



Synthesis of hydrothermally stable mesoporous aluminosilicates by using urea as additive

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HIGHLIGHTS

- Hydrothermally stable Mesoporous materials were prepared via mother liquor recycling method.
- Urea is employed as additive to alter the properties of surfactant solutions.
- P123 utilization efficiency is drastically increased.

ARTICLE INFO

Article history:

Keywords:

Mesoporous aluminosilicates
Mother liquor recycling
Urea
Hydrothermal stability

ABSTRACT

Mesoporous aluminosilicates (MAs) with high hydrothermal stability by assembly Y precursors have been a promising materials for cracking heavy oil. A means to reduce the template consumption and water discharge is of vital importance in synthesis of MAs. Mother liquor recycling (MLR) is an eco-friendly and effective method to synthesize (MAs) with largely reduced template consumption and water discharge. However, inorganic salts accumulation especially for SO_4^{2-} in the mother liquor with continuous recycling has a negative influence on the micellization of the surfactants. The P123 molecules tend to aggregate into much larger particles and the assembly mother solution becomes cloudy. Less ordered MAs with poor hydrothermal stability would be obtained. In this work, well-ordered MAs with high hydrothermal stability were synthesized via MLR method by introducing urea as additives. Urea acting as salting-in additives behaves opposite to the inorganic salts, which could clear the assembly mother solution by breaking down the P123 aggregates into micelles. After hydrothermal treatment in 100% water vapor at 800 °C for 16 h, the obtained sample maintains 37.7% of specific surface area and 62.1% of total pore volume. In contrast, the sample prepared without adding urea just maintains 15.0% of specific surface area and 20.0% of total pore volume. This strategy provides a high efficiency and low cost route to the synthesis of MAs, which sheds a light on the practical application of MAs.

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1. Introduction

Since the discovery of one family of mesoporous silicates named SBAs [1], which were paid considerable attention because of their potential applications as catalysis or catalyst supports in some processes involving large reactant molecules such as heavy oil cracking. However, as compared with conventional microporous zeolite, these mesostructured materials have poor hydrothermal

stability, which can be attributed to the amorphous nature of the pore walls [2]. Extensive efforts have been made toward to rational design and synthesis of mesostructured materials with excellent hydrothermal stability. One might expect to improve the hydrothermal stability of mesostructured materials by introducing the microporous zeolite primary and secondary units into the mesoporous walls via employment of self-assembly of microporous zeolite precursors [3–6]. The hydrothermal stability of obtained mesoporous aluminosilicates (MAs) is comparable to that of USY and the prepared catalysis exhibited excellent catalytic performance in heavy oil catalytic cracking test [7]. But there still have two shortcomings: low utilization efficiency (only 0.52 g MA was

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obtained per gram of P123) and high water discharged in production of MAs (86 g wastewater per gram of MAs was discharged), which make these MAs far from meeting the demand of practical application in the industrial scale. Tremendous effort has been made to solve these problems, which includes steam-assisted conversion route [8–10], microwave-assisted route [11] and crystal-seed method [12]. Although, generally successful in terms of increasing the utilization efficiency or decreasing the water consumption, neither of these method could solve the problems together.

Mother liquor recycling (MLR) is one approach that can reuse the remaining reactants (such as Al, Si, templates) and water, which is widely used for the synthesis of microporous zeolites such as NaY [13], ZSM-5 [14], TS-1 [15,16], and aluminophosphates [17]. Our previous study [18] had reported that mesoporous aluminosilicates could be synthesized through the MLR method utilizing the nonreacted templates in the mother liquor. The consumption of templates and water discharge could be drastically reduced to 51.5% and 27.3% of those of traditional synthesis route. Meanwhile, the product yield is 4.8 times that of conventional MAs (102.66 g/L vs 21.4 g/L). Unfortunately, after being hydrothermally treated in 100% water vapor at 800 °C for 16 h, the obtained MAs just preserved 15.0% surface area and 20.0% total pore volume, which cannot face the extremely harsh terms of heavy oil cracking. This is due to that inorganic salts accumulation especially for SO_4^{2-} in the mother liquor with continuous recycling has a negative influence on the micellization of the surfactants. It would sharply decrease the critical micelle concentration (CMC) and cloud point (CP) of P123, resulting in that the P123 molecules aggregate into much large particles and tend to be “salt-out” from the mother liquor [19–22]. Meanwhile, the aggregation of micelles does not favor the well-ordered MAs with excellent hydrothermal stability. It is expected that eliminating the negative effect of SO_4^{2-} is the key point to successfully synthesize hydrothermally stable MAs via MLR method.

