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Gas–oil cracking activity of hydrothermally stable aluminosilicate mesostructures (MSU-S) assembled from zeolite seeds: Effect of the type of framework structure and porosity

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Abstract

Aluminosilicate mesostructures (MSU-S_{BEA}) assembled from zeolite Beta (BEA) seeds exhibited relatively high hydrothermal stability and were significantly more active in the cracking of gas–oil compared to MCM-41 after severe steaming pretreatment. The MSU-S_{BEA} mesoporous materials with wormhole framework structure and those having morphology of solid nanoparticles with high interparticle mesoporosity were more steam-stable and more active after severe steaming than those with hexagonal pore structure. Differences in acid sites strength between the MSU-S_{BEA} materials and MCM-41 could not be probed by the complex reaction system of the large hydrocarbon molecules of gas–oil.

Keywords: Mesoporous catalysts; Zeolite seeds; Acidity; Gas–oil; Cracking

1. Introduction

The potential use of the aluminium-substituted MCM-41 materials, discovered by Mobil in 1992 [1], in the conversion of residual oil fractions to valuable lighter products, such as gasoline and diesel, has been one of the recent research and technological goals in fuels industry [2]. However, early works showed that the calcined, proton-exchanged H^+/Al-MCM-41 materials are mildly acidic [3,4] and they exhibit very low (hydro)thermal stability, especially at higher Al loadings [3], as compared to typical USY zeolite catalysts.

Significant advances have been made recently in improving both the hydrothermal stability and acidity of Al-MCM-41 mesostructures through the supramolecular assembly of aluminosilicate zeolite precursors or ‘‘zeolite seeds’’, which contain the secondary building blocks of the zeolite structures that they normally nucleate [5]. The first demonstration of this approach utilized faujasitic zeolite seeds (FAU) to construct the walls of a hexagonal Al-MCM-41 structure with high aluminum content [5a], while other zeolite seeds (MFI, BEA) containing the five-ring subunits of pentasil zeolites have also been utilized to synthesize hexagonal, wormhole or cellular foams structures [5b–d]. In addition to the exceptional hydrothermal stability of the above aluminosilicate mesostructures, named MSU-S (from Michigan State University), it was also shown that their cumene cracking activity was higher than that of a conventional Al-MCM-41 material.

With regard to the cracking of gas–oil, there is a limited number of studies which show that the calcined H^+/Al-MCM-41 is active and selective, but it loses almost all of its activity when it is subjected to severe hydrothermal treatment [3,6]. In a more recent study [7], the moderately steam-deactivated MSU-S aluminosilicate mesostructures synthesized from zeolite Beta seeds, exhibited higher gas–oil cracking activity when compared to a similarly steamed amorphous silica–alumina catalyst. Also, the MSU-S mesostructures were more selective towards the production of LCO, propylene and butylenes compared to an H–Y zeolite catalyst at the same gas–oil conversion percentage.

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In this work, the gas–oil cracking activity of fresh and hydrothermally treated MSU-S mesoporous aluminosilicates synthesized from zeolite Beta seeds and having different particle morphology and framework pore structures, was compared to that of a conventional Al-MCM-41 material. Porosity and acidity characterization results for the mesoporous materials were used to rationalize the observed differences in catalytic activity.

2. Experimental

2.1. Synthesis-preparation of catalytic materials

The MSU-S aluminosilicate mesostructures tested in this work were synthesized through the molecular assembly of zeolite Beta (BEA) seeds (with Si/Al = 49) by using two different mesoporous structure directing agents, the cetyltrimethylammonium bromide (CTAB) which produced an hexagonal pore structure (sample MSU-S/H_{BEA}) [5b] and the tallow tetraamine which produced an HMS-type *wormhole-like* mesostructure (sample MSU-S/W_{BEA}) [5c]. The zeolite Beta (BEA) seeds were prepared by a procedure analogous to those described previously [5d], using tetraethylammonium ions as BEA-structure directors, and tetraethyl orthosilicate (TEOS) and aluminum tri-*sec*-butoxide as silicon and aluminium sources, respectively. A third sample (MSU-S/S_{BEA}) was synthesized from BEA seeds which had been digested at 150 °C for 20 h and were further washed, dried and calcined at 600 °C for 4 h, without the use of any surfactant as mesoporous structure directing agent. A conventional Al-MCM-41 (2% Al) sample with hexagonal pore structure was also synthesized for comparison. All the synthesized materials were calcined to combust the organic templates and to produce their H^+-form and they were further steamed at 800 °C for 3 h at different steam partial pressures (10%, 40% steam in nitrogen or 100% steam).

