Métodos Físicos em Química Inorgânica (119.229 e 314.889)

Prof. José Alves Dias

Tópicos a serem descritos (continuação)

- 6. Exemplos Selecionados de Aplicações de RMN em Estado Sólido

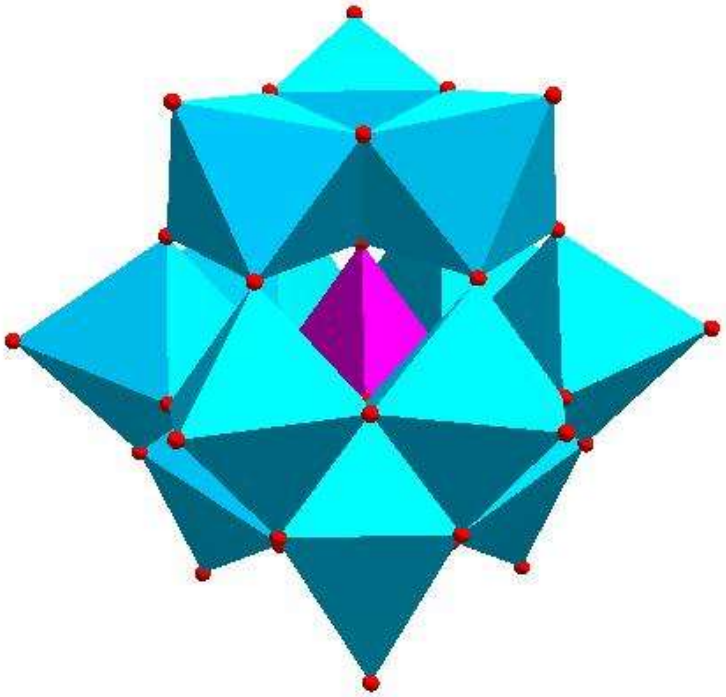
MAS-RMN de ^{31}P: Polioxometalatos

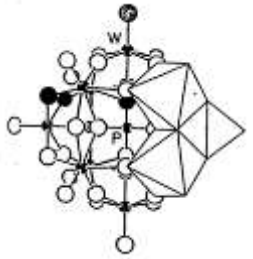
- Sólidos iônicos composto por ânions poliméricos formados pela condensação de dois ou mais oxoânions diferentes, representados pela fórmula geral $[X_xM_mO_y]^{q-}$ ($x \leq m$), onde:

- X = variedade de elementos dos grupos 11 a 17 (usualmente P, Si, As, Sb, Ge, etc.)

- M = Mo, W, V, Nb, Ta, ou misturas destes elementos em seus estados de oxidação mais elevados (d^0, d^1).

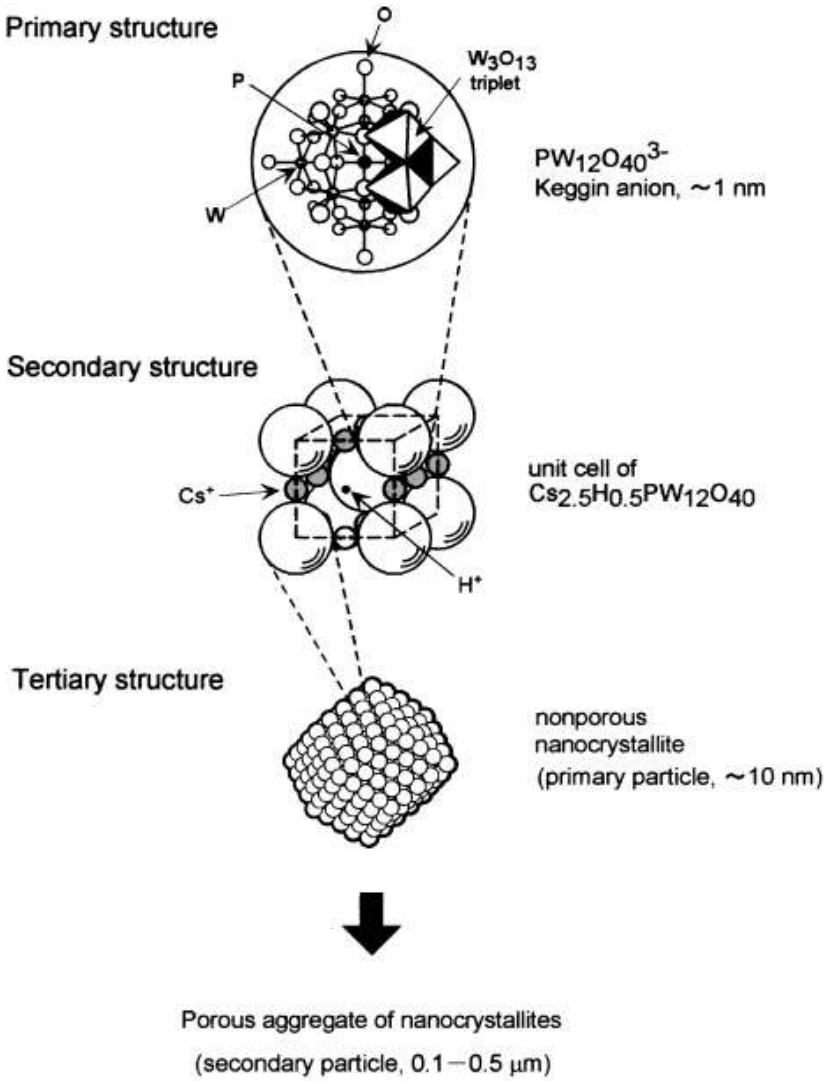
Estrutura de Keggin (Poliânion, $XM_{12}O_{40}$)





(Primária)

Coordenação tetraédrica do heteroátomo (T_d)


Primary structure
O
P
W
W_3O_{13} triplet
$PW_{12}O_{40}^{3-}$
Keggin anion, ~1 nm
Secondary structure
Cs^+
H^+
unit cell of
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$
Tertiary structure
nonporous
nanocrystallite
(primary particle, ~10 nm)
Porous aggregate of nanocrystallites
(secondary particle, 0.1−0.5 μm)

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0103 - 5053 $6.00+0.00

Article

Acidity and Characterization of 12-Tungstophosphoric Acid Supported on Silica-Alumina

Flávia C. G. de Mattos, Eduardo N. C. B. de Carvalho, Elon F. de Freitas, Mateus F. Paiva, Grace F. Ghesti, Julio L. de Macedo, Sílvia C. L. Dias and José A. Dias**

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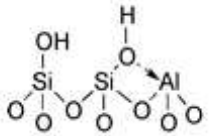
This work deals with preparation and characterization of $H_3PW_{12}O_{40}$ (H_3PW) supported on silica-alumina. Impregnation of H_3PW (15, 20, 30 and 40 wt.%) on commercial silica-alumina support in acidic aqueous solution is effective for preparing this catalyst keeping its Keggin structure, according to different methods of characterization. The catalysts were tested in a model reaction of acetic acid with ethanol and 30 wt.% H_3PW/SiO_2-Al_2O_3 had the highest activity under the conditions: catalyst calcination at 300 °C, temperature of 100 °C, acetic acid:ethanol molar ratio of 2:1 and catalyst:acetic acid mass ratio of 10 wt.%. The reaction yield was 79 and 100% selectivity for ethyl acetate over three reutilizations, for reaction time of 2 h. The calculated total acid site distribution was 0.299 mmol g^{-1} (97% of the theoretical probed by pyridine), and most of these (0.236 mmol g^{-1}) were Brønsted weak-medium strength (pyridine desorption between 300 and 500 °C).

