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Assessment of surface acidity in mesoporous materials containing aluminum and titanium

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ABSTRACT

The surface acidity of mesoporous molecular sieves of aluminum and titanium was evaluated using four different techniques: *n*-butylamine volumetry, cyclohexylamine thermodesorption, temperature-programmed desorption of ammonia and adsorption of pyridine. The nature, strength and concentration of the acid sites were determined and correlated to the results of a probe reaction of anthracene oxidation to 9,10-anthraquinone (in liquid phase). In general, the surface acidity was highly influenced by the nature, location and coordination of the metal species (Al and Ti) in the mesoporous samples. Moderate to strong Brönsted acid sites were identified for the Al-MCM-41 sample in a large temperature range. For mesoporous materials containing Ti, the acidity was represented by a combination of weak to moderate Brönsted and Lewis acid sites. The Ti-HMS sample exhibits a higher acidity of moderate strength together with a well-balanced concentration of Brönsted and Lewis acid sites, which enhanced both conversion and selectivity in the oxidation reaction of anthracene.

1. Introduction

There has been an increasing need for processes to treat bulky organic molecules such as polycyclic aromatics (PAHs) or large substituted hydrocarbons (nitrogenates, oxygenates, sulfurates, etc.), not easily converted by conventional microporous catalysts [1]. Both in laboratory and commercial scale, several organic reactions of industrial interest have been catalysed by zeolitic materials, for instance the selective oxidation of monoaromatics using H_2O_2 as oxygen donor. Titanium molecular sieves (TS1, Ti-Beta) have been effective for oxidations with H_2O_2 [2,3], while mesoporous materials, usually doped with aluminum and transition metals (Ti, Zr, V, Cr, etc.), are more indicated for organic media without water, for hindered molecules, or when tert-butylhydroperoxide is used as oxygen donor [4,5]. In this scenario, the synthesis of siliceous mesoporous materials, first reported by Mobil researchers [6], has enabled new adsorption and catalysis studies for molecules of large dimensions. These materials, designated as M41S family (MCM-41, MCM-48 and MCM-50), present a regular hexagonal pore structure with high surface area (>1000 m^2/g). MCM-41 molecular sieves are usually obtained by hydrothermal synthesis at 373–393 K, or by the sol–gel method at room temperatures. Their properties are highly affected by the synthesis condition, such as pH, temperature, surfactant or template, presence of electrolytes, reaction time, aging period, etc. [7–9]. In general, the catalytic and adsorptive properties of these materials can be intrinsically related to their acid properties (nature, strength and distribution of their acid sites).

In this study we report surface acidity assessed by four different analytical techniques: *n*-butylamine (*n*BuA) volumetry, cyclohexylamine (CHA) thermodesorption, temperature-programmed desorption of ammonia (NH_3), adsorption of pyridine coupled to IR spectroscopy for MCM-41 and HMS mesoporous materials containing Al and Ti. The acidity values are related to the results

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obtained for the oxidation of anthracene in liquid phase using t-butylhydroperoxide as oxidant. We believe that the assessment of the surface acidity is crucial in understanding the structure and catalytic behavior of these materials in processes involving cracking, substitution or oxidation of large organic molecules.

2. Experimental

2.1. Synthesis and characterization

Samples were prepared using the sol–gel methodology originally reported by Aguado et al. [10] and modified by us as previously reported [11,12] with acid and alkaline hydrolysis of the aluminum and titanium alkoxydes (aluminum triisopropoxide and titanium tetraisopropoxide, respectively). The silicon, aluminum and titanium sources were tetraethylorthosilicate (TEOS), aluminum triisopropoxide and titanium tetraisopropoxide, respectively. The molar composition of the synthesis gel was approximately 1.00 TEOS; 0.10 Al triisopropoxide; 0.33 dodecylamine (S^+I^-); 5.21 ethanol; 23.00 H_2O, for the Al-MCM-41, and 1.00 TEOS; 0.33 Ti tetraisopropoxide; 0.33 dodecylamine (S^+I^-); 5.21 ethanol; 23.00 H_2O, for the Ti-MCM-41. Additionally, a sample of pure silica (without Al or Ti) and a sample of mesoporous titanium oxide (using primary dodecylamine as template, S^0I^0) were also prepared at the same molar compositions of the doped MCM-41 samples. According to Tanev and Pinnavaia [13], mesoporous materials that are obtained using a neutral template route (S^0I^0) tend to present larger wall thicknesses and surface areas than similar samples obtained using cationic surfactants (S^+I^- route) that having the same number of hydrocarbons. The resulting solids were filtered, rinsed with deionized water and dried at 378 K for approximately 12 h, after which they were calcined at 823 K for at least 2 h. The calcined samples, in their acid forms, were labeled as Si-MCM-41, Al-MCM-41(10), Ti-MCM-41(30) and Ti-HMS(30). The numbers in parenthesis represent the stoichiometric Si/heteroatom molar ratio in the synthesis gel. The samples were characterized by the usual techniques: X-ray diffraction in a Philips X'PERT MPD powder diffractometer using Cu Kα (λ = 1.5418 Å) radiation; Fourier transform infra-red in a spectrophotometer BIO-RAD FX-3000; and N_2 adsorption at 77 K using a Quantachrome NOVA 2000 apparatus. The chemical composition of the samples was estimated using ICP-OES in a Perkin-Elmer OPTIMA 4300.

