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Synthesis of silicalite-1 using fluoride media under microwave irradiation

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ABSTRACT

Robust hydrophobic zeolites are targeted for biomass and heavy oil upgrading, which involve large content of water. Silicalite-1 (Si-MFI) zeolite has been synthesized successfully with short synthesis time under microwave irradiation using two different sources of mineralizer agents at 180 °C. The effects of mineralizer agents on the synthesis of silicalite-1 and their effects on the phase produced, particle size and morphology were studied carefully. Eight new formulations were investigated to synthesize silicalite-1 with different strategies: (i) in the presence of both fluoride and hydroxide sources or (ii) in the presence of fluoride only or (iii) in the presence of hydroxide only. In addition, it was confirmed from our synthesis results that the synthesis of silicalite-1 in the absence of both fluoride and sodium hydroxide was possible. It was also noticed that the flexibility of adding ammonium fluoride to the synthetic gel was limited as compared to both sodium and potassium fluoride. It was observed that an addition of fluoride to the synthesis mixture led to an increase of particle size. In opposite, when only sodium hydroxide was added as a mineralizer agent, an increase of sodium hydroxide concentration led to a decrease in the particle size and favored the irregularity of silicalite-1 morphology.

1. Introduction

Zeolites are used as heterogeneous catalysts in chemical industries due to their adsorption properties of hydrocarbon molecules [1]. Zeolites have been used extensively in many refining and petrochemical processes, including isomerization, alkylation, cracking, steam cracking, viscosity reduction of heavy oil or long hydrocarbons and methanol to olefins (MTO). Furthermore, for certain applications such as biomass and heavy oil upgrading, further modifications are required to overcome the possible degradation of zeolite due to the presence of water. These requirements encouraged zeolite scientists to produce robust zeolites using different strategies such as different synthesis methods, different source of starting materials and changing the additive concentration. In the presence of steam or water, it was claimed that a hydrophobic zeolite can be used to eliminate the degradation of the zeolite and enhance its stability.

Zeolite can be modified using different methods such as adding chemical compounds with hydrophobic nature. For instance, adding silane group such as tetraethyl orthosilicate (TEOS) and octadecyltrichlorosilane (OTS) can add a hydrophobic nature to the synthesized zeolite [2,3]. On the other hand, zeolite can be produced in the presence of different mineralizer agents such as fluoride and hydroxide media. It is well known that hydrophobicity of zeolites can be enhanced by partial or total replacement of hydroxide media with fluoride media such as sodium fluoride (NaF), potassium fluoride (KF) and ammonium fluoride (NH_4F) [4–8].

Zeolites are available with different properties, frameworks and pores. More than 200 frameworks are available right now [9]. Among these zeolites, the most famous zeolite industrially is ZSM-5 (MFI) zeolite. Its importance is due to its activity in many catalytic reactions [10]. ZSM-5 (MFI) was firstly synthesized by Mobil Research and Development scientists [11]. The framework of ZSM-5 has a three-dimensional pore system with 10 membered-rings (MR) and pore size of (0.51 × 0.55 nm) in [100] direction [12]. Many studies were conducted in the synthesis of ZSM-5 using different heating method and different kind of chemical sources. Recently, several zeolites such as MTT, MFI, NaA and Zeolite Y were synthesized under microwave irradiation due to its advantages such as shorter synthesis time, shorter particle size and the particles have a uniform shape [13–20].

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In this study, ZSM-5 (MFI) zeolite was synthesized under microwave irradiation. The possibility of producing ZSM-5 with different silica to aluminum ratio was studied. The aim of the study is to confirm (i) the possibility of producing silicalite-1(Si-MFI) in the presence of different concentration of sodium hydroxide, (ii) the addition of different fluoride sources to the synthesis of silicalite-1 with different concentrations, (iii) the reduction or removing of sodium hydroxide content in the presence of fluoride media, and (iv) the possibility of varying the fluoride media in the absence of sodium hydroxide.

2. Experimental

2.1. Reactants

Some chemicals were used as raw materials in the synthesis of silicalite-1 included the following: (1) colloidal silica (40 wt. % in water, Sigma–Aldrich), (2) aluminum sulfate octahydrate ($Al_2(SO_4)_3.18H_2O$, Acros), (3) tetrapropylammonium hydroxide (TPAOH, 25% in water, Acros), (4) sodium hydroxide (NaOH, Panreac), (5) sodium fluoride, (6) potassium fluoride, (7) ammonium fluoride.