Keywords: supported heteropolyacid, 12-tungstophosphoric acid, silica-alumina, ethanol, esterification of acetic acid with ethanol



Silica–alumina

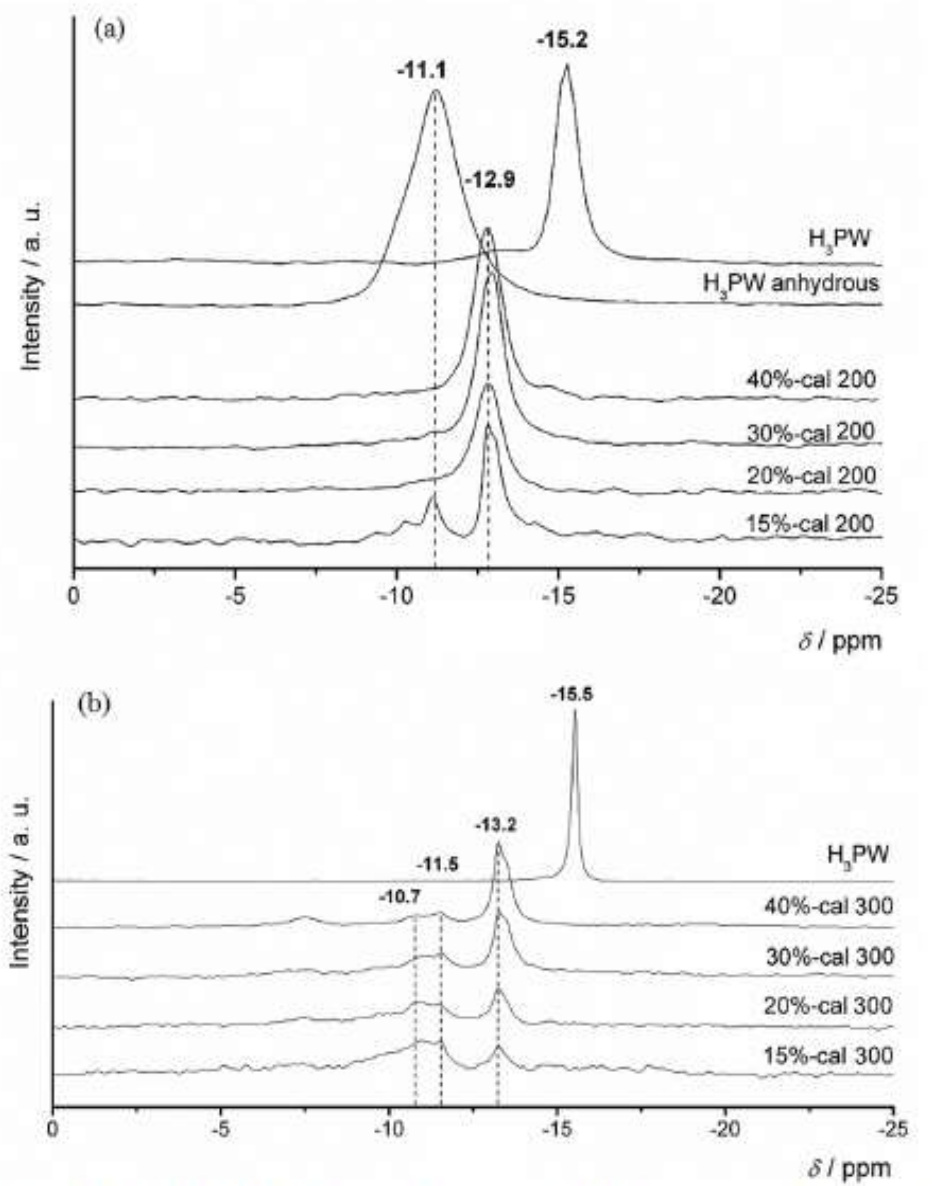


Figure 3. ^{31}P MAS NMR spectra of x wt.% H_3PW/SiO_2-Al_2O_3 referenced to 85% H_3PO_4: (a) samples calcined at 200 °C for 4 h and obtained at 7.05 T, and (b) samples calcined at 300 °C for 4 h and obtained at 14.1 T.

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Esterification of oleic acid with ethanol by 12-tungstophosphoric acid supported on zirconia☆

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ABSTRACT

Esterification of organic acids with alcohols produces an industrially important class of substances with a variety of applications. This work presents an impregnation route to support $H_3PW_{12}O_{40}$ (H_3PW) on zirconia (ZrO_2) in acidic aqueous solution (HCl 0.1 mol L^{-1}) at different ratios (5, 10, 15, 20, 25, 40 and 60 wt%), which were further applied in the esterification of oleic acid with ethanol. Impregnated samples calcined at 200 °C for 4 h were characterized by FTIR, FT-Raman, XRD, ^{31}P MAS NMR and BET surface area. No decomposition of the Keggin anion structure was observed under these conditions. The XRD results, surface area determination and catalytic tests pointed out that H_3PW was well dispersed over the support and only a monoclinic phase of the commercial ZrO_2 was detected. An optimum reaction performance (88% of oleic acid conversion) was achieved at 20 wt% loading, 100 °C, 4 h reaction and 1:6 (acid:ethanol) molar ratio. A small leaching of 8 wt% of the initial mass of this catalyst (i.e., the actual loading was 18.4 wt%) was also observed at the end of reaction, which affects the reaction kinetics. Thermal stability studies of 20%H_3PW/ZrO_2 catalyst, determined by ^{31}P MAS NMR, XRD and FT-Raman revealed that Keggin anion decomposition begins at ca. 500 °C, which was confirmed by the respective decrease of the catalytic activity. A preliminary study of recyclability indicated that a treatment of the spent catalyst involving a sequence of washing with n-hexane, drying at 100 °C and calcining at 300 °C for 4 h, recovered conversion values as high as 70%.

