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Studies on MeAPSO-5: An investigation of physicochemical and acidic properties

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Abstract

This work reports physicochemical and acidic properties of MeAPSO-5 (Me = chromium or iron), regardless their performance in the production of isobutane. Chromium and iron were partially introduced in SAPO-5 by direct hydrothermal synthesis. The solids were characterized by XRD, chemical analysis, N_2 adsorption isotherms, EPR, XPS, and calorimetry of ammonia adsorption. Their activity was also evaluated in the isomerization of *n*-butane. The purity of hydrothermally synthesized SAPO-5 was identified in all solids. EPR and XPS showed that chromium and iron exist as Cr_2O_3 and Fe_2O_3, respectively, mostly distributed on the solid surface. However, no reflections characteristic of these oxides were found in the XRD patterns. The chromium and iron cause different effects on the acidity: chromium increases the solid acidity whereas iron reduces drastically the acidic features. While distinct activity were observed between CrSAPO-5 and the FeSAPO-5 in *n*-butane isomerization, it is noteworthy that the pure SAPO-5 is not active in the reaction due to the too low strength of its acid sites. Results suggest that the *n*-C_4 isomerization activity of CrSAPO-5 may be ascribed to its enhanced acidity while, contrary to what was observed in the case of mordenite or sulfated zirconia, Iron addition to SAPO-5 did not enhance the catalytic activity via a possible participation of redox steps.

Keywords: SAPO-5; Chromium; Acid properties; Iron; *n*-Butane

1. Introduction

Silicoaluminophosphates (SAPOs) were first reported by Union Carbide in 1984 [1,2] and they have been widely studied since then. These microporous solids exhibit not only characteristics of zeolites, but also novel physicochemical traits that are related to their unique compositions [3–5].

SAPO-5 (IUPAC structure type AFI) with 12-ring straight channels is the interest of many researchers because substitution of silicon in a neutral aluminophosphate generates acid sites of different strengths, which may provide a much stronger interaction with the hydrocarbons [2,5]. The acid properties of SAPO strictly depend on the Si content, sitting and ordering in the lattice [5–8]. The literature reports the theoretical possible isomorphous substitution mechanisms (SM) in SAPO-5 materials [6]: Si substitutes Al (SM1), Si replaces P (SM2) and also, two Si atoms can substitute one Al atom and one P simultaneously (SM3).

SM1 provides a framework of possible changes that have to be neutralized by anions. However, the SMl substitution cannot occur practically because Si–O–P linkages are considered unlikely [8,9]. In contrast, by SM2, a PO_2^+ tetrahedron is replaced by SiO_2 then, the cation exchange capacity is generated because the framework becomes negatively charged. The potential Brønsted site per Si atom should be generated by SM2 mechanism because this substitution introduces one negative charge, which can be compensated by a proton to form an acid site [6,7]. The substitution of two Si atoms for a pair of Al and P (SM3) atoms cannot occur independently because of the formation of undesirable Si–O–P linkages like SMl. Indeed, the simultaneous substitution of one AlO_2^- and one adjacent PO_2^+ tetrahedron by (SM3) does not involve changes in the lattice charge. However, SM3 can take place in combination with SM2 to avoid the formation of Si–O–P [9,10]. Although

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the latter substitution mechanism should lead to less than one acid site per framework Si atom, the resulting strength should be higher than the one arising from the SM2 substitution, as has already been discussed [2–9].

Some reports have noticed the simultaneous generation of Brønsted and Lewis acid sites during the preparation of SAPO-5, MeAPSO-5, MeAPO-5 (metal substituted in the SAPO and AlPO framework, respectively) that seems to be associated with active sites of enhanced catalytic activity. Therefore, a wide distribution of acid sites and the one-dimensional nature of the pore system appear to contribute to their performance in important applications including lube dewaxing, ammoxidation, adsorption studies [3,5,9–12].

In another way, transition metals are usually used to modify the catalysts' properties. When metal ions like Mg, Co, Fe, Zn, Mn are introduced in the molecular sieve framework, they may enhance significantly the activity of the undoped molecular sieve for oxidation, alkylation and isomerization reactions [12–15].

