

# The novel acid catalysts — framework zirconium phosphates: the bulk and surface structure

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## Abstract

Structural features and surface properties of framework zirconium phosphates synthesized via mechanochemical activation (MA) and sol–gel (SG) route were studied using XRD, TEM, <sup>31</sup>P MAS NMR, IR and ESR spectroscopy and compared with their catalytic performance in the reaction of hexane isomerization. A high initial isomerization activity of crystalline zirconium phosphates prepared via MA can be determined by a larger share of the strong Lewis centers probed by TEMPON test molecule. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

Framework zirconium phosphates of the NZP type have a stable flexible structure enabling to conduct homovalent as well as heterovalent cation substitution, and thus to generate both local and cooperative distortions of the lattice affecting both concentration and strength of the surface Lewis and Brönsted acid centers [1]. H-forms of framework zirconium phosphates

possessing fast proton conductivity could be considered as solid superacids [2]. Therefore, catalysts on the basis of these thermodynamically stable systems appear to be promising for the acid-catalyzed processes of hydrocarbons transformation including isomerization and alkylation.

Previous studies [3,4] showed that highly dispersed crystalline framework zirconium phosphates could be prepared hydrothermally in the presence of polyethylene oxide (PEO) from precipitated amorphous sols or water suspensions of the products of mechanical activation (MA) of the solid salts mixtures. This paper reports

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results of studying the main structural features of a basic  $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$  system and that modified by La obtained at different pH both via MA route and sol–gel method followed by hydrothermal treatment (HTT) and comparing ones with their surface properties and catalytic performance in the reaction of hexane isomerization.

## 2. Experimental

Starting materials and some synthesis parameters are presented in Table 1. Two series of samples were prepared using a traditional sol–gel method (SG) and MA. The procedures of preparation were the same as in previous reports [3]. To prepare SG samples, a solution of

$\text{ZrO}(\text{NO}_3)_2$  was titrated with a stoichiometric volume of  $(\text{NH}_4)_2\text{HPO}_4$  or  $\text{NH}_4\text{H}_2\text{PO}_4$ , while the solution was constantly stirred. As a result, the gelatinous amorphous precipitate was obtained and further washed with deionized water. In MA series, the stoichiometric mixture of starting compounds (Table 1) were activated in the high power EI-2  $\times$  150 mill. Suspensions of sols and activated mechanical mixture in distilled water with addition of polyethylene oxide (PEO) and  $\text{HNO}_3$  to regulate pH were loaded into teflon-lined Parr acid-digestion bombs and kept at 175–200°C for 5–7 days. For sample MA-2\*, pH was low as a result of using in starting mixture  $\text{NH}_4\text{H}_2\text{PO}_4$  (Table 1). After HTT, solids were washed with ethanol and distilled water, dried at 120°C and calcined at 400°C.

Table 1  
Parameters of synthesis and some properties of samples calcined at 400°C

Sample <sup>a</sup>	Starting compounds	pH before HTT	Specific surface ( $\text{m}^2/\text{g}$ )	Phase composition by X-ray diffraction
SG-6	$\text{ZrO}(\text{NO}_3)_2$ $(\text{NH}_4)_2\text{HPO}_4$	5	130	Amorphous + $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ cubic (traces)
SG-7	–	1	28	$\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ rhombohedral
SG-7# <sup>b</sup>	–	1	33	$\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ rhombohedral + layer and unknown phases
SG-8	–	3	114	amorph. + $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ rhombohedral
MA -2	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} (\text{NH}_4)_3$	7	60	$\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ cubic + orthorhombic phase
MA -2*	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ $\text{NH}_4\text{H}_2\text{PO}_4$	1	39	$\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ rhombohedral + $\text{LaPO}_4$
MA-3	$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ $\text{ZrO}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O}$ $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$	7	67	$\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ cubic + orthorhombic phase
MA -5	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$	7	40	$\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ cubic + orthorhombic phase <sup>c</sup>
MA -5*	–	1	9	$\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ rhombohedral

<sup>a</sup>SG — samples prepared via sol–gel method, MA — ones prepared via mechanochemical activation.