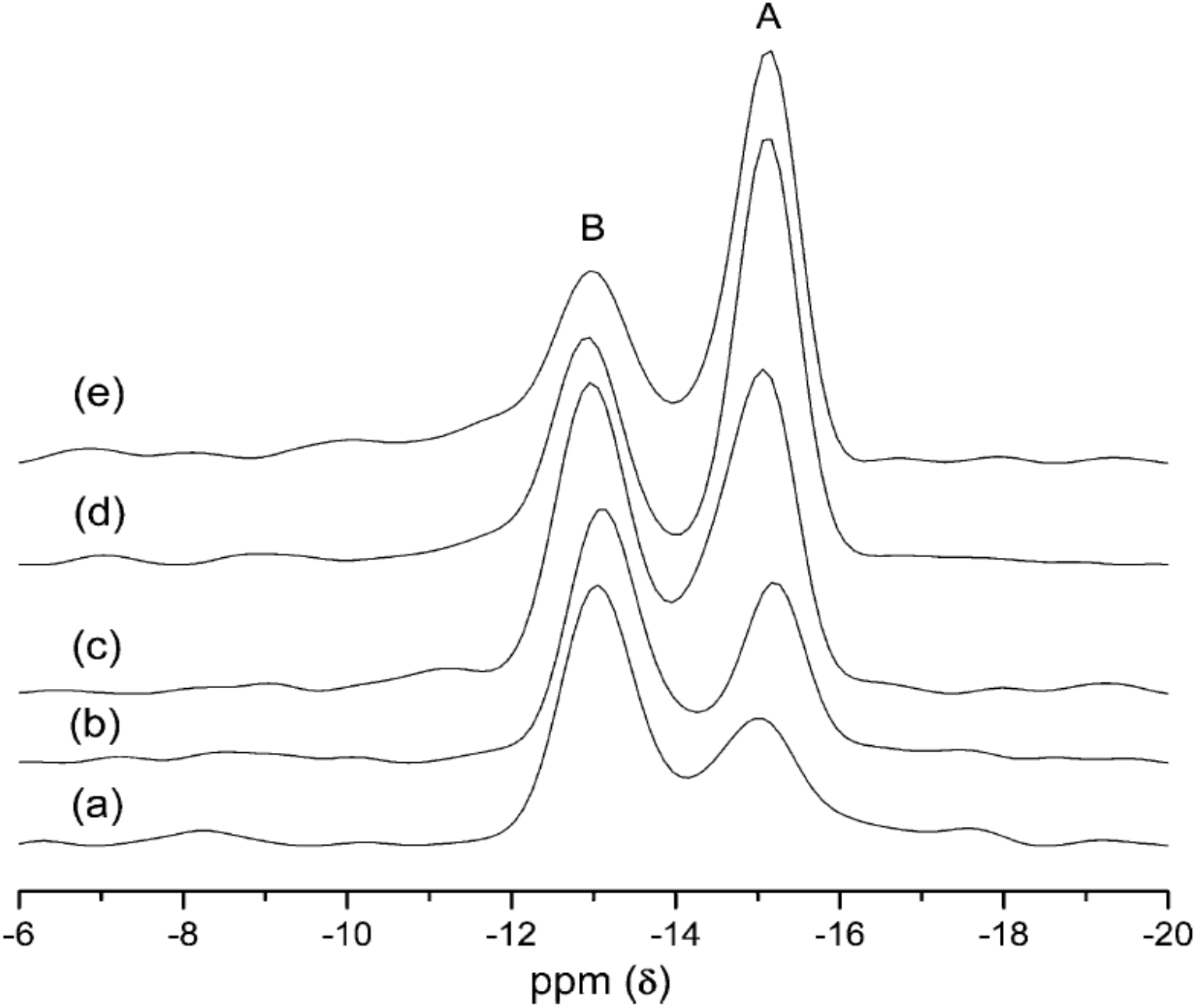

Fig. 4. ^{31}P MAS NMR spectra of H_3PW/ZrO_2 with: (a) 5 wt%; (b) 15 wt%; (c) 20 wt%; (d) 25 wt% and (e) 40 wt% of H_3PW.

- Dois tipos de ambientes do H_3PW:

- A: sinal no MAS-RMN de ^{31}P em -15 ppm $\Rightarrow$ equivalente ao H_3PW cristalino.

- B: sinal no MAS-RMN de ^{31}P em -13 ppm $\Rightarrow$ H_3PW interagindo na superfície do ZrO_2 $\Rightarrow$ espécies como $\{[\equiv Zr{-}OH_2]^{n+}[H_{3-n}PW_{12}O_{40}]^{n-3}\}$

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Effects of cesium ion exchange on acidity of 12-tungstophosphoric acid

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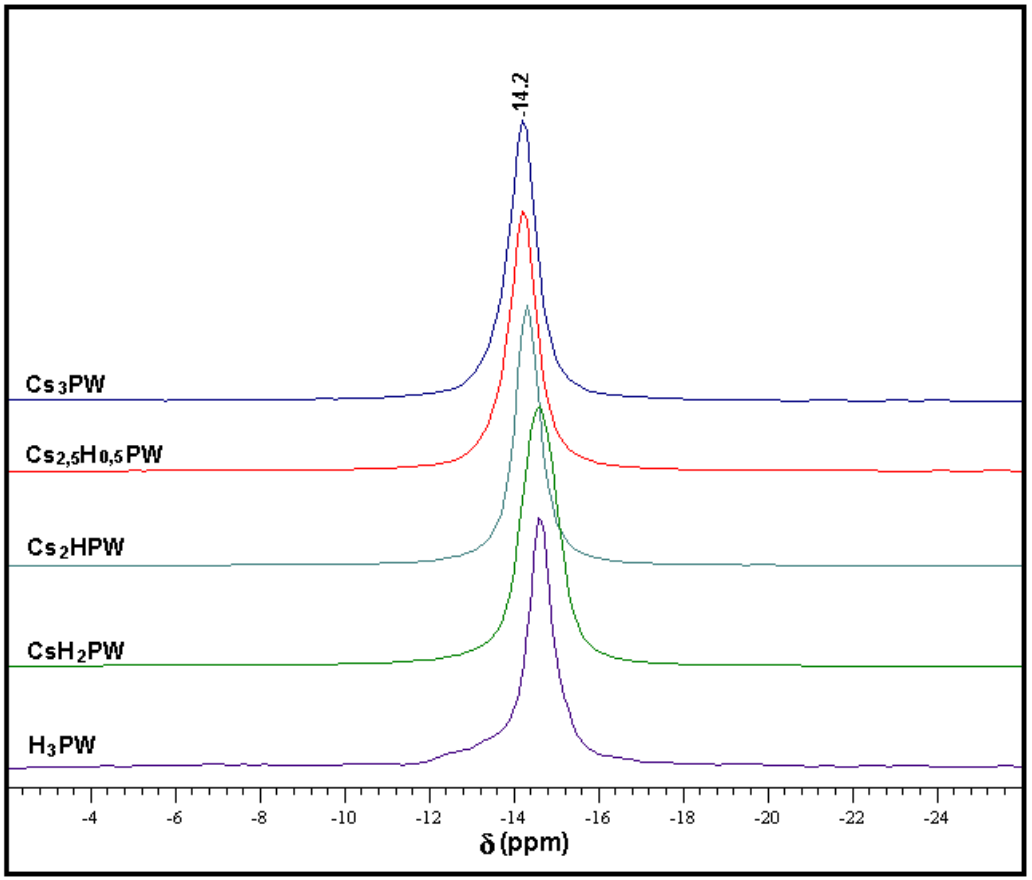
Abstract

