

Cheap zeolite catalyst ($\text{Na}_3\text{PO}_4/\text{NaX}$) for toluene/methanol side chain alkylation

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Abstract— A new zeolite catalyst ($\text{Na}_3\text{PO}_4/\text{NaX}$), which is low in cost, environment-friendly and also gives higher conversion of methanol, was prepared by the impregnation method and catalytic performance was tested for side-chain alkylation of toluene with methanol. From the characterization of the catalysts by Temperature-programmed desorption (TPD- CO_2), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) method we found that when the concentration of Na_3PO_4 was 0.1 mol/L, the yield of styrene and ethylbenzene, and conversion of methanol reached 39.4% and 100%. It was determined that as the loading of Na_3PO_4 onto the NaX surface enhanced, the amount and the strength of middle base sites significantly increased, which is favorable for the toluene/methanol side chain alkylation.

Keywords— zeolite catalyst, side-chain alkylation, middle base sites, styrene.

I. INTRODUCTION

Styrene is a significant chemical material that might be used to produce a wide range of polymers that are utilized in many applications, including toys, food packaging, medical equipment, and paper coverings [1]. Sidorenko et al. first reported styrene production by toluene/methanol side-chain alkylation [2]. Since then, this reaction has involved wide-ranging attention because this method of producing styrene offered economic benefits [3,4] and was supposed as a reliable one step substitute for the existing two-step method over alkylation of benzene with ethylene and followed by the catalytic dehydrogenation of ethylbenzene [5,6].

Many scientists have explored the mechanism of toluene/methanol side-chain alkylation reaction to invent an efficient catalyst for the toluene/methanol side chain alkylation [7]. It is usually recognized that the alkylation of toluene with methanol over basic zeolites can catalyze side-chain alkylation while acidic zeolites can catalyze to the ring of toluene [8]. Toluene/methanol side chain alkylation is a well-known acid-base synergistic catalysis process [9-11]. Usually, acidic sites can stabilize and adsorb toluene; however the function of base sites is to trigger the carbon atom of the side chain of toluene followed by the methanol to formaldehyde

dehydrogenation. Formaldehyde formed by the dehydrogenation of methanol acts as an actual alkylating agent for side-chain alkylation [12] and it can decompose into CO and H_2 on-basic sites [13,14]. A series of side reactions occur during toluene/methanol side chain alkylation process. Ethylbenzene was supposed to produce through the hydrogenation of styrene with hydrogen, which in turn produced by methanol dehydrogenation to formaldehyde and auxiliary formaldehyde decomposition [15]. It was suggested from previous research that the main reaction pathway for ethylbenzene formation is the hydrogenation of styrene with methanol [16]. Besides xylene formed through toluene disproportionation during the ring alkylation with methanol that existed at acid sites must not be ignored either [17].

There has been extensive study of catalysts for toluene/methanol side chain alkylation [18]. A noble catalyst for toluene/methanol side-chain alkylation was reported to have the following characteristics (1) appropriate strength of base to dehydrogenate methanol to formaldehyde, (2) polarization and stabilization of methyl group of adsorbed toluene, and (3) balanced reactant sorption stoichiometry [3,19]. From previous studies it was found that the catalyst prepared by CsX modified by K_3PO_4 could enhance the amount and strength of the

middle base on the catalyst and reduce the number of acid sites leading to the improved catalytic effect in toluene/methanol side chain alkylation [20]. Although this system (CsX modified by K_3PO_4) was energy-efficient however, the major drawback for using K_3PO_4 was the higher cost of the raw materials.

In order to solve the problem of raw materials cost we supposed to use Na_3PO_4 modified NaX molecular sieve in our current study, which is cheaper than K_3PO_4 system and investigated the effect of Na_3PO_4/NaX in the toluene/methanol side chain alkylation for the production of styrene. The results of our study showed that as the concentration of Na_3PO_4 increased, the amount of middle base sites also increased leading to the higher yield of ethylbenzene and styrene signifying that the strength and amount of middle base sites is a crucial factor for the toluene/methanol side chain alkylation.

II. EXPERIMENTAL SECTION

2.1 Materials:

Zeolite NaX (Si/Al = 1.25) was attained from Nankai University's Catalyst Plant. Methanol, and Toluene, with a purity of 99%, were obtained from Tianjin Kemo Chemical Reagent Co., Ltd.

