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ACID PROPERTIES OF SiMCM-41 MESOPOROUS MOLECULAR SIEVE

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Abstract

The SiMCM-41 mesoporous molecular sieve was synthesised by the hydrothermal method. The physicochemical characterisation by infrared spectroscopy, X-ray diffraction and thermogravimetry, showed that the material presents a well-defined structure. In this study, the determination of the total acidity and relative strength of the acid sites of the SiMCM-41, was performed by desorption of adsorbed *n*-butylamine combined with thermogravimetric measurements. The total acidity, determined by means of the amount of amine desorbed normalised by mass of solid, was equivalent to 0.927 mmol g^{-1}, in the temperature range from 96 to 235°C. By using the Flynn and Wall integral kinetic model, at 5, 10 and 20°C min^{-1} heating rates, it was determined that the activation energy to desorb *n*-butylamine was 90.7 kJ mol^{-1}, in the same temperature range, evidencing that SiMCM-41 presents only weak acid sites on its surface.

Keywords: acidity, Flynn and Wall model, MCM-41, thermogravimetry

Introduction

In the 90's, scientists from Mobil Oil, used supramolecular surfactant agents and obtained a new class of mesoporous materials [1–3]. This class was denominated as M41S family, in which the main structures are: hexagonal phase MCM-41; cubic phase MCM-48; and MCM-50, a non stable lamella phase. Since then, the unique ultra large zeotypes were metalophosphates ALPO-4, VPI-5, cloverite and JDF-20. According to IUPAC rules [4], mesoporous (or nanoporous) materials present pore diameters ranging from 2 to 50 nm. The MCM-41 species is the more important structure of the family presenting arrange of ordered crystallographic channels, and disordered atomic arrange, similar to that of amorphous silica. Its structure is shown in Fig. 1.

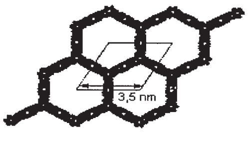

Fig. 1 Structure of the MCM-41 molecular sieve [5]

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These materials present values of surface areas ranging from 1000 to 1500 $m^2\ g^{-1}$, attracting attention of a lot of researchers. Recently, scientists have got progress in the synthesis of these materials by the use of different methods, inorganic fonts of Al, Si, P, metal transitions and surfactant structural as templates [6–9]. Due to the high surface area and great accessibility of their pore system, these materials are being promising as acid catalysts in many petrochemical processes [10–13], so the study of its acid properties is of great importance. In general, spectrophotometric methods and adsorption of gaseous basic compounds are commonly used to study these properties [14, 15], relative not only to the acid sites density and the strength, but also the nature of the acid sites. However, by using this method, it is not possible to determine acidity in the real working conditions of the catalyst.

Thermal analysis is one of the most valuable techniques for the characterization of an acidic surface [16–18]. In this case, the most frequently bases used are: ammonia (pK_b=4.75) and pyridine (pK_b=8.75). The pyridine can be used to determine the presence of Brönsted and Lewis acid centers, applying infrared spectroscopy [19]. The *n*-butylamine (pK_b=3.23), which is a relatively strong base, has been used in several titration methods using colors indicators [20]. This base reacts with weaker acid sites than either pyridine or ammonia. Infrared spectroscopy has also been used to characterize *n*-butylamine adsorbed on several surfaces [21–23]. In all these cases, it is considered that basic molecules interact with all the acid sites present on the solid surface, and the number of acid sites can be determined from the amount of base required to reach the saturation point. There are some doubts on the real determination of the total acidity of surfaces by using *n*-butylamine titration in a non-aqueous media, using Hammett indicators [24–26].

The aim of this work is to study the acidity of SiMCM-41 by means of *n*-butylamine adsorption by using thermogravimetry and differential thermogravimetry (TG/DTG). The activation energy to desorb *n*-butylamine from SiMCM-41 was determined by applying the Flynn and Wall multiple heating rates kinetic model.

Experimental

Synthesis

The SiMCM-41 was synthesized from the following materials: sodium silicate (Merck), silica (Aerosil), distilled water, cethyltrimethylammonium bromide (CTMABr) as surfactant, and trimethylammonium hydroxide (TMAOH) as mineralizer. These reactants were mixed in order to obtain a hydrogel with the following molar composition:

$$1SiO_2:0.11Na_2O:0.263TMAOH:0.175CTMABr:27.4H_2O$$

To the synthesis procedure, firstly, a suspension of Na_2SiO_3, was added to 25%TMAOH, and stirred until the pH stabilization. SiO_2 was added to this mixture with continuous stirring, for 45 min. Finally, CTMABr and water was added. The gel was aged for 90 min. The reactive hydrogel was charged into a PTFE-lined autoclave, and submitted to a hydrothermal treatment, at 140°C, under autogeneous pressure, for a period of 18 h. Then, the product was filtered, washed with deionized water, and dried in static atmosphere. The calcination was carried out in two steps: at 500°C, at a heating rate of 5°C min^{-1}, in dynamic nitrogen atmosphere, for 2 h. Then, at the same temperature in dry air, for an additional period of 6 h.