2.2. Materials characterization and catalytic cracking tests

The catalytic materials tested in this work were characterized for: (a) chemical composition by ICP-AES measurements (Plasma 40, Perkin-Elmer instrument), (b) structural properties by powder XRD measurements (Rigaku Rotaflex diffractometer), (c) the surface area and pore volume/size by N_2 adsorption–desorption experiments at −196 °C (Micromeritics ASAP 2000 sorptometer), (d) the particle morphology and pore structure by TEM images (JEOL JEM-100CX II microscope), and (e) the number of acid sites by NH_3-TPD experiments using a commercial TPD apparatus (Altamira AMI-1) and an on-line mass spectrometer (Baltzers, Omnistar) for a detailed analysis of all the desorbed gases.

The catalytic testing of the materials in the cracking of gas–oil was performed on a fully automated short-contact-time microactivity test (SCT-MAT) unit. The reaction temperature was 560 °C, reaction time 12 s and cat-to-oil 2.3. The feedstock was a vacuum gas–oil (VGO) with conradson carbon 0.29, specific gravity 0.9365 and mean average boiling point 454 °C. Gaseous and liquid products were analyzed by advanced gas-chromatography techniques.

3. Results and discussion

3.1. Characterization of mesoporous catalytic materials

Detailed characterization data on the structure and morphology of the MSU-S mesostructured aluminosilicates synthesized from zeolite Beta seeds have been previously reported [5b–d]. In brief, the low-angle XRD patterns (not shown) of both the as-synthesized and the calcined MSU-S aluminosilicates showed the formation of different mesostructures (hexagonal or wormhole-like), as a result of using different structure directing agents (surfactants). In addition, no Bragg peaks were observed in the high-angle XRD region of the zeolite seeds and of the produced MSU-S materials proving the absence of any crystalline zeolitic phases; however, the formation of secondary zeolitic subunits was verified by the IR band in the 550–600 cm^{-1} region, which is characteristic of five-membered ring subunits of BEA and MFI structures.

The differences in the framework/pore structure of the MSU-S materials can also be clearly seen from the nitrogen adsorption–desorption isotherms in Fig. 1. The sample MSU-S/H_{BEA} which was synthesized from zeolite Beta seeds and with the use of CTAB as structure directing agent exhibits a typical well-ordered hexagonal mesopore structure, similar to that of the classical MCM-41 material. Both these samples show very narrow pore size (diameters) distributions with maxima at ~3.0 nm (inset in Fig. 1). For the synthesis of the sample MSU-

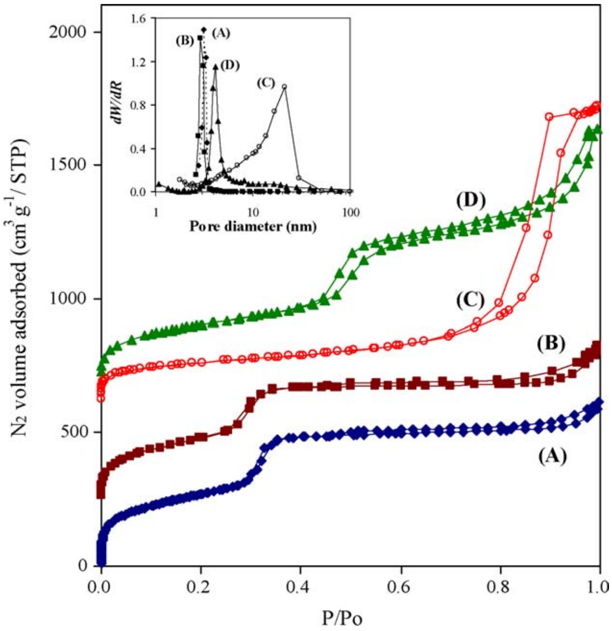

Fig. 1. N_2 adsorption-desorption isotherms for calcined forms of (A) MCM-41, (B) MSU-S/H_{BEA}—hexagonal (isotherm offset by 200 $cm^3 g^{-1}$), (C) MSU-S/S_{BEA}—solid nanoparticles (offset by 600 $cm^3 g^{-1}$), (D) MSU-S/W_{BEA}—wormhole-like (offset by 650 $cm^3 g^{-1}$). Inset: BJH pore size distributions obtained from the corresponding adsorption isotherms.

