



Para-selective methylation of toluene with methanol over nano-sized ZSM-5 catalysts: Synergistic effects of surface modifications with SiO₂, P₂O₅ and MgO



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ARTICLE INFO

Article history:

Received 22 November 2013

Received in revised form 8 April 2014

Accepted 26 April 2014

Available online 5 May 2014

Keywords:

Nano-sized ZSM-5
Single modification
Multiple modification
Para-selectivity
Synergistic effect

ABSTRACT

The nano-sized ZSM-5 catalysts were modified by surface coating with SiO₂, P₂O₅, MgO and their combinations; the catalytic properties were investigated in the shape-selective methylation of toluene with methanol. The catalysts were characterized by XRD, XRF, N₂ adsorption–desorption, temperature programmed desorption of ammonia (NH₃-TPD), Fourier-transform infrared spectra of adsorbed pyridine/2,6-di-tert-butylpyridine, and adsorption of n-hexane/cyclohexane. The passivation of Lewis acid sites occurs prior to that of the Brønsted acid sites over ZSM-5 modified by SiO₂, while P₂O₅ or MgO preferentially neutralizes the Brønsted acid sites of ZSM-5. The deposition of MgO is more efficient in passivating the acid sites and narrowing the pore openings, compared to SiO₂ or P₂O₅ modification with the same oxide content (<9 wt%). The single modification could not completely passivate the external surface acid sites and simultaneously narrow the pore openings to a proper extent; so the selectivity to para-xylene does not exceed 90% even at the highest oxide loading. The multiple modification by SiO₂, P₂O₅ and MgO, with a suitable sequence can efficiently eliminate external surface acid sites, and simultaneously narrow the pore openings, which led to a higher para-selectivity (~98%). The combined modification with SiO₂, P₂O₅ and MgO in a proper sequence can lead to a synergistic effect for tailoring the acid property and pore mouth of the catalyst, thus enhancing the para-selectivity to ~98% and improving catalytic stability, as demonstrated by flow test for 1000 h on stream.

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1. Introduction

Para-xylene is a very important starting material for production of terephthalic acid and polyethylene terephthalate [1]. It is primarily produced as a component in mixtures by catalytic reforming and thermal cracking of naphtha, along with benzene, toluene and other xylene isomers [1,2]. However, in these processes, toluene is produced in excess and para-xylene in deficit for the market demand. Therefore, the conversion of the surplus toluene into value-added para-xylene by toluene disproportiona-

tion [1–3] or transalkylation of trimethylbenzene [1,2,4] is a potential way to balance the deficiency of aromatic production in chemical industries. The shape-selective alkylation of toluene with methanol [5–12] is also a promising way of producing para-xylene as compared with toluene disproportionation, and hence, the process has been the focus of industrial and academic research for the last few decades. However, up to now, the shape-selective methylation process has not been commercialized yet, because there is no highly efficient catalyst that has high enough selectivity for this process.

The alkylation of toluene with methanol, as a well-known acid-catalyzed carbenium ion reaction, produces primarily a mixture of xylenes, and the product distribution largely depends on the characteristics of the catalyst. Beside alkylation, side reactions such as isomerization also take place. Compared with other zeolites (such as zeolite Y, mordenite, MCM-22, TNU-9, SSZ-33) and the

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silicoaluminophosphate molecular sieve (HSAPO-5) [5–12], ZSM-5 has attracted more attention as para-selective alkylation catalyst, due to its unique pore size comparable to the molecular dimension of para-xylene [10,11]. However, the composition of xylenes produced is close to the thermodynamic equilibrium distribution (23% para, 54% meta, 23% ortho at 500 °C) over nano-sized HZSM-5 catalyst [10]. In order to improve the selectivity to para-xylene, the acidity and pore structure of zeolite need to be modified properly [13]. On one hand, active sites on the external surface should be passivated to prevent undesired methylation and secondary isomerization of p-xylene to m-xylene and further to o-xylene via 1,2-methyl shift. On the other hand, pore entrances should be narrowed to further increase the differences among xylene isomers regarding the diffusion barriers.

In earlier studies, the para-selectivity approaching 100% could be obtained by modifying HZSM-5 with single modifier such as P, Mg, B, Sb, and La [14–26], and further, by optimizing the process variables [27,28]. Unfortunately, the conversion of toluene and the stability of the catalyst were not satisfactory under high para-selectivity conditions. The precoking modification could also enhance the para-selectivity [29,30], but the method is difficult to control. Aboul-Gheit et al. [31,32] found that the increase of the Pt or Pd content could enhance the para-selectivity by narrowing the pore openings, but the overall selectivity to para-xylene was lower than 40%. Although, numerous prior studies focused on single modification of ZSM-5 to increase para-selectivity, low activity and bad stability are inevitable.