Physicochemical characterization

The obtained material was characterized by X-ray diffraction (XRD), infrared spectroscopy (FT-IR), and thermal analysis (TG/DTG). The XRD analysis was recorded in a Rigaku diffractometer, using nickel-filtered CuK_α ($\lambda\text{Cu} = 0.15406$ nm) in the 2Θ ranging from 0 a 10° low angle region. From FT-IR spectra, it was determined the structural features of the materials. The spectra was recorded in a FT-IR MIDAC model, using the KBr technique, in the 1300–400 cm^{-1} region. The TG measurements was used to determine the quantity of adsorbed water molecules, and the effective participation of the surfactant on the materials. This analysis was carried out on a TA-951 thermobalance, with ca. 10 mg of sample, at a heating rate of 10°C min^{-1}, under dynamic dry air atmosphere flowing at 60 $\text{cm}^3\ \text{min}^{-1}$.

Determination of the acidity

The acidity properties of the catalyst were determined by thermogravimetry TG/DTG using *n*-butylamine as molecular probe, as reported by Araujo *et al.* [17]. The adsorption system is shown in Fig. 2.

The calcined sample was dried at 100°C, in a 60 $\text{cm}^3\ \text{min}^{-1}$ nitrogen stream for 2 h. Then, vapors of *n*-butylamine were directed to the sample at 95°C, until complete saturation of the acid sites of the sample. Afterward, the sample saturated with *n*-butylamine was purged with pure nitrogen at the same temperature, for 30 min, in order to remove the physically adsorbed base. After this treatment, the temperature programmed desorption of *n*-butylamine was initialized by heating the saturated sample in the thermobalance, at a heating rate of 10°C min^{-1} up to 500°C in the same nitrogen flow. The acid sites were determined as the quantity, in mmols of the desorbed *n*-butylamine, per gram of catalyst, being expressed in mmol g^{-1}, in a specific temperature range. By using the Flynn and Wall multiple heating rate integral kinetic model, where was considered the remotion of *n*-butylamine at different degree of conversions, in the same range of temperature and heating rates of 5, 10 and 20°C min^{-1}, was determined the activation energy necessary to remove the *n*-butylamine from the acid sites.

Results and discussions

The studied mesoporous material has basically a silicates structure with a MCM phase. This was prepared in aqueous media, in presence of alkyltrimethylammonium bromide surfactant. Mechanically, the surfactant template suffered self-organization to a liquid crystal phase, being successively encapsulated by inorganic species that condensed and formed rigid walls [27]. Thus, occurred the interaction process of the inorganic-surfactant mesophase, obtaining the desired morphology. In the case of SiMCM-41, the mesophase is formed by the arrange of the silicate layers. The use of silica promote the formation of the ordered structures [28]. The pH of the gel was ca 11. The hydrothermal treatment of a gel at basic conditions carry to a MCM-41 formation with good yield [29].

From the characterization of the synthesized SiMCM-41, by DRX, FT-IR and TG, it was verified that the hydrothermal method has been efficient to obtain the MCM mesophase. The FT-IR spectra of the SiMCM-41 shown a strong absorption band at 960 cm^{-1}, due to Si–OH groups, and others at the 1080, 800 and 465 cm^{-1} regions, which are characteristics of the material. Also, these bands are present in pure silica [2].

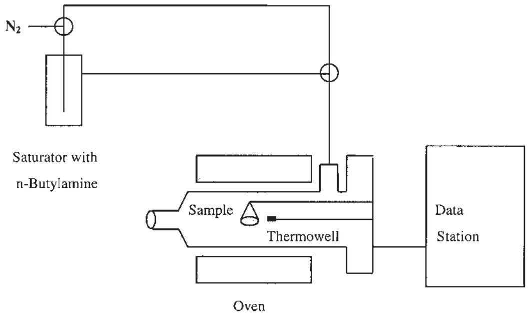

Fig. 2 Adsorption system used to study the acid properties of the catalyst

The X-ray diffractogram to MCM-41 shown a very strong 100 peak, at 1.6° 2Θ, due to the little ordered pore system [29]. Also, it was distinguished three weak peaks characteristic of the family, at 2.8, 3.2 and 3.6°, suggesting a hexagonal symmetry [2].

From thermogravimetry, it was verified that both tensoactive and mineralizer directed the synthesis of the SiMCM-41. The TG curve of the as-synthesized sample is visualized in Fig. 3. Three mass losses were observed, assigned as (a) due to desorption of water molecules, (b) and (c), due to decomposition of organic materials ($CTMA^+$ and TMAOH). The solid has high porosity, as can be estimated by the total mass loss, of ca. 45.9%, corresponding to 6.8% of water, observed in the 28 to 112°C temperature range, and 39.1% of organic volatile, from 112 to 340°C. The final residue was ca. 54.1%, which is the SiMCM-41 without tensoactive.

