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SYNTHESIS AND CHARACTERIZATION OF Al- AND Ti-MCM-41 MATERIALS: APPLICATION TO OXIDATION OF ANTHRACENE

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Abstract - The synthesis and characterization of new molecular sieves of the MCM-41 type are presented in this study. Samples were obtained from the alkoxides of Si, Ti and Al and different long-chain amine and alkylammonium salts surfactants, by the sol-gel method, through moderate agitation at room temperature. The reactions were conducted in two steps, acid hydrolysis (pH=2) and alkaline condensation (pH=10), both taking about 90min. The synthesized crystals were characterized using infrared spectroscopy, thermogravimetry and X-Ray diffraction. Pore diameters and surface areas were measured by N_2 adsorption at 77K. Catalytic tests were conducted for anthracene oxidation using different oxidants (H_2O_2, alkylhydroperoxide) and organic solvents (benzene, tetrahydrofuran).

Keywords: Synthesis; Characterization; MCM-4; Anthracene oxidation.

INTRODUCTION

Porous solids are widely used in industrial applications related to the preparation of adsorbents, catalysts and ion-exchangers as well as for future use in advanced technologies involving semiconductors, photoreceptors, and enzymatic complexes (Sayari, 1996). Zeotypical structures with pore diameters ranging from 2 to 12Å have traditionally been used in catalytic processes. These materials are subdivided into three main categories: zeolites (e.g., A, X, Y), aluminum phosphates (AIPO´s) and metalophosphates with large pores (VPI-5, JDF-20, etc). Several industrial processes use microporous zeolites with pore diameters ranging from 0.5 to 0.6nm in the separation and catalysis phases (e.g. catalytic cracking, xylenes separation and isomerization) (Reddy and Song, 1996; Selvam et al., 2000; Corma et al., 1994). This structural characteristic is a limiting factor for the processing of higher molecular weight hydrocarbons (Biz and Occelli, 1998). In 1992 a significant change took place in nanoporous science when Mobil researchers reported an aluminosilicate synthesis with uniform size in the mesoporous materials range (2 to 50nm) (Beck et al., 1992; Kresge et al., 1992). These materials, named M41S, have structural characteristics directly related to the conditions of the synthesis: nature of the surfactant, pH, presence of electrolytes, temperature, solvents, and time of reaction (Cassiers et al., 2000; Ryoo and Kim, 1995; Arnold et al., 1999).

The main difference in the preparation of zeolites and of M41S-type materials consists in the action of directing surfactant agents (templates), which

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*To whom correspondence should be addressed organize themselves in water solution forming either specific compositions or liquid crystals (Sayari, 1996). According to this mechanism, the Mobil scientists found three different forms: a hexagonal phase, a hexagonal arrays of molecules (MCM-41 family); a cubic phase (MCM-48 family); and an unstable lamellar phase (MCM-50 family). Various synthesis strategies are used in the preparation of the mesostructured materials, especially the following: the hydrothermal method (typically described as the treatment of a silicate solution between 80 and 140ºC for two or more days) and the sol-gel method (related to the hydrolysis and condensation of metallic alkoxides at specific pHs).

There has recently been an increased interest in the insertion of metals with high redox potentials (V, Cr, Ti, Fe, Ni, etc) into the original structure of the MCM-41 type (Ulagappan and Rao, 1996; Rodriguez-Castellón et al., 2003; Tuel, 1999; Blasco et al., 1995). These metals produce isomorphic substitutions that increase the catalytic activity in oxidative processes involving organic molecules of commercial interest, such as phenols, bulky aromatics, and terpineols (Kondam and Song, 1996).

This study will present results of synthesis and characterization of Aluminum and Titanium MCM-41 materials prepared in our laboratory using different surfactants and evaluated for the reaction of anthracene oxidation using different oxidants and solvents.