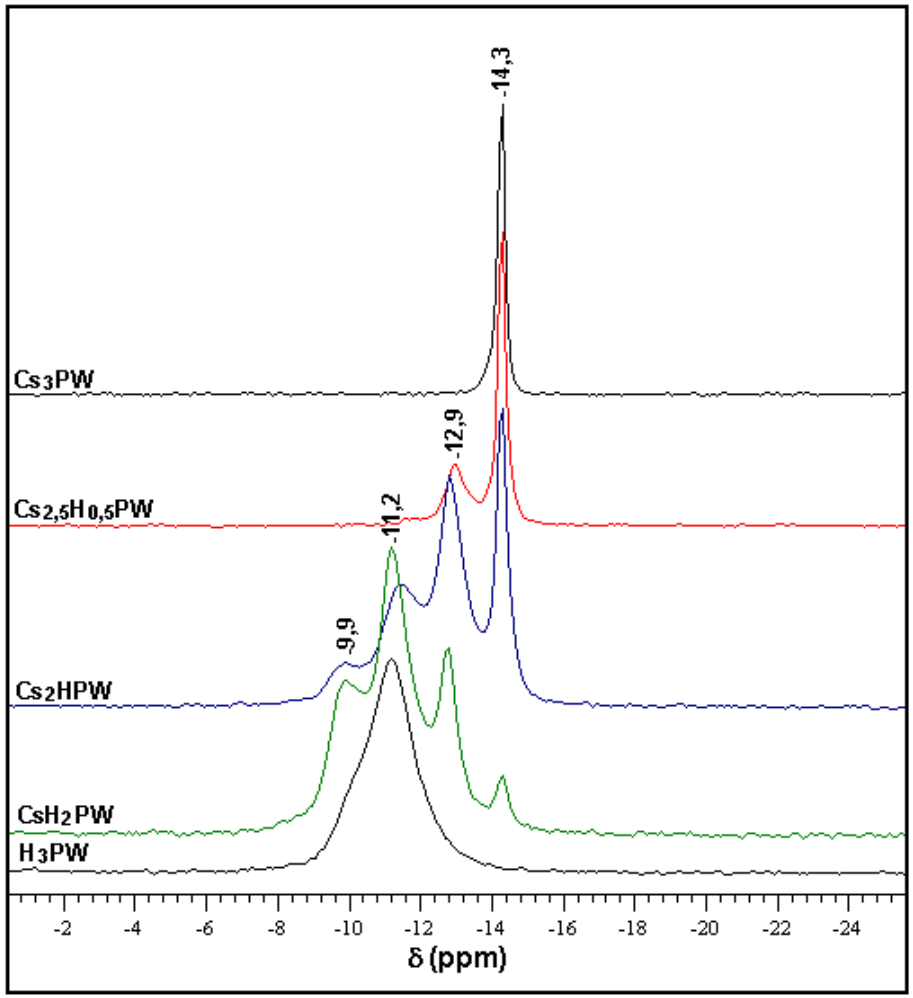
The acidity of heteropolytungstic acids containing cesium is of great interest because of their unique catalytic and physical properties. Preparation and characterization of $Cs_xH_{3-x}PW_{12}O_{40}$ ($x = 1$, 2, 2.5 and 3) have been performed using FTIR for functional groups, XRD for crystal structure, ^{31}P MAS NMR for the environment of the phosphorous. Calorimetry and adsorption of pyridine interaction in cyclohexane slurry (Cal–ad method) was used to quantify the number of acid sites and the corresponding enthalpy of adsorption. The distribution of proton and cesium ions in the salt structures is nearly homogeneous, as confirmed by XRD, ^{31}P MAS NMR and enthalpy measurements. The acidity, systematically obtained in this work, indicates different proton strengths, with the following order: $H_3PW > Cs_2HPW \cong Cs_{2.5}H_{0.5}PW > CsH_2PW \gg Cs_3PW$, with $\Delta H_1 = -32.7$, -28.3, -27.4, -20.8 and $-7.8\,kcal\,mol^{-1}$, respectively. These enthalpies are strongly influenced by an endothermic term related to interstitial expansion of the structure by entrance of the pyridine molecule, which is evidenced by XRD results. The total amount of protons titrated by pyridine in all solids is larger compared to the calculated population on surface. This supports penetration by the polar probe into all of the solids. For $Cs_{2.5}H_{0.5}PW$ the strongest protons are exposed nearly exclusively on the surface of this solid, as demonstrated by Cal–ad results for site-1 calculation. The combination of FTIR and adsorption site density demonstrated the effect of substituting Cs for H, changing the Brønsted acid site density to hydrogen-bonded ones.

Keywords: Cesium heteropolytungstates; 12-Tungstophosphoric acid; Solid acids; Cal–ad method; Ion exchange

Espectros de MAS-RMN de ^{31}P das amostras de $Cs_xH_{3-x}PW$ antes da calcinação



Espectros de MAS-RMN de ^{31}P das amostras de $Cs_xH_{3-x}PW$ após calcinação (200 ºC)



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Solvent effect on the preparation of $H_3PW_{12}O_{40}$ supported on alumina

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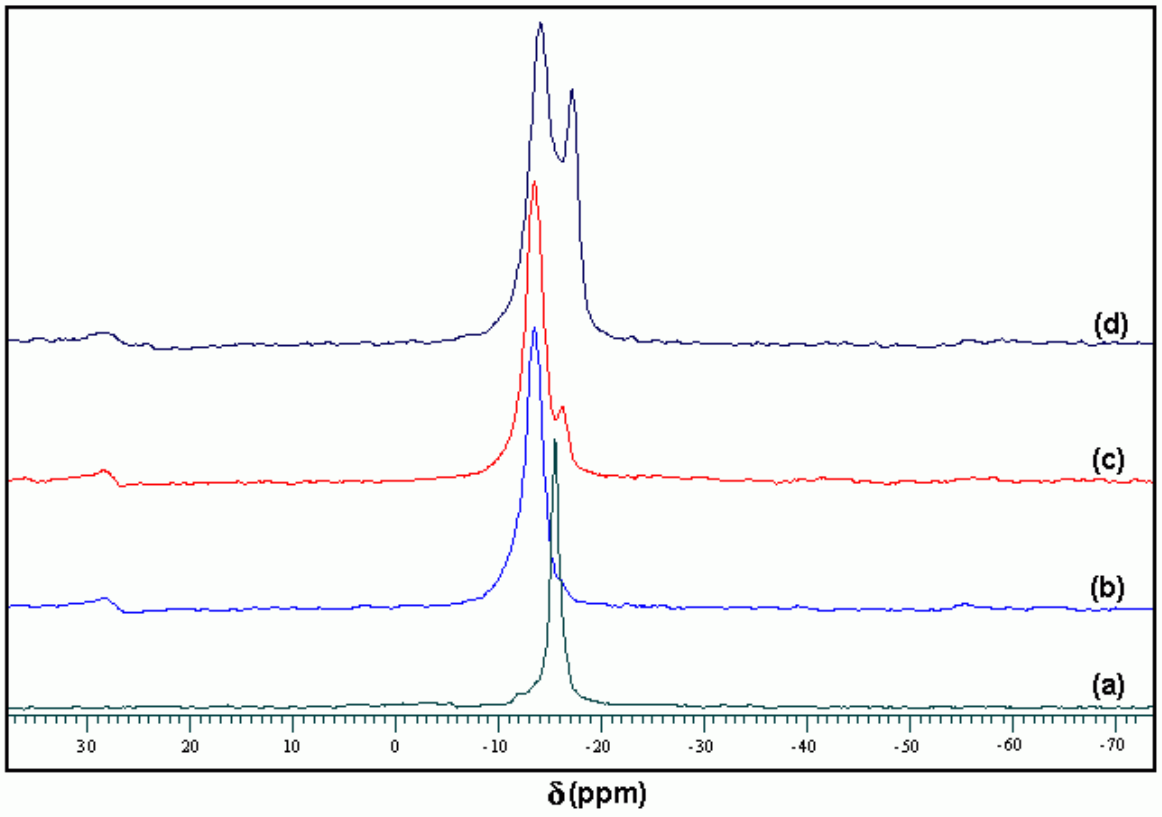
Available online 19 August 2005

Abstract

Preparation, structural characterization and solid acidity studies of $H_3PW_{12}O_{40}$ (H_3PW) supported (20, 40, 50 and 80 wt.%) on γ-alumina have been performed. Impregnation of H_3PW on γ-alumina was performed by the evaporation technique using water (acidified with HCl), ethanol and acetonitrile as solvents. The presence of the Keggin anion on alumina surface is very dependent upon the preparation conditions and pH, as indicated by partial decomposition in water solution. High acid concentration in aqueous solutions is required to obtain intact the Keggin anion. Ethanol showed the formation of distinct species on the alumina surface. In contrast, acetonitrile has not displayed any significant decomposition of the Keggin anion. All these conclusions are based on FTIR, Raman, ^{31}P MAS–NMR, XRD and SEM–EDX measurements. The presence of the Keggin structure on the alumina surface can be followed by those techniques, eliminating any doubt about collapse of the supported anion. Calorimetric and adsorption of pyridine interactions in cyclohexane slurry (Cal-ad method) showed that the catalyst H_3PW/Al_2O_3 is a weaker acid than pure H_3PW or supported on silica, but stronger than alumina. The enthalpies indicated partial neutralization of the most basic sites of alumina at the expense of the strongest protons of H_3PW.