In particular, direct transformation of *n*-butane to isobutane is an important reaction from industrial and academic points of view [13–16]. There are several studies focusing on the reaction of *n*-butane to isobutane over acidic catalysts [17–21]. Most of academic findings have reported the use of *n*-butane as a test reaction for evaluating the relative acidic properties of sulfated zirconia, heteropolycompounds, and zeolites such as H-mordenite. In particular, Fe and/or Mn addition in sulfated zirconia (ZS) was reported to rise significantly the activity of ZS in n-C_4 isomerization [16,22]. Additionally, the influence of synthesis variables of transitions metal ion containing SAPO-5 on their catalytic performances has been reported [13,14,23]. There are, however, only a few studies published in the open literature on the influence of metal incorporation (chromium and iron) in the synthesis of silicoaluminophosphate molecular sieves applied to the transformation of *n*-butane.

Therefore, in this work we have attempted the metal (Cr,Fe) isomorphous substitution in the AFI structure and studied the influence of the metal on the physicochemical, acid and catalytic properties of SAPO-5. The reaction of isomerization of *n*-butane into isobutane was used as a test reaction to investigate the catalytic property of CrSAPO-5, FeSAPO-5 with respect to pure SAPO-5.

2. Experimental

2.1. Synthesis of MeAPSO-5

Silicoaluminophosphate molecular sieves SAPO-5 were synthesized hydrothermally using the following gel composition 0.2 SiO_2:Al_2O_3:P_2O_3:1.5 TEA:40H_2O, using a modified recipe of literature [24,25]. In a typical synthesis, 4.5 g of aluminum hydroxide (pseudoboehmite Condea) was dispersed into about one half of the total amount of water. The mixture was stirred and ortho-phosphoric acid (85% Aldrich) diluted in water 1:1 (v/v) was added drop by drop on the aluminum slurry under vigorous stirring until a homogeneous mixture was obtained. The gel was further mixed for 30 min. 7.0 mL of triethylamine was added and stirring was maintained for 30 min more. After the addition of the organic template, the silicon source (Aerosil 200, Degussa) was added, keeping the agitation for 10 min more. The pH of the gel was 5 and the resultant material was transferred into a stainless-steel autoclave, sealed and placed in an oven and maintained at 170 °C for 48 h. The solid thus obtained was filtered, washed with distilled water and dried. Finally, it was calcined at 500 °C in air for 12 h (heating rate: 1 °C min^{-1}).

Chromium and iron were introduced in SAPO-5 by direct hydrothermal synthesis, following the same recipe as that described above. The metals (chromium acetate or iron nitrate) were mixed to the final gel after the addition of silica. Both metals contents were 1 wt.%.

2.2. Characterization

Solids were characterized by XRD, chemical analysis, nitrogen adsorption isotherms, calorimetry adsorption of ammonia, electron paramagnetic resonance (EPR), X-ray photoelectron spectroscopy (XPS) and evaluated in *n*-butane isomerization as test reaction.

The purity of hydrothermally synthesized SAPO-5 and metals modified SAPO-5 were analyzed using a Bruker (Siemens) D5005 X-ray diffractometer, using Ni filtered Cu Kα radiation. XRD experiments were performed in the range of 2θ between 5° and 80°.

The chemical analysis was performed in Carry AAS/ICP-OES in a PerkinElmer, Arl 3410 model instrument. Each sample was dissolved in a concentrated hydrofluoric acid solution and heated in a sand bath at 200 °C. The solvent was completely evaporated and then hydrochloric acid and water were added to the precipitate, before measurement of the chemical composition.

BET measurements were recorded on Micromeritics ASAP 2002 equipment. Samples were first treated in vacuum to remove the gaseous impurities (300 °C, 6 h, 10^{-3} Torr) and the textural features were studied using nitrogen adsorption at 77 K.

EPR experiments were performed in order to study the oxidation state of the metals present in the solids. EPR spectra were taken in quartz tubes of 4 mm inner diameter at room temperature and also at N_2 liquid temperature on an upgraded Varian E9 spectrometer, operating at 100 kHz field modulation, in the X-band mode. DPPH was used as a standard for *g*-value determinations. Experiments were performed for selected samples that contain the transitions metals.

