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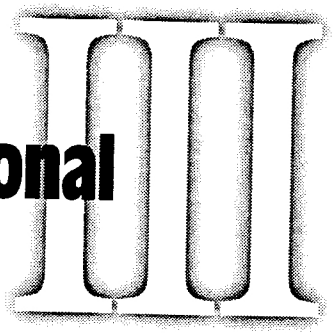

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SYNTHESIS AND ACIDITY CHARACTERIZATION OF CoAPO-37

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ABSTRACT

A well-crystallized sample of CoAPO-37 was prepared. The incorporation of cobalt in the FAU structure framework was indirectly shown by FTIR spectroscopy, which shows peaks assigned to Bronstëd acid sites. Pyridine adsorption reveals the presence of both Bronstëd and Lewis acid sites. Catalytic tests reveal activity for the 1-butene and m-xylene isomerization, indicating that acid sites of CoAPO-37 are stronger than those of SAPO-37 and similar to those found in the studied Y zeolite sample.

INTRODUCTION

Microporous materials with a faujasite-type structure were first prepared with an aluminosilicate composition (X and Y zeolites). In 1984, B. M. Lok et al. [1] at the Union Carbide laboratories prepared a silicoaluminophosphate material with a faujasite structure (SAPO-37), using organic molecules as templates. More recently (1994), L. Sierra et al. [2] reported the synthesis of MeAPO-37 and MeAPSO-37 materials. The metals incorporated into the framework were cobalt and zinc.

The acidic properties of these later materials have not been published in the scientific literature, so far. The aim of this paper is to report the first results of the study of the acidic properties of CoAPO-37 by FTIR spectroscopy and model reactions, and compare the results with those obtained for materials with the same structure but different composition: SAPO-37 and Y zeolite.

The synthesis of a pure sample of CoAPO-37 could not be achieved in our laboratory following the conditions reported by L. Sierra et al. [2] and new conditions had to be optimized. Some results of this process are also reported.

EXPERIMENTAL

For the synthesis of CoAPO-37, the sources of aluminum, phosphor and cobalt were pseudoboehmite (PURAL SB, Condea), ortho-phosphoric acid (Merck, 85 %) and cobalt acetate (Carlo Erba, RPE), respectively. The templates were the tetrapropylammonium and tetramethylammonium ions, the first in the hydroxide and in the bromide forms (TPAOH, 40% aq. sol., ALFA and TPABr, > 99 %, Merck) and the second in the hydroxide form (TMAOH, 10 % aq. sol., Merck). The gel preparation followed closely the procedure described for the synthesis of CoAPO-40 [3].

Based on preliminary experiments, the following gel composition for the initial gel was selected: $Al_2O_3 : P_2O_5 : 0.1\ CoO : (TPA)_2O : 0.05(TMA)_2O : 80\ H_2O$. At that stage of the study the experimental variables optimized were the pH, by adjusting the TPABr/TPAOH ratio, and the crystallization time. The crystallization temperature was 150°C. A small quantity of CoAPO-37 seeds, obtained from one of the preliminary non-reproducible experiments, was used in selected syntheses.

SAPO-37 was prepared according B. M. Lok et al [1], with the composition $(Si_{0.10}Al_{0.50}P_{0.40})O_2$ and NH_4NaY zeolite (Si/Al=2.5) was purchased from Aldrich.

All samples were checked for crystallinity and purity by X-ray powder diffraction (XRD) on a Rigaku difractometer using CuKα radiation filtered by Ni. Selected samples were also analyzed by scanning electron microscopy on a Hitachi S2400 microscope. The composition of the sample used for the IR and catalytic studies, as determined by ICP, was $(Co_{0.02}Al_{0.48}P_{0.50})O_2$.

FTIR spectroscopy studies were carried out using an all-glass high-vacuum cell and were conducted on self-supported wafers (ca. 18 mg, 16-mm diameter). All the spectra were recorded at ambient temperature. The materials were heated under vacuum in the infrared cell for 8h at the desired temperature (500°C for Y zeolite and 550°C for CoAPO-37 and SAPO-37), followed by a treatment under oxygen (100 Torr) at the same temperature for 2h and an evacuation at ca. $5x10^{-6}$ Torr for 1h. The CoAPO-37 sample was further reduced by H_2 (100 Torr for 5h at the same temperature), followed by a new evacuation under high vacuum. A reference spectrum was then recorded. The wafer was then contacted with pyridine vapor at RT for 30 min, by equilibrating the catalyst wafer at a pressure of 1.5 Torr. Then, an evacuation was conducted at RT for 8h, after which the temperature was raised stepwise to 550°C. The vacuum was maintained for 30 min at each temperature. The spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer and collected at $2cm^{-1}$ resolution. In order to analyze the influence of oxidative and reductive treatments on the OH groups and potential acid sites of CoAPO-37, spectra were recorded after oxidation under oxygen and after the reductive treatment under hydrogen.

