDA with a mass ratio of NH₄-IM-5: PDDA aqueous solution = 1: 50. After 1 h stirring, the functionalized NH4-IM-5 was obtained after centrifugal washing three times and drying at 80 °C overnight. Thirdly, 1.2 g of as-prepared functionalized NH₄-IM-5 was added to the mixture solution (240 mL ethanol, 300 mL deionized water, 4.0 g ammonia aqueous solution (28 wt%) and 1.2 g CTAB). The suspension was dispersed by ultrasonic treatment for 1.0 h. Then, TEOS (1.2-3.6 g) was added into the suspension dropwise under vigorous stirring at room temperature. After stirring for 5 h, the sample was filtered and washed with ethanol and deionized water, dried at 110 °C overnight and finally calcined at 550 °C for 6 h to eliminate the organic template. Five H-IM-5@meso-SiO₂ samples (IM-S) with different amounts of TEOS (1.2, 1.8, 2.4, 3.0 and 3.6 g) were synthesized and named IM-1.2S, IM-1.8S, IM-2.4S, IM-3.0S and IM-3.6S respectively. For comparison, the functionalized NH4-IM-5 (1.2 g) was modified with amorphous silica by chemical liquid deposition using TEOS (2.4 g) by referring to the method reported by Zheng et al.⁴¹ and named as IM-2.4S-CLD.

2.3. Synthesis of the Phosphorus Modified H-IM-5@meso-SiO₂ Samples

Five phosphorus modified IM-2.4S samples (IM-2.4S-P) with different phosphorus content (0.5, 1.0, 1.5, 2.0 and 2.5 wt%) were synthesized by impregnating with certain amounts of phosphoric acid on the IM-2.4S sample and named as IM-2.4S-0.5P,

60

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IM-2.4S-1.0P, IM-2.4S-1.5P, IM-2.4S-2.0P and IM-2.4S-2.5P respectively.⁽⁴⁾ Meanwhile, a comparison sample with 2.0 wt% phosphorus content was prepared by the same impregnation method on the H-IM-5 zeolite without coating of meso-SiO₂ shell. The comparison sample was named as IM-2.0P. All the impregnated samples were dried at 110 °C overnight, and calcined at 500 °C for 5 h.

2.4. Materials Characterization

The X-ray diffraction (XRD) patterns were collected using a Rigaku Ultima IV diffractometer with Cu Ka radiation (40 kV, 44 mA). The chemical composition of samples were obtained on an Agilent 725 ICP-OES. N2 adsorption-desorption isotherms were collected using a Micromeritics ASAP-2020 system. The BET specific surface area (S_{BET}), micropore specific surface area (S_{micro}), mesopore specific surface area (S_{meso}), micropore volume (V_{micro}) and mesopore volume (V_{meso}) were derived from the corresponding N₂ adsorption-desorption isotherms. The pore size distributions were derived from adsorption branches of isotherms using the NL-DFT method. Scanning electron micrographs (SEM) were obtained on Hitachi S-4800 operating at a field emission electron acceleration voltage of 5-15.0 kV. Transmission electron microscopy (TEM) images were obtained on a JEOL-2010F electron microscope operated at 200 kV. The X-ray photoelectron spectroscopy (XPS) was obtained by using a Perkin-Elmer PHI 5000C ESCA system equipped with Mg anode. The binding energy was calibrated by C 1s at 284.6 eV. The solid-state MAS NMR spectra was performed on a Bruker AVANCE III 500 spectrometer.

NH₃-TPD was performed on Auto Chem 2910 (Micromeritics, USA) and the

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desorbed NH₃ were detected using a thermal conductivity detector (TCD). The¹⁰ acta^{(C9NJ02440A} type and accessibility of samples were tested by pyridine/2,4,6-collidine-FTIR (Py/Coll-IR) using a Nicolet IS-10 equipped with an in situ reaction cell. The number of Lewis and Brønsted acid sites were quantified according to the Lambert-Beer formula: $\xi = A \cdot S/n$, in which ξ is extinction coefficient, A is the corresponding absorbance, S is surface area of the wafer, and n is amount of the adsorbate substance. For Py-IR, $\xi_{Bronsted}$ (1541) = 1.02 cm/µmol and ξ_{Lewis} (1443-1453) = 0.89 cm/µmol were used to quantify Brønsted and Lewis acid sites, respectively.⁴²⁻⁴⁴ The total and strong acids were measured at 200 and 450 °C, and their difference was the weak acids. For Coll-IR, $\xi(1632-1648) = 10.1$ cm/µmol was applied to quantify external surface acids of the samples.^{42,44}

Temperature programmed desorption (TPD) of p/m-xylene was performed on Auto Chem 2910 (Micromeritics, USA). The diffusion of m-xylene into ZSM-5 pores is limited at lower temperatures. Therefore, the adsorption of p/m-xylene was carried out at 80 °C to ensure that p/m-xylene could diffuse into the pores. The sample was pretreated at 450 °C with helium flow for 60 min, and then the temperature cooled to 80 °C for the adsorption of p-xylene or m-xylene. Then the temperature cooled to 40 °C. Finally, the TPD curves were collected from 40 to 500 °C with varying heating rates (8-20 °C/min).

