Advanced Powder Technology 27 (2016) 1738–1749

Contents lists available at ScienceDirect

Advanced Powder Technology

journal homepage: www.elsevier.com/locate/apt

Original Research Paper

Effect of template combinations (TEA/MOR, TEA/DEA, DEA/MOR) in synthesis of nanostructured CoAPSO-34 catalyst used in conversion of methanol to light olefins

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ARTICLE INFO

Article history:
Received 27 November 2015
Received in revised form 28 April 2016
Accepted 3 June 2016
Available online 16 June 2016

Keywords:
CoAPSO-34
MTO
Dual template
Ethylene
Propylene

ABSTRACT

Current research was focused on the synthesis of CoAPSO-34 catalysts with various templates combination with the aim of reducing the preparation cost and implemented in methanol conversion to light olefins reaction. Three sets of mixed templates are taken into account for CoAPSO-34 synthesis, being TEA/morpholine, TEA/DEA and DEA/morpholine with constant composition of 50%:50%. The catalysts were prepared via hydrothermal method and characterized with XRD, FESEM, PDS, EDX, BET, FTIR and NH_3-TPD techniques. Nanostructured catalyst synthesized with DEA/morpholine mixture exhibited the highest crystallinity evidenced by XRD analysis. The catalyst prepared with TEA/DEA mixed template has the smallest particle size and the most uniform particle size distribution. The highest value of Si incorporation was obtained for the catalyst prepared with DEA/morpholine mixture shown by EDX analysis. Methanol to light olefins reaction was carried out at different reaction temperatures. The stability test was conducted maintaining at constant temperature, molar feed ratio and GHSV to distinguish the effect of time on stream. In comparison, later emergence of DME in the products stream for the catalyst prepared with DEA/morpholine can be due to its higher crystallinity, specific surface area, better Si distribution and higher structural OH bands evidenced by XRD, BET, EDX and FTIR techniques, respectively.

1. Introduction

Ethylene and propylene are important commodity petrochemicals useful in a variety of processes for making plastics and other chemical compounds. The petrochemical industry has known for some time that oxygenates, especially alcohols, are convertible into light olefins which are traditionally produced from petroleum feedstock by catalytic or steam cracking processes [1–3]. The preferred methanol conversion process is generally referred to as a methanol-to-olefin(s) process MTO, where methanol is converted to primarily ethylene and/or propylene in the presence of a molecular sieve [4–12]. Molecular sieves are porous solids having pores of different sizes such as zeolites or zeolite-type molecular sieves [13–15]. Some of the most useful molecular sieves for converting methanol to olefins are the silicoaluminophosphates (SAPOs) [4,9,10,16–24]. SAPO molecular sieves contain a three dimensional micro porous crystal framework structure of [SiO_2], [$A1O_2$] and [PO_2] corner sharing tetrahedral units [25–27].

SAPO molecular sieves having the CHA framework type and especially SAPO-34 are particularly important catalysts [28–30]. The pore openings of the structure are defined by eight member rings having a diameter of about 4.0 A [31–33]. Cages are cylindrical with the dimensions of approximately 10×6.7 A. SAPO-34 crystals have a cubic-like morphology and typically crystallize as cubes, partial cubes, platelets or flakes, depending on the height of the crystals [4,21,24,34]. Most of the SAPO-34 molecular sieves were synthesized under hydrothermal conditions by using different kinds of amines like, tetraethyl ammonium hydroxide (TEAOH), diethylamine (DEA), triethylamine (TEA), morpholine, dipropylamine (DPA), isopropyl amine (IPA) and piperidine [4,7,16,21,34–37]. Furthermore, TEAOH was commonly used in lab and showed excellent catalytic performance for MTO reaction [36]. However, its relative higher cost would be a significant obstacle to commercial production. Consequently, applying mixed templates compared to those prepared with single template resulted in the reduction in catalyst preparation costs. Different mixed

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http://dx.doi.org/10.1016/j.apt.2016.06.005
0921-8831/

templates were taken into account in the SAPO-34 synthesis with the aim of reducing the portion of TEAOH in the synthetic gel to cope with the high preparation costs. Various mixed templates have been applied in SAPO-34 synthesis being TEAOH/TEA, TEAOH/DEA, TEAOH/morpholine, TEA/DEA and TEAOH/dipropylamine [4,7,19,21,34,35].

During preparation of the synthesis gel, an organic molecule is added to the mixture in order to ensure complete crystallization, increase the probability of producing the desired phase, balance the framework charge and fill voids in the framework. Organic molecules, which are used as a template in synthesis, have a significant influence not only on the crystallinity of the framework but also on the properties, such as the silicon distribution in a SAPO material [4,21,34,35]. The suitability of a material as a catalyst is determined by its activity, selectivity, accessibility and stability. SAPO-34 is a potentially suitable catalyst based on first two characteristics. But, stability and accessibility issues were taken into account because of rapid deactivation due to coke formation [38,39] and higher cost of organic template, respectively. Cost-effective SAPO-34 material can be achieved by excluding TEAOH from the template mixture. To improve the stability of the catalyst, we need to understand how it works as a catalyst at an atomic scale. A method of enhancing the catalyst stability and simultaneously avoiding the formation of methane during the MTO process is metal introduction into the SAPO-34 framework. In recent years, transition metals were used to incorporate into SAPO-34 to improve the catalysts performance. In the present work, cobalt was chosen to be used for the SAPO-34 synthesis due to its proven excellent performance in MTO reaction [8,12,18,37,40–44]. It indicated that most of the mixtures include the expensive TEAOH template. In the present contribution, SAPO-34 catalysts were synthesized with organic template mixtures excluding TEAOH to eliminate the synthesis costs. Thus, we conducted research on the preparation of SAPO-34 without TEAOH containing mixtures.

