



MTW zeolites for reducing cold-start emissions of automotive exhaust

Z. Sarshar^a, M.H. Zahedi-Niaki^a, Q. Huang^b, M. Eić^b, S. Kaliaguine^{a,*}

^a Department of Chemical Engineering, Université Laval, Québec, Canada, G1K 7P4

^b Department of Chemical Engineering, University of New Brunswick, Fredericton, N.B., Canada, E3B 5A3

ARTICLE INFO

Article history:

Received 27 June 2008

Received in revised form 12 August 2008

Accepted 21 August 2008

Available online 3 September 2008

Keywords:

Hydrocarbon trap

ZSM-12

Ion-exchange

Isomorphous substitution

Cold-start emissions

Temperature-programmed desorption

Single-file diffusion

Adsorption

ABSTRACT

Increasingly strict environmental legislations have led to the need for better control of vehicle cold-start emissions. In this research work, a series of one-dimensional channel molecular sieves with 12 oxygen ring apertures (12R) having MTW structure (MTW is the designation for ZSM-12 in the IZA nomenclature of zeolite structures), have been synthesized and characterized by different techniques such as: XRD, SEM, BET surface area, elemental analysis by atomic absorption spectroscopy, FTIR of adsorbed pyridine and temperature-programmed desorption (TPD). The synthesized samples were tested as hydrocarbons (HCs) trap adsorbents using toluene and ethylene as heavy (aromatic) and light (olefin) probe molecules present in the exhaust stream at engine cold-start. TPD tests were performed after adsorption under four different mixture conditions: binary (toluene–ethylene), ternary (toluene–ethylene–CO₂), ternary (toluene–ethylene–H₂O) and quaternary (toluene–ethylene–CO₂–H₂O). The results demonstrated that a silver exchanged MTW zeolite, Al-ZSM-12 (Ag) exhibited high and stable trapping capacities for both probe molecules in all mixtures investigated in this study, thus showing essentially no sensitivity to CO₂ and/or H₂O. Moreover, a high desorption temperature, particularly for toluene, was associated with the large amount of strong Lewis and Brønsted acid sites. Isomorphous substitution of Al by Fe in MTW structures did not lead to drastic changes in adsorption capacities and desorption temperatures of the two sorbates.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Over the recent years, the low emission standards have forced automobile and catalyst manufacturers to focus on reducing the cold-start hydrocarbons (“HCs”) emissions. Cold-start is referring to the short time period of 1–2 min, after engine ignition, before the three-way catalyst reaches its light-off temperature. During this period about 70–80% of the total hydrocarbons are released without converting due to sluggish catalyst activity at low temperature. Different approaches have been attempted to solve this problem including combustion heated catalyst (CHC) [1], electrically heated catalyst [2–5], close-coupled catalyst [6,7], exhaust-gas ignition (EGI) [8,9] and heat storage devices but all these solutions encountered difficulties such as: cost, complexity in design and fabrication and durability. It has been found that the effective solution to the cold-start problem is to design a system employing an adsorbent which traps the hydrocarbons temporarily, followed by their gradual desorption from the porous structure upon increasing exhaust temperature. For this solution,

zeolites have been found preferred adsorbent materials due to their thermal stability and their thermodynamic affinity to HCs. The critical factors for any emission trap are the adsorption capacity and desorption temperature which must be higher than the catalyst light-off temperature [10].

A series of zeolites BEA, MFI, MOR and X [11–13] and silicoaluminophosphate molecular sieves [14] were investigated regarding their hydrocarbon adsorption capacities, under a variety of conditions [15]. Bruke et al. [16] reported that beta zeolite (BEA) is a promising material for this application, while Elangovan et al. [17] found that Standard Oil Synthetic Zeolite-thirty-three (SSZ-33) is superior to BEA based on their adsorption studies of a series of medium and large pore silicoaluminate zeolites. On the other hand, Czaplewski et al. [18] observed an interesting phenomenon of trapping molecules within the one-dimensional channel of EUO and MOR zeolites, as compared to more typical three-dimensional zeolites. This phenomenon was designated as the single-file diffusion mechanism, which prevents the passage of molecules by one another inside the micropores of the one-dimensional zeolites.

In a previous work we have studied a number of one-dimensional zeolites which could potentially be employed as adsorbents for HC traps during cold-start. ZSM-12 was selected as a promising candidate from these preliminary screening tests, based on its high

* Corresponding author.

E-mail address: Serge.Kaliaguine@gch.ulaval.ca (S. Kaliaguine).

trapping capacity and desorption temperature [19,22]. In particular ZSM-12 was found to be hydrothermally stable up to 973–1073 K in the presence of 10% water vapour in helium [22]. In the present study, the influence of isomorphous metal substitutions, cation exchange and acid properties of synthesized ZSM-12 (MTW) samples on trapping capacities and desorption temperatures of both probe molecules were investigated.