2.5. Catalytic Measurements

The characteristic of modified samples were studied by alkylation of toluene with methanol in a quartz tube reactor (length: 500 mm; internal diameter: 9 mm). A

certain amount of samples (20-40 mesh) were packed into the constant temperature section of the reactor and the rest spaces were filled with quartz sands (20-40 mesh). The samples were preheated at the reaction temperature for 1 h in N₂ flow to ensure that the water and volatile organic compounds adsorbed in the pores were completely removed. The reactants, mixture of toluene with methanol, were then pumped into the reactor at certain reaction temperatures and WHSV with N₂ flow (40 mL/min). Products were directly delivered into a gas chromatograph equipped with a flame

3. Results and Discussion

ionization detector and innowax column.

3.1. Texture and Catalytic Properties of H-IM-5 and H-ZSM-5

Fig. 1A exhibited the XRD patterns of H-IM-5 and H-ZSM-5 zeolites, which peak positions matched the characteristics of IMF and MFI topologies as described in the literatures, respectively.^{40,45} As exhibited in Fig. 1B, the N₂ adsorption-desorption isotherms of H-IM-5 and H-ZSM-5 zeolites can be attributed the mixture of type I and IV isotherms,⁴⁴ in which the micropores were filled at $P/P_0 < 0.1$ and the addition N₂ uptake at P/P_0 of 0.45-0.95 confirmed the presence of irregularly shaped intergranular mesopores. The S_{micro} and V_{micro} of H-IM-5, shown in Table S1, were close proximity to that of the H-ZSM-5. The NH₃-TPD curves (Fig. 1C) of these two zeolites exhibited two same NH₃ desorption peaks at 202 and 406 °C, and the peak areas were basically the same, indicating similar acid sites amount and acid strength on these two zeolites. The catalytic performance of toluene alkylation with methanol on these two zeolites were obtained as shown in Fig. 1D. Compared with H-ZSM-5, H-IM-5

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possessed higher toluene conversion and xylene selectivity, which may be related to^{7/C9NJ02440A} its unusual channel system with large internal cavities and numerous high acidic Al, H-sites.³⁴ The selectivity of p-xylene on these two zeolites were basically the same, which were closely to thermodynamic equilibrium value. In the subsequent study, H-IM-5 was modified with coating of mesoporous silica and impregnation of H₃PO₄ to improve its para-selectivity.



Fig. 1 (A) XRD patterns, (B) N₂ adsorption-desorption isotherms isotherms, (C) NH₃-TPD profiles, (D) Catalytic performance of H-IM-5 and H-ZSM-5 zeolites. S_X-Selectivity of xylene; S_{PX}-Selectivity of p-xylene.

3.2. Texture and Acid Properties of H-IM-5@meso-SiO₂ Samples

Fig. 2 exhibited the XRD results of H-IM-5@meso-SiO₂ samples with different TEOS weight varying from 1.2 g to 3.6 g. The wide-angle XRD patterns exhibited apparent diffraction peaks contributed by the core IM-5 zeolite, which were

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completely consistent with the topological structure of IM-5. However, the peak intensities decreased with the increasing of TEOS weight, i.e. the increase of meso-SiO₂/IM-5 mass ratio, which may be caused by the coating of meso-SiO₂. Since the framework of meso-SiO₂ shell is amorphous, there was no obvious diffraction peak of meso-SiO₂ in the wide-angle XRD patterns of H-IM-5@meso-SiO₂ samples. As shown in Fig. 2, the low-angle XRD of H-IM-5@meso-SiO₂ samples presented (100) peak at about 2.4° without the appearance of (110) and (200) peaks, suggesting the existence of short-range ordered mesoporous structure.^{46,47} The intensity of this (100) peak increased with the increasing of TEOS weight, indicating the proportion of meso-SiO₂ shell to the core H-IM-5 became higher. As shown in the electron microscopy images (Fig. 3), the parent H-IM-5 was in the morphology of rod-like crystals. After the coating of meso-SiO₂, the crystal size increased obviously and the crystal particles were prone to agglomeration. The TEM images of IM-2.4S sample, shown in Fig. 3 (T2 and T3), confirmed that the core-shell structure with H-IM-5 crystals for the core and meso-SiO₂ for the shell. XPS spectra of Al 2p was carried out and displayed in Fig. S1. It can be clearly observed that the characteristic binding energy at 74.5 eV of Al 2p was easily recognized in the spectra of H-IM-5 zeolite.^{48,49} However, the Al 2p signal on IM-2.4S sample was barely detectable by XPS measurement, which suggested that the core H-IM-5 crystals were completely coated with the meso-SiO₂ shell.