1-Butene isomerization and m-xylene isomerization were chosen as test reactions to compare the acidity of the studied catalysts. The catalytic tests were carried out at atmospheric pressure in a dynamic flow reactor. Catalytic activity is expressed as mmoles of transformed reactant per hour and mass of catalyst. Reaction products were analyzed by gas chromatography.

1-Butene isomerization was carried out at 150°C, N_2/HC molar ratio of 49 and a WHSV of 0.9 h^{-1}. m-Xylene isomerization was carried out at 350°C, N_2/HC molar ratio of 7.5 and WHSV of 17.4 h^{-1}.

RESULTS AND DISCUSSION

The pH value of the initial synthesis gel had a strong influence on the purity and crystallinity of the desired material as already observed for the synthesis of related metallo-aluminophosphate of various aluminophosphate-based structures [3]. It was observed that a better crystallization of the FAU structure is obtained when the pH value is around 6.3-6.7. The pH changes in this system could be achieved by simply changing the TPABr/TPAOH ratio keeping constant the total amount of TPA. The desired pH value was obtained with a TPABr/TPAOH ratio of 0.3.

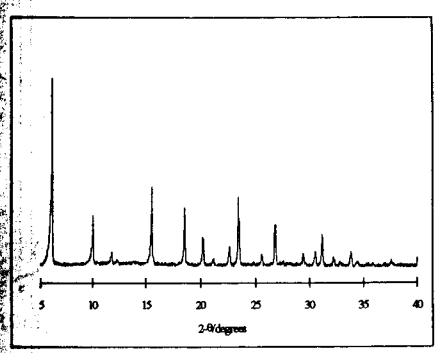

Figure 1. XRD pattern of CoAPO-37 sample (6h crystallization at 150 °C)

Figure 2. SEM of a CoAPO-37 sample (6 h crystallization at 150 °C)

The synthesis conditions used in this study were very close to those used for the synthesis of MeAPO-40 and, as a result, the CoAPO-40 phase is often present as the main crystalline side phase. In the absence of seeding, XRD analysis indicates the presence of this impurity phase

already at 24 h heating. In addition, the crystallinity of the CoAPO-37 phase was very low. In order to increase the quality of the synthesized product, a small amount of CoAPO-37 crystals was added to the synthesis gel. By this seeding process, the crystallization rate of the FAU structure was dramatically increased and a product with a good crystallinity was obtained after 6 h crystallization, as shown by XRD and SEM in Figure 1 and Figure 2, respectively. The XRD pattern of a CoAPO-37 sample after 6h crystallization corresponds to that of the faujasite structure and the SEM analysis of the same sample shows a well-crystallized material with the typical octahedral morphology crystals and with a mean size of about 5μm. For higher crystallization periods, CoAPO-40 phase is also present, as shown by XRD. This can also be due to the presence of small crystals of CoAPO-40 in the seeds which could not be detected by XRD.

Figure 3 shows the FTIR spectra of the OH stretching mode region of HNaY, SAPO-37 and CoAPO-37 samples after the pretreatments. The two major peaks that appear in the spectra of Y zeolite and SAPO-37 are usually assigned to OH groups located in the large α cages (peaks at 3649 and 3642 cm^{-1}) and small β cages (peaks at 3549 and 3574 cm^{-1}) respectively [4].