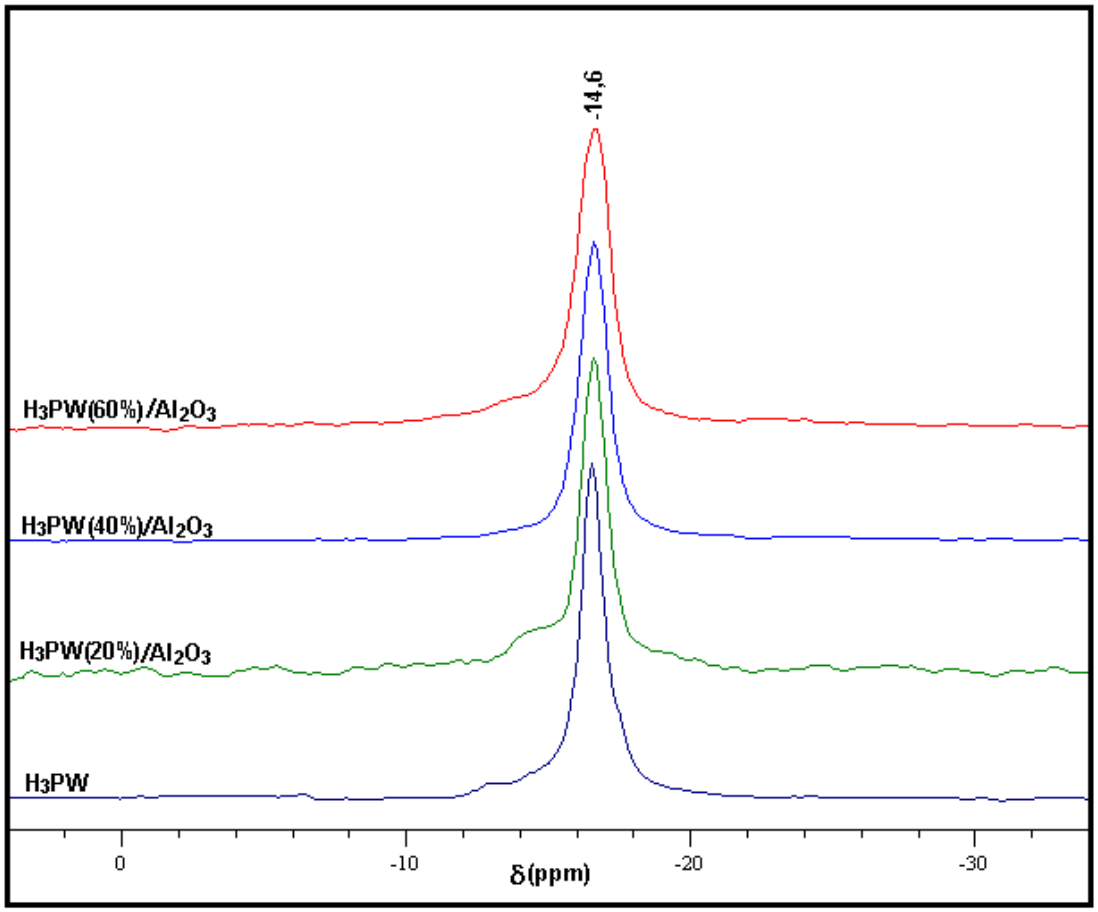
Keywords: 12-Tungstophosphoric acid; Alumina; Supported heteropolyacid; Acidity; ^{31}P MAS–NMR

Espectros de MAS-RMN de ^{31}P das amostras de H_3PW suportado em Al_2O_3, preparadas em solução aquosa ácida (HCl 0,1 mol L^{-1})

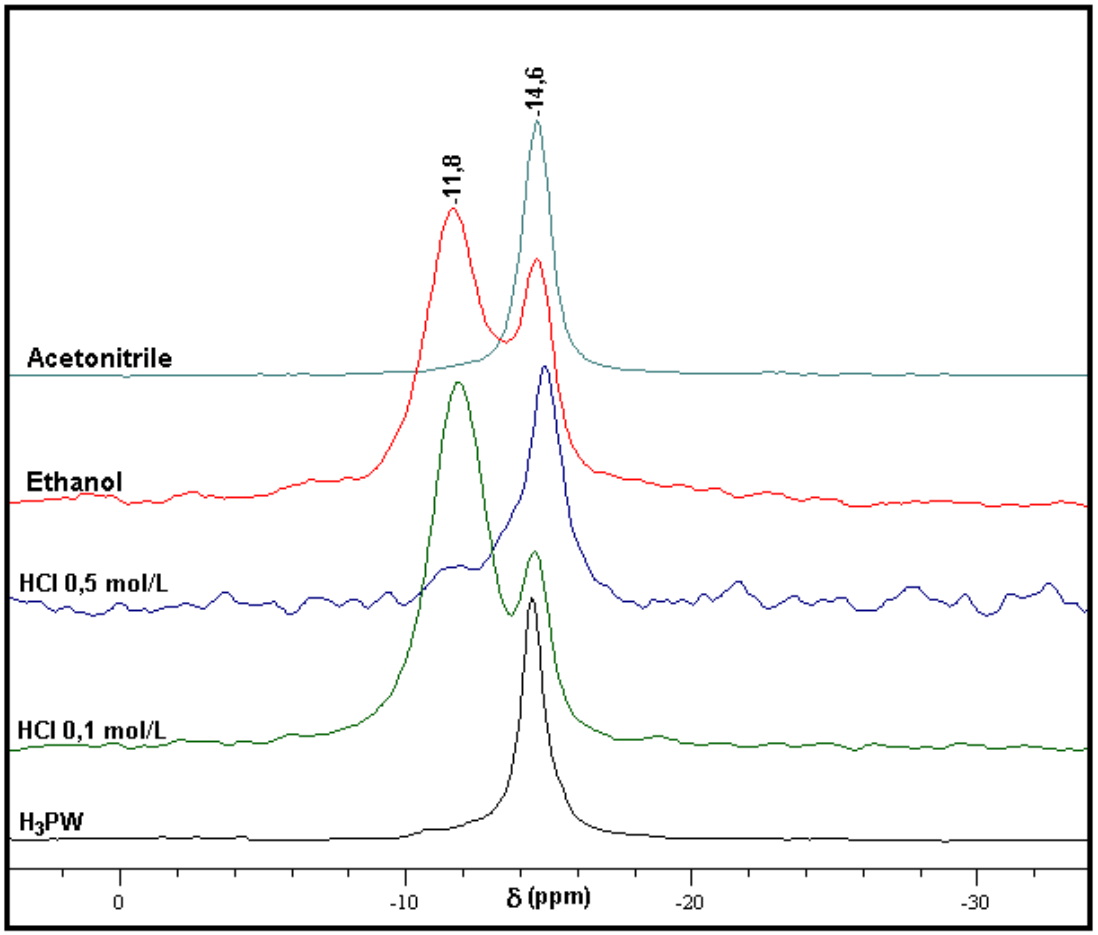


a) H_3PW hidratado; H_3PW/Al_2O_3 com: b) 20%; c) 40%; d) 50%

Espectros de MAS-RMN de ^{31}P das amostras de H_3PW suportado em Al_2O_3, preparadas em CH_3CN

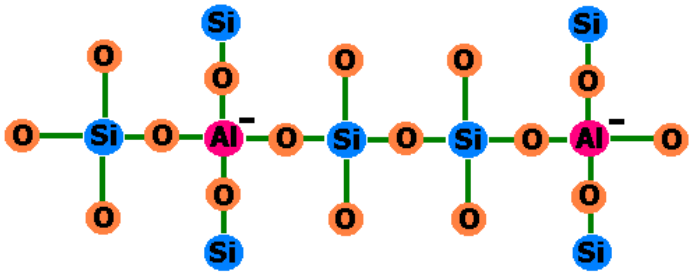


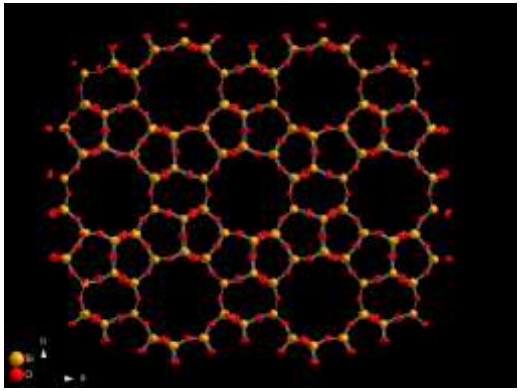
Espectros de MAS-RMN de ^{31}P das amostras de 40% H_3PW suportado em Al_2O_3, preparadas em diferentes solventes



MAS-RMN de ^{29}Si e ^{27}Al: Zeólitas

- Esqueleto cristalino formado pela combinação de tetraedros TO_4 (T = Si, Al, B, Ga, Ge, Fe, P, Co) unidos entre si através de átomos de oxigênio comuns.
- Estrutura apresenta canais e cavidades de dimensões moleculares nos quais estão os cátions de compensação, moléculas de água ou outros adsorbatos.