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Fig. 2 XRD patterns of H-IM-5 and H-IM-5@meso-SiO₂ samples: (a) H-IM-5, (b) IM-1.2S, (c)

IM-1.8S, (d) IM-2.4S, (e) IM-3.0S, (f) IM-3.6S.



Fig. 3. SEM images: (A) H-IM-5 (×20.0K), (B) IM-1.2S (×30.0K), (C) IM-1.8S (×30.0K), (D) IM-2.4S

(×30.0K), (E) IM-3.0S (×30.0K), (F) IM-3.6S (×30.0K). TEM images: (T1) H-IM-5, (T2, T3) IM-2.4S.



Fig. 4 (A) N_2 adsorption-desorption isotherms of the samples, (B) The corresponding pore size distributions based on the adsorption isotherms. The pore size distributions in the inset were offset along the y-axis for visual clarity.

Samples	SiO ₂ /Al ₂ O ₃	$S_{BET} \ ^b$	$S_{micro}{}^{c}$	S _{meso} ^c	V _{total}	V_{micro} ^c	V _{meso} ^c
	ratio ^a	$(m^2 g^{-1})$	$(m^2 g^{-1})$	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	$(cm^3 g^{-1})$	$(cm^3 g^{-1})$
H-IM-5	47	382.477	286.107	96.370	0.355	0.142	0.213
IM-1.2S	58	499.009	194.133	304.876	0.404	0.106	0.298
IM-1.8S	65	547.098	184.067	363.031	0.423	0.097	0.326
IM-2.4S	73	598.365	174.993	423.372	0.445	0.089	0.356
IM-3.0S	79	638.119	166.772	471.347	0.477	0.077	0.400
IM-3.6S	86	707.043	159.288	547.755	0.485	0.071	0.414

 Table 1
 Structural properties of H-IM-5 and H-IM-5@meso-SiO2 samples

^a Calculated by ICP-OES; ^b Calculated by the BET method; ^c Calculated using the t-plot method.

For the sample without PDDA pretreatment, the coating of meso-SiO₂ onto the H-IM-5 crystals also happened. Nonetheless, partial silica self-assembled in sphere form outside the bulk phase of the desirable H-IM-5@meso-SiO₂ core-shell composite (Fig. S2). Therefore, the external surface of H-IM-5 crystals functionalized

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to positively charged was more conducive to attract negatively charged silica species^{/C9NJ02440A} in basic media. And then H-IM-5 crystals were coated with the meso-SiO₂ shell by layer-by-layer electrostatic adsorption.

N₂ adsorption-desorption was carried out to determine the texture properties of the samples. As exhibited in Fig. 4A, the isotherms for all the samples can be attributed to the mixture of type I and IV isotherms. The isotherms for H-IM-5@meso-SiO₂ samples showed a steep increase at $P/P_0 = 0.2-0.4$ confirmed the presence of meso-SiO₂ corresponding to pore size distributions at $2.0 \sim 3.5$ nm (Fig. 4B inset). Same as the H-IM-5 isotherm, H-IM-5@meso-SiO2 samples also exhibited obvious H4 hysteresis loops at P/P_0 of 0.45-0.95, which indicates the presence of irregularly shaped intergranular mesopores caused by H-IM-5 crystals. In contrast to the parent H-IM-5 zeolite, the pore size distributions of H-IM-5@meso-SiO2 exhibited two peaks, in which the peak at ~ 0.87 nm was ascribed to the micropores of core H-IM-5 and the other at around 2.5 nm was related to the meso-SiO₂. As shown in Table 1, the SBET and total pore volume (Vtotal) of H-IM-5 zeolite were 382.477 m² g⁻¹ and 0.355 cm³ g⁻¹, respectively, which were mainly derived from micropores. In the H-IM-5@meso-SiO₂ samples, the contribution of micropores to SBET and Vtotal decreased with the increase of TEOS weight, while the contribution of mesopores at the range of 2.0~3.5 nm increased obviously and became the main contributor. The results of N₂ adsorption-desorption suggested that the core H-IM-5 was well-connected with the meso-SiO₂ shell and micropores of the core were accessible to the outside. For further confirmation of the accessibility of core H-IM-5, NH₃-TPD

 and FT-IR measurements were carried out.

As exhibited in Fig. 5A, the NH₃-TPD curves presented two NH₃ desorption peaks which were related to weak and strong acids. For H-IM-5, the peaks at 203 and 409 °C were attributed to weak and strong acids, respectively.⁵⁰ Compared with H-IM-5, the peak intensity of H-IM-5@meso-SiO₂ samples decreased and the peak value shifted to lower temperature slightly, indicating a decrease of acid amount and decline of acid strength. It should be attributed to the coating of meso-SiO₂ shell which are extremely low in acidity.



Fig. 5 A) NH₃-TPD, B) Coll-IR at 200 °C, C) Py-IR at 200 °C and D) Py-IR at 450 °C. The

spectra of samples: a) H-IM-5, b) IM-1.2S, c) IM-1.8S, d) IM-2.4S, e) IM-3.0S and f) IM-3.6S.

