Petroleum Research

Petroleum Research 2018 (August-September), Vol. 28, No. 99. 37-40

DOI: 10.22078/pr.2018.2475.2146

Hydrothermal Synthesis of Zn-ZSM5 Catalyst for Xylene Isomerization

Milad Rasouli[1], Nakisa Yaghobi[2]*, Hossein Atashi[1], and Davod Mohebbi-kalhori[1]

1. Department of Chemical Engineering, Faculty of Engineering, University of Sistan and Baluchestan, Zahedan, Iran

2. Department of Petrochemical, Iran Polymer and Petrochemical Institute, Tehran, Iran

N.yaghobi@ippi.ac.ir

DOI: 10.22078/pr.2018.2946.2375

Received: October/18/2017 Accepted: March/11/2018

Abstract

The addition of Zinc to the synthesis of ZSM-5 catalysts (Si/Al=21) was studied in xylene isomerization reactions. Physicochemical characteristics of the prepared catalysts were evaluated by XRD, BET, SEM, FTIR, NH3-TPD and TG analyses. Zn incorporation strongly increased the strong acid (Brønsted) sites and reduced the weak acidity (Lewis). Higher strong acidity led to higher PX yield and Lower weak acidity led to lower coke formation and more catalytic stability. (0.5 wt.%) Zn-ZSM-5 as an efficient and stable catalyst for xylene isomerization reactions demonstrated high PX yield (18.5 wt.%), high EB conversion (43.6%) and low xylene loss (3.3 %).

Keywords: ZSM5, Isomerization, Para-xylene, Xylene Loss, Catalyst Stability.

INTRODUCTION

Separation of PX from C8 aromatics can be carried out through different processes such as crystallization or by adsorption over zeolite adsorbents ; moreover, the raffinate is sent to the isomerization unit where additional PX is achieved by equilibrium reaction [1]. Wichterlova et al [2] synthesized bimetallic Ni-exchanged HZSM-5 catalyst (Si/Al = 13.6) with different sources of Ni salts such as; Ni $(CH_3COO)_2$, $NiCl_2$, $NiSO_4$, and NiO. Ion-exchange with $NiCl_2$ indicated the decrease in strong acid skeletal OH groups and uniform dispersion of metallic Ni (0.102 mmol Ni/g zeolite) into the zeolite cationic sites which are active for xylene isomerization reactions. Rane and coworkers [3] reported that the combination of 10% HZSM-5 and 90% ZSM-35 catalyst increases EB conversion more than 20% and indicated much more catalytic stability and PX selectivity in comparison with the pure ZSM-35.

In the present study, the bifunctional Zn-ZSM-5 nanocatalysts were hydrothermally prepared with different amounts of zinc and then platinum was incorporated to the zeolites with partial vacuum impregnation method. The main focus was on the adjusting nanocatalyst acidity using various contents of zinc and the role of platinum active species on the catalytic behavior of Zn-ZSM-5 nanocatalysts in PX yield, EB conversion and xylene loss in xylene isomerization reactions.

EXPERIMENTAL

CATALYST PREPARATION

Zn-ZSM-5 nanocatalysts (Si/Al = 21) were synthesized by hydrothermal method. The synthesis solution included the determined content of tetraethylorthosilicate (TEOS) aluminum isopropoxide (AIP) and tetrapropylammonium hydroxide (TPAOH), deionized water and zinc nitrate $(Zn(NO_3)_2)$. The mixture was kept at 180 °C in a Teflon lined autoclave for a period of 120-150 hours. After filtration and washing, the nano-catalysts were dried over the night at 95 °C [4]. The amount of zinc in the prepared nanocatalysts was calculated to be 0.2, 0.5 and 1.0 wt%. Pt impregnation on the HZSM-5 support was conducted according to our previous work [5] through a partial vacuum impregnation method using $H_2(PtCl_6)6H_2O$ salt. The prepared nanocatalysts indicated 0.1wt% Pt promoter.