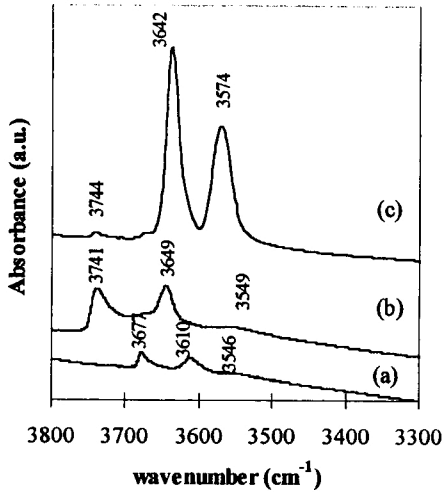

Figure 3. FTIR spectra of (a) CoAPO-37 after a preliminary oxidative/reductive treatment (b) Y zeolite and (c) SAPO-37 after pretreatment

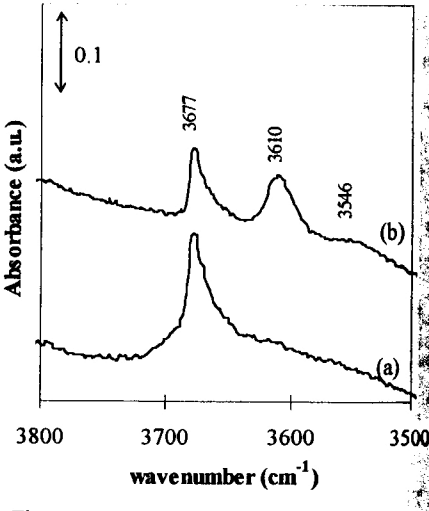

Figure 4. FTIR spectra of CoAPO-37 after (a) oxidative treatment under oxygen and, (b) reducing treatment under hydrogen

The spectrum of CoAPO-37, recorded after the hydrogen treatment, clearly shows the presence of at least 2 peaks in that region: 3677 and 3610 cm^{-1} and a shoulder at 3546 cm^{-1}. The peak at 3677 cm^{-1} can be assigned to terminal Al-OH and P-OH groups [3-5]. Relatively to the bands in the other solids, the peaks of CoAPO-37 are less intense. However, the peak at 3610 cm^{-1}, which can be assigned to Bronstëd acid sites [6, 7], indicates that the framework incorporation of cobalt has occurred.

The influence of the thermal treatments, under oxidative and reductive conditions, on the framework cobalt, has been also evaluated by FTIR spectroscopy. Figure 4 shows the CoAPO-37 spectra of the OH stretching mode region of CoAPO-37 after an oxidative and after a reductive treatment. It is clearly shown that the peak at 3610 cm^{-1} and the shoulder at 3546 cm^{-1} completely disappear if the treatment is carried out in oxidative conditions. These peaks are restored after the reductive treatment.

This behavior can be rationalized if the possibility of oxidation (from Co^{II} to Co^{III}) and reduction (from Co^{III} back to Co^{II}) of the framework cobalt is considered [3, 8-11]. The presence of framework Co^{II} generates a negatively charged framework. These charges are compensated by protons (resulting from the template decomposition), thus giving rise to Bronstëd acid sites. On the other hand, if the Co is in the oxidation state +3, the lattice is neutral and no Bronstëd acid sites are generated. The IR results reported here agree with the hypothesis of the reversible oxidation of framework cobalt.

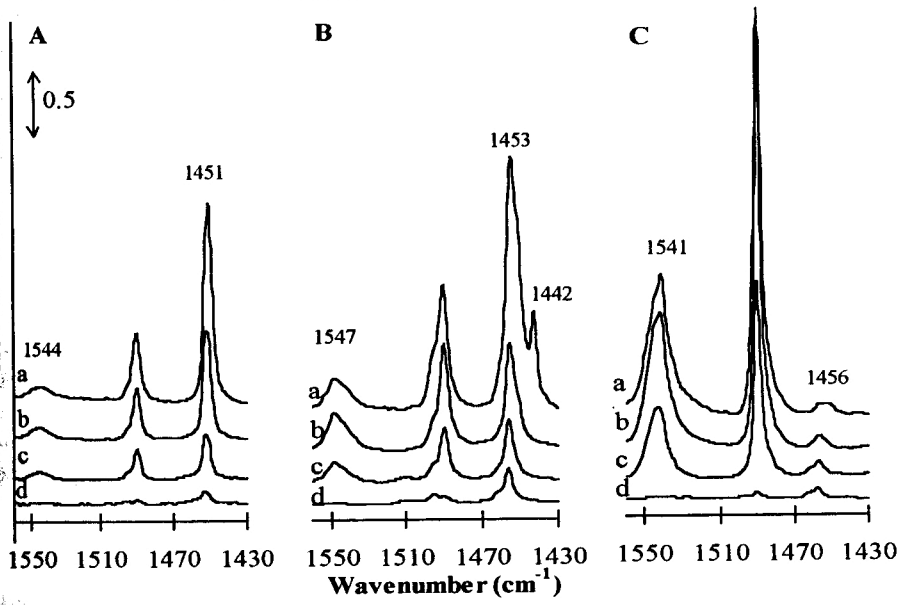

Figure 5. Difference IR spectra of pyridine adsorption on (A) CoAPO-37, (B) HNaY zeolite and (C) SAPO-37, followed by evacuation at (a) 100°C, (b) 200°C, (c) 300°C and (d) 400°C