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 Table 2
 The Brønsted/Lewis amount determined by Py-IR (mmol Py g⁻¹-cat) and Coll-IR (mmol Py g⁻¹-cat)

			Acid	dity ^a		Adsorbed pyridine	External	Adsorbed collidine	
Sample	T ^a	Sp	Wp	Ç.	Wr	per core H-IM-5 °	surface	per core H-IM-5 °	
		DB	// B	D_{L}	"L	(mmol-Py·g ⁻¹ -IM-5)	acidity ⁶	(mmol-coll·g ⁻¹ -IM-5)	
H-IM-5	1.235	0.349	0.584	0.190	0.112	1.235	0.231	0.231	
IM-1.2S	0.889	0.243	0.41	0.142	0.094	1.138	0.112	0.143	
IM-1.8S	0.796	0.213	0.373	0.122	0.088	1.130	-	-	
IM-2.4S	0.725	0.201	0.326	0.112	0.086	1.131	0.088	0.137	
IM-3.0S	0.662	0.189	0.287	0.104	0.082	1.125	-	-	
IM-3.6S	0.610	0.178	0.260	0.091	0.081	1.122	0.069	0.127	

^a Determined by Py-IR. ^b Determined by Coll-IR. ^c The number of adsorbed pyridine or collidine per core H-IM-5 was calculated by dividing the amount of total acid or external acid with the proportion of core H-IM-5 in the samples, respectively. *T*-Total acid; S_L and S_B -Strong Lewis and Brønsted acid; W_L and W_B -Weak Lewis and Brønsted acid.

The acidic type and accessibility of the samples were determined by Py-IR and Coll-IR, in which Py-IR results reflected the sample acidity without differentiating the internal or external surface acids, while Coll-IR can only access to the external surface acidity of H-IM-5 crystals.^{44,51-53} The Py-IR spectra at 200 and 450 °C were obtained as shown in Fig. 5C and D. The peak at 1451 cm⁻¹ can be related to the Lewis acid sites. Another characteristic peak at around 1540 cm⁻¹ was related to the vibration of pyridine molecules bonded to Brønsted acid sites.⁵⁴ The relative intensities of these two peaks decreased obviously as the temperature rose from 200 to 450 °C, indicating desorption of weakly adsorbed pyridines. Fig. 5B presents Coll-IR spectra of the samples at 200 °C. As demonstrated by N. S. Nesterenko et al.,⁴² peaks

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at 1632 and 1648 cm⁻¹ were related to adsorption of 2,4,6-collidine at Lewis and Brønsted acid, which were subsequently used to quantify the external surface acidity. As indicated by Coll-IR spectra in Fig. 5B, the coating of meso-SiO₂ shell resulted in a dramatically decrease of peak intensities at 1632 and 1648 cm⁻¹, which can be due to the increase of meso-SiO₂/IM-5 mass ratio and passivation of the external surface acid sites by silica shell. The detailed Py/Coll-IR results were analyzed with the previously established methods and compiled in Table 2. The total acid amount calculated by pyridine exhibited the same tendency as the results of NH₃-TPD. In contrast to H-IM-5, the total acids of IM-2.4S decreased by 41%. It was assumed that the meso-SiO₂ shell had no acid center and only the core H-IM-5 could adsorb the pyridine molecules. In that way, the number of adsorbed pyridine per core H-IM-5 in the IM-2.4S sample was 1.131 mmol-Py·g⁻¹-IM-5, which was about 8% less than that of parent H-IM-5 zeolite. The external surface acids on the IM-2.4S sample calculated by Coll-IR was 0.088 mmol Coll·g⁻¹-cat and the adsorbed collidine per core H-IM-5 was 0.137 mmol-Coll g⁻¹-IM-5. The relative decrement of external surface acids was 0.094 mmol-Coll g⁻¹-IM-5 which accounted for 7.6% of the total acids. Therefore, it can be deduced that the decrement of the number of adsorbed pyridine per core H-IM-5 was mainly due to the decrease of external surface acids caused by the coating of meso-SiO₂. The results of N₂ adsorption-desorption and acid analysis confirmed that the meso-SiO₂ shell did not result in blockage of pores of core crystals and the micropores of the core H-IM-5 were accessible to the outside.

3.3. Texture Properties of Phosphorus Modified H-IM-5@meso-SiO₂ Samples

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N₂ adsorption-desorption was carried out to determine the texture properties of the ^{INCOND2440A} phosphorus modified samples. The isotherms for phosphorus modified IM-2.4S-P samples (Fig. S3) were similar to that of IM-2.4S which can be attributed to the mixture of type I and IV isotherms. As illustrated in Table 3, the S_{BET} and V_{total} of the IM-2.4S-P samples, as well as the S_{micro} and V_{micro}, decreased with the increasing of phosphorus impregnation amount. It indicated that the phosphate ions entered into pores of the sample and resulted in the narrowing of the channel. The XRD patterns (Fig. S4) exhibited the typical IMF topology without distinct peaks for phosphorus species. Nevertheless, compared with the IM-2.4S sample, the crystallinity of phosphorus modified samples decreased with the increasing of phosphorus impregnation amount, which was mainly attributed to the dealumination caused by H₃PO₄.

