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The beneficial use of ultrasound in synthesis of nanostructured Ce-doped SAPO-34 used in methanol conversion to light olefins

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ABSTRACT

Methanol to olefins process is an interesting route for synthesis of light olefins over nanostructured catalysts. The present research deals with catalyst development by sonochemical method for methanol to olefins reaction with the aim of reaching the most efficient catalyst. The CeSAPO-34 catalyst was prepared via ultrasound assisted hydrothermal method and characterized by XRD, FESEM, PSD, EDX, BET and FTIR techniques. The characteristics and performance of this sample were compared to the catalyst prepared by conventional hydrothermal method. XRD patterns reflected the higher crystallinity of the catalyst synthesized by ultrasound application. In comparison, particles with smaller sizes obtained by applying ultrasonic irradiation. The catalyst obtained using ultrasound had the longer lifetime and sustained desired light olefins at higher values.

1. Introduction

The depletion of oil reserves and the increasing demand for ethane and propene, initiated the quest for chemical processes based on alternative feedstock [1–5]. Methanol has been attracted due to its potential to transform into gasoline (methanol to gasoline or MTG) and/or olefins (methanol to olefins or MTO) when reacted over acidic zeolite catalysts. Methanol is an interesting alternative to crude oil which can be obtained from any gasifiable carbon-rich feedstock, such as natural gas, coal and biomass.

Different acidic microporous catalysts have been reported for MTO process [6–12]. Reaction over medium-pore zeolites (like ZSM-5) produces extensive amounts of aromatics and paraffins and in the case of large-pore zeolites rapid coke formation results [7,9,13–21]. The silicoaluminophosphate, SAPO-34, was reported to be the most promising catalyst giving maximum light olefins selectivity up to 80%. Using the SAPO-34 catalyst with small particle sizes enhances the accessibility of methanol into its cages, resulting in better catalytic performance. Investigations about the effect of particle size show the best performance for SAPO-34 catalyst with smaller particle size [22–26].

Over the last few years, great attention has been paid to the use of ultrasound energy in material chemistry and considered a very interesting technique to prepare novel supported materials with particular properties [14,21,27–31]. The main advantages of catalysts prepared by ultrasound energy are: an increase of specific surface area, smaller particle size and enhanced catalytic performances [32–35]. All the enhanced characteristic of catalysts synthesized using the ultrasound application would resultantly make them an outstanding catalysts for the catalytic processes [36–38]. Several studies evidenced that the activity of the ultrasound-assisted catalysts retains their activity for longer time [14,21]. In the preparation of heterogeneous catalysts the beneficial effect of ultrasound are derived from acoustic cavitation. It can be defined as the tendency of formed bubbles by ultrasonic waves to collapse preferentially near the solid surfaces. Consequently, collapsing bubbles generate localized hot spot. [14,21,27–29,31,39]. As a result, a temperature and pressure of about 5000–25,000 K and 180 MPa are produced [32]. This hot spot is estimated to have radius smaller than 299 nm with a lifetime of less than 2 μs. Thus, the major reason for the enhanced chemical reaction caused by the ultrasonic energy can be the high local temperature produced during the bubble collapse. It will result in dissociation of the reactant molecules and better dispersing of the metal heteroatoms in the initial gel. Furthermore, ultrasonic processing prohibits the further growth of the particles and their agglomeration. Moreover, attaining smaller particles is commonly the dominant factor to supress the secondary reactions

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in the MTO process. The effect of acoustic cavitation is favored by the presence of dissolved noble gases like argon, increasing the temperature of the collapsing bubbles generated by ultrasound [21,29,31,39]. In addition, catalyst preparation can be accomplished much faster using ultrasound irradiation. Thus, objective of this research is to assist the traditional hydrothermal method using ultrasound energy in the preparation of catalysts for MTO process.

The biggest challenge facing MTO commercialization is about the achievement of the highest lifetime of the catalyst. Rapid deactivation by coke is the major drawback of SAPO-34 utilization in MTO process and resultantly makes short lifetime for this catalyst [40–45]. Metal incorporation into silicoaluminophosphate framework influences properties of resulting samples [8,14,41–44,46–48]. MeSAPO-34s synthesis has been attracted due to their obtained longer lifetime compared to conventional SAPO-34. It is well-recognized that template plays important roles in the synthesis of molecular sieves and it may be dominating factor in the particle size of the catalyst. SAPO-34s templated with TEAOH showed smaller particle size compared to that of the sample synthesized with morpholine. In this research, the catalysts were prepared by morpholine as template to cope with higher cost of TEAOH. The ultrasound energy was applied to enhance the product morphology. There is no report available for the use of ultrasound irradiation in the synthesis of Ce incorporated into SAPO-34 framework. To correlate the modification of the catalysts features with their performance in MTO reaction, characterizations by XRD, FESEM, PSD, EDX, BET and FTIR techniques have also been performed. Performance tests were carried out to investigate the influence of different temperatures on the catalyst activity. In addition, the stability test was conducted to address the time on stream performance.