This topic has been the focus of our group. The main objective of this work is the synthesis of CoAPSO-34s with mixed templates excluding TEAOH. To the best of our knowledge, SAPO-34s modified by Co addition have not been synthesized by mixed templates. Up to now, investigations were mainly focused on achieving the optimized ratio of the binary template mixture. The catalytic evaluation of SAPO-34s synthesized with different mixed templates and under the similar conditions can be the named the major novelty of the present work. Three samples were synthesized with TEA/morpholine, TEA/DEA and DEA/morpholine mixtures with simultaneous Co metal addition. Physiochemical properties of the catalysts were identified by XRD, FESEM, EDX dot-mapping, BET, FTIR and NH_3-TPD techniques. The characterization of materials followed by the testing of samples for catalytic performance qualities such as reactivity (activity and selectivity) and stability (lifetime) allows us to gain deeper insights into the relationship between structure and catalytic properties. The stability test was conducted to investigate the effect of time on stream.

2. Materials and methods

2.1. Materials

The reactants used for preparing the CoAPSO-34 samples are aluminum isopropoxide (Aldrich, 98+ %), fumed silica (Aldrich, 99.9%), phosphoric acid (Merck, 85%), cobalt nitrate hex hydrate (Merck) as the sources of Al, Si, P and Co, respectively. TEA (Aldrich, 99.9%), DEA (Aldrich, 99.9%) and morpholine (Aldrich, 99.9%) were used as the organic templates. The synthesized catalysts with TEA/morpholine, TEA/DEA and DEA/morpholine mixtures were denoted as CoS/TE-MO, CoS/TE-DE and CoS/TE-DE, respectively.

2.2. CoAPSO-34 preparation and procedures

The gel recipe and the crystallization conditions for the CoAPSO-34 molecular sieves synthesized with mixed templates are shown in Fig. 1. The molar composition of synthesis solution was $1SDA^1{:}1SDA^2{:}1Al_2O_3{:}0.6SiO_2{:}0.05Co_2O_3{:}1P_2O_5{:}70H_2O$. In detail, weighted aluminum isopropoxide was dissolved in distilled water under vigorous stirring for 90 min at room temperature. Phosphoric acid aqueous solution was added to the solution under stirring by a drop-wise addition for 60 min. Fumed silica, cobalt nitrate and template mixture were added in turn and it was continually stirred for 24 h. The resulting gel was transferred into autoclave and heated at 200 °C for 48 h. The resulting solids were collected by centrifugation, then washed with water and dried overnight at 110 °C. Finally, the catalyst sample was calcined at 550 °C for 6 h to remove organic template and trapped water within the micro pores of the as-synthesized solid.

2.3. CoAPSO-34 characterization techniques

XRD patterns of the SAPO-34 catalysts were recorded on a Bruker D8 Advance diffractometer operated at 40 kV and 40 mA with Cu Kα radiation (1.54178 Å) to identify crystal phases. The phase identification was made by comparison to the Joint Committee on Powder Diffraction Standards (JCPDSs). The average crystal size was calculated using the half-width at half-height of most intense peaks of diffraction pattern and well-known Debye–Scherrer equation. Diffraction peaks recorded in a 2θ range between 5° and 50°. It is worthy to note that the calculated crystallinity is relative crystallinity. It is estimated by the intensity of the major peaks. The morphology of the samples was observed by the Field Emission scanning electron microscope (FESEM) on a HITACHI S-4160 (Japan). The FESEM is equipped with an Energy Dispersive X-ray (EDX) analyzer to take dot maps and to know the dispersion of the various metals. The specific surface area of the sample was determined by N_2 adsorption–desorption method at 196 °C (Quantachrome ChemBET-3000). FT-IR spectra of the samples were recorded on a UNICAM 4600 FT-IR spectroscopy using KBr pellet. Degassing is performed to eliminate air and moisture from the KBr powder. Catalysts acidity was measured by ammonia temperature programmed desorption using BELCAT analyzer with a TCD detector. Before analysis, 0.1 g of calcined sample was preheated at 550 °C for 60 min under a 50 cm^3/min helium gas flow. Ammonia adsorption was made from a mixture of 5% (molar basis) of ammonia in helium under total flow rate of 50 cm^3/min at 100 °C. After adsorption of ammonia, the samples were kept under a helium gas flow at 100 °C to remove physically adsorbed gases. Finally, the helium flow (50 cm^3/min) was passed through the sample with increasing temperature up to 800 °C at a rate of 10 °C/m.

2.4. Experimental setup for catalytic performance test

A laboratory plant with a continuous down flow packed bed reactor used for this study is presented in Fig. 2. Catalytic reaction studies were performed in electrically heated fixed bed reactor under atmospheric pressure. The gases are mixed and passed to the reaction section. Catalyst was loaded and previous to the reaction preheated in 70 ml/min Argon at 550 °C for 60 min to remove the adsorbed water. After the temperature of reactor was decreased to 300 °C, methanol and H_2O was fed to the reactor using a saturator. The products were analyzed on gas chromatograph (GC Chrom, Teif Gostar Faraz, Iran) with flame ionization detector (FID) using Plot-U column (Agilent) column by programming the oven temperature between 40 °C and 180 °C. Argon was used as a carrier for gas chromatograph and hydrogen