Samples	P content ^a	S _{BET} ^b	S _{micro} ^c	S _{meso} ^c	V _{total}	V _{micro} ^c	V _{meso} ^c
ł	(wt%)	$(m^2 g^{-1})$	$(m^2 g^{-1})$	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	$(cm^3 g^{-1})$	$(cm^3 g^{-1})$
IM-2.4S	-	598.365	174.993	423.372	0.445	0.089	0.356
IM-2.4S-0.5P	0.43	577.267	159.742	417.525	0.426	0.079	0.347
IM-2.4S-1.0P	0.95	559.013	149.972	409.041	0.405	0.072	0.333
IM-2.4S-1.5P	1.41	539.072	137.351	401.721	0.389	0.065	0.324
IM-2.4S-2.0P	2.07	510.365	117.427	392.938	0.371	0.055	0.316
IM-2.4S-2.5P	2.42	479.253	100.712	378.541	0.350	0.047	0.303

Table 3	Structural	properties	of IM-2.4S and	phosphorus	s modified	samples
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^a Determined by ICP-OES; ^b Calculated by BET method; ^c Calculated by t-plot method.



Fig. 6 ²⁷Al and ³¹P MAS NMR spectra of the samples: a) IM-2.4S, b) IM-2.4S-1.0P, c) IM-2.4S-1.5P, d) IM-2.4S-2.0P, e) IM-2.4S-2.5P.

As exhibited in Fig. 6, the ²⁷Al spectrum of IM-2.4S showed an intense peak at 54 ppm corresponds to the tetra-coordinated framework aluminum (FAL) and the weaker peak at 0 ppm typically related to the octahedral extra-framework aluminum (EFAL).⁵⁵ Similar spectra for the IM-2.4S-P samples were observed, while the relatively weak peak of octahedral Al shifted from 0 to -14 ppm, indicating the octahedral Al attached to phosphorous and the higher signal at -14 ppm of IM-2.4S-P samples indicated more octahedral Al due to the dealumination from zeolite caused by phosphoric acid.⁵⁶ Meanwhile, a broad band appeared at ~ 36 ppm in the spectrum of IM-2.4S-2.5P sample can be attributed to either twisted tetra-coordinated FAL and/or classical penta-coordinated aluminium.^{55,57} As shown in the ³¹P MAS NMR spectrum (Fig. 6), the -6 ppm signal was assigned to phosphorus in H₄P₂O₇, pyrophosphates or short-chain polyphosphates not connected to Al,⁵⁵ whereas the -14 ppm signal was related to the short-chain polyphosphates connected to Al,^{55,56} The peaks at -32 and

New Journal of Chemistry

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-40 ppm were related to highly condensed polyphosphates or polyphosphoric species $^{0.01023/C9NJ02440A}$ connected to Al.^{55,58} It is clear that the phosphoric acid on the samples decomposed into H₄P₂O₇ and its derivatives after the calcination treatment. As shown in Fig. 6, when the phosphorus content was less than 2.0 wt%, there was a predominance of the peaks in the range of -6 ~ -14 ppm, corresponding to more phosphorus existed as pyrophosphoric acid or short-chain polyphosphates. The proportion of peak area in the range of -32 ~ -40 ppm increased with the increase of phosphorus content, indicating more highly condensed polyphosphates bonded to Al atoms.

The acidity of the phosphorus modified IM-2.4S-P samples were measured using Py-IR and NH₃-TPD. Fig. S5 displayed the Py-IR spectra of phosphorus modified IM-2.4S-P samples at 200 and 450 °C, and the detailed acid amounts were listed in Table 4. As shown in Table 4, both the total and strong acids decreased with the increase of phosphorus content, while the weak acids exhibited a variation tendency to increase first and then decrease. These two different variation tendencies had been confirmed in the NH₃-TPD profiles (Fig. S6) that the peak intensity of strong acid decreased with increasing of phosphorus content, while the weak acid peak intensity increased first and then decreased. Furthermore, the peak value shifted to lower temperature slightly after the modification of phosphorus. Combined with the analysis of ³¹P NMR, the variation of acidity due to the phosphorus impregnation can be explained by the model proposed by Lercher et al.⁵⁹ that a bond was formed between the P and O of the Si-O-Al group and the P-OH had a lower acid strength than the Si-OH-Al group. When the P content was lower than 1.0 wt%, the quantity of P-OH

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could compensate for the loss of Si-OH-Al. And as a consequence, the amount of weak acids increased, while the strong acids and acid strength decreased. However, when the P content was higher than 1.0 wt%, the P species not only interacted with Al but also with the P species via the oxygen bridge, indicating more condensed polyphosphates which resulted in the decrease of P-OH amount. Eventually, the acid sites decreased as the condensed polyphosphates increased.