Zeólita ZSM-5

MAS-RMN de ^{29}Si e ^{27}Al: Zeólitas

- RMN de ^{29}Si é de grande utilidade no estudo de estruturas e superfícies de sílica gel, silicatos, aluminossilicatos (zeólitas) e cimentos hidráulicos.
- Os desvios químicos isotrópicos observados em silicatos é de cerca de 60 ppm (-60 a –120 ppm) em relação ao TMS.
- Os deslocamentos são dependentes do grau de condensação dos tetraedros Si-O.
  - Q_0 – monossilicatos = tetraedro simples
  - Q_1 – dissilicatos = tetraedro duplo
  - Q_2 – estruturas em cadeia
  - Q_3 – estruturas ciclicas em camadas
  - Q_4 – estruturas tridmensionais

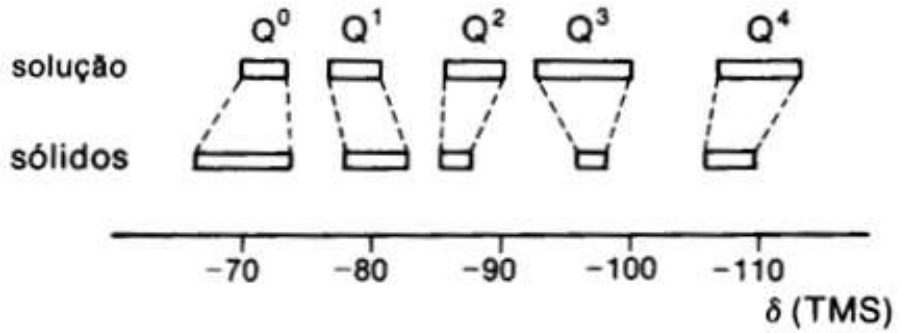


FIG. 10.46. Gama de desvios químicos do ^{29}Si para diferentes unidades estruturais de aniões de silicatos em solução e em sólidos, assim como alguns exemplos.

Exemplos						Tipo de tetraedro SiO
NaH_3SiO_4	−66,4					simples (Q^0)
$Ca_6(OH)_6[Si_2O_7]$		−82,6				duplo (Q^1)
$K_4H_4[Si_4O_{12}]$			−87,5			ciclotetra (Q^2)
$Ca_2(OH)_2[SiO_3]$ (hillebrandite)			−86,3			cadeia simples (Q^2)
$Ca_6(OH)_2[Si_6O_{17}]$ (xonotlite)			−86,8	−97,8		cadeia dupla (Q^2 e Q^3)
$Mg_3(OH)_2[Si_4O_{10}]$ (talco)				−98,1		camada (Q^3)
SiO_2 (quartzo)					−107,4	espiral (Q^4)

- Os aluminossilicatos de fórmula geral $M_{x/n}[(AlO_2)_x(SiO_2)_y]\ nH_2O$ (e.g., feldspatos, zeólitas) podem ser estudados pela combinação de RMN de ^{27}Al e ^{29}Si, obtendo-se a distribuição detalhada dos átomos de Al e Si. A coordenação do Al resulta diretamente do desvio químico no espectro de ^{27}Al.

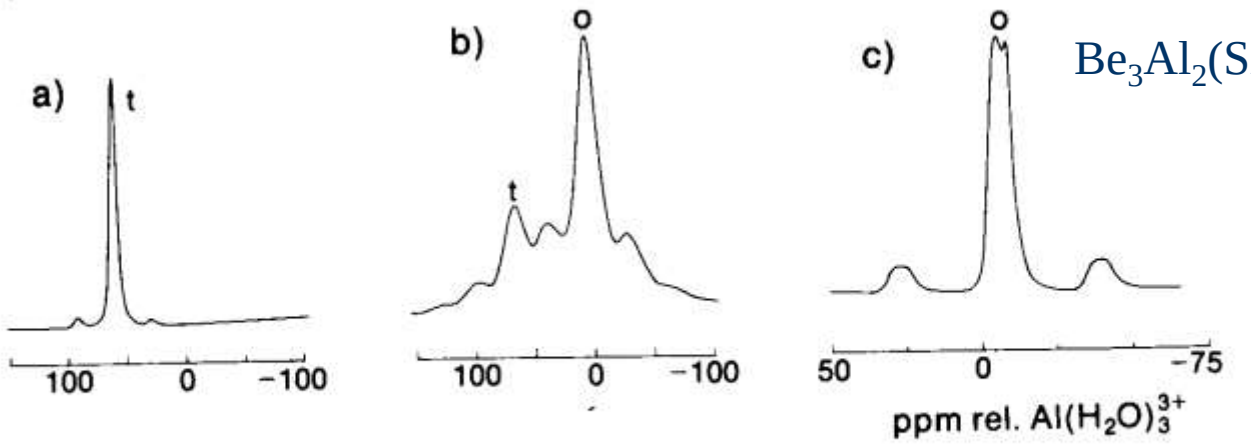


FIG. 10.47. Espectro de ^{27}Al de a) Zeolite NaY; b) Alumina; c) Berilo, t−coordenação tetraédrica, o−coordenação octaédrica (Adapt. da ref. 60).

- Os espectros de ^{29}Si mostram que os respectivos desvios químicos distribuem-se em cinco regiões distintas, correspondentes aos ambientes do Si tetraédrico Si(nAl) (n = 0, 1, 2, 3, 4), sendo *n* o número de átomos de Al (T_d) ligados ao Si (T_d).

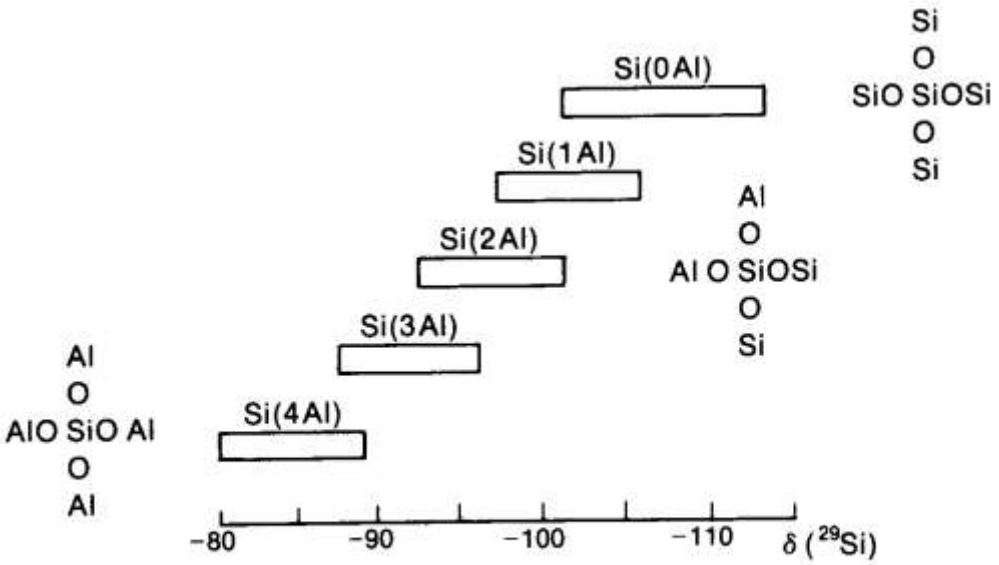


FIG. 10.48. Gama de desvios químicos para os cinco possíveis ambientes do Si em aluminossilicatos.