It is important to note that the intensity of the bands assigned to the Bronstëd acid sites slightly decreases after each oxidation/reduction cycle, which could be an indication that part of the framework cobalt was lost during these treatments.

The lower frequencies at which the Bronstëd acid sites vibrate in CoAPO-37, when compared to Y zeolite, indicate that different acid sites are present and that their strength is over enhanced with respect to aluminosilicate FAU materials. Similar observations were made in the case of CoAPO-40 [3] that involves stronger acid sites than SAPO-40.

Figure 5 shows the spectra of CoAPO-37, HNaY zeolite and SAPO-37 after pyridine adsorption (difference spectra with respect to the reference). The peak at ca. 1545 cm^{-1} is usually assigned to the presence of pyridinium ion and consequently to the presence of Bronstëd acid sites. The peak at ca. 1453 cm^{-1} is assigned to the pyridine molecule adsorbed on Lewis acid sites [12-14]. These spectra indicate that CoAPO-37 and HNaY zeolite samples, involve more Lewis acid sites than Bronstëd acid sites, in contrast to SAPO-37.

Figure 6 shows the integrated intensity of IR bands assigned to (A) Bronstëd acid sites (bands at 1541-1548 cm^{-1}) and (B) Lewis acid sites (bands at 1451-1457 cm^{-1}) as a function of the evacuation temperature. These figures also confirm that CoAPO-37 sample involvs a small number of Bronstëd sites, similar to the tested Y zeolite. Oppositely, it presents a quite large number of Lewis acid sites. The evaluation of the acid sites strength on the different catalysts is not possible, due to the reduced number of sites presented at higher temperatures

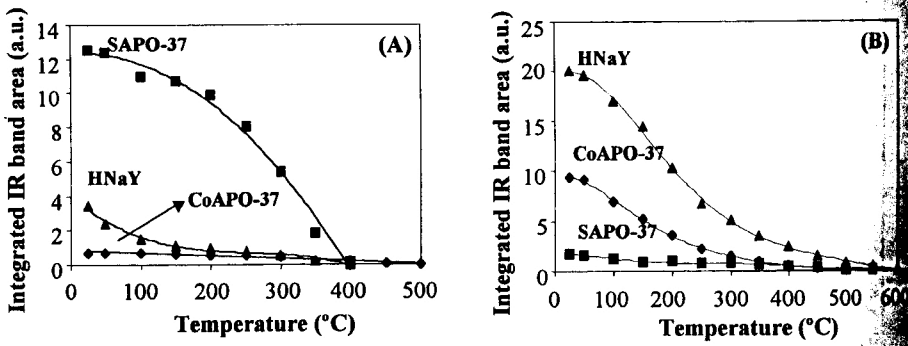

Figure 6. Dependence of the integrated intensity of IR bands assigned to (A) Bronstëd acid sites (bands at 1541-1548 cm^{-1}) and (B) Lewis acid sites (bands at 1451-1457 cm^{-1}) on the evacuation temperature

To better define, characterize and compare the catalytic sites existing in the above materials, we examined the skeletal isomerization of 1-butene into isobutene, the double bond isomerization to cis- and trans-2-butene and the isomerization of m-xylene.