In our previous work [33,34], we have reported that the SiO₂, P₂O₅ and MgO modified nano-sized ZSM-5 catalyst exhibited the high para-selectivity of 98%. Recently, an enhancement of the stability of modified small sized HZSM-5 in hydrogen atmosphere by surface SiO₂ deposition together with P–Ni doping has been reported [35]. The conversion of toluene was 31%, and the selectivity to p-xylene was around 91%. However, the difference between the single and multiple modification, and the effect of the different sequences of modification on surface acidity and the pore structure in the alkylation reaction have not been reported.

In this paper, we investigated the effects of the surface modifications of nano-sized ZSM-5 with single modifiers SiO₂, P₂O₅ and MgO and their combinations in different sequences on the acid property and pore opening of the catalyst in detail. The modification

procedures are illustrated schematically in Fig. 1. By integrating the results from infrared spectroscopy (IR) of adsorbed probe-molecules, temperature programmed desorption of ammonia (NH₃-TPD), N₂ physical adsorption, and the adsorption of n-hexane and cyclohexane in combination with the results of catalyst testing for toluene methylation, it was found that there is a synergistic effect between the modifiers SiO₂, P₂O₅ and MgO which tailors the acid property and pore mouth of the catalyst leading to a much better para-selectivity and high stability.

2. Experimental section

2.1. Catalyst preparation

Na-ZSM-5 zeolite of SiO₂/Al₂O₃ = 26 (Si/Al of the zeolite measured by NMR was about 30.5, seen in Fig. S1) was hydrothermally synthesized according to the procedure reported previously [36]. By extruding the mixture of nano-sized Na-ZSM-5 with alumina as binder (Al₂O₃/Na-ZSM-5 = 25 wt%) and lanthanum-rich mixed rare earth carbonate (industrial grade, contained 40 wt% La₂O₃ in rare earth oxide) (mixed rare earth/Na-ZSM-5 = 10 wt%) using a 0.5 mol/L HNO₃ solution as adhesive, the extrudate of nano-sized Na-ZSM-5 catalyst was obtained, dried at 120 °C for 12 h, and calcined in air at 540 °C for 4 h. Then by ion exchange with a 0.5 mol/L NH₄NO₃ solution at room temperature for three times followed by washing, drying at 120 °C for 12 h, and calcining in air at 540 °C for 4 h, H-ZSM-5 zeolite was obtained, which is labeled as ZSM-5.

In this work, the modified nano-sized ZSM-5 catalysts were prepared according to the procedures described in our previous investigations [33,34,36]. The ZSM-5 catalysts with single modifiers SiO₂, P₂O₅, and MgO were prepared by impregnating the nano-sized ZSM-5 with tetraethyl orthosilicate (TEOS) dissolved in cyclohexane, aqueous solution of monoammonium phosphate, and aqueous solution of magnesium acetate at room temperature, respectively, followed by drying at 120 °C and calcining in air at 540 °C for 4 h. These catalysts were denoted as xSi/ZSM-5 (x = 3, 6, 9, 12), yP/ZSM-5 (y = 5, 10, 15, 20) and zMg/ZSM-5 (z = 3, 6, 9, 12), respectively, where x, y, z are the nominal weight percentage of the modifier. The multiple modified nano-sized ZSM-5 catalysts by SiO₂, P₂O₅ and MgO, were prepared according to the above procedure. The different methods and sequences of modification

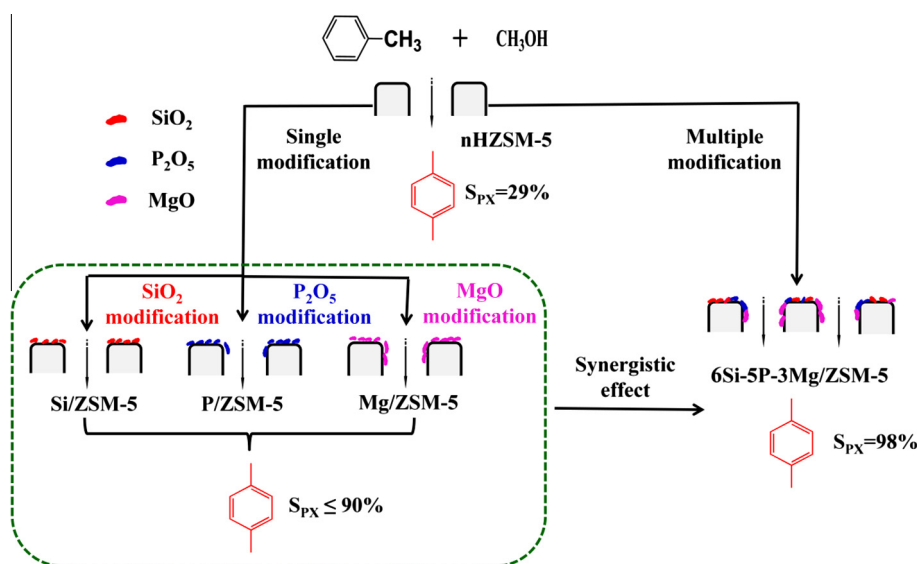


Fig. 1. Modification procedure for preparation of modified ZSM-5 catalysts.

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