- Cálculo da Razão Si/Al: Regra de Lowenstein = dois átomos de Al não podem estar adjacentes (não existem ligações Al-O-Al)

$$(\mathrm{Si}/\mathrm{Al}) = \frac{\sum_{n=0}^{4} I_{\mathrm{Si(nAl)}}}{\sum_{n=0}^{4} (1/4)\, n I_{\mathrm{Si(nAl)}}}$$

Zeólita NaX

Zeólita NaY

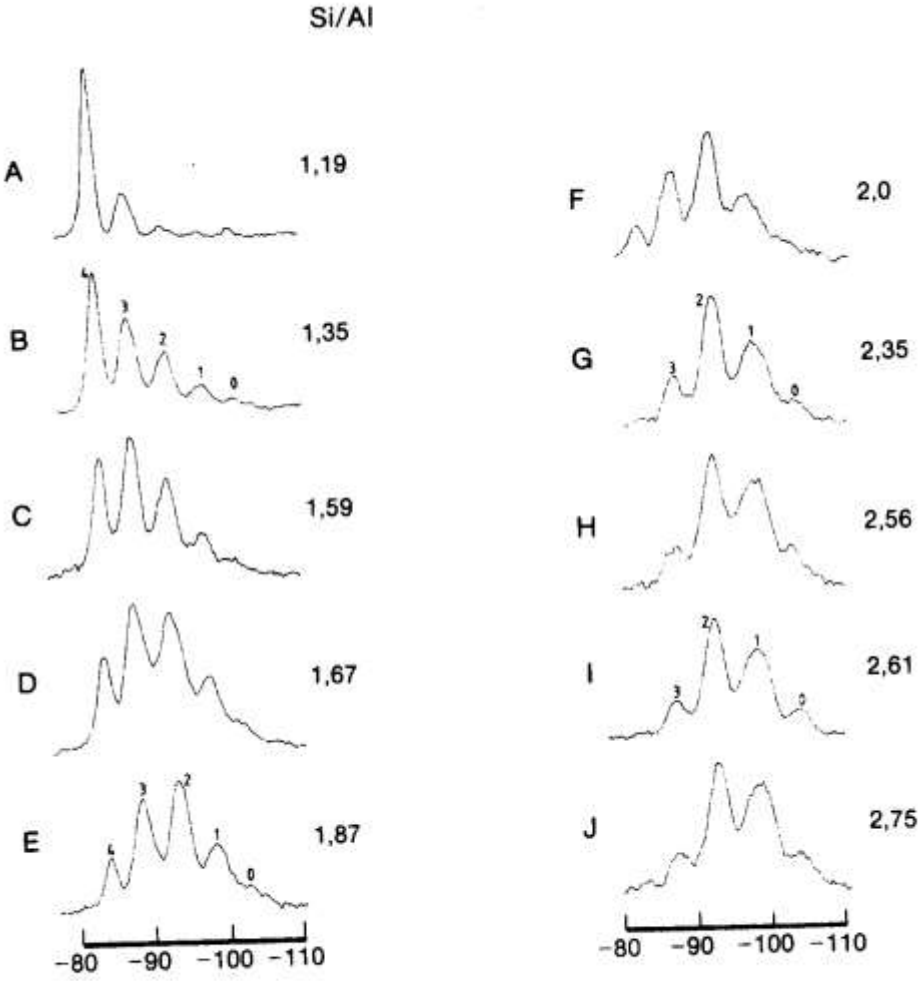


FIG. 10.49. Espectros de ^{29}Si de zeolitos do tipo Faujasite em função da razão Si/Al. A – E) zeolitos NaX; F – J) zeolitos NaY (Adapt. da ref. 60).

MAS-RMN de ^{29}Si e ^{27}Al permite estudar o mecanismo de reorganização estrutural em zeólitas calcinadas

Zeólita Y

400 °C/1 h

700 °C/ 1 h + H_2O

Troca Iônica + HNO_3

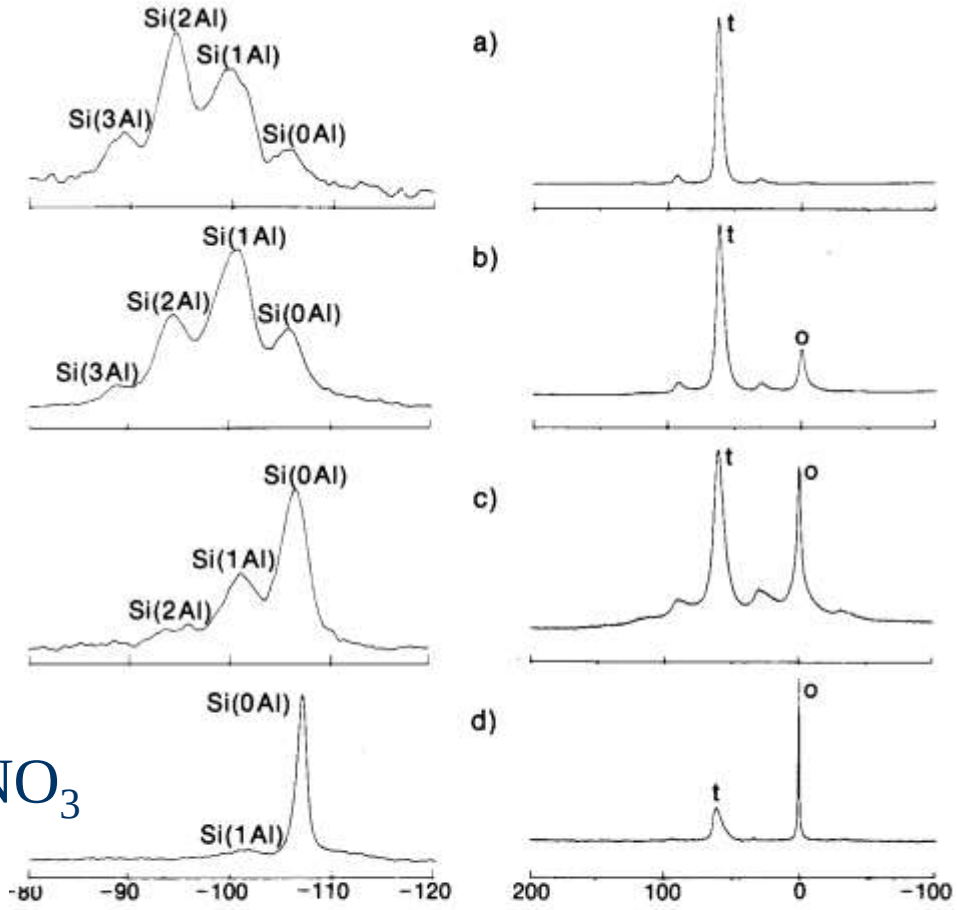


FIG. 10.50. Estudo da estabilização da zeolite Y por RMN de ^{29}Si e ^{27}Al. a) Espectro da zeolite Y; b) Após calcinação durante 1 h a 400°C; c) Após aquecimento 1 h a 700°C na presença de vapor; d) Após permuta iônica, aquecimento e lavagem com ácido nítrico (Adapt. da ref. 73).