S/W$_{(BEA)}$, instead of CTAB a neutral amine surfactant (tallow tetraamine) was used, resulting in an HMS-type wormhole mesostructure with pore diameters of ~4.0 nm. The nitrogen isotherms of the third sample MSU-S/S$_{(BEA)}$, which was synthesized by thermal treatment of zeolite Beta seeds without the use of surfactant, show a sharp increase of adsorbed nitrogen volume at high partial pressures ($P/P_0 \sim 0.8$) which corresponds to a large mesopore volume with a relatively narrow distribution of pore diameters in the range 3–30 nm with a maximum at ~21 nm. This type of sorption properties has been previously reported for nanosized (fundamental particle sizes smaller than ca. 20 nm) crystalline or amorphous Beta and MFI zeolite-based materials, and is attributed to interparticle mesoporosity [8–11]. The TEM images (not shown) of MSU-S/S$_{(BEA)}$ verified the formation of fundamental nanoparticles of 10–15 nm in size closely interconnected and capable of generating interparticle mesoporosity with pore diameters in the range 3–30 nm, in accordance with nitrogen sorption data.

The surface area values of the fresh-calcined and severely steamed mesoporous materials are given in Table 1. It can be clearly seen that the MSU-S/H$_{(BEA)}$ and MSU-S/W$_{(BEA)}$ samples that were synthesized by the use of structure director–surfactant molecules present large surface areas (1017 and 928 m^2/g, respectively), similar to MCM-41 (990 m^2/g), while MSU-S/S$_{(BEA)}$ which consists mainly of X-ray amorphous solid nanoparticles presents lower surface area (541 m^2/g). After severe steaming at 800 °C for 3 h and 100% steam, the two hexagonal mesostructures MSU-S/H$_{(BEA)}$ and MCM-41 are almost completely destroyed resulting in very low surface areas, with the MSU-S sample showing a nearly double (57 m^2/g) area compared to MCM-41 sample (30 m^2/g). On the other hand, the MSU-S/W$_{(BEA)}$ sample with the wormhole-like mesostructure and the solid nanoparticles sample MSU-S/S$_{(BEA)}$ retain considerably higher surface area (145 and 116 m^2/g, respectively). Although these surface area values when compared to those of typical fresh-calcined mesostructures appear to be very small, in the fluid catalytic cracking (FCC) process they could be considered of high importance since the equilibrium FCC catalysts usually present surface areas in the range of 100–200 m^2/g.

The total aluminum content of the fresh-calcined samples is ~0.8–0.9 wt.% and the sodium content is very low ($\leq$0.03 wt.%), as can be seen in Table 1. The total acid sites of the fresh samples are also similar, while after severe steaming they retain a very small amount of residual acidity with differences between the samples that could be considered as insignificant (Table 1).

Table 1
Chemical composition, total acid sites and surface area of fresh-calcined and steamed (800 °C, 3 h, 100% steam) mesoporous aluminosilicate materials

Catalyst	Chemical composition (wt.%)		Acid sites (μmol NH$_3$ g^{-1})		Surface area (m^2/g)	
	Al	Na	Fresh	Steamed	Fresh	Steamed
MSU-S/W$_{BEA}$	0.90	0.03	237	31	928	145
MSU-S/H$_{BEA}$	0.69	0.03	202	22	1017	57
MSU-S/S$_{BEA}$	0.81	0.03	219	32	541	116
MCM-41	0.77	0.02	198	17	990	30

3.2. Gas–oil cracking activity of fresh and steamed mesoporous catalytic materials

Our previous studies have shown that the MSU-S aluminosilicate mesostructures synthesized from zeolite Beta seeds, after moderate steam deactivation at 800 °C for 3 h and 10–20% steam in nitrogen flow, exhibited higher gas–oil cracking activity when compared to a similarly steamed amorphous silica–alumina catalyst [7]. However, the above steaming conditions are not representative of the (hydro)-thermal deactivation that the commercial FCC catalysts undergo in the regeneration step of the overall cracking process. The more severe steaming conditions that were applied in this study (100% steam at 800 °C) can better simulate the industrial process. Fig. 2 presents a comparison of the gas–oil cracking activity of the classical hexagonal mesoporous MCM-41 aluminosilicate material and the wormhole-like mesoporous MSU-S/W$_{(BEA)}$ aluminosilicate synthesized from zeolite Beta seeds. When the samples were tested in their fresh-calcined form or after relatively moderate steaming they exhibited similar gas–oil cracking activity (gas–oil conversion > 55% at cat-to-oil = 2.3). However, at higher steaming severities the MSU-S/W$_{(BEA)}$ was considerably more active than MCM-41; after the most severe steaming treatment the MSU-S sample retained 36% of its activity in the calcined form while MCM-41 retained only 13% (Fig. 2).