2.2. Synthesis of MFI zeolites

Many procedures are available for the synthesis of MFI zeolite with different approaches [14,21–23]. In our experiments, MFI zeolite was synthesized as follows. Sodium hydroxide (X g) was dissolved in 42.22 g of deionized (DI) water, followed by adding Y g of either sodium fluoride, potassium fluoride or ammonium fluoride. Aluminum sulfate octahydrate (Z g) was then dissolved in the solution. Then, 7.04 g of TPAOH was added and stirred for a few minutes followed by the addition of colloidal silica (13 g). For example, in one of the procedures to synthesize ZSM-5 zeolites, X = 0.14 g, Y = 0.20 of sodium fluoride and Z = 0 g. The reaction mixture was stirred vigorously at ambient temperature for 2 h. The general gel composition was 1.0 SiO_2: 0.1 TPAOH: z Al_2O_3: x NaOH: 35.5 H_2O: y wF, where w is (Na, K or NH_4). Experiments were carried out with different molar ratios as shown in Table 1.

The synthesized gel was transferred to 100 ml Teflon bottle and heated to 180 °C for 2 h with string speed of 300 rpm under microwave irradiation. The product was collected and washed thoroughly with DI water to reduce the pH. The samples were dried then the samples were calcined at 650 °C for 10 h.

2.3. Ion exchange

Sodium ions in Na-ZSM-5 zeolite were exchanged with NH_4 using 2 M of ammonium nitrate under microwave irradiation at 85 °C for 10 min. Ion exchange was performed under microwave irradiation. A 20 g of the solution was added to each 1 g of the zeolite. The samples were centrifuged and ion-exchanged again. Then the samples washed twice with deionized water and re-calcined again at 550 °C for 12 h.

2.4. Characterization

The crystallinity and the phase identification were determined using X-ray diffraction (XRD) with CuKα radiation. The scanning step and speed was 0.02 and 3° per min, respectively. Crystal morphologies and particle sizes were investigated using field-emission scanning electron microscopy (FE-SEM).

3. Results and discussion

3.1. Effect of synthesis time

The synthesis procedure for ZSM-5 was modified from a formula reported by Konno et al. [24]. Konno et al. synthesized ZSM-5 zeolite by the hydrothermal oven at 150 °C for 72 h. In our modified protocol, we synthesized ZSM-5 zeolite with a SiO_2/Al_2O_3 ratio of 300 in the gel mixture at 180 °C under microwave irradiation with a stirring speed of 300 rpm. The synthesis was performed under microwave irradiation to guarantee the uniformity of the particle size and to shorten the synthesis time. Since the required synthesis time under microwave irradiation is significantly shorter than the one in hydrothermal oven, it is worthy to find the corresponding required synthesis time using microwave irradiation. To identify the required temperature, ZSM-5 zeolite was synthesized with different synthesis time in the range of 1–6 h. In all these cases, samples were synthesized without aging prior to the synthesis. It was possible to obtain pure ZSM-5 zeolite in 1 h synthesis time as confirmed by XRD as shown in Fig. 1. However, the lack of zeolite yield after both 1 h and 2 h synthesis time forced us to adapt our synthesis time to 3 h.

3.2. Effect of silica to aluminum (Si/Al) ratio

The second modification was performed by varying the silicon to aluminum ratio (Si/Al) ratio in the solution. Based on our target to produce a hydrophobic ZSM-5 zeolite, it is worthy to add the feature of hydrophobicity by changing the Si/Al ratio. It is well known that as silicon to aluminum ratio increases, the hydrophobicity and stability of the zeolite increases [25]. Based on this fact, we tried to synthesize ZSM-5 zeolite with high range of the silicon to aluminum ratio between 150 and infinity with the synthesis time of 3 h without aging prior to the synthesis under microwave irradiation. We were able to obtain pure ZSM-5 in the whole range and the XRD patterns were preserved as shown in Fig. 2.

Table 1
Molar ratio of modified formulations in the synthesis of silicalite-1.

Identification for formula	Mineralizer agent				Formulation
	NaOH	NaF	KF	NH_4F	
1	Yes	No	No	No	1 SiO_2: 0.1 TPAOH: (0–0.0033) Al_2O_3: 0.0405 NaOH: 35.5 H_2O
2	Yes	No	No	No	1 SiO_2: 0.1 TPAOH: (0.0–0.5) NaOH: 35.5 H_2O
3	Yes	Yes	No	No	1 SiO_2: 0.1 TPAOH: 0.0405 NaOH: 35.5 H_2O: (0.0–0.413) NaF
4	Yes	No	Yes	No	1 SiO_2: 0.1 TPAOH: 0.0405 NaOH: 35.5 H_2O: (0.0–0.55) KF
5	Yes	No	No	Yes	1 SiO_2: 0.1 TPAOH: 0.0405 NaOH: 35.5 H_2O: (0.0–0.083) NH_4F
6	No	Yes	No	No	1 SiO_2: 0.1 TPAOH: 35.5 H_2O: (0.0–0.413) NaF
7	No	No	Yes	No	1 SiO_2: 0.1 TPAOH: 35.5 H_2O: (0.0–0.413) KF
8	No	No	No	Yes	1 SiO_2: 0.1 TPAOH: 35.5 H_2O: (0.0–0.083) NH_4F