EXPERIMENTAL SECTION

Materials

All the reactants (alkoxides, solvents, oxidants, amine, alkylammonium salt, hydrocloric acid, ammonium hydroxide, anthracene and 9,10-anthraquinone), of analysis grade (> 98%), were supplied by ACROS ORGANICS® with analytic purity degree (and used without any further purification.

Methods

a) Synthesis

The MCM-41 metal samples were prepared by the sol-gel method with the use of the alkoxides tetraethyl orthosilicate-TEOS (silicon), aluminum triisopropoxide (aluminum), and titanium tetraisopropoxide (titanium), and the surfactant agents dodecylamine (DA), dodecylamine hydrocloride (DAC1), and cetiltrimethyammonium chloride (CTACl). The typical procedure involves addition of alkoxides of Ti or Al to the TEOS in a Teflon flask, followed by dilution of the mixture with ethanol. For the initial mixture of Si+Al alkoxides, a water solution of cetiltrimethylammonium chloride was added. For the Ti-MCM-41 samples, either an alcohol solution of dodecylamine or an acid water solution (pH=1) of dodecylamine (salt preparation in situ) was added. The molar composition of the synthesis gel was 1 TEOS : 0.033 alkoxide (Ti or Al): 0.30 Surfactant: 5.2 Ethanol: 23 H_2O. The reaction was initially conducted at pH 2.0 (alkoxide hydrolysis) for about 90min under moderate agitation. At the end of the operation, the pH of the solution was adjusted to 10 with 30% ammonium hydroxide. The time of agitation varied between 75 and 90 min. Once the alkaline phase had ended, the material was left still for 20h at room temperature. Later the following phases were carried out: filtration in vacuum, washing with deionized water, drying (6h at 105ºC), and calcination (550-600ºC in air atmosphere). The synthesized samples were named Al-CTACl, Ti-DA, and Ti-DACl.

b) Characterization

The samples were characterized by four analytical techniques as follows: X-Ray diffraction (DRX) in a Philips X’PertPro diffractometer using CuKα radiation (40KV and 40mA); infrared spectroscopy (FTIR) in a Bio-Rad spectrophotometer, using the attenuated total reflection technique (ATR); thermogravimetric analysis (TG/DTG) in a Shimadzu 5OH system with a platinum crucible, a synthetic air atmosphere, a 50cc/min flow; and specific surface area (A_{BET}) in a QuantaChrome Nova 2000 system. The same equipment was used to calculate the pore distribution by the BJH method.

c) Catalytic Tests and Product Analysis

Anthracene oxidation was used as a model reaction (see Figure 1) to assess the catalytic activity of the synthesized mesoporous materials. Batch catalytic tests were carried out in a bottom flask under magnetic agitation with anthracene dissolved in a solvent (either benzene–C_6H_6 or tetrahydrofuran–THF), followed by addition of the catalyst and the oxidant (either H_2O_2 30% or tert-butyl hydroperoxide–TBHP 70%). The reaction mixture was then left under reflux, while the change in the typical brown color of the quinones was observed. The reaction conditions used were as follows: catalyst/anthracene mass ratio of 1:1; solvent volume of 10mL; molar ratio anthracene/oxidant of 1:10; and time of reaction of 20h (Srinivas et al., 2002). The reaction was followed by high performance liquid chromatography using a Varian ProStar 150 model with a isocratic mode of 1mL/min flow of a mixture CH_3CN-H_2O 80:20, λ = 254nm.

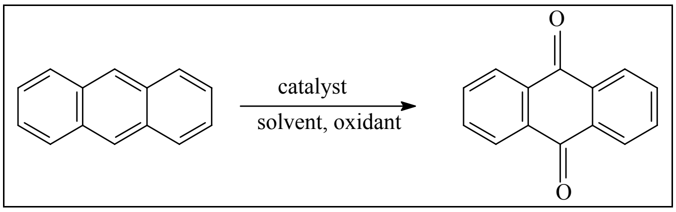

Figure 1: Model reaction used in the catalytic tests (anthracene → 9,10-anthraquinone)