The gas–oil cracking activity (expressed as wt.% conversion of gas–oil) and products yields of all the fresh-calcined and steamed mesoporous aluminosilicates tested, are shown in Table 2. The gas–oil cracking activity of the hexagonal MSU-S/H$_{(BEA)}$ material was similar to that of MCM-41 both in their

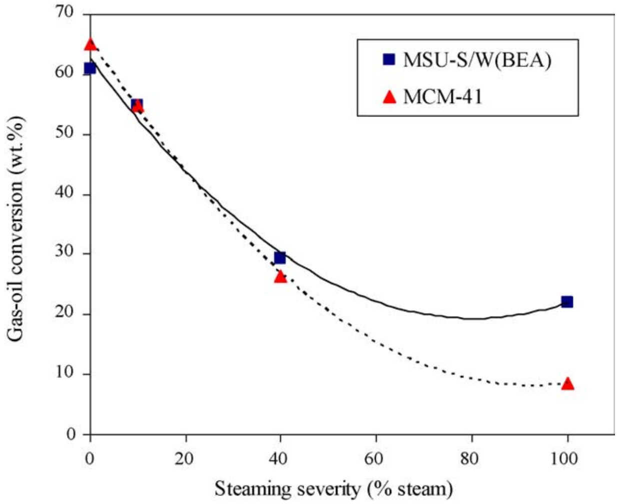

Fig. 2. Comparison of gas–oil cracking activity between the classical MCM-41 aluminosilicate and the wormhole-like MSU-S/W$_{BEA}$ synthesized from zeolite seeds, at different steaming severities (increasing % steam in steam–nitrogen mixtures, 800 °C, 3 h).

Table 2
Gas–oil cracking activity and products yields of the fresh-calcined and the severely steamed mesoporous aluminosilicate catalytic materials

	Catalysts							
	MSU-S/W_{BEA}		MSU-S/H_{BEA}		MSU-S/S_{BEA}		MCM-41	
	Fresh	Steamed	Fresh	Steamed	Fresh	Steamed	Fresh	Steamed
Conversion (wt.%)	61.0	22.1	59.3	8.6	53.6	20.6	65.1	8.5
Gasoline (wt.%)	35.0	15.0	34.8	5.2	27.8	14.7	37.6	4.8
LCO[a] (wt.%)	19.3	15.3	17.9	3.6	17.6	11.3	17.5	3.5
LPG[b] (wt.%)	18.8	3.45	16.8	1.44	19.6	2.99	18.4	1.56
Dry gases[c] (wt.%)	2.68	1.62	2.93	1.24	2.81	1.59	3.32	1.24
Coke (wt.%)	4.35	1.92	4.66	0.64	3.32	1.20	5.48	0.82

[a] LCO = light cycle oil.
[b] LPG = liquified petroleum gases ($C_3 + C_4$).
[c] Dry gases = $H_2 + C_1 + C_2$.

fresh-calcined form as well as after severe steaming. On the other hand, the MSU-S/$S_{(BEA)}$ sample retained considerably high activity after severe steaming, similar to that of MSU-S/$W_{(BEA)}$. By comparing the activities of all the MSU-S fresh-calcined mesoporous catalytic materials it can be suggested that both the hexagonal and the wormhole-like mesopore structures with framework pore diameters in the range of 3–4 nm are more effective than the solid nanoparticles of sample MSU-S/$S_{(BEA)}$ which possesses larger mesopores with mean diameter of ∼21 nm. However, easier accessibility of the gas–oil molecules to the acid sites of MSU-S/$S_{(BEA)}$ due to its larger pores, leads to higher LPG production, lower gasoline and relatively high LCO yields, compared to the rest of the mesoporous catalysts.

From the data in Tables 1 and 2, it can also be seen that the activity of MCM-41 is similar to those of MSU-S/$H_{(BEA)}$ and MSU-S/$W_{(BEA)}$, all of them having similar number of total acid sites. This result is in contradiction with the clearly observed superior cracking activity of both the hexagonal and wormhole-like MSU-S mesostructures synthesized from Beta seeds compared to the classical MCM-41 aluminosilicate in the cumene cracking reaction [5b,c]. The above discrepancy could be possibly attributed to the presence of zeolitic acid sites in the framework of the MSU-S materials which are easily accessible by the small cumene molecule but are difficult to be reached by the large hydrocarbon molecules of gas–oil. However, what is of most importance to the FCC process is the higher surface area that the MSU-S/$W_{(BEA)}$ (wormhole-like structure) and the MSU-S/$S_{(BEA)}$ (solid nanoparticles) samples retain after severe steaming, compared to the two hexagonal mesostructures, leading to significantly higher gas–oil cracking activity with the former two steamed MSU-S catalytic materials compared to MCM-41.

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