2.2. Surface acidity measurements

Four different techniques were used to identify and quantify the nature of the acid sites in the samples under study: *n*-butylamine volumetry, cyclohexylamine thermodesorption (CHA-TD), temperature-programmed desorption of ammonia (NH_3-TPD), and adsorption of pyridine coupled to infrared spectroscopy (Py-FTIR).

The measurement of acidity using *n*-butylamine volumetry involves the interaction of the acid surface with adsorption indicators at specific pK_a's [14,15]. Anthraquinone (pK_a = −8.2), p-benzo-azodiphenylamine (pK_a = 1.5) and p-dimethylaminoazobenzene (pK_a = 3.3) were used as indicators (0.1% in iso-octane). The acidity values (corresponding to the pK_a of the indicators) were obtained from the titration with *n*-butylamine using an automatic titrator Metrohm 751 GPD Titrino. This technique fundamentally allows the determination of the total quantity of Brönsted acid sites and their distribution. The cyclohexylamine thermodesorption was used to estimate the number of acid sites, mainly protons (Brönsted acid sites), that are able to interact with this base (CHA) after treatment at 523 K, according to a procedure described by Mokaya and Jones [16]. A thermogravimetric analyzer TGA50H-Shimadzu (heating rate: 20 K/min; N_2 flow rate of 25 mL/min) was used to follow the weight loss caused by the desorption of CHA. For the temperature-programmed desorption of ammonia, which was used to measure total surface acidity, the samples were heated at 823 K under N_2 flow in order to remove previously adsorbed impurities, followed by adsorption of ammonia at 373 K. The system was kept at this temperature for about 30 min, to ensure adsorption equilibrium (saturation). The base was then desorbed by increasing the temperature from 373 to 823 K at a rate of 10 K/min and ammonia concentration was detected on line in a Shimadzu GC-14A gas chromatograph using a thermal conductivity detector. For the adsorption of pyridine, employed to evaluate Lewis acidity, pyridine was used as probe molecule. The IR spectra of the adsorbed pyridine were recorded on a Shimadzu MPC 3100 spectrometer. Self-supported wafers of the samples were placed in a glass cell under vacuum. The samples were evacuated at 623 K and maintained at that temperature under high vacuum overnight. Then they were exposed to pyridine vapors at room temperature for 30 min, followed by outgassing at 373 K.

2.3. Catalytic measurements

In order to evaluate and compare the results obtained from the different acidity techniques used in our samples, the model reaction of oxidation of anthracene was chosen. The reaction was conducted at 348 K under reflux following the procedure described by Srinivas et al. [17]. Benzene and t-butylhydroperoxide (tBHP) were used as solvent (at a molar ratio of 8:1 with respect to anthracene) and oxidant, respectively. The chemical analysis of reactants and products was performed by liquid chromatography (Varian ProStar 150), equipped with a UV–vis detector, and/or by gas chromatography (Varian CP3800) coupled with a mass spectrometry detector (Saturn 2000 MS/MS).

3. Results and discussions

The employed synthesis method resulted in materials with high incorporation of Al and Ti, but with poor textural properties, as shown in Table 1. Particularly, analyses by X-ray photoelectronic spectroscopy (XPS) – not shown – confirm the presence of a very small amount of extra framework alumina and titania. Further details on textural properties and XPS characterization of these samples may be found in previous studies [11,12].

The results for the acidity measurements of synthesized samples using the four different techniques are summarized in Table 2. It may be observed that, in general, acidity increases with the incorporation of heteroatoms to the framework. This may be due to the increase of Brönsted acidity (C_B), which is associated with the formation of acidic hydroxyl groups bonded to the metal (AlOH and TiOH) or due to the formation of isolated Lewis acid sites (C_L) from low coordinated cations (Al or Ti).

In the nBuA volumetry technique, the acid sites are related to the process of protons transfer (Brönsted acidity) between the adsorbed indicator and the titration base. The numbers in parentheses shown in the "nBuA volumetry" column stand for the moles of nBuA

Table 1
Textural properties of synthesized samples.

	Si-MCM-41	Al-MCM-41(10)	Ti-MCM-41(30)	Ti-HMS(30)
$(Si/metal)_{product}$	∞	10	40	30
$d_{1\,0\,0}$ (Å)[a]	37.3	28.9	30.4	38.4
a_0 (Å)[b]	43.1	33.4	35.2	44.3
Surface area (m^2/g)	545	569	657	746
d_{pore} (Å)	41.4	32.4	31.1	28.1
V_{pore} (cm^3/g)	0.56	0.46	0.51	0.52

[a] Interplanar (planes 1 0 0) distance.

[b] Mesoporous parameter (distance between adjacent pores in the hexagonal arrangement).