RESULTS AND DISCUSSION

Synthesis of Mesoporous Materials in Different Surfactant Media

The main characteristic of catalyst preparation by the sol-gel method is the presence of an acid phase that keeps the Al^{+3} and Ti^{+4} ions in solution. For the titanium catalysts this is a compulsory phase, since carrying out the process (hydrolysis and condensation) in a purely alkaline medium would produce the direct precipitation of titanium oxide, or TiO_2, from the alkoxide (Luo et al., 2002). The types of gel initially elaborated were viscous suspensions that were easy to filtrate. After removal of the surfactants through calcination at 600ºC, an extremely thin white powder was obtained. All samples were prepared using Si/metal molar ratios of approximately 30:1 in the synthesis gel.

Characterisation by XRD, BET, TG/DTG, FTIR

a) X-Ray Diffraction

The diffraction profiles of the three synthesized samples are presented in Figure 2. It is possible to observe a peak for 2θ between 2° and 3°, which is characteristic of the Bragg plane reflection (100). This is sufficient evidence of the presence of the MCM-41 structure (Blasco et al., 1995). There are no (110), (200), and (210) Bragg planes, which demonstrates poor ordering of the pore structure of our synthesized samples.

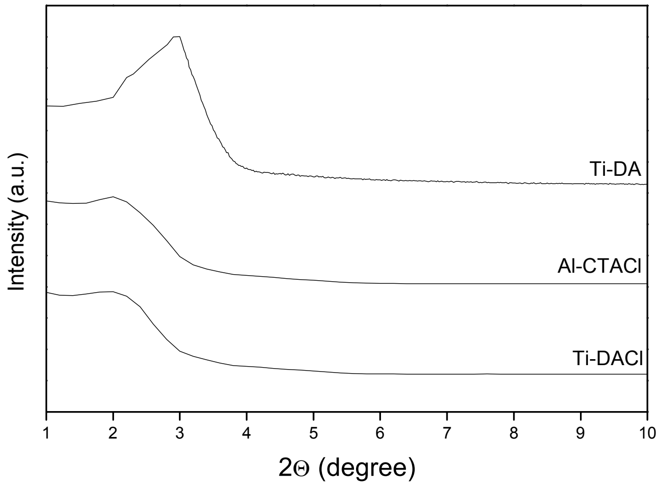

Figure 2: X-Ray profiles of the calcined samples.

b) N_2 Adsorption

Surface areas (A_{BET}) were determined from N_2 adsorption at 77K in a BET plot linear band ($P/P_0 = 0.05-0.30$). The isotherms obtained were of type IV, in accordance with the IUPAC classification for mesoporous materials (Sing, 1998). The physical properties of the synthesized samples are listed in Table 1. The values for surface areas and pore diameters confirm the mesoporous nature of the synthesized materials, despite lower than usual values observed for the surface areas that were measured. This can be related to the lower crystallinity that was observed in the X-ray diffraction analysis indicative of the poor ordering of the pore structure of our samples. The pore diameters (between 2.8 and 3.2 nm) are in the range usually observed for MCM-41 samples (Corma et al., 1994; Chen et al., 1999; Aguado et al., 2000).

Table 1: Properties of calcined Al-MCM-41 and Ti-MCM-41 samples.

Properties	Samples		
	Ti-DA	**Ti-DACl**	**Al-CTACl**
d_{100} (Å)	37.5	36.2	33.1
a_0^* (Å)	43.3	41.8	38.3
A_{BET} (m^2/g)	726	657	595
Pore diameter (Å)	28.1	31.1	32.0

* $a_0 = 2d_{100} / 3^{1/2}$ (unit hexagonal cell parameter)

c) Thermal Analysis (TG/DTG)

The thermogravimetric curves (TG) and the respective differential curves (DTG) are shown in Figure 3. In all samples, thermal degradation peaks are observed, between 150 and 370ºC, corresponding to the removal of the surfactant. It may also be observed that moderate losses are noted between 550 and 600°C, which may be attributed to dehydration and condensation of silanol groups at the surface of the samples (Cesteros et al., 2001).