XPS spectra were recorded on a VG ESCALAB 200 R spectrometer provided by an electron analisator using a hemispherical analyzer with a pass energy of 20 eV. A Mg Kα X-ray source (1253.6 eV) was used for the analyses. All binding energy measurements were corrected for charging effects with reference to the carbon 1s binding energy fixed to 284.6 eV. The pressure used was lower than 5×10^{-9} Torr.

For calorimetry of ammonia adsorption, the catalyst was placed in a glass tubular cell for a preliminary pretreatment at 400 °C under vacuum for 2 h. The cell was then introduced in the calorimeter at 80 °C and the experiment was performed: successive ammonia injections were done until complete saturation of the sample.

2.3. Catalytic measurements

n-Butane isomerization was used as test reaction in order to study the acidity of the solids. 100 mg of the samples were placed in a tubular quartz reactor and pretreated at 400 °C under air flow ($0.3\ \mathrm{L\,h^{-1}}$ for 2 h). The reaction was carried out at 200 °C, using a butane/nitrogen mixture (5% *n*-C_4 in N_2, total flow rate = $1.28\ \mathrm{L\,h^{-1}}$) and products were analyzed by a DELSI chromatograph equipped with a flame ionization detector coupled to a MERCK D2500 integrator.

Also, a reference catalyst, Fe-mordenite was evaluated in the reaction at the same temperature.

3. Results and discussion

3.1. Physicochemical properties of the solids

3.1.1. XRD

The crystal phase of the calcined silicoaluminophosphates was analyzed by XRD and the results are shown in Fig. 1.

The diffraction patterns of the solids present the peaks characteristic of SAPO-5 materials that are consistent with those reported by Flanigen et al. [2], indicating that the 3 samples are well-crystallized.

Any peak assignable to crystalline chromium or iron oxide can be observed in CrSAPO-5 and FeSAPO-5 samples, respectively, indicating that these phases are in a too low quantity or in an amorphous phase that cannot be detected by XRD. It is not easy to ascertain the last possibility, and hence, other techniques besides XRD are required to provide the necessary information about the nature of the metal phases in these solids.

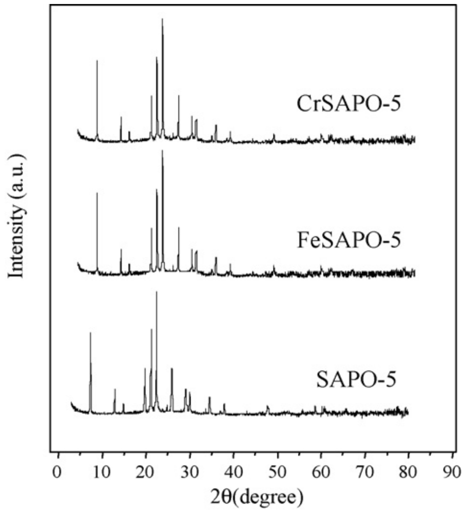

Fig. 1. XRD patterns at high diffraction angles for pure SAPO-5 (SAPO-5), iron SAPO-5 (FeSAPO-5) and chromium SAPO-5 (CrSAPO-5) samples.

3.2. Chemical analysis

The iron and chromium contents, as well as the Si/Al ratio of the solids are given in Table 1.

According to the table, the expected isomorphous substitution was efficient to obtain silicoaluminophosphates samples. In all solids, molar ratios are close to those of the starting solution. Note that the Si/Al ratio slightly decreased upon metal introduction. However, in case of FeSAPO-5, the iron content (0.55%) was lower than that of the starting gel (1 wt.%). This relates to the fact that part of the metals may be leached during the washing steps.

The hypothesis above is supported by the Pauling chemical bond theory [26] that establishes the isomorphous substitution of a heteroatom in a zeolite or silicate structure is facilitated, if the metal–oxygen ratio $r(M^+)/r(O^{2-})$ is 0.225 and 0.414. The changes in the coordination sphere of the cation substitute can be caused by changes in the oxidation state. It is a result of the calcination process that is generally used to remove the template and water of the as-synthesized zeolite.

Indeed, the geometry assumed by the metal substitute, the chemical bond stability of the incorporated metal and also the crystalline lattice solids, as well as the incompability of the latter and the metal substitute result in the structural defects causing the metal leaching [26,27].