2. Materials and methods

2.1. Materials

In a typical synthesis, morpholine template, γ-Al_2O_3 (Merck), silicic acid (Merck, 98%), cerium nitrate hexahydrate (Merck) and phosphoric acid (Merck, 85%) were used as the sources of aluminium, silicon, cerium and phosphorus, respectively. All the materials were used as received without any further treatments. The catalysts synthesized by conventional and ultrasound assisted hydrothermal methods denoted as CeSAPO34-H and CeSAPO34-UH, respectively.

2.2. Catalyst preparation and procedures

For the successful synthesis, appropriate order of mixing and suitable precursors for each of the samples was employed as demonstrated in Fig. 1. In detail, weighted amount of γ-Al_2O_3 dissolved in distilled water under stirring for 40 min. Phosphoric acid aqueous solution was added to the solution under stirring by a dropwise addition for 40 min. Afterward, silicic acid and cerium nitrate were added in turn. Finally, morpholine was gradually added to the precursor solution and stirred for 24 h. The chemical composition of synthetic gel was $1Al_2O_3$:$0.6SiO_2$:$1P_2O_5$:$0.006CeO_2$:3Morpholine:$50H_2O$. As illustrated in Fig. 2, the ultrasound treatment has been performed using an ultrasonic generator with a frequency of 20 kHz, an effective input power of 90 W. The precursors solution has been sonicated by a 13-mm solid probe standard titanium horn in argon atmosphere. The use of this gas enhances cavitation effect because increases the temperatures of the collapsing bubbles generated by ultrasound. Temperature was maintained at constant temperature (30 ± 2 °C) and checked

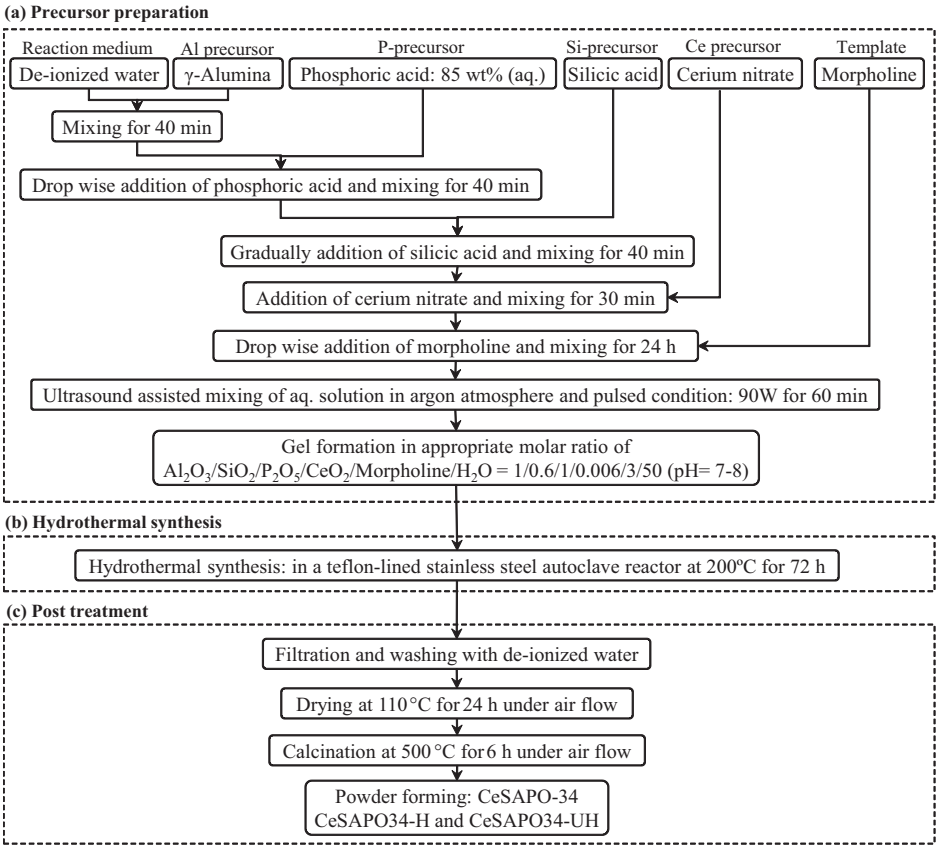

Fig. 1. Preparation steps of nanostructured CeSAPO-34 catalyst using ultrasound energy and hydrothermal method.