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Synthesis, Characterization, and Catalytic Performance of Fe-Cr Nano Oxide/ZSM-5 Composites for Styrene Production

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Abstract

In this article, at first ZSM5- zeolite using metakaolin as a source of alumina was synthesized by using a microwave oven. In this regard, ZSM5- zeolites with high purity and in relatively short time (25 min with microwave irradiation) were successfully prepared. Then nano particle Fe-Cr/ZSM5- zeolite composite catalysts were prepared via Solid State Dispersion (SSD) and encapsulation methods. Samples were prepared by mixing different weight ratios of Fe_2O_3, Cr_2O_3, and K_2CO_3 powders with ZSM5- zeolites at the first method, and for the second one, the metal complexes were encapsulated within the ZSM5- zeolite pores. Prepared catalysts then characterized via EDX, SEM, XRD and FT-IR techniques. The catalytic performance of the synthesized catalysts was evaluated in ethylbenzene dehydrogenation to styrene in the presence of steam at 610 °C under atmospheric pressure. The results demonstrate that ZSM5- oxide loaded catalysts have better performance than bare zeolite. In addition, samples with Fe_2O_3 nano particles also act more effectively than Cr_2O_3 loaded zeolites. It was shown that styrene yield was significantly been influenced by loading Fe_2O_3, Cr_2O_3 and K_2CO_3 materials. The comparison between performance of SSD and encapsulation method was shown that the second one with smaller particle size and high Fe-Cr oxide dispersion has higher yield and conversion toward styrene production.

Keywords: Styrene, Ethylbenzene, ZSM-5 Zeolite, Fe-Cr Nano Oxide, Encapsulation.

Introduction

The catalytic dehydrogenation of ethylbenzene to styrene is of increasing interest due to growing demand for styrene. This valued product is an important raw material for production of acrylonitrile–butadiene–styrene resins, expandable styrene–butadiene latex, and a variety of synthetic polymers [1,2]. At industrial scale, the ethylbenzene dehydrogenation reaction is carried out over Fe–K based catalyst in the presence of superheated steam, which does not participate in the reaction but increases the activity and selectivity of the catalyst [3,4]. Although the commercial catalysts show high activity and selectivity, however there are some important disadvantages such as: low specific surface area, easy deactivation of iron based active sites, high toxicity and environmental pollution due to the chromium compounds [5,6]. In this context, the search for new catalytic systems is of high interest in today's research in catalysis. Therefore, in the present contribution, several types of nano particle Fe-Cr/ZSM-5 zeolite composite catalysts were prepared via Solid State Dispersion (SSD) and encapsulation methods. Their catalytic performance is addressed in ethylbenzene dehydrogenation in a fixed bed reactor.

Experimental

Catalyst preparation

Zeolites with ZSM-5 structure were prepared from silicic acid and alumina as Si and Al sources, respectively. Firstly, the solution of silicic acid, tetrapropylammonium bromide and sodium hydroxide in distilled water was added to the solution of sulfuric acid, n-propyl amine and metakaolin. The obtained mixture was stirred for 24 h at room temperature, transferred in to the Teflon-lined autoclave and heated under microwave radiation for 25 minutes. The synthesized sample was filtered, washed with distilled water, and dried for 3h in air at about 120°C. The template was removed by calcining the sample in air at 550°C for 5 h. To minimize the effect of the released steam on the zeolite structure a heating rate as low as 4°C/min was applied. The following methods were used to preparation of Fe-Cr nano oxide/ZSM-5 composite catalysts: Samples of Z-D_2 to Z-D_6 were prepared via SSD (Solid State Dispersion) method in which, a certain amount of Fe_2O_3 Cr_2O_3 and K_2CO_3 powders rubbed with ZSM-5 zeolites in the mortar and after adding of ethanol, calcinated at 600°C. Samples of Z-D7 to Z-D_{11} were prepared via encapsulation method. As first, K3[$Cr(C_2O_4)_3$] complex was synthesized in the zeolite pores. Prepared sample dried in air at about 100°C and Z-D7 catalyst produced after calcination in air at 600°C for 5 h.

Catalytic activity test

Catalytic experiments were carried out on catalysts, pelletized, crushed, and sieved at about 0.5–1 mm diameter under atmospheric pressure in a continuous-flow apparatus with a fixed bed stainless steel reactor (i.d. 10 mm and length 500 mm) placed inside an electrically heated furnace. Because of the low reactor pressure gradients of the catalyst bed in the reactors favored the yield and selectivity for styrene formation, in the industry, catalyst extrudate or pellet was used. Our synthesized catalysts are supplied in the form of cylindrical pellets of 1 mm diameter and 0.7 cm length. Prior to dehydrogenation of ethylbenzene, the reactor was loaded with 2.0 g of catalyst sample with support of quartz beads.

The catalysts were activated at 610°C. It was carried out in a flow of N_2 (100 ml min−1) for 60 min.