Table 1: Catalytic activity and selectivity calculated at 10 and 120 min time on stream: T = 150°C, N_2/HC = 49, WHSV = 0.9 h^{-1}

	t = 10 min				t = 120 min			
Sample	Activ. (mmol/g/h)	Selectiv. isobutene (%)	Selectiv. cis-2but. (%)	Selectiv. trans-2-but. (%)	Activ. (mmol/g/h)	Selectiv. isobutene (%)	Selectiv. cis-2-but. (%)	Selectiv. trans-2-but.(%)
Y zeolite	21	1.2	26	49	14	0.3	44	54
CoAPO-37	20	1.4	30	60	20	0.4	39	60
SAPO-37	21	2.0	33	61	21	0.4	36	62

The results shown in Table 1, which refer to the isomerization of 1-butene, reveal that CoAPO-37 sample was as active for 1-butene isomerization as Y zeolite and SAPO-37. However, the overall strength of the acid sites of all the samples seems to be weak because the skeletal isomerization is very low, this value being slightly higher for SAPO-37 than for CoAPO-37 and HNaY zeolite. This could be related to the larger number of Bronstëd acid sites present on that sample.

The variation of the catalytic activity with time on stream for the isomerization of m-xylene is shown in Figure 7.

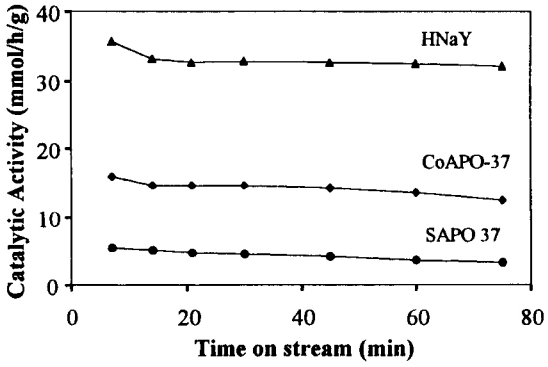

Figure 7. Catalytic activity for the m-xylene-isomerization for the studied catalysts, as a function of time on stream: T = 350°C, N_2/HC = 7.5, WHSV = 17.4 h^{-1}

For this reaction, which is believed to be sensitive to the strength of the Bronstëd acid sites [15], the catalytic activity of CoAPO-37 is higher than that of SAPO-37, in spite of the larger number of Bronstëd acid sites present in SAPO-37 sample. These results are probably an indication that the acid sites generated by the framework cobalt in the FAU structure are probably stronger than those generated by framework silicon, as already observed for AFR structure [3]. The difference in the catalytic activity of CoAPO-37 and the HNaY zeolite, for the

m-xylene isomerization, is probably also due to the larger number of acid sites present in HNaY

CONCLUSIONS

The results reported in this paper show the possibility of preparing a well-crystallized CoAPO-37 material. FTIR characterization indicates the incorporation of cobalt in the FAU structure and the presence of both Bronstëd and Lewis acidities. Catalytic tests show that CoAPO-37 was active for the isomerization of 1-butene and m-xylene, confirming the presence of Bronstëd acid sites generated by the framework incorporation of cobalt.

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PULSED LASER DEPOSITION OF MOLECULAR SIEVE FILMS AND MEMBRANES

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ABSTRACT

An excimer laser (KrF*, 248 nm) has been employed to deposit thin continuous films of all silica, aluminosilicate and magnesium aluminophosphate molecular sieves on a variety of substrates including Si, Pt, TiN, ITO, Al_2O_3, Mylar, glass and porous stainless steel. Both as-synthesized and calcined materials such as UTD-1, MCM-41 and MAPO-39 have been laser irradiated. The deposition of the silicate based materials depended on the presence of an organometallic (uv absorbing) template in the pores of the material. In the absence of the template, the laser irradiated molecular sieve materials photoluminesced rather than ablate. We have termed this modification as guest assisted laser ablation (GALA). In the case of UTD-1 and MAPO-39 oriented films are obtained following a post hydrothermal treatment. Results from characterization of the PLD molecular sieve films by x-ray diffraction and scanning electron microscopy are presented.

INTRODUCTION

Thin films composed of crystalline all silica and aluminosilicate zeolites as well as phosphate based molecular sieves have attracted interest because of their potential applications in areas such as separations, catalysis and sensors [1]. Molecular sieves offer several advantages over dense phase inorganic or polymeric thin film materials which include high selectivity due to uniform pore size, thermal stability and facile diffusion. Several techniques have been developed for the preparation of continuous molecular sieve films [2] such as deposition and growth of crystals from solution on a substrate. This method generally results in isolated crystals that must be grown sufficiently large so as to merge and form a continuous film [3]. Recent efforts using nanoseeds have resulted in thin oriented films of molecular sieves such as zeolite A [4]. However, it is unclear how universally applicable this method will be since it appears to rely on

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