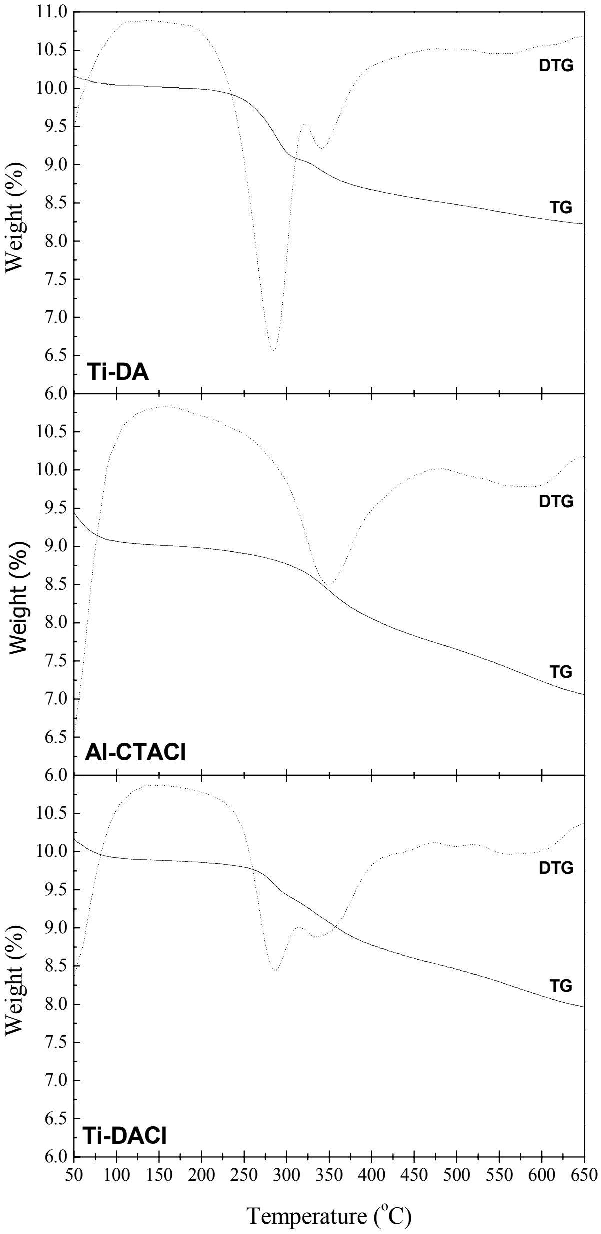

Figure 3: TG/DTG analyses of the dry samples.

d) IR Spectroscopy (FTIR)

The infrared spectra of the synthesized samples are shown in Figure 4. Special attention should be paid to a few points. First, the presence of an intense band between 4000 and 3000 cm^{-1} in all samples which corresponds to the internal and external hydroxyl groups of the mesoporous structure. Second, a band between 1050 and 1250 cm^{-1} which is associated to asymmetrical tensions of Si-O-Si in the framework structures. Finally, the presence of a weak band situated between 960 and 970 cm^{-1}, which is associated with the Si-O-R stretching, where R = H^+, Ti^{+4}, or Al^{+3}. The intensity of this band may be related to the amount of metals (Ti or Al) incorporated to the framework structure (Zholobenko et al., 1997; Chen et al., 1997).