CATALYTIC PERFORMANCE

The gas phase xylene isomerization reactions were carried out in a fixed bed, continuous-flow reactor. 2 g of each nanocatalyst with the particle size of 0.5-0.7 mm diameter was packed in a stainless steel reactor with an inner diameter of 1 cm for catalytic measurements. The feed mixture including 85% MX and 15% EB was introduced to the reactor using a dosing system (Harvard Apparatus, 0.00044-77 ml min-1). The reaction was carried out at a temperature in the range 400-500 °C and the pressure of 7-10 bar with an H_2/HC of 2-3 mol min^{-1}. PX yield (wt. %) was measured as the amount of PX in the products.

RESULTS AND DISCUSSION

CATALYST CHARACTERIZATION

CATALYST STRUCTURE, MORPHOLOGY, AND TEXTURAL PROPERTIES

The XRD analyses (Figure 1) did not show any diffraction peak attributed to the metallic species while the intensity of nanocatalysts decreased slightly with introducing zinc during synthesis, which could be interpreted by a higher adsorption coefficient of Zn oxide for X-ray radiation.

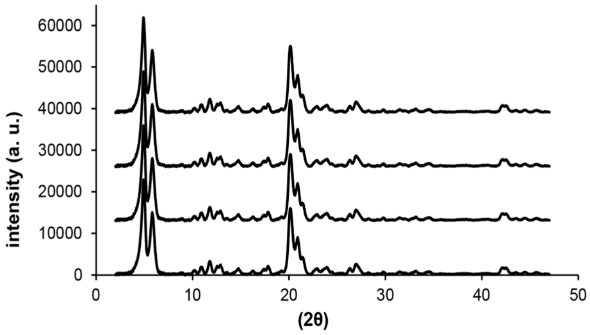

Figure 1: XRD of the prepared catalysts.

ACIDITY

The NH3-TPD spectra for the parent and metal-containing nanocatalysts are given in Figure 2. Based on the results, it can be deduced that the strong acid site density increased as the platinum is introduced to the nanocatalyst.

CATALYST PERFORMANCE

The results in Figure 3 a. illustrated the initial PX yield catalyzed by P/0.2ZZ5, P/0.5ZZ5, and P/1.0ZZ5 nanocatalysts were found to be 14.9%, 18.5%, and 22.6%, respectively, and indicated to be much more than Pt-free nanocatalysts. It can be inferred from the results that P/0.5ZZ5 nanocatalyst maintained the highest reactivity and stability among all the prepared nano-catalysts. It can be deduced from the results that an increase in Zn loading led to a higher initial PX yield and a lower xylene loss that can be attributed to the high level of strong acid sites and lower amount of weak acidity which are main sites for xylene isomerization and coke deposition, respectively.

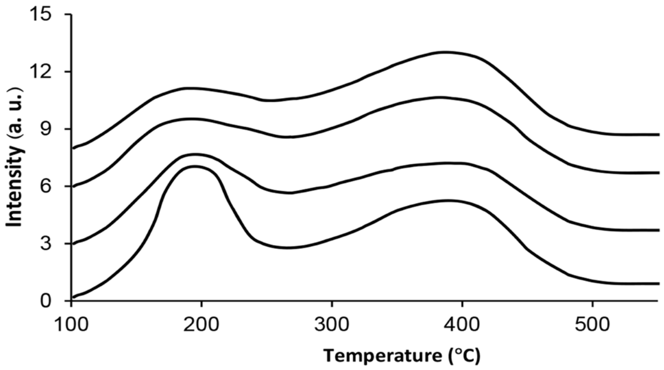

Figure 2: NH3-TPD of the prepared catalysts.