<sup>b</sup>Sample was prepared using unwashed sol.

<sup>c</sup>Sample contains admixture of layered acid zirconium phosphate and, after calcination at 400°, a small amount of  $\text{ZrP}_2\text{O}_7$ .

The phase composition of samples was examined by the X-ray diffraction method combined with the infrared spectroscopy. The microstructure of samples was studied using transmission electron microscopy (TEM, Jeol 200 C, 200 kv).  $^{31}\text{P}$  MAS NMR (CXP-300 Bruker spectrometer, 121.47 MHz, 3.2 MHz spinning rate) was used to characterize a local coordination of phosphate groups [3]. Surface properties were probed as in Ref. [4] by the IR spectroscopy of surface hydroxyls (Brönsted acid centers) and CO test molecule adsorbed at coordinatively unsaturated cations — Lewis acid centers. To measure concentrations of the most strong Lewis acid centers TEMPON test molecule was adsorbed from hexane solution, and ESR spectra were acquired using a ERS 221 spectrometer [5].

Catalytic transformation of n-hexane in the range of 250–550°C was studied in a pulse and flow regime using a flow reactor loaded with 0.05–0.5 g of catalyst pretreated in the nitrogen flow at 450°C for 30 min. In pulse mode, 1 mL of hexane was fed into the flow of nitrogen at velocity of 20–40 cm<sup>3</sup>/min. For the flow regime, the reaction mixture (H<sub>2</sub>/hexane = 4:1) feed was 8.3 cm<sup>3</sup>/min. The product gases were analyzed by GC.

### 3. Results and discussion

#### 3.1. The phase composition and bulk structure

For La-containing SG samples, in acid suspensions, orthorhombic zirconium hydroxo-orthophosphate  $\alpha\text{-ZrPO}_4(\text{OH})$  is formed [3]. As follows from the data presented in Table 1, undoped SG samples prepared at low pH contain crystalline  $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$  phase of the rhombohedral type. Therefore, for sol-gel samples, phase-pure  $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$  is formed during HTT only if suspension of the washed sol with pH  $\sim 1$  was used (sample SG-7). According to XRD and IR data, SG-7# sample prepared at the same pH from the unwashed sol, besides rhombohedral  $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$  phase,

contains also a layer acid zirconium phosphates of the  $\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$  type as deduced from the presence of diffraction peak corresponding to interlayer distances  $\sim 8\text{--}9 \text{ \AA}$  and a narrow IR band at 1223 cm<sup>-1</sup> attributed to bulk acidic phosphate groups. In the XRD pattern, a number of the low intensity reflexes is also present testifying the admixtures of unknown phases. The increase of pH during HTT reduces the amount of crystalline phase and gives rise to amorphous phase as was revealed in broadening of the phosphate group absorption band at  $\sim 1050 \text{ cm}^{-1}$ . According to EXAFS data, X-ray amorphous samples prepared at pH 5 possess a disordered structure, which was reflected in the decrease of the Zr–O and Zr–P coordination numbers [4]. However, even in such samples, TEM revealed the admixture of crystalline phase presented as thin needles.

Dispersed crystalline samples are easily obtained even at pH  $\sim 7$  via HTT of suspensions of MA products in the presence of PEO. This feature is explained by formation of zirconium phosphate nuclei in the course of solids activation [3].  $^{31}\text{P}$  MAS NMR characteristics of phosphate groups, namely, emergence of several equidistant lines after MA (Fig. 1), indicate a step-wise change of their coordination environment due to interaction with zirconium cations. As a result, after HTT the cubic phase of the

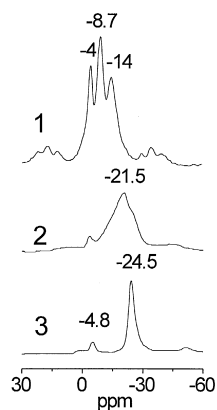


Fig. 1.  $^{31}\text{P}$  MAS NMR spectra for MA-2 (1) and MA-2\* (2,3) prepared at different pH at various stages of synthesis. 1,2 — after mechanical activation. 1,3 — after hydrothermal treatment.

