Evaluation of silanization of Na-Fe-silcalite-1 and Na-Fe-ZSM-5 on the oxidation of n-octane to C8 oxygenates

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1. Introduction

Linear oxygenates have many applications in pharmaceutical and chemical industries [1] Zeolite materials can be used to increase the production of linear oxygenates since they provide a shape selectivity to mimic the enzymatic environment. One of the special properties of these zeolite materials is the possibility of substituting Al with metals like Fe, Co, Mn etc. into the framework of the zeolite [2]. However, the substitution of these metals may lead to uncontrolled and undesired reactions because of the substituted metals on the external surface of the material [3]. Therefore, there is sometimes a need to deactivate the external surface to control the size shape selectivity that is provided by zeolite materials. Silanization is one of the common approaches that is used to achieve this purpose [4-7]. It has been reported that modification of the zeolite pore opening also occurs during the application of the silanization process. This is due to deposition of silica on the entrance of the channel resulting in reduced pore entrance sizes [8,9]. Therefore, it is necessary to use a bulky agent like TEOS for this purpose.

2. Experimental (or Theoretical)

The catalyst material, Na-Fe-Silicalite-1 and Na-Fe-ZSM-5, were synthesised using the modified solid gel method [10, 11]. The synthesised catalysts were calcined at 550 °C to remove the organic template.

Furthermore, materials were modified in their Na form by the process of silanization to deactivate the external surface of zeolites. A mass of 2.5 g of parent Na-Fe-Silicalite-1 or Na-Fe-ZSM-5 was stirred for 21 hours in 4 wt % tetraethoxysilane (TEOS) diluted in 96 mL hexane at room temperature [12]. After the sample was stirred for 24 hours, it was filtered, dried and calcined under air at 550 ºC to yield Na-Fe-Silicalite-5(80:Sil), Na-Fe-Silicalite-1(128:Sil), Na-Fe-ZSM-5(78:Sil) and Na-Fe-ZSM-5(128:Sil), respectively. Note: Sil = Silanized. All

3. Results and discussion

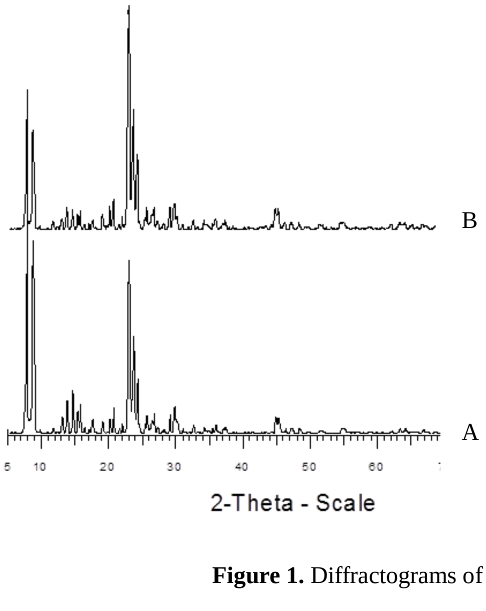

Figure 1. Diffractograms of A) Na-Fe-Silicalite-1(80) and B) Na-Fe-Silicalite-1(80:Sil)

Table 1: Conversion of n-octane and selectivity to terminal products

Catalysts	Conversion	Selectivity to terminal products
[a]Na-Fe-Silicalite-1(80)	2.8	28.1
[a]Na-Fe-Silicalite-1(80:Sil)	3.1	14.3
[a]Na-Fe-Silicalite-1(128)	1.6	17.6
[a]Na-Fe-Silicalite-1(128:Sil)	1.3	12.3
[b]Na-Fe-ZSM-5(78)	6.3	24.5
[b]Na-Fe-ZSM-5(78:Sil)	10.3	25.7
[b]Na-Fe-ZSM-5(126)	1.7	20.7
[b]Na-Fe-ZSM-5(126:Sil)	4.3	27.3

[a]Numbers in brackets represents Si/Fe ratio

[b]Numbers in brackets represents Si/Fe ratio which is the same as Si/Al ratio

Conditions: 0.22g catalyst, 7 mmol octane, 2.3 mmol H_2O_2(30 wt%), 80 ml CH_3CN at 80 °C

The XRD analyses show that only the ZSM-5 phase was present in all the catalysts. These catalysts were tested in the oxidation of n-octane in MeCN using H_2O_2 as an oxidant. It was found that the selectivity to terminal products increased with increasing the volume of MeCN. Furthermore, the Na-Fe-Silicalite-1(80), Na-Fe-Silicalite-1(80:Sil), Na-Fe-Silicalite-1(128) and Na-Fe-Silicalite-1(128:Sil) show terminal selectivities of 28.1, 14.3, 17.6 and 12.3 % respectively. In contrast Na-Fe-ZSM-5(78), Na-Fe-ZSM-5(126), Na-Fe-ZSM-5(78:Sil), and Na-Fe-ZSM-5(126:Sil) show terminal selectivities of 24.5, 25.7, 21.3 and 27.3 % respectively

4. Conclusions

The XRD results showed that only the ZSM-5 phase was present in all the Fe-Silicalite-1 and Fe-ZSM-5 catalysts even after silanisation. Furthermore, the increase in Si/Fe ratio from the ICP results confirmed that the silanisation process was successful. All catalysts were effective in the selective oxidation of n-octane to C8 oxygenates. The catalysts with Al showed a better selectivity to terminal products after silanisation compared to those without Al.

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