In our work, in case of FeSAPO-5, there was no change in the iron oxidation state upon calcination. However, the calcination process probably leads to the migration of part of iron species out of the framework [26].

Literature reports that materials in which chromium is incorporated by isomorphous substitution, contain Cr^{3+} cations the as-synthesized form, that are oxidized to Cr^{5+} or Cr^{6+} upon

Table 1
Chemical composition of the silicoaluminophosphates

Sample	% Fe (±0.05)	% Cr (±0.05)	Si/Al
SAPO-5	–	–	0.42
CrSAPO-5	–	1.02	0.41
FeSAPO-5	0.55	–	0.38

Samples: pure SAPO-5 (SAPO-5), SAPO-5 containing chromium and iron, respectively, CrSAPO-5 and FeSAPO-5.

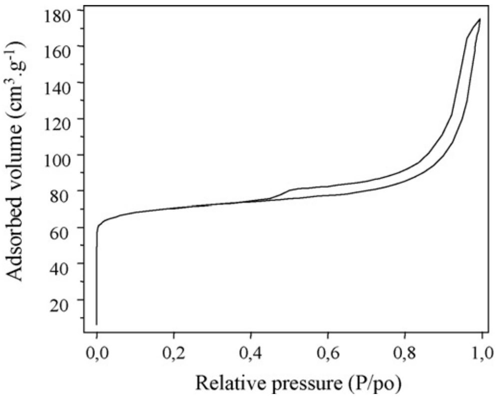

Fig. 2. Adsorption–desorption isotherm at N_2 liquid temperature of SAPO-5 sample.

Table 2
BET surface, pore volume and size of the silicoaluminophosphates

Sample	BET surface ($m^2 g^{-1}$)	Pore volume ($cm^3 N_2 g^{-1}$)	Pore size (Å)
SAPO-5	249	0.11	7.4
CrSAPO-5	273	0.13	8.5
FeSAPO-5	122	0.05	7.5

Samples: pure SAPO-5 (SAPO-5), SAPO-5 containing chromium and iron, respectively, CrSAPO-5, FeSAPO-5.

calcination at 500 °C [27]. The change in oxidation state generates structural defects in the framework.

3.3. N_2 adsorption isotherms

The textural parameters of the solids were studied though the N_2 adsorption isotherms. The N_2 adsorption–desorption isotherm of the SAPO-5 material is shown in Fig. 2.

SAPO-5 has a surface area of 249 $m^2 g^{-1}$ and a pore volume of 0.11 $cm^3 g^{-1}$ (Table 2). It is in very good agreement with adsorption data of the corresponding material described in literature [1,2].

By the way, the presence of iron provides a decrease in both surface area and pore volume, probably, due to a lower crystallinity as compared to the other samples. Indeed, the metal content is too low to assign the modification of the adsorption properties to a partial blocking of the mesopores by extraframework species. By contrast, incorporation of chromium leads to an increase of textural parameters, and CrSAPO-5 possesses the largest pore size (8.5 Å) among the series of compounds, as seen in Table 2.

3.4. XPS and EPR experiments

XPS experiments were performed to get information on the chemical composition and oxidation state of the metals present on the surface of FeSAPO-5 and CrSAPO-5. The binding energy related to Si, Al, P, O, C and Cr in CrSAPO-5 sample is summarized in Table 3.

The binding energy (BE) is determined by reference to the 2p level of Al at 75.2 eV, in agreement with literature [28]. Generally, in Cr_2O_3 (Cr^{3+}) Cr2p3/2 binding energy is around 576.9 eV whereas Cr^{6+} species (in CrO_3) has Cr2p3/2 binding energy tabulated near of 580 eV [28–30]. The binding energy obtained for the CrSAPO-5 sample has an intermediate value (577.4 eV) and the Cr2p peak can be deconvoluted in two components that are attributed to Cr^{3+} and Cr^{6+}. The major component is Cr^{3+}, as seen in Fig. 3. This is also confirmed by the yellow-green color of the sample. Indeed, the ratio Cr/Si is 0.06, indicating that most of the chromium is on the surface of the solid. The XPS spectrum of CrSAPO-5 is seen in Fig. 3.