2.2 Catalyst Preparation:

A series of Na_3PO_4 catalysts were produced by loading different concentrations of Na_3PO_4 on NaX zeolite ($SiO_2/Al_2O_3 = 2.4$) at $80^\circ C$. Procedures followed are described below:

Different concentrations of Na_3PO_4 solution (solid/liquid ratio, 10g/100ml) were loaded three times on 10g of NaX at $80^\circ C$ for 2 h. The Buchner funnel was used to filter the slurry. The cake obtained as a result of filtration was absorbed again in an aqueous solution of Na_3PO_4 (100 ml, 0.5M) and agitated for 2 h at the same temperature. Filtration and absorption processes were repeated further two times. The resulting residue was filtered. The mixture was dehydrated at $80^\circ C$ for 12 h followed by the calcination at 3 K/min. After 3 hours of calcination at $500^\circ C$, the resulting powder was crushed, pelletized and sieved to obtain the zeolite catalyst with a size between 40 mesh and 60 mesh. The powder obtained was ready for reaction and referred to as Cat-n, where n is the concentration of Na_3PO_4 in the catalyst.

2.3 Characterization of Catalysts:

The X-ray diffraction (XRD) of catalysts were recorded on a Rigaku D/max 2500 X-ray diffractometer using Ni-filtered Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm), activated at 100 mA and 40 kV. A $10^\circ/\text{min}$ scanning rate was used for Bragg's angles $2\theta = 5-80^\circ$.

Temperature-programmed desorption (TPD) of adsorbed CO_2 was done on a TP-5080 to analyze the basic sites. The sample (0.1 g) was pretreated at $450^\circ C$ for 103 min in a He stream before taking measurements and cooled down to the required temperatures. The samples were exposed to pure CO_2 at $100^\circ C$ for 30 min. The samples were heated to $810^\circ C$ with a temperature ramp at $10^\circ C \text{ min}^{-1}$ after purging with helium.

A Quanta-chrome Autosorb QDS-30 physical adsorption analyzer system at $-196^\circ C$ was used to attain N_2 adsorption-desorption isotherms. The samples were degassed under vacuum at $200^\circ C$ for 4 hours prior to taking a measurement. Pore volumes and Specific surface areas were determined by BJH method and Brunauer-Emmett-Teller (BET) method separately.

Scanning electron microscopy SEM images of catalysts were obtained by a JESOL JSM-6010PLUS/LV scanning microscope. The samples were loaded onto the sample holder, seized with conductive aluminum tape and vacuum coated gold film with Cressington sputter ion coater prior to taking SEM photographs. Magnification was 5000, with an acceleration voltage of 20kV.

2.4 Catalytic Tests:

For the toluene/methanol side chain alkylation, Na_3PO_4/NaX powder was crushed, pressed, and sieved (40-60 mesh). A fix bed reactor was used to carry out the reaction, and 1.2 g of the catalyst was positioned in the center of a stainless-steel tube having 7 mm inner diameter, and the catalyst was supported by quartz sands at the outlet of the reaction tube, and separated by quartz cotton at both ends to prevent catalyst from blowing into GC columns. Nitrogen was the carrier gas and the flow rate was 10.0 mL/min, the molar ratio of toluene to methanol was 5:1, and the mass space velocity was 1.0 h^{-1} . The catalyst was activated at $450^\circ C$ for 2 h under an atmospheric nitrogen atmosphere and then lowered to $425^\circ C$ for evaluation. The reaction products were quantitatively examined online by Haixin GC950 gas chromatograph equipped with an HP-FFAP column ($0.53 \text{ mm} \times 50 \text{ m}$), and the products were detected by a hydrogen flame ionization detector (FID). Since the access of toluene in the reaction system was used, the conversion rate, product selectivity, and yield were calculated based on methanol given in the equation below.

$$X_{MET} = \left(1 - \frac{MET \text{ outlet}}{MET \text{ inlet}} \right) \times 100\%$$

$$S_X = \left(\frac{X}{MET \text{ inlet} - MET \text{ outlet}} \right) \times 100\%$$

$$Y_X = S_X \times C_{MET}$$

III. RESULTS AND DISCUSSION

3.1 TPD-CO₂

To examine the base properties of the catalysts, we conducted Temperature-programmed desorption (TPD) experiments of CO₂, and TPD-CO₂ spectra of all catalysts such as NaX, cat-0.01, cat-0.05, cat-0.075, cat-0.1 were shown in Fig.1. Three kinds of desorption peaks were seen for all catalysts. The first region was at a low-temperature range between 50°C-250°C correspond to the weak base site; the second region ranges between 250°C-500°C indicates a middle base site while the third region is the strong base site at around 500°C-800°C. As the loading of Na₃PO₄ enhanced, the CO₂ desorption peak area of the middle base site increased and shifted towards higher temperature while the desorption peak area decreased at low temperatures indicating that during the impregnation process, the amount of base sites of support enhanced. It can be elucidated from these results that a suitable amount of Na₃PO₄ may considerably increase the amount and the strength of middle base sites on the surface of the catalysts.