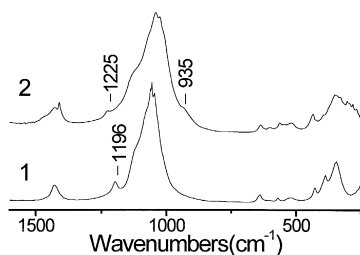


Fig. 2. IR spectra of the samples MA-5 (1) and MA-5\* (2) after hydrothermal treatment.

$\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$  type along with admixtures of high-pressure orthorhombic  $\beta\text{-Zr}(\text{OH})\text{PO}_4$  phase are formed. It can be due to specific mechanism of crystallization during HTT of MA product suspensions proceeding at neutral pH via stacking of primary particles dispersed in water [3]. It should be mentioned that sample without La (MA-5) also contains admixtures of layered acid zirconium phosphates as judged by the presence of a low-angle XRD reflex corresponding to  $d \sim 11 \text{ \AA}$  and IR absorption bands of acidic phosphate groups at  $1225$  and  $935 \text{ cm}^{-1}$  (Fig. 2).

HTT of suspensions of mechanically activated mixtures of salts at low pH yields rhombohedral  $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$  phase as in the case of SG method. For La-containing MA-2\* sample, provided acid ammonium phosphate was used in the starting mixture, even at the stage of MA, a broad  $^{31}\text{P}$  NMR peak at  $-21.5 \text{ ppm}$  typical to  $\text{HPO}_4^{3-}$  group in the layer acid zirconium phos-

phate [6] was developed (Fig. 1). A similar peak was detected for sol obtained at low pH. It implies that in strongly acidic media, formation of crystalline phase proceeds via the same dissolution–precipitation mechanism for both sols and MA products.

According to EXAFS data, for all samples, a mean Zr–O distances are in the range of  $\sim 2.06 \text{ \AA}$ . For samples of cubic structure, Zr–O coordination numbers were found to be lower as compared with those typical for the rhombohedral samples (6.7 and 8, respectively) thus evidencing a greater degree of Zr–O polyhedra disordering. For cubic samples without La, the appearance of the Zr–Zr distances at  $2.9 \text{ \AA}$  corresponding to Zr cations in positions of Na in the parent  $\text{Na}_2\text{Zr}_4\text{P}_6\text{O}_{24}$  structure, also evidences a site occupation disordering. In contrast, for samples with the cubic structure, Zr–P coordination numbers (at  $\sim 3.63 \text{ \AA}$  distance) approach values typical for high-temperature NZP samples [7]. In La-containing samples of the cubic structure (MA-2, MA-3), phosphate groups are in general not acidic and situated in a rather symmetric environment. For sample without La (MA-5), IR band of phosphate groups (Fig. 2) as well as  $^{31}\text{P}$  MAS NMR peaks [3] are split, evidencing variation of their cationic environment and the presence of considerable amount of acidic phosphate groups. Such acidic groups are absent in samples of rhombohedral

Table 2  
The density of Lewis centers and activity of the samples in hexane isomerization

Sample	Lewis centers concentration $\text{mol CO/m}^2 \cdot 10^{17}$ (IRS)	Share of SLC <sup>a</sup>	$X_{\text{pulse}}$ (%) 450°C	Yield <sub>pulse</sub> of isomers (2,3-DMB + 2-MP) (%)	$X_{\text{flow}}$ (%) 550°C
MA-2	1.6	0.25	64 <sup>b</sup>	53	48
MA-3	1.44	0.42	90	90	30
MA-5	0.78	0.83	91	90	30
SG-6	5.5	0.16	50	50	30
SG-7	7.7	0.1	40 <sup>c</sup>	40	75
SG-8	7.1	0.17	40	40	22

<sup>a</sup>The ratio of the densities of Lewis acid sites estimated by ESR and IRS.