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Multiple adsorption process description of zeolite mordenite acidity

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Abstract

Sodium and protonic exchanged mordenite zeolites were characterized by XRPD, ICP-AES, TGA/DTA, ^{29}Si and ^{27}Al solid-state NMR, FTIR, DRIFTS, and Cal–Ad (calorimetric and adsorption studies of pyridine interaction with the solid in cyclohexane slurry). To describe the acidic site of |H| [Al–Si–O]-MOR, a two site adsorption process showed the best results: 0.081 mmol g^{-1} of Brønsted sites ($\Delta H_1 = -82.9$ kJ mol^{-1}) and 0.422 mmol g^{-1} of Lewis sites ($\Delta H_2 = -36.7$ kJ mol^{-1}). These results were confirmed by FTIR experiments. In the protonic sample, only 18% of tetrahedral Al were assigned as Brønsted sites, while 56% of the sites (Brønsted and Lewis) are located in the main channels. ^{29}Si CP/MAS NMR spectra showed the presence of silanol groups and ^{27}Al MAS NMR spectra showed the presence of non-framework penta-coordinated Al species and/or non-framework amorphous silica–alumina. These species probably caused an overestimation of framework Si/Al calculation by ^{29}Si MAS NMR. The framework Si/Al ratio was calculated using ICP-AES and ^{27}Al MAS NMR, and the dealumination process was observed by both ^{29}Si CP/MAS and ^{27}Al MAS NMR.

Keywords: Mordenite zeolite; Adsorption; Calorimetry; Acidity; Cal–Ad

Cálculo da Razão Si/Al

MAS-RMN e CP/MAS-RMN de ^{29}Si

Na-MOR

H-MOR

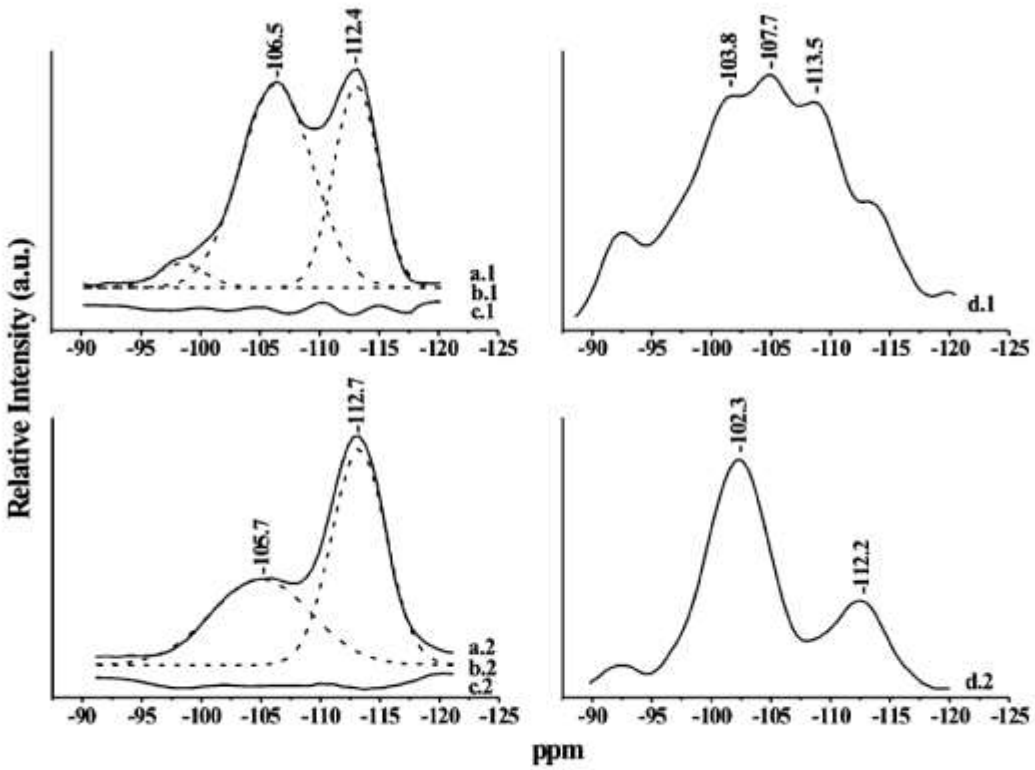
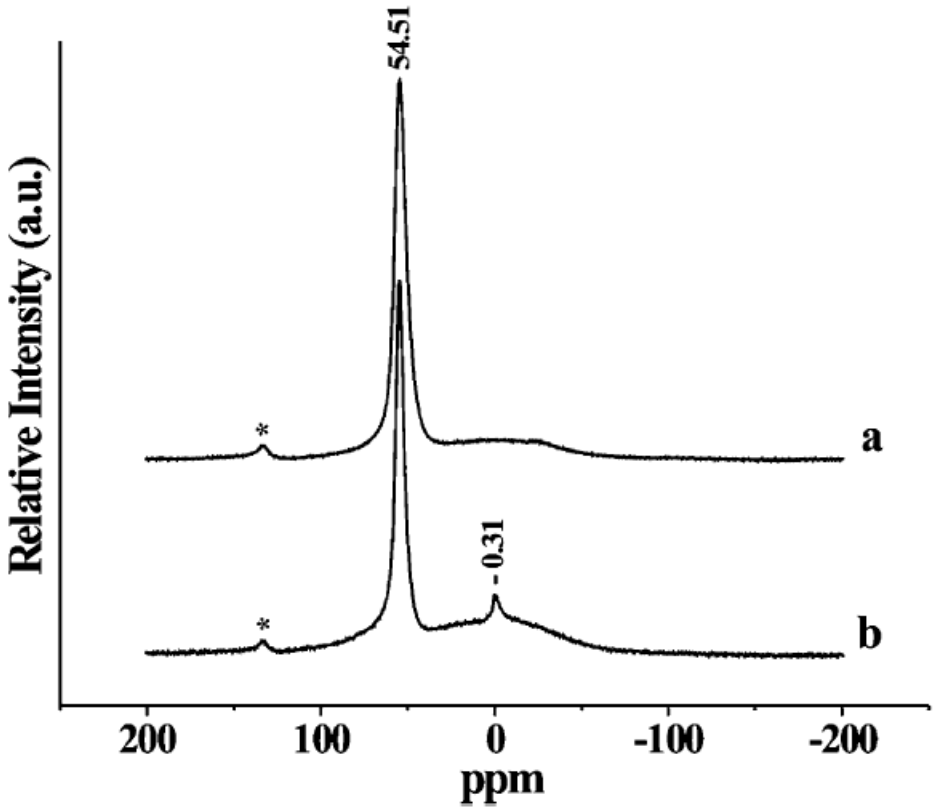


Fig. 1. ^{29}Si NMR spectra of |Na|[Al–Si–O]-MOR (1) and |H|[Al–Si–O]-MOR (2): (a) MAS, (b) deconvolution of different peaks, (c) difference between measured and deconvolved, (d) CP/MAS.

RMN de ^{27}Al



Na-MOR

H-MOR

Fig. 2. ^{27}Al MAS NMR spectra: (a) |Na| [Al–Si–O]-MOR, (b) |H| [Al–Si–O]-MOR. (∗) indicates side bands.

Table 1. Chemical and structural analyses of the samples.

Sample	$(Si/Al)_{global}$[a]	%C[b]	$(Si/Al)_{framework}$ ^{29}Si NMR deconvolved	$(Si/Al)_{framework}$ ^{27}Al NMR & ICP-AES[c]	Al_{T_d} (%)
|Na| [Al-Si-O]-MOR	6.8 ± 0.4	100.0	5.9	9.1	74.5
|H| [Al-Si-O]-MOR	16.3 ± 1.2	107.5	9.5	33.5	48.7

a. ICP-AES.
b. % of cristallinity calculated by XRPD.
c. Calculated by using equation 4.

$$(Si/Al)framework = (Si/Al)global[(IAl(tet) + IAl(oct))/ IAl(tet)] \quad (4)$$