 Table 4
 The Brønsted/Lewis amount determined by Py-IR for the samples after modification of
 phosphorus.

Samples	Т	T_B	T_L	S_B	W_B	S_L	W_L
IM-2.4S	0.729	0.530	0.199	0.201	0.329	0.113	0.086
IM-2.4S-0.5P	0.723	0.557	0.166	0.135	0.422	0.075	0.091
IM-2.4S-1.0P	0.719	0.576	0.143	0.091	0.485	0.051	0.092
IM-2.4S-1.5P	0.637	0.517	0.120	0.054	0.463	0.036	0.084
IM-2.4S-2.0P	0.462	0.387	0.075	0.015	0.372	0.012	0.063
IM-2.48-2.5P	0.364	0.298	0.066	0.009	0.289	0.007	0.059

T-Total acid; T_B and T_L -Total Brønsted and Lewis acid; S_B and S_L -Strong Brønsted and Lewis acid; W_B and W_L -Weak Brønsted and Lewis acid.

3.4. Catalytic Performance of H-IM-5@meso-SiO₂ and Phosphorus Modified H-IM-5@meso-SiO₂ Samples in Alkylation of Toluene with Methanol

3.4.1. Catalytic performance of H-IM-5@meso-SiO₂ samples



Fig. 7 Catalytic properties of H-IM-5 and H-IM-5@meso-SiO₂ samples: a) H-IM-5, b) IM-1.2S, c) IM-1.8S, d) IM-2.4S, e) IM-3.0S, f) IM-3.6S, g) IM-2.4S-CLD. Reaction temperature = 440 °C, T/M = 2.0 and WHSV = 2.0 h⁻¹.

The texture and acidic properties of catalyst have significant effects on the para-selectivity in the alkylation of toluene with methanol. As shown in Fig. 7A, the parent H-IM-5 exhibited the highest catalytic activity of toluene conversion, but the worst selectivity of xylene and p-xylene. For the H-IM-5@meso-SiO₂ samples, the average toluene conversion decreased from 55.2% to 44.4% with the increase of TEOS weight from 1.2 g to 3.6 g, which was mainly due to the decrease of core H-IM-5 proportion in the composite. Meanwhile, due to the passivation of meso-SiO₂ shell to the external surface acid sites, the p-xylene selectivity improved above the thermodynamic equilibrium (24%) with the increase of meso-SiO₂/IM-5 mass ratio. For the IM-2.4S sample, the average toluene conversion, selectivity of p-xylene and xylene were 51.6%, 40.3% and 74.3%, respectively. As demonstrated in Fig. 7D, the

yield of p-xylene was significantly improved for samples with TEOS weight less than //csNJ02440A 2.4g, and the yield of xylene was basically unchanged. In contrast, the IM-2.4S-CLD sample exhibited higher selectivity of xylene and p-xylene, but its toluene conversion decreased to 9.5% after 8 hours of catalytic reaction, indicating that the amorphous silica obtained by chemical liquid deposition blocked the entrance of pores to a large extent as exhibited in Fig. S7. Although the coating of meso-SiO₂ shell can improve the yield of p-xylene, the selectivity of p-xylene still needs to be further improved. The IM-2.4S sample showed the best yield of p-xylene among all the H-IM-5@meso-SiO₂ samples. Therefore, IM-2.4S sample was selected and further modified with phosphorus.





Fig. 8 Catalytic properties of IM-2.4S and phosphorus modified IM-2.4S-P samples: a) IM-2.4S,
b) IM-2.4S-0.5P, c) IM-2.4S-1.0P, d) IM-2.4S-1.5P, e) IM-2.4S-2.0P, f) IM-2.4S-2.5P, g) IM-2.0P.
Reaction temperature = 440 °C, T/M = 2.0 and WHSV = 2.0 h⁻¹.

New Journal of Chemistry

Fig. 8 exhibited the effects of phosphorous content on catalytic propertie^{CO} of the^{CONJO2440A} phosphorus modified IM-2.4S-P samples. It can be seen from Fig. 8 that the p-xylene selectivity of the phosphorus modified samples improved significantly with loss of catalytic activity. The p-xylene selectivity of IM-2.4S-2.0P sample was above 60% with a xylene selectivity of more than 88%, and its p-xylene yield reached the maximum. However, the yield of xylene decreased with increasing of phosphorus content, mainly due to the loss of acid sites which resulted in the weaken of catalytic activity. Further increasing phosphorus content to 2.5 wt% resulted in an increase of p-xylene selectivity to ~ 70%, while the toluene conversion decreased to 14.6% after 8 hours of catalytic reaction. As shown in Fig. 8, the IM-2.0P sample obtained by phosphorus modification without coating of meso-SiO₂ shell exhibited the worst selectivity and yield of p-xylene with a relatively high yield of xylene.