2. Experimental details

2.1. Al-ZSM-12 synthesis

Al-ZSM-12 was synthesized using a method proposed by Ernst et al. [20]. In a typical preparation, 80.9 g of a sodium silicate solution (Merck, 28.5 wt.% SiO₂, 8.8 wt.% Na₂O, 62.7 wt.% H₂O) was mixed with 80 g distilled water. To this, a solution of 30 g methyltriethylammoniumchloride (Fluka) in 100 g water was added, under stirring, followed by adding a solution containing 2.4 g Al(NO₃)₃·9H₂O (Merck) in 30 g H₂O. Afterwards, 4.7 g H₂SO₄ (Merck, 98%) was added under vigorous stirring. In the next step, the gel was transferred into a Teflon-lined stainless steel autoclave and the crystallization was conducted in a furnace at 433 K without agitation for 7 days. The final products were separated by centrifugation and then repeatedly washed with distilled water, followed by drying in air at 343 K overnight. Finally, calcination at 823 K was carried out overnight. The molar composition of the resulting gel was calculated as SiO₂/Al₂O₃ = 120, OH⁻/SiO₂ = 0.3, Na₂O/(MTEA)₂O = 1.5 and H₂O/OH⁻ = 125.

2.2. Ion exchange of ZSM-12

The calcined zeolites were three-fold ion-exchanged at room temperature with 0.1 M ammonium nitrate solution. Ag incorporation was carried out by ion-exchange in the liquid phase using silver nitrate over H-form of zeolite samples. For this, the solution was stirred at 353 K for 2 h. Thereafter, the samples were centrifuged and washed with distilled water and then dried overnight at 373 K.

2.3. Fe-ZSM-12 synthesis

The hydrothermal synthesis of Fe-ZSM-12 was carried out by modifying the procedure reported by Ernst et al. for the synthesis of ZSM-12. In a typical preparation of Fe-ZSM-12 [21], a required amount of sodium silicate (27.8 wt.% SiO₂, 8.8 wt.% Na₂O and 63.4 wt.% H₂O) in 40 g H₂O was added slowly under stirring to another solution comprising specified amount of Fe(NO₃)₃·9H₂O, 40 g H₂O and 3.0–4.0 g H₂SO₄ (96–98 wt.%). To the above mixture adequate amount of methyltriethylammoniumchloride (MTEA-Cl, Fluka) in 40 g H₂O was added under vigorous stirring. The pale lemon-coloured gel, so obtained, was stirred for about half an hour before transferring into a Teflon-lined stainless steel autoclave.

The typical molar gel composition was: SiO₂/Fe₂O₃ = 140, SiO₂/MTEA⁺ = 2.5, SiO₂/Na⁺ = 1.67, OH⁻/SiO₂ = 0.214 and H₂O/SiO₂ = 47. The crystallization was carried out at 433 K for 5 days. The colour of the crystalline product was white. The final products were separated by centrifugation and then repeatedly washed with distilled water, followed by drying in air at 343 K overnight. Thereafter, calcination was carried out at 873 K overnight. The gel compositions of the different samples are presented in Table 1.

3. Structural characterization

3.1. XRD

In X-ray diffraction (XRD) patterns the unique structures of the different zeolites, in terms of atom positions and unit cell dimensions, are reflected in characteristic positions and relative intensities of observed peaks. Powder X-ray diffraction patterns of the as-synthesized and calcined samples were recorded using a Siemens D5000 powder diffractometer with Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$).

3.2. SEM

Scanning electron micrographs were recorded to determine the crystallite size and characterize the morphology of the materials, using a JEOL JSM-840A SEM operated at 15–20 kV.

3.3. Elemental analysis

The bulk chemical compositions of the samples were determined by elemental analysis. The bulk composition of the calcined samples (practically Si/M atomic ratio = y/x) was determined by the so-called wet analysis method. A complete acid digestion prior to analysis by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) or flame atomic absorption spectroscopy (AAS) was required. The AAS analysis was carried out using a PerkinElmer 1100B atomic absorption spectrometer. The ICP analyses were carried out using a P40 spectrometer also from PerkinElmer.

3.4. Nitrogen adsorption

The sorption isotherms of nitrogen measured at its condensation temperature (77 K) reflect the textural characteristics of the materials. In this work, the nitrogen adsorption measurements were performed to characterize the textural properties of the calcined samples, including the total BET surface area and the micropore volume.

The adsorption and/or desorption isotherms of nitrogen at 77 K were obtained using an Omnisorp-100 automatic analyzer after degassing the calcined samples at 573 K for at least 4 h under vacuum 0.013–0.0013 Pa. The linear part of the Brunauer–

Table 1
Gel composition of synthesized samples

Sample	Acronym	Si/Al	Si/Fe	Gel composition ^a				
				r	x	y	z	m
ZS1-29	Al-ZSM-12	60		1.0	0.016	0.000	1.89	226.13
ZS1-26	Fe-ZSM-12		40	1.0	0.000	0.030	2.39	122.10
ZS1-36	Fe-ZSM-12		50	1.0	0.000	0.024	2.39	122.10
ZS1-24	Fe-ZSM-12		70	1.0	0.000	0.017	2.39	122.10
ZS1-28	Al-Fe-ZSM-12	40	40	1.0	0.014	0.014	2.39	122.10
ZS1-32	Al-Fe-ZSM-12	60	60	1.0	0.010	0.010	2.39	122.10

^a rR:xAl₂O₃:yFe₂O₃:zSiO₂:mH₂O; R = MTEA-Cl.

Download English Version:

<https://daneshyari.com/en/article/48107>

Download Persian Version:

<https://daneshyari.com/article/48107>

[Daneshyari.com](https://daneshyari.com)