3.2 XRD Diffraction

Fig. 2 depicts the XRD patterns of different catalysts (NaX, cat-0.01, cat-0.05, cat-0.075, cat-0.1). It could be perceived from our results that all the catalysts showed diffraction peaks of the faujasite framework signifying a typical arrangement of X-zeolite. However, in comparison with NaX zeolite, the relative diffraction peak intensity of cat-0.05, and cat-0.1 slightly decreased at 26.7°. This might happen because the zeolite structure was slightly damaged in the process of impregnation. Except for zeolite X, there were no other noticeable peaks seen in all XRD patterns, suggesting that the assembly of NaX was not destroyed during the catalyst preparation process, and Na₃PO₄ has well dispersed on the surface of NaX zeolite.

3.3 SEM

Fig 3 shows SEM images cat-0.01, cat-0.05, cat-0.075, cat-0.1. All the catalysts had same size distribution and irregular octahedron structures. The catalysts were mainly made up of crystallites having size about 2 to 3 μm and small particles. SEM images of cat-0.01 (a) and cat-0.075 (c) are similar. Fig. 3.4(d) represents that there were a huge number of white particles which showed the loading of Na₃PO₄ on NaX zeolite surface and also represented a uniform mixing which might be the reason of stability and high catalyst performances. Based on the results we elucidated that more the dispersion of the particles on the surface, higher the performance of the toluene/methanol side chain alkylation.

3.4 BET

The pore volume, pore diameter, and total surface area of all the catalysts are given in Table 1. It can be perceived from these results that pore volume and catalyst surface area was considerably reduced with an increase in the concentration of Na₃PO₄ as displayed in Fig 4. It might be because Na₃PO₄ occupied some parts of the zeolite pores. Combined these results with the catalytic performance, catalyst with concentration 0.1 mol/L showed best ability to catalyze the reaction indicating that small pore volume having microporous structure might be suitable for the toluene/methanol side chain alkylation