The TG curve, representing the *n*-butylamine desorption from the acid sites of the SiMCM-41, is shown in Fig. 4. One can see that there are two mass losses in the TG curve, and a corresponding temperature range. They were assigned as: peak (a) ranging from room temperature to 97°C, desorption of physisorbed amine; peak (b), from 96 to 235°C, dissociation of *n*-butylamine on the acid sites. In this temperature range, the total acidity of the SiMCM-41 was quantitatively determined by means of the amount of *n*-butylamine desorbed divided by mass of sample, being equivalent to 0.927 mmol g^{-1}. The presence of strong acid sites was not observed.

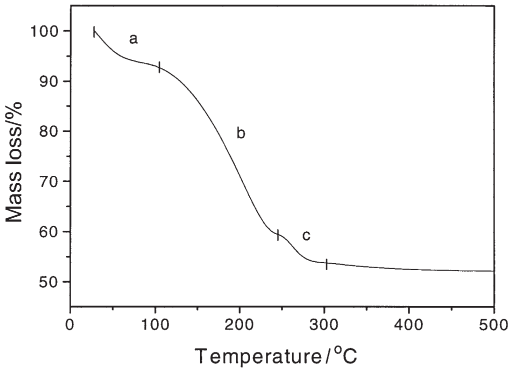

Fig. 3 TG curve of the as-synthesized SiMCM-41: a – water molecules; b and c – organics from the template. Heating rate: 10°C min^{-1}

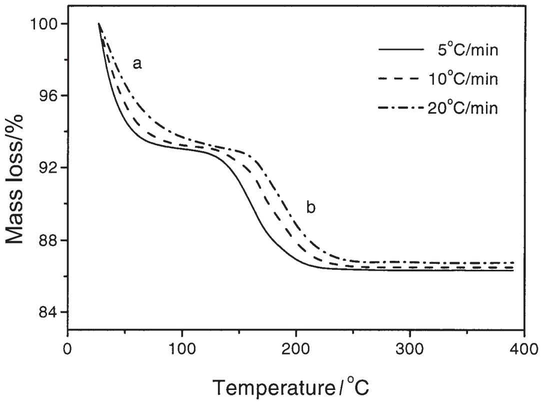

Fig. 4 TG curves of *n*-butylamine adsorbed on SiMCM-41, showing mass losses from: a – physisorbed base; and b – *n*-butylamine desorption from the acid sites

The Flynn and Wall kinetic model [30] is normally used to determine the activation energy (*E*) relative to decomposition in a solid state, which uses integral TG curves, at several heating rates. In this work, this model was used to determine the *E* relative to deamination process from the acid sites of SiMCM-41 material, according to the following decomposition process:

$$[n\text{-butylamine}]\text{-SiMCM-41} \rightarrow n\text{-butylamine}_{(g)} + \text{SiMCM-41}_{(g)} \tag{1}$$

According to the Flynn and Wall model [30, 31], the heating rate (β), absolute temperature and activation energy (*E*) are related by the Eq. (2).

$$\frac{\partial \log \beta}{\partial 1/T} \cong -\left[\frac{0.457}{R}\right]E \tag{2}$$

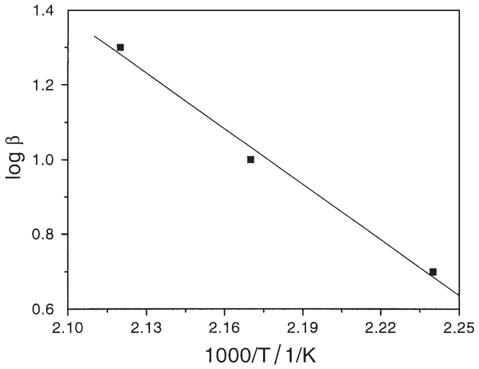

Fig. 5 Logarithm of heating rate in function of the inverse of the absolute temperature

Substituting the gas universal constant value (R=1.987 cal mol^{-1}K^{-1}), we have:

$$E \cong -435\frac{\partial \log \beta}{\partial 1/T} \tag{3}$$

Thus, 'E' due to n-butylamine desorption from the acid sites on SiMCM-41 surface, was determined from the slope of the log of heating rate (logβ) *vs*. the inverse of the absolute temperature (1/K) curve (Fig. 5). The obtained value was E=90.7 kJ mol^{-1}, measured in the temperature range from 383 to 493 K. This value evidences that the SiMCM-41, synthesized as described, presents only weak acid sites on its surface.

Conclusions

The SiMCM-41 material, synthesized using cethyltrimethylammonium bromide and trimethylammonium hydroxide presented good quality. The effective participation of these templates on the MCM-41 structure was quantitatively verified by thermogravimetry. The calcination of the SiMCM-41 under nitrogen and air atmospheres resulted in the generation of the acid sites. Thermogravimetric analysis of n-butylamine desorption showed that SiMCM-41 has only weak acid sites on its surface. By using the multiple heating rate Flynn and Wall kinetic model, was possible to determine the activation energy (90.7 kJ/mol) which corresponds to n-butylamine desorption from the acid sites. This value gives the relative acid strength of the sites on the surface of the SiMCM-41 in a specific temperature range, which can be useful for some catalytic applications.

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