Table 3
Binding energy related to the peaks of chromium, oxygen, carbon, phosphorous, silicon and aluminum

Peak	Centre	% [AT]
Cr 2p	577.36	1.050
O 1s	531.86	66.612
C 1s	284.56	3.408
P 2p	134.06	4.008
Si 2p	102.66	17.125
Al 2p	74.16	7.796

Total area of the peaks (AT).

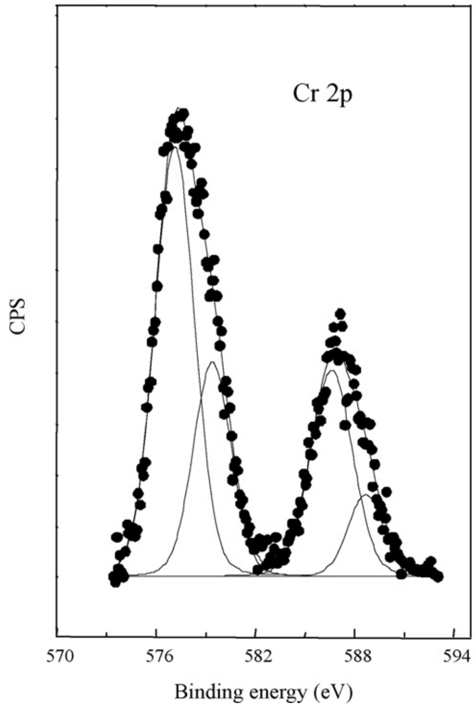

Fig. 3. XPS spectra of chromium 2p level. Sample: CrSAPO-5.

It was not possible to know the iron chemical environment in FeSAPO-5 by XPS, due to the low quantity of iron (0.55 wt.%) in this sample. This was done using EPR, which is a more sensitive method. The EPR spectra are shown in Fig. 4. The X-band EPR spectra of high-spin Fe^{3+} ions in diamagnetic low field media like zeolites are usually composed of four component lines [31].

The hump observed at $g = 2.0–2.6$ is generally attributed to extra framework iron species, in the form of oxide/hydroxide clusters [31]. This suggests that iron oxide in the hematite form (α-Fe_2O_3) is distributed on the solid surface, which is supported by the brown color of the calcined sample.

CrSAPO-5 displayed one broad singlet (Fig. 4b) with a *g*-value of 1.98 attributed to Cr^{3+} species present as ion-exchange cations or oxide-like compounds. The orange yellow-green color of the sample indicates the presence of Cr^{6+} species, in agreement with XPS results. Spectra possess similar features at different temperatures.

By XPS and EPR investigations, it was found that chromium oxidation states in CrSAPO-5 sample were Cr^{3+} and Cr^{6+}, assigned mainly to partly oxidized Cr_2O_3 clusters, while FeSAPO-5 sample showed Fe^{3+} related to hematite (α-Fe_2O_3), mostly distributed on the solid surface.

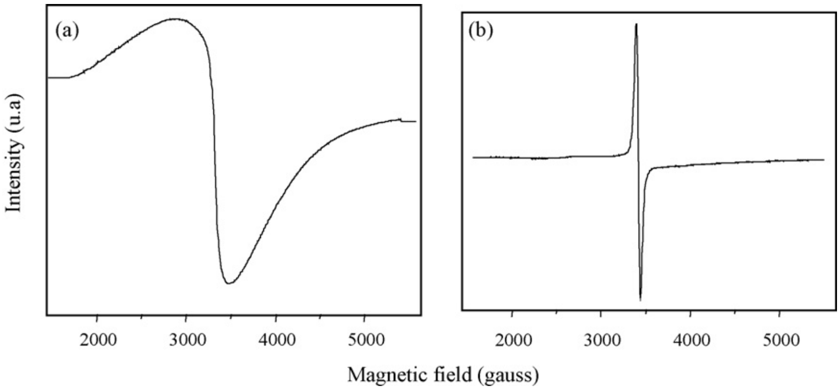

Fig. 4. EPR spectra of (a) FeSAPO-5 and (b) CrSAPO-5 samples.