Combined with the analysis of N₂ adsorption-desorption and acidity, it can be deduced that the meso-SiO₂ shell could passivate the external surface acids of sample crystals, which reduced the isomerization of p-xylene and improved the selectivity of p-xylene. The phosphorus modification method was mainly used to reduce the strong acids, which could inhibit the occurrence of side reactions. In addition, the phosphorus species could enter the pores of sample and narrow the pore-opening size, which ultimately improved the selectivity of target product. However, the selectivity and yield of p-xylene cannot be improved effectively only by coating of meso-SiO₂ shell or phosphorus modification alone. Therefore, the combination modification of meso-SiO₂ shell and phosphorus could adjust the surface acidity as well as the size of

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pores and pore-opening simultaneously, and enhance the selectivity of target product product eventually.

3.4.3. Effects of methanol/toluene (T/M) feed ratios on the activity and selectivity of

the sample



Fig. 9 Effects of T/M feed molar ratios on the activity and selectivity of the IM-2.4S-2.0P sample. Reaction temperature = 440 °C and WHSV = 2.0 h⁻¹. S_X-Selectivity of xylene; S_{PX} -Selectivity of p-xylene.

Fig. 9 showed the catalytic performance of IM-2.4S-2.0P sample at different T/M ratios. The toluene conversion decreased with the increase of T/M molar ratio, while the selectivity of xylene and p-xylene were improved. In the absence of side reactions, the maximum toluene conversion was theoretically 100% at a T/M = 1.0. But the actual toluene conversion was around 36.1%, indicating that only 36.1% of methanol could involve in the alkylation of toluene. When the T/M molar ratio was 2.0, approximately 64.1% methanol involved in the alkylation reaction, indicating that methanol could be more effective for the alkylation reaction at a higher T/M molar ratio was a second second reaction.

ratio. In addition, the higher methanol feed concentration could accelerate

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Fig. S8 illustrated the TG curves of IM-2.4S-2.0P sample after 24 h alkylation reaction at different T/M feed molar ratios. And the weight loss ratio increased with the decline of T/M molar ratio, which confirmed a faster coke formation rate at lower T/M feed molar ratios.

3.4.4. Effects of reaction temperature on the activity and selectivity of the sample



Fig. 10 Effects of reaction temperature on the activity and selectivity of the IM-2.4S-2.0P sample. T/M = 2.0 and WHSV = 2.0 h⁻¹. S_X-Selectivity of xylene; S_{PX}-Selectivity of p-xylene.

Fig.10 exhibited the effects of reaction temperatures carried out in the range of 360-480 °C on the IM-2.4S-2.0P sample. The results revealed that the catalytic activity increased due to the improvement of diffusion rate and reaction rate of toluene at higher reaction temperature, while p-xylene exhibited higher selectivity due to the restrain of isomerization at the lower reaction temperature. But the sample could deactivate faster at higher temperatures. Hence, the optimal reaction

temperature for the IM-2.4S-2.0P sample could be selected at 440 °C.

3.4.5. Effects of WHSV on the activity and selectivity of the sample

Fig. 11 showed the effects of WHSV ranging from 1.0 to 4.0 h⁻¹ at 440 °C on the IM-2.4S-2.0P sample and the T/M molar ratio was 2.0. As shown in Fig. 11, the average toluene conversion decreased from 34.9% to 25.1% when the WHSV increased from 1.0 to 4.0 h⁻¹, which was mainly due to the shorten of contact time between reactants and acid sites. Meanwhile, the shorten of contact time between products and acid sites inhibited the isomerization of products, which was conducive to improve the selectivity of p-xylene.



Fig. 11 Effects of WHSV on the activity and selectivity of the IM-2.4S-2.0P sample. Reaction temperature = 440 °C and T/M = 2.0. S_X-Selectivity of xylene; S_{PX}-Selectivity of p-xylene.

3.5. Diffusion of p/m-xylene in the samples

The TPD methods have been acknowledged a useful technique for surface analysis, which can be applied to the study of desorption and diffusion processes.^{60,61} The experiments were carried out on the TPD device at different heating rates using the

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New Journal of Chemistry

View Article Online diffusion equation reported by D. Fraenkel et al.,⁶⁰ in which the activation energy for

New Journal of Chemistry Accepted Manuscript

diffusion (E) can be formulated,
$$\ln \frac{RT_m^2}{\beta} = \ln \left(\frac{r_0^2 E}{1.44\pi^2 D_0} \right) + \frac{E}{RT_m}$$

where D_0 is the intrinsic diffusion coefficient, E is the activation energy for diffusion, β is the heating rate, R is a gas constant, r_0 is radius of zeolite particle, T_m is the peak desorption temperature. The calculation of D_0 involves the radius of the crystal which is difficult to achieve accurately. Therefore, a plot of $\ln\left(\frac{RT_m^2}{\beta}\right)$ versus $1/T_m$ could

obtain the line with slop E/R, which can be used to calculate the E.