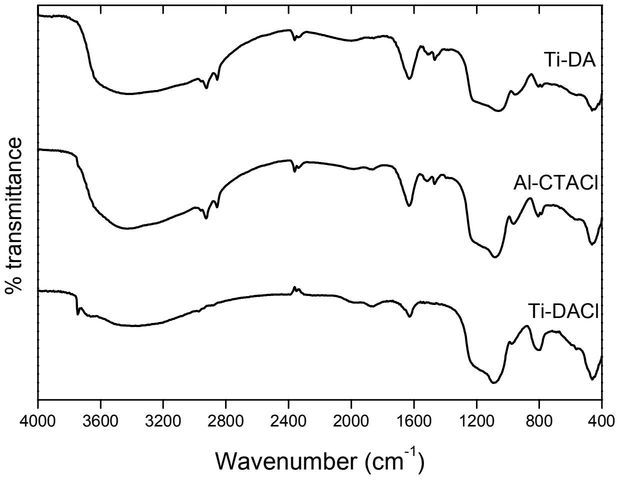

Figure 4: Infrared spectra of the Ti-DA sample after calcination

Catalytic Results

We performed comparative oxidation reaction tests using the samples we synthesized at the same reaction conditions as reported by Srinivas et al. (2002). We also carried out the reaction at the same conditions in the absence of a catalyst (with insignificant conversion to 9,10-anthraquinone), and using a commercial Y microporous zeolite (Si/Al=1.6), to compare with our samples. All results of conversion and selectivity are listed in Table 2. It may be observed that all mesoporous samples have better selectivity and conversion than the Y microporous zeolite for this reaction. It may also be noted that the sample entitled Ti-DA (titanium MCM-41 prepared using dodecylamine as surfactant) yielded the higher values for conversion and selectivity (71.2% and 98.8%, respectively) of the three mesoporous samples, and was thus selected for the studies of oxidant and solvent effects that followed. For comparison, Srinivas et al. (2002) using a Ti-MCM-41 sample in a system with TBHP and benzene observed conversion and selectivity of 6.7% and 33.1%, respectively.

To evaluate the effect of solvent and oxidant type on the anthracene oxidation reaction, we performed similar tests using benzene (C_6H_6) and tetrahydrofurane (THF) as solvents, and hydrogen peroxide (H_2O_2) and tert-butyl hydroperoxide (TBHP) as oxidants. Table 3 shows all the conversion and selectivity results. The best combination was for benzene as solvent and TBHP as oxidant, which yielded the best combined results of conversion and selectivity. It may be noted that for the benzene-H_2O_2 system, where the polarities of the species are too different, the conversion and selectivity to 9,10-anthraquinone proved to be insignificant.

Table 2: Effect of the type of catalyst on anthracene oxidation. Conditions: benzene 10mL, anthracene/TBHP 1:10 (molar), 0.1g catalyst, 0.1g anthracene, reaction time 20h.

Catalyst	Conversion (%)	Selectivity (%)
Al-CTACl	55.7	78.1
Ti-DACl	48.2	97.2
Ti-DA	**71.2**	**98.8**
Y	23.1	52.1
no catalyst	0.62	0.82

Table 3: Effect of solvent and oxidant type on anthracene oxidation. Conditions: solvent 10mL, anthracene/oxidant 1:5 (molar), 0.1g Ti-DA, 0.1g anthracene, reaction time 20h.

Solvent/Oxidant	Conversion (%)	Selectivity (%)
C_6H_6 /H_2O_2	8.2	3.3
THF /H_2O_2	72.1	44.3
C_6H_6/TBHP	71.2	98.8
THF /TBHP	70.8	50.2

CONCLUSIONS

Al-MCM-41 and Ti-MCM-41 samples were synthesized using the sol-gel method and different surfactants. The samples were characterized by infrared spectroscopy, N_2 adsorption, X-ray diffraction, and thermal analysis. The samples were also tested for a previously reported oxidation reaction of anthracene to 9,10-anthraquinone (Srinivas et al., 2002) and evaluated with regards to solvent and oxidant effect. Our results indicate much better conversions and selectivities for our mesoporous samples as compared to a microporous zeolite, which may be further studied to try to more deeply understand the effect of the metal exchange in the framework structure.

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NOMENCLATURE

a_o	unit hexagonal parameter	Å
d_{100}	interplanar distance	Å
P	equilibrium pressure	kPa
P/P_o	equilibrium relative pressure	(-)
A_{BET}	specific surface área	m^2/g

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