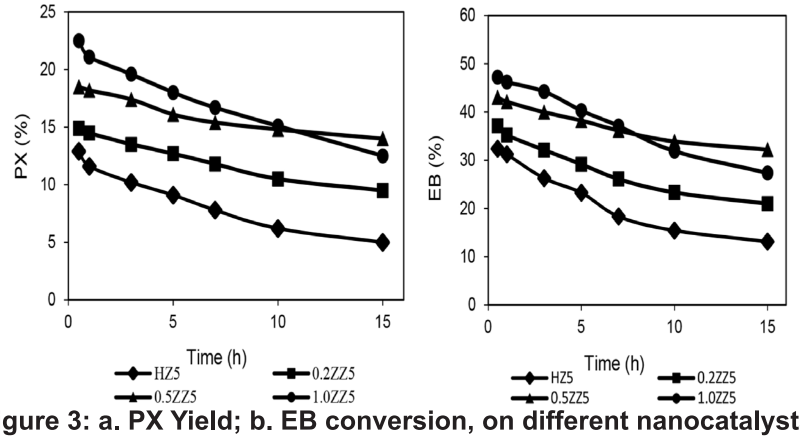

Figure 3: a. PX Yield; b. EB conversion, on different nanocatalysts.

Figure 3 b. shows the EB conversion on the prepared nanocatalysts. EB reforming which produces xylene mixture mainly occurs on bifunctional catalysts. Therefore, the balance between metal and acid function of prepared bifunctional nanocatalysts is an important factor for high catalytic activity. As shown in Figure 3. b. P/1.0ZZ5 indicated higher initial EB conversion (47 wt.%) with respect to other nanocatalysts because of higher acidity, whereas, the gradual reduction was observed with time on the stream. It is clear that EB conversion onto maximum Zn loading (1.0 wt.%) started to reduction after 1 hour on stream while the nanocatalyst with lower Zn content (0.5 wt.%) indicated approximately stable behavior with TOS. The reason for this reduction is attributed to undesirable side reactions such as EB disproportionation and dealkylation catalyzed by the acid function of catalyst, and also higher coke formation due to a high level of Lewis acid sites [7]. P/0.5ZZ5 nanocatalyst with the high strength to weak acid ratio demonstrated a higher level of EB conversion with a low amount of xylene loss with respect to other prepared nanocatalysts (P/0.2ZZ5 and P/1.0ZZ5). P/0.5ZZ5 nanocatalyst also showed the highest reaction activity and stability even at TOS of 15 hours.

CONCLUSIONS

The Zn-containing ZSM-5 nanozeolites with different amount of zinc have been hydrothermally synthesized and used as the support for platinum impregnation in xylene isomerization reactions. For the zinc-containing ZSM-5 nanozeolites, TPD-NH3 and FI-IR methods confirmed the existence of zinc species into the structure of nanocatalysts. Introduction of Zn into ZSM-5 nanozeolite structure led to a lower coke formation by decreasing the weak acidity. Finally, Zn-ZSM-5 nanocatalysts demonstrated higher EB conversion and more catalytic stability compared to that of Zn-free samples with time on stream. Moreover, the lower weak acid sites explained the lower coke formation rate and consequently more reaction activity and stability.

REFERENCES

[1]. Ono Y., *"A survey of the mechanism in catalytic isomerization of alkanes,"* Catalysis Today, Vol. 81, pp. 3-16, 2003.

[2]. Bauer F., Chen W. H., Ernst H., Huang S. J., Freyer A. and Liu S. B., *"Selectivity improvement in xylene isomerization,"* Microporous and Mesoporous Materials, Vol. 72, pp. 81-89, 2004.

[3]. Nasiru M. and Tukura, Al-Khattaf S., *"Comparison studies of Xylene isomerization and disproportionation reactions between SSZ-33, TNU-9, mordenite and ZSM-5 zeolite catalysts,"* Chemical Engineering Journal, Vol. 166, pp. 348-357, 2011.

[11]. Wang G. L., Wu W., Zan W., Bai X. F., Wang W. J., Qi X. and Kikhtyanin O. V., "*Preparation of Zn-modified nano-ZSM-5 zeolite and its catalytic performance in aromatization of 1-hexene*," Vol.25, pp. 1580-1586, 2015.

[4]. Rasouli M., Atashi H., Mohebbi-kalhori D. and Yaghobi N., *"Bifunctional Pt/Fe-ZSM-5 catalyst for Xylene isomerization,"* Journal of the Taiwan Institute of Chemical Engineering, Vol. 78, pp. 438-446, 2017.