Table 5 $T_{\rm m}$ of p/m-xylene at different heating rates and E on the H-IM-5, H-ZSM-5, IM-2.4S

and	IM-2	.4S-2	2.0P	sampl	les.
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	$T_{\rm m}$ (K) of p-xylene at					Tm	(K) of m	-xylene	E of	E of	
Samples different β (K/min)					di	fferent β	(K/min)	p-xylene	m-xylene		
	8	12	16	20	8		12	16	20	(kJ/mol)	(kJ/mol)
H-IM-5	419.0	427.9	435.3	442.2	427	.5	436.3	444.2	450.1	53.9 ± 2.6	57.1 ± 2.1
H-ZSM-5	400.8	412.3	420.9	430.3	407	.6	418.9	427.7	435.5	38.1 ± 2.2	41.6 ± 2.0
IM-2.4S	419.5	428.6	435.7	442.5	428	.9	437.4	445.1	451.0	54.7 ± 2.2	59.0 ± 2.4
IM-2.4S-2.0P	416.7	426.6	433.8	441.5	426	5.7	435.8	442.8	449.3	50.0 ± 2.5	57.7 ± 2.0

The TPD curves of p/m-xylene on the H-IM-5, H-ZSM-5, IM-2.4S and IM-2.4S-2.0P samples at the different heating rates were shown in Fig. S9. As shown in the Fig. S9, the TPD patterns for p-xylene exhibited only one obvious peak. Whereas, the TPD patterns for m-xylene showed two distinct peaks, one of which appeared at lower temperature was attributed to the m-xylene adsorbed on the external

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surface of sample crystals and the other peak arose at high temperature was due to the m-xylene adsorbed in the zeolite channels.⁶² So the diffusion parameters of m-xylene in the zeolite channels were calculated by the second desorption peak temperatures. In addition, the adsorption capacity of xylene on the IM-2.4S-2.0P samples decreased obviously, especially the m-xylene, indicating that the diffusion of m-xylene into the micropores was hindered by the phosphorus modification. The values of E obtained from the linear $\ln\left(\frac{RT_m^2}{\beta}\right)$ versus $1/T_m$ plots according to the equation were given in Table 5. The E of p-xylene on H-ZSM-5 was 38.1 ± 2.2 kJ/mol, which was higher than the literature data (30.0 kJ/mol).^{63,64} The differences can be explained from the interaction between π -electrons of benzene ring and protonic acidity on H-ZSM-5 zeolite.65 Moreover, the asymmetrical distribution of methyl groups enables m-xylene higher polarity and alkaline, which can be used to explain the higher E of m-xylene on the samples than that of p-xylene.⁶² Compared with H-ZSM-5 zeolite, xylene on H-IM-5 zeolite showed higher diffusion activation energy, which may be caused by its unusual channel system. As shown in Table 5, there was a slight increase in the E of p/m-xylene after the coating of meso-SiO₂, which was mainly due to the diffusion resistance of the silica shell. Compared with IM-2.4S sample, the E of p/m-xylene after phosphorus modification decreased due to the neutralization of acid sites on H-IM-5, which was consistent with the reported literature.⁶⁶ In addition, the phosphorus modification had little effect on the E of m-xylene. It may be attributed to the reason that phosphorus deposition narrowed the pore-opening size and increased the diffusion resistance of m-xylene in the pores of sample, which could partially

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compensate for the loss of *E* caused by acid neutralization. Thus, the interactions^{2/C9NJ02440A} between diffusing molecule and sample surface acidity as well as the geometric factors play important roles in the diffusion process.

4. Conclusions

A core-shell H-IM-5@meso-SiO2 composite with hierarchical pores was successfully obtained via a method of reversing the external surface of IM-5 crystals to positively charged by PDDA, which could induce an oriented self-assembly formation of meso-SiO₂ shell. The as-synthesized H-IM-5@meso-SiO₂ composite was thereafter modified with phosphorus species to adjust the acidity on the internal surfaces as well as the size of pores and pore-opening. Combined with the physicochemical structure and catalytic performance evaluation, the meso-SiO₂ shell passivated the external surface acidity of zeolite crystals without blockage of pores and the phosphorus modification method reduced the strong acids which could inhibit the side reactions. Therefore, the combination modification of meso-SiO₂ shell and phosphorus could adjust the surface acidity as well as the size of pores and pore-opening simultaneously, and enhance the selectivity of target product eventually. The TPD of xylene analysis showed that the interactions between diffusing molecule and sample surface acidity as well as the geometric factors play important roles in the diffusion process.

Conflicts of Interest

There are no conflicts to declare.

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Supplementary Material

Supporting information is available in the Electronic Supplementary Information (ESI).

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Catalytic Performance of Phosphorus Modified H-IM-5@meso-\$1022

Composite in Alkylation of Toluene with Methanol

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A phosphorus modified H-IM-5@meso-SiO₂ was synthesized with its acidity and pore channels modified to enhance the selectivity of target product.

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