IV. FIGURES AND TABLES

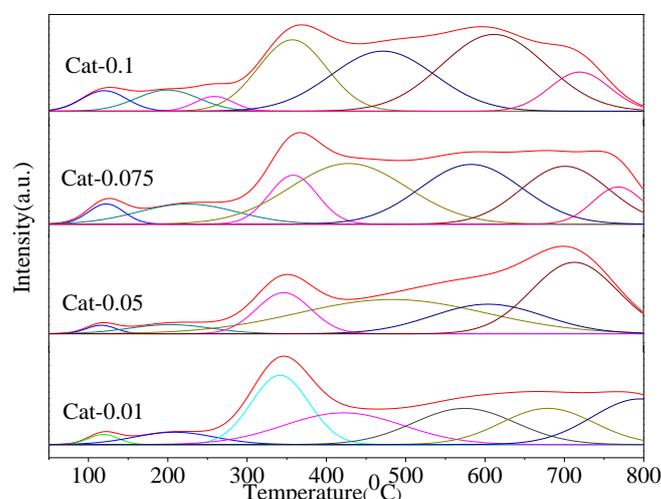


Fig 1. TPD-CO₂ profile of catalysts cat-0.01, cat-0.05, cat-0.075 and cat-0.1

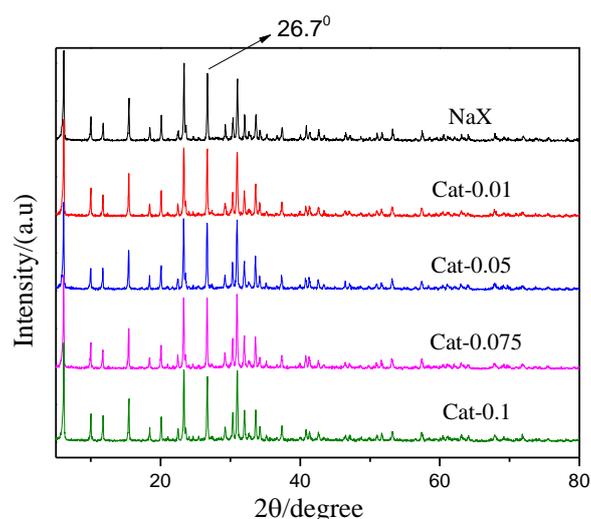


Fig 2. XRD patterns of catalysts NaX, cat-0.01, cat-0.05, cat-0.075, and cat-0.1

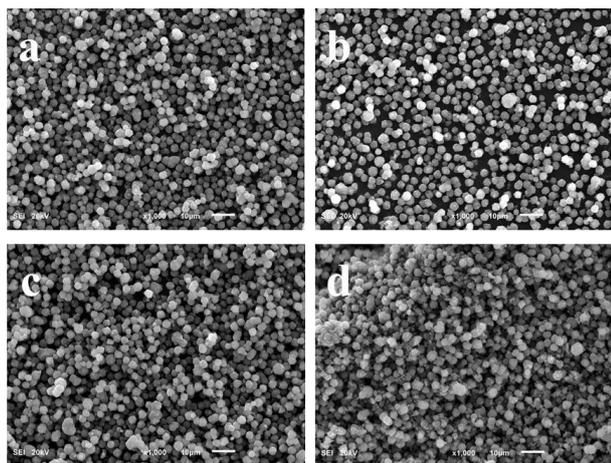


Fig 3. SEM images of catalysts (a) cat-0.01, (b) cat-0.05, (c) cat-0.075, and (d) cat-0.1

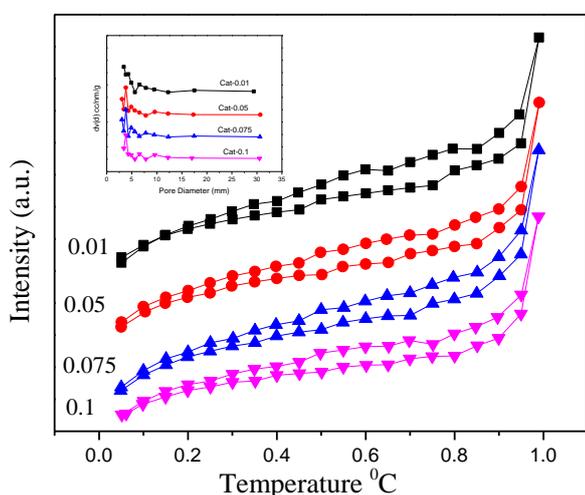


Fig 4. BET images of catalysts cat-0.01, cat-0.05, cat-0.075, and cat-0.1

Table.1: Textural properties of different catalysts

Catalysts	Pore Volume cm ³ /g	Pore Diameter nm	Total surface area m ² /g
0.01M	0.032	3.408	595.85
0.05M	0.029	3.819	553.79
0.075M	0.033	3.825	610.66
0.1M	0.025	3.820	541.14

Where: M= mol/L, cat-0.01=0.01M, cat-0.05=0.05M, cat-0.075=0.075M, cat-0.1=0.1M

Table.2: Performance of Catalyst

Catalyst	Reaction Temp(°C)	MET conv%	Selectivity of products Yield of products (%)				
			of products (%)				
			S _{EB}	S _{STY}	Y _{EB}	Y _{STY}	Y _(EB+STY)
0.01M	425	96.9	18	2.2	17.9	2.1	20
0.05M	425	100	23	3.8	23.5	3.8	27.3
0.075M	425	100	15	2.6	15.3	2.6	17.9
0.1M	425	100	31	7.5	31.9	7.5	39.4

Where: M= mol/L, cat-0.01=0.01M, cat-0.05=0.05M, cat-0.075=0.075M, cat-0.1=0.1M

V. CATALYTIC REACTION

The reaction performance for the toluene/methanol side chain alkylation over a series of catalyst Cat-n (n represents loading of Na₃PO₄) is shown in Table 2. Ethylbenzene and styrene were regarded as the main products for the toluene/methanol side chain alkylation while there exist some byproducts such as methane and xylene. With the loading of Na₃PO₄ by impregnation method, methanol conversion reached up to 99%, and the selectivity and yield of styrene and ethylbenzene were also expressively increased. The activity of the catalyst and the yield of styrene and ethylbenzene were enhanced considerably when the concentration of Na₃PO₄ was 0.1 mol/L, i.e., yield (Ethylbenzene + Styrene) 39.4%. At this concentration of Na₃PO₄, the conversion of methanol was 100%.

The catalytic activity data in Table 2 and TPD-CO₂ (Fig. 1) showed that selectivity (ethylbenzene + styrene) and the activity of the catalyst has improved with an appropriate amount and strength of middle base sites, which suggested the middle base sites were advantageous for the toluene/methanol side chain alkylation reaction.

VI. CONCLUSION

In this work, a cheap and new zeolite catalyst containing different concentrations of Na₃PO₄ supported on NaX has successfully synthesized and characterized by TPD-CO₂, XRD, SEM, and BET. The TPD-CO₂ results revealed that as the loading of Na₃PO₄ on NaX zeolite enhanced, the amount of middle base sites also increased which led to the higher yield of ethylbenzene and styrene i.e, the yield of ethylbenzene and styrene, and conversion of methanol reached 39.4% and 100% signifying that the presence of amount of middle base sites on the surface of the catalyst was crucial factor for the toluene/methanol side chain alkylation.

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