Results and Discussion

Phase composition analysis

Figure 1 shows the X-ray powder diffraction patterns of prepared samples. It can be seen from the figure that all samples have ZSM-5 structure with four strong peaks at 2θ=7.92°, 8.84◦, 23.12◦ and 23.8◦, could be indexed as 0 1 1, 0 2 0, 0 5 1 and 0 3 3 reflections, respectively. the peaks at 2θ=24.14°, 33.15◦, 35.61°, 40.85°, 49.48°, 54.09°and 63.99° obtained in Z-D_4, Z-D_6, Z-D_4, Z-D_8 and Z-D_9 samples can be well fitted to the data of the presence of hematite, α-Fe_2O_3 (JCPDS 33-0664 and h k l: 0 1 2, 1 0 4, 1 1 3,0 2 4, 1 1 6, 3 0 0, respectively). On the XRD patterns of the ZSM-5 type samples, no other diffraction peaks except those of the ZSM-5 structure were observed.

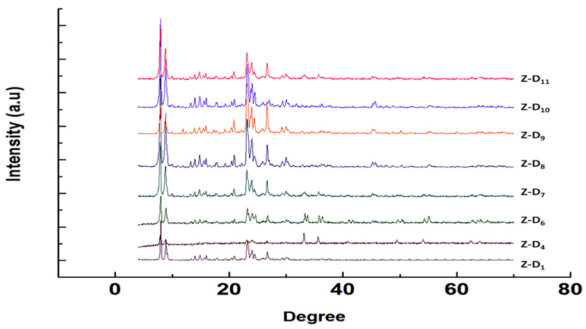

Fig. 1. XRD patterns of synthesized samples

Catalytic performances

As shown in figures 2 and 3, the prepared zeolites were tested as catalysts of the dehydrogenation of ethylbenzene in the presence of H_2O (14 ml h−1). According to the figure 2, Z-D_1 shows the lowest selectivity to styrene, while other catalysts with Fe_2O_3 particles show the high selectivity. It was found that the styrene yield of catalysts related to the SSD method increased in the following order:

Z-D_4> Z-D_2> Z-D_6> Z-D_5> Z-D_3> Z-D_1

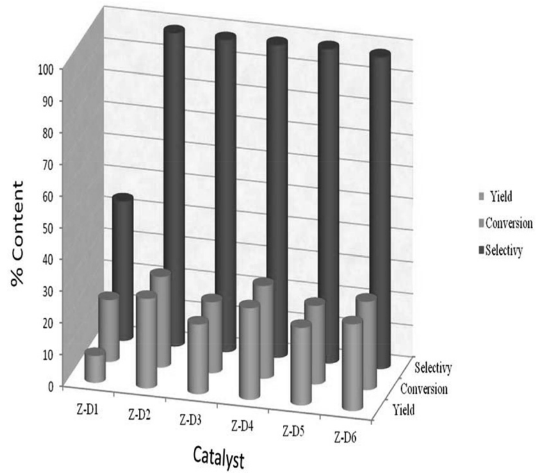

Fig. 2. The performance of various catalysts prepared with SSD method for the dehydrogenation of ethylbenzene in the presence of steam at 610◦C.

The variation of ethylbenzene conversion, styrene selectivity and styrene yield versus catalyst type prepared with encapsulation method are illustrated in Fig. 3. As shown, Z-D_{11} catalyst has the highest initial conversion and styrene yield but the lowest selectivity to styrene.

The styrene yield for the catalysts is in the order of:

Z-D_{11}> Z-D_9> Z-D_{10}> Z-D_7> Z-D_8> Z-D_1

Compared with SSD method, with encapsulation method, ethylbenzene conversion and styrene yield increased remarkably.

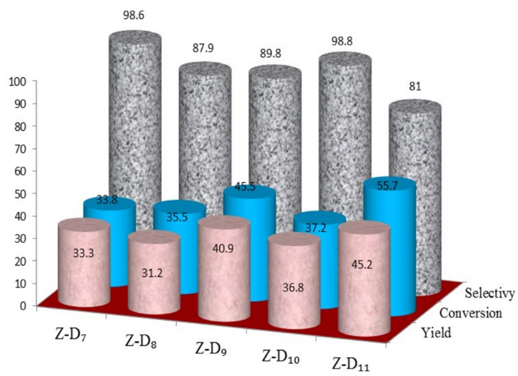

Fig. 3. The performance of various catalysts prepared with encapsulation method for the dehydrogenation of ethylbenzene in the presence of steam at 610°C.

Conclusion

In this article ZSM-5 zeolites with high purity and in relatively short time (25 min with microwave irradiation) were successfully prepared. Then nano particle Fe-Cr/ZSM-5 zeolite composite catalysts were prepared via Solid State Dispersion (SSD) and encapsulation methods. Samples were prepared by mixing different weight ratios of Fe_2O_3 ،Cr_2O_3 and K_2CO_3 powders with ZSM-5 zeolites at first method and for the second one, the metal complexes were encapsulated within the ZSM-5 zeolite pores. Prepared catalysts then characterized via EDX, SEM, XRD and FT-IR techniques. The catalytic performance of the synthesized catalysts was evaluated in ethylbenzene dehydrogenation to styrene in the presence of steam at 610°C under atmospheric pressure. The results demonstrate that ZSM-5 oxide loaded catalysts have better performance than bare zeolite. In addition, samples with Fe_2O_3 nano particles act more effectively than Cr_2O_3 loaded zeolites. It was shown that styrene yield significantly influenced by loading Fe_2O_3 Cr_2O_3 and K_2CO_3 materials. The comparison between performance of SSD and encapsulation method was shown that the second one with smaller particle size and high Fe-Cr oxide dispersion has higher yield and conversion toward styrene production.

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