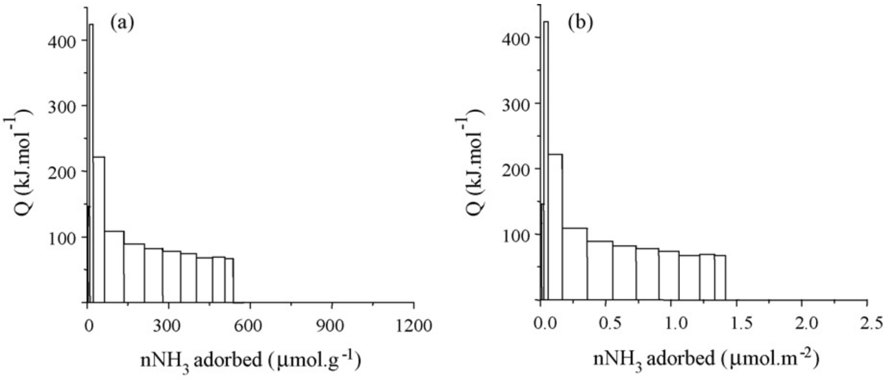

Fig. 5. Calorimetry diagram of the chromium SAPO-5 sample (CrSAPO-5). Micro mol of ammonia adsorbed per gram of the catalyst (a). Micro mol of ammonia adsorbed per meter square of the catalyst (b).

3.5. Acidity measurements—calorimetry

Calorimetry is a technique well suited to probe the acid sites concentration and strength on the surface of solid catalysts. SAPO-5 is a solid that possesses a low acidity. Therefore, the experiment was performed on the more acidic FeSAPO-5 and CrSAPO-5 samples. Calorimetry results are shown in Fig. 5.

According to Fig. 5a, incorporation of chromium produces a few amount of sites that would possess a high strength. Indeed, we can note an intense differential heat of adsorption for low ammonia coverage (see the beginning of Fig. 5). That suggests that chromium and ammonia can form a complex providing such unusual exothermic phenomena. However, further addition of ammonia doses, results in the determination of a significant

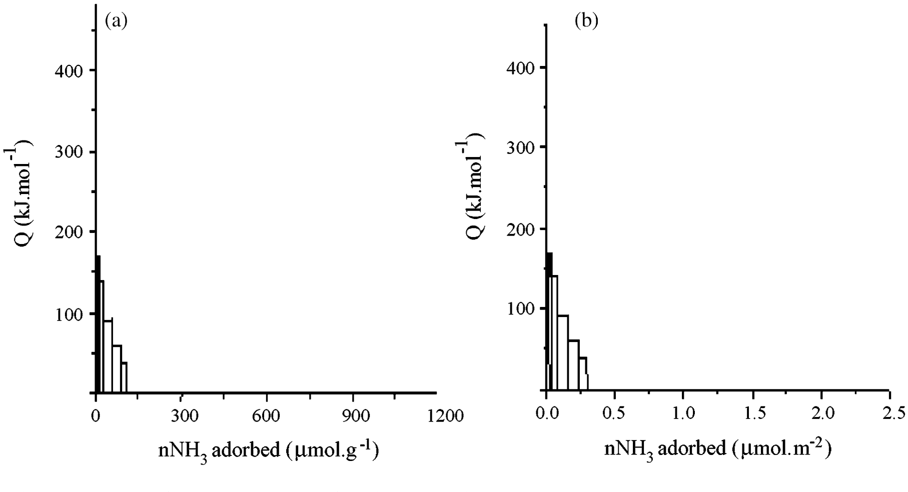

Fig. 6. Calorimetry diagram of the iron SAPO-5 sample (FeSAPO-5). Micro mol of ammonia adsorbed per gram of the catalyst (a). Micro mol of ammonia adsorbed per meter square of the catalyst (b).

