Ammoxidation of propane over Fe-silicalite activated by nitridation

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Introduction

Ammoxidation of propane to acrylonitrile is a promising alternative to currently used process, ammoxidation of propylene. Although in last years great attention has been devoted to this economically more convenient process, the published results are still too modest. Among the well studied systems belong mixed metal oxides [1-4] and zeolite doped with iron [5,6]. Recently, new class of catalyst, VAlON, prepared by nitridation of the V-Al precursor, gave very good results in the ammoxidation of propane [7]. In our laboratory we have investigated the catalytic behavior of the Fe-silicalite activated by nitridation.

Experimental

[Fe]-MFI zeolite (4300 ppm of Fe, Si/Fe = 210) was prepared by hydrothermal synthesis of the mixture containing TEOS, aqueous solution of $FeCl_3$.6 H_2O, 1M solution of TPAOH and 10% solution of NaOH. The synthesis was carried out in the autoclave at 160 °C for 48 hours. The catalyst was subsequently treated at 540 °C for various times in flow of NH_3 and propane, the total flow was 100 cm^3/min with 5 vol. % of NH_3 and 5 vol. % of propane in helium. Ammoxidation of propane was carried out in a fixed bed through-flow microreactor at atmospheric pressure. The amount of catalyst used was 80 mg. The total flow rate was 100 cm^3/min, the feed composition was 2.5 vol. % of propane, 5 vol. % of NH_3 and 5 vol. % of O_2 in helium. The reaction was measured at the temperature of 540 °C.

Results/Discussion

In recent years Fe-zeolites were studied in the ammoxidation of propane and although quite interesting results were achieved, these systems suffered from some drawbacks such as: (i) the need of use N_2O as a (co)-oxidant in order to achieve high catalytic activity and (ii) the selectivity to the by-product, acetonitrile, was too high (acrylonitrile to acetonitrile ratio range from 1 to 3)[5,6]. Parent [Fe]-zeolites are usually activated by steaming in the water vapor (10-30 vol. % in N_2) at high temperature (600 °C). We found out that nitridation is better way for activation. The nitridated catalyst is able to selectively ammoxidize propane using only molecular oxygen as the oxidizing agent and moreover, high ratio of acrylonitrile to acetonitrile can be obtained. The selectivity to acrylonitrile was 42% at propane conversion of 26 % leading to yield of 11% which is 2.5 times higher as compared to results obtained over steamed catalysts reported in literature [5]. Acrylonitrile to acetonitrile ratio was almost three times higher over our catalyst than over steamed one (8.4 vs. 3). The productivity of the reported catalyst was as high as 9.3 mol*h*kg(cat)$^{-1}$. Once nitridated Fe-silicalite, the material is stable in the reaction and there is no change in the distribution of the products with the reaction time at least for 6 hours of reaction.

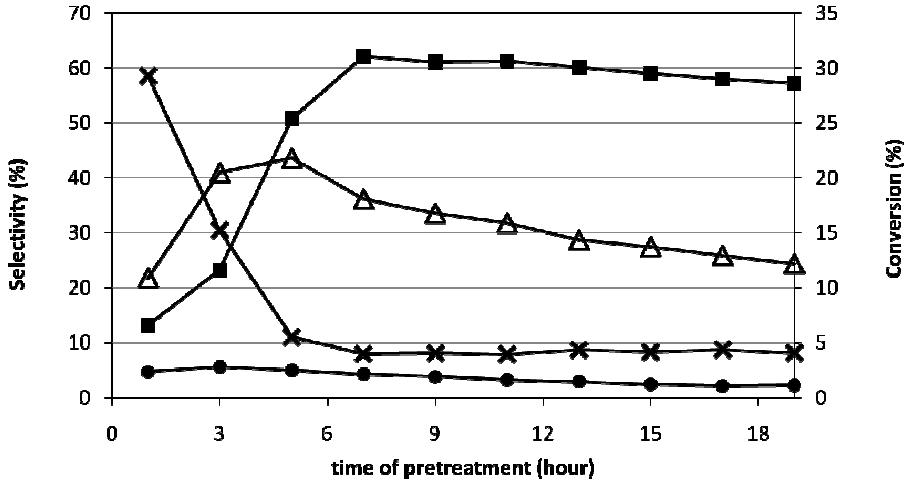

Figure 1: Ammoxidation of propane over Fe-silicalite, effect of the time of the nitridation after 50 minutes of the reaction, legend: ■ conversion of propane, Δ selectivity to acrylonitrile, ✖ selectivity to propylene, ● selectivity to acetonitrile

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