Urea and its derivatives are well-known denaturants of proteins [23], because of their ability to enhance hydrophilic interactions in aqueous solution. For the same reason, it is expected that urea could be used to alter the properties of surfactant solutions by slightly changing the balance of hydrophobic/hydrophilic interactions of surfactants with water [24]. Bahadur's group [20] reported that urea behaved opposite to the inorganic salts. The presence of urea is interpreted in terms of improved solubility of poly(propylene oxide) (PPO) moiety and also poly(ethylene oxide) (PEO) moiety of P123 micelles. Some studies [25] using ^1H NMR spectroscopy showed that urea working as salting-in additive, enhance the solubility of nonionic surfactants in the water solution, through the formation hydrogen bonds between urea molecular and PEO moiety. Two different mechanisms for urea action in aqueous micellar solutions have been proposed: (1) an indirect mechanism, urea changes the “structure” of water to facilitate the solvation of a hydrocarbon chain of nonpolar solute [26]; (2) a direct mechanism, urea replaces some of the water molecules in the hydration shell of the solute but has almost no effect on the water structure [27]. However, a fundamental understanding that addition of urea could increase the CMC of nonionic surfactant and raises the CP is widely admitted.

In the present investigation, we employed urea as additive in the MLR system to change the hydrophilic-hydrophobic balance of P123 micelles. Well-ordered MAs with excellent hydrothermal stability were synthesized. According to our knowledge, it is demonstrated for the first time that MAs were synthesized using urea as additives in MLR process. A combination of a urea-assisted and precursor self-assembly process is believed to be the key to realizing industrial production of MAs.

2. Experimental section

2.1. Materials

Triblock copolymer P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, MW = 5800) was purchased from Sigma-Aldrich Co. LLC. Water glass contained 28.3% SiO_2 and 8.8% Na_2O , sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), Urea ($\text{CO}(\text{NH}_2)_2$), and aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) were obtained from the Tianjin Guangfu Co.

2.2. Preparation of Y zeolite precursors

Y precursors were prepared according to literature [28]. The mixtures of Na_2SiO_3 , $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, and NaOH solution with a molar ratio of $\text{Al}_2\text{O}_3/\text{SiO}_2/\text{Na}_2\text{O}/\text{H}_2\text{O} = 1/16/15/320$ were prepared. After being stirred for 40 min, it was aged under stirring at 98 °C for 8 h to obtain a sticky solution, called the “Y precursors”.

2.3. Multiple assembly process

- (1) 300 g zeolite Y precursors and 6 M H_2SO_4 were simultaneously added into the P123 solution (40 g P123 dissolved in 1500 mL water) at pH 1.5–1.8. The mixture gel was assembled at 30 °C for 20 h to obtain “assembly product” and “assembly mother liquor”. Assembly mother liquor and assembly product (filter cake 1) were separated by filtration.
- (2) Prior to the second cycle, 10 g of urea and 15 g of P123 were added into 1500 mL assembly mother liquor obtained in the last step under stirring. After 6 h, 240 g Y precursors were added. Meanwhile, H_2SO_4 was slowly added under stirring adapting the pH of mixtures in range of 1.5–1.8. After the same assembly process with that of step (1), assembly mother liquor and assembly product (filter cake 2) were separated by filtration.
- (3) The third, fourth, and fifth assembly cycles were repeated as the procedure described in step (2) except for adding urea. The assembly products obtained from the third, fourth and fifth cycles will be denoted as “filter cake 3”, “filter cake 4”, and “filter cake 5”.

2.4. Crystallization

Portions of filter cakes 1, 2, 3, 4, and 5 were taken out and mixed with mother liquor (the recycling liquor in cycles 1) and then transferred to five 100 mL Teflon autoclave respectively. The remaining portions of five filter cakes were mixed with the mother liquor (the recycling liquor in cycles 1) and then transferred to 1 L Teflon autoclave. The six mixtures were crystallized at 120 °C for 24 h. After filtration, washing, drying and calcination at 550 °C for 5 h, the final products were obtained and denoted as U-x, (x being 1, 2, 3, 4, 5, and 6). For comparison, WU-x (x being 1, 2, 3, 4, 5, and 6) was synthesized as the same procedures of U-x except for adding urea in the second cycle.

2.5. Hydrothermal stability of MAs

In order to evaluate the hydrothermal stability of MAs, U-6 and WU-6 were hydrothermally treated in 100% water vapor at 800 °C for 16 h. And the obtained materials were denoted as HU-6 and HWU-6 respectively.

2.6. Characterization

X-ray diffraction (XRD) patterns of the synthesized

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