<sup>b</sup> $\text{C}_6\text{H}_6$  formed (selectivity 14%).

<sup>c</sup>550°C.

structure as judged by IR (Fig. 2) and  $^{31}\text{P}$  MAS NMR (Fig. 1) data.

### 3.2. Surface properties and catalytic activity

For all samples, no universal correlation between isomerization activity or selectivity and the densities of Lewis or Brönsted acid sites estimated by FTIRS was found. Hence, activity was suggested to be determined by the strongest Lewis centers (SLC) probed by ESR of nitroxide molecules [5]. In Table 2, the concentration of Lewis centers estimated by IRS of CO adsorbed at  $\text{Zr}^{4+}$  and the share of SLC determined as the ratio of the densities of Lewis centers estimated by ESR and IRS as well as the activity of samples in pulse and flow regime are presented. In general, MA samples of cubic structure possess a lower density of acid sites, that can be explained by a higher coordination number [4], i.e., higher degree of bulk and surface coordination saturation. Meanwhile, the share of SLC probed by the TEMPON molecule for MA samples is higher than that for SG samples being dependent upon composition of starting materials (Table 1). For crystalline samples, the initial activity ( $X_{\text{pulse}}$ ) increases with the density of SLC, while the steady-state hexane conversion ( $X_{\text{flow}}$ ) declines. This trend can be explained by the surface coking favored by SLC. The most effective catalyst for isomerization of hexane in the flow regime is MA-2 showing the highest yield of isomers  $\sim 11\%$ . Among sol–gel samples, crystalline SG-7 of rhombohedral type structure has the highest  $X_{\text{flow}}$  and cracking selectivity, whereas isomerization selectivity is rather low.

## 4. Conclusions

Framework zirconium phosphates structural features and surface properties were studied and compared with catalytic performance in the reactions of hexane isomerization. The high initial isomerization activity of crystalline zirconium phosphates prepared via MA can be determined by the larger share of the strong Lewis centers probed by TEMPON test molecule.

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## References

- [1] J. Alamo, R. Roy, *J. Mater. Sci.* 21 (1986) 444–450.
- [2] J.B. Goodenough, H.J. Hong, J.A. Kafalas, *Mater. Res. Bull.* 11 (1976) 173.
- [3] V.A. Sadykov, S.N. Pavlova, G.V. Zabolotnaya, R.I. Maximovskaya, S.V. Tsubulya, E.B. Burgina, V.I. Zaikovskii et al., *Mater. Res. Innov.* 2 (1999) 328.
- [4] V.A. Sadykov, S.N. Pavlova, G.V. Zabolotnaya, D.I. Kochubei, R.I. Maximovskaya, V.I. Zaikovskii, S.V. Tsubulya et al., in: *Adv. Catal. Mater.*, P.W. Lednor, D.A. Nagaki, L.T. Thomphson (Eds.), *Mater. Res. Soc. Symp. Ser.* 549/1999.
- [5] V.A. Bolshov, A.M. Volodin, G.M. Zhidomirov, A.A. Shubin, A.F. Bedilo, *J. Phys. Chem.* 98 (1994) 7551.
- [6] N.J. Clayden, *J. Chem. Soc., Dalton Trans.* (1987) 1877.
- [7] S.N. Pavlova, V.A. Sadykov, E.A. Paukshtis, E.B. Burgina, S.P. Degtyarev, D.I. Kochubei, N.F. Saputina, A.V. Kalinkin, R.I. Maximovskaya, V.I. Zaikovskii, R. Roy, D. Agrawal, *Stud. Surf. Sci. Catal.* 119 (1998) 759.