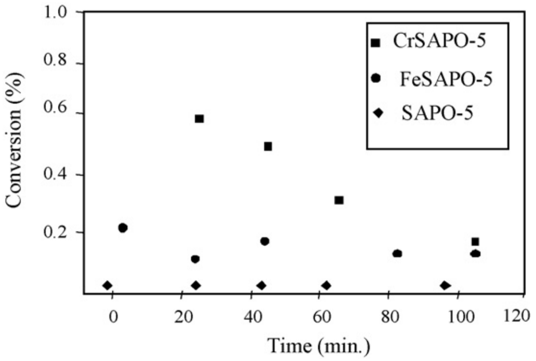

Fig. 7. The performance of the solids in the isomerization of *n*-butane. Samples: (●) iron SAPO-5, (■) chromium SAPO-5 and (✶) pure SAPO-5.

amount of sites, of homogeneous energy, characterized by differential heat of adsorption between 80 and 100 kJ mol^{-1}.

On the other hand, the adsorption profile observed on FeSAPO-5 shows a fast decrease which evidences the poor acidity of this sample (Fig. 6).

In general, the presence of chromium provides a significant amount of acid sites with homogeneous acidity. By contrast, iron introduction decreases drastically both the number and the strength of the acid sites.

3.6. Performance in n-butane isomerization

The isomerization of *n*-butane to isobutane was chosen as model reaction to test the catalytic activity of the samples. For this reaction, strong acid sites are generally required [16]. The catalytic performance of the silicoaluminophosphates is shown in Fig. 7.

SAPO-5 is inactive in the reaction. It is generally believed that Brønsted acid sites of medium strength can catalyze the transformation of *n*-butane, depending of the Brønsted acid density [16–18]. However, most likely, the low density of weak acid sites in pure SAPO-5 was not able to catalyze the isobutane production whatever be the mechanism involved.

On the other hand, the silicoaluminophosphates containing transition metals were slightly more active in the transformation of *n*-butane. CrSAPO-5 sample showed the highest conversion whereas FeSAPO-5 showed a lowest one but stable activity with time.

The nature and the strength of the acid sites present in the metal incorporated silicoaluminophosphates were expected to influence the rate of isobutane formation. However, the conversion level for the two samples cannot be understood only in view of their acidity difference. CrSAPO-5 shows a significant initial activity due probably to the presence of some acid sites with sufficient strength, identified by calorimetric results. However, CrSAPO-5 experienced a fast deactivation due probably to sites poisoning [32]. In contrast, the catalytic performance was modest with FeSAPO-5.

From these results, we can conclude that, in general, the CrSAPO-5 showed a better performance in the C_4 transformation due to its higher acidity compared to the FeSAPO-5 and pure SAPO-5. In case of CrSAPO-5, the chromium species generate significant amount of acid sites with medium strength and then, a significant catalytic activity is observed. At this stage, it cannot be stated if or not, the redox properties of Cr^{3+}/Cr^{6+} couple participate to the reaction.

It was seen previously that the isobutane rate of formation was generally increased in iron presence, i.e. when the reaction is conducted with iron modified mordenite zeolite or sulfated zirconia [20,22]. By contrast, in case of silicoaluminophosphates materials, which have acid sites with too low strength, the iron presence does not favor the *n*-C_4 isomerization.

4. Conclusions

The following conclusions can be outlined from our study:

We tried to incorporate transition metal in catalysts based on silicoaluminophosphates by isomorphous substitution. These materials possess the characteristic phase of SAPO-5 silicoaluminophosphates. No peaks corresponding to chromium or iron oxides were seen by XRD analysis. However, iron and chromium oxides were found as Cr_2O_3 and α-Fe_2O_3 particules, mostly distributed on solid surface, as seen in XPS and EPR results.

The presence of transitions metals strongly influences the textural features of the silicoaluminophosphates. Iron presence decreases both textural parameters, while chromium provides an increase of the textural features of the solid.

The presence of chromium and iron lead to different effects on the acidity: the chromium mainly generated significant amount of acid sites with medium strength while iron addition led to a quite non-acidic material.

Pure SAPO-5 and MeAPSO samples were evaluated in *n*-butane isomerization. The non-modified SAPO-5 sample is not active in this reaction, essentially because of the too low acidity strength. The metal modified samples showed much higher activity in the C_4-hydrocarbon transformation than SAPO-5. For CrSAPO, this can be ascribed to an enhanced acidity. But, contrary to what is observed in the case of mordenite of sulfated zirconia, Iron addition to SAPO-5 did not promote the catalytic activity.

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