Journal of Thermal Analysis and Calorimetry, Vol. 85 (2006) 2, 329–333

THERMAL TREATMENT ON COMPOSITE γ-ZIRCONIUM PHOSPHATE-SILICA

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The prepared amorphous γ-ZrP\$SiO_2$ composite had a complicated composition, since a part of γ-ZrP is converted to α-form during the exfoliation of it. The γ-ZrP\$SiO_2$ composite have specific surface area of 421 $m^2 g^{-1}$. The acidic P–OH groups of the lamellae species placed on the surface (it is ≈1.0 meq g^{-1}), do not destroy until the temperature of 1030 K. During the thermal treatment the total mass loss of 7.79% was found. This value corresponds to 0.42 mole of H_2O per molecule unit. The water loss process was found very slow, because of the placing of bilamellar species in the composite.

Keywords: *phosphate, silica, thermal analysis, zirconium*

Introduction

The inorganic ion exchangers had own interest in fifties in nuclear industry, because of their extremely good resistance against ionisation radiation. These materials were generally amorphous. Among them the zirconium phosphate (hereafter α-ZrP) had favoured interest. Later, in 1964 α-ZrP was synthesised in crystalline form and its layered structure was investigated in detail [1]. In the following years this material was widely investigated by various laboratories. The scope of these works became clear that α-ZrP are of interest as acid catalyst, especially due to the presence of acid P–OH groups on the structure surface [2, 3]. Connection with this recognition many researches were already been carried out between 1979–2000. The greater part of the mentioned works initially restricted to amorphous [4, 5], and then to crystalline α-ZrP [6–13].

Relatively little consideration has been given to layered γ-zirconium phosphate (hereafter γ-ZrP), to the other crystalline modification of zirconium phosphate, although it was known since 1968 [14]. The reason could be that its structure and chemical formulation elucidated recently [15]. To use these materials as catalyst in reactions going at a relatively higher temperature there are necessary to know their thermal behaviour. In connection with this item there was found only few works [16–19]. Only Yamanaka *et al.* reported its use as a catalyst [20, 21].

One of the problems of using layered zirconium phosphates as acid catalyst, is their low specific surface area. To increase the surface was prepared composite on SiO_2.

In this paper presented the data corresponds to the thermal treatment of this composite in comparison with that of for α-ZrP and γ-ZrP.

Experimental

Sample preparation

The composition γ-ZrP\SiO_2 was prepared as follows: 100 cm^3 of the exfoliated γ-ZrP dispersion was added, at room temperature, under vigorous stirring, to 10 g of silica solution and then coagulation was obtained by rapidly adding 0.1 M acetic acid (0.34 cm^3 for 1 g of silica solution). The gel was first dried at 353 K, then calcified overnight remove organic material [22].

Methods

The powder diffraction patterns were recorded using a computer controlled powder diffractometer (DRON-2). The measurements were performed with a goniometer speed of 1° cm^{-1}, and β-filtered CoK_α radiation (λ=1.7890), in the range of 2θ=3–110° at 295 K temperature (exception of γ-ZrP/SiO_2 composite, in this case the measurement was finished at 2θ=60). The powder diffraction patterns were evaluated by 'EXRAY' peak searching software [23].

The specific surface area of the samples was determined by the so called 'dynamic' method, using Chrompac 9001 type gas chromatograph as follows:

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1388–6150/$20.00

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100 mg of sample was placed in a gas stream of H_2(30%)+N_2(70%) at 78 K. The gas adsorption was measured then the apparatus was heated to 298 K and the gas desorption is determined. The surface area value was obtained by three adsorption/desorption cycles. The accuracy of the measurement was ~0.5%.

The Hamett acidity of the samples was determined by amine titration method as described previously [22].

Solid State ^{31}P NMR investigations were carried out by NMR service at ISRIM (Terni) with Varian 400 type spectrometer: The spectra were obtained at 161.9 MHz, and they were referenced to 80% H_3PO_4.

Thermal analysis were carried out in a temperature range of 298–1200 K, with a Mettler TA-1-HT computer controlled thermobalance that simultaneously provided DTA and TG data. The heating rate was chosen 278 K min^{-1}, the reference material was Al_2O_3, ambience: air and the experiments were carried out in Pt crucible. The data were evaluated by means of computer software.

Results and discussion

The majority of the particles (~85%) were found in sizes of 5–15 μm.

Based on analytical data, for the γ-ZrP/SiO_2 composite the following composition was found:

Component	Molar composition	Mass of the comps./g g^{-1} composite
γ-$\mathrm{ZrPO_4[O_2P(OH)_2]_{0.3}}$ $\mathrm{[O_2(OH)P{-}O{-}P(OH)O_2]_{0.25}}$	$1.10\cdot10^{-3}$	0.29
α-$\mathrm{Zr(HPO_4)_2}$	$2.80\cdot10^{-4}$	0.08
SiO_2	$1.10\cdot10^{-2}$	0.63
total	–	1.00

Figure 1 shows the XRD patterns of γ-ZrP/SiO_2 composite in comparison with that of the α- and γ-ZrP-s, and with the latter in calcined form (c). Evaluate the peaks of XRD pattern of α-ZrP (a) we found monoclinic structure with cell parameters of a=0.981, b=0.551, c=1.521 nm and β=110°. The calculated interlayer distance was 0.756 nm. The same evaluation of curve (b) result also monoclinic structure with cell parameters of a=0.559, b=0.864, c=2.531 nm and β=101°. The calculated interlayer distance of 1.22 nm, was found, while that is for calcined form was found to 0.88 nm. Against them the XRD pattern of γ-ZrP/SiO_2 composite showed any peak in range of 2θ=5–60°.

Since a completely amorphous material was found, it can be concluded that the greater part of γ-ZrP is present as monolamellar species or packets of only few lamellae. The peak found at low angle could be related to fact that the dispersion of γ-ZrP lamellae maintains a certain degree of order in SiO_2. In other words the γ-ZrP/SiO_2 composite could be seen as SiO_2 intercalated γ-ZrP. In any case, the composite could have a complicated composition (see above), since it is known that exfoliated γ-ZrP can partially transformed in stable α-crystalline form ZrP [2].

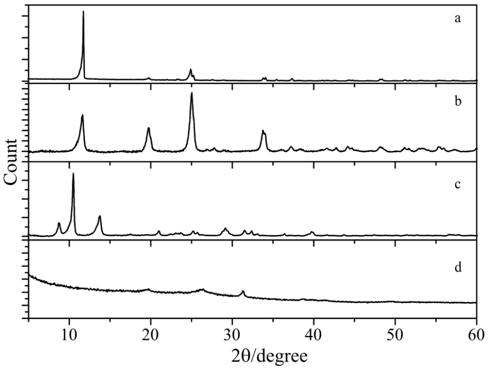

Fig. 1 A fragment of X-ray powder diffraction pattern of the investigated samples; a – α-$\mathrm{Zr(O_3P{-}OH)_2\cdot H_2O}$, b – γ-$\mathrm{ZrPO_4[O_2P(OH)_2]\cdot 2H_2O}$, c – γ-ZrP$_{\mathrm{calc.}}$ and d – γ-ZrP\\$SiO_2$composite

Useful information on the nature of the phosphate species present in the composite was obtained by solid-state NMR investigations. The ^{31}P MASNMR spectrum of the composite was quiet complex. Comparing the spectra of γ-ZrP/SiO_2 composite (Fig. 2a) and the thermally treated γ-ZrP (Fig. 2c) with that of the γ-ZrP (Fig. 2b), and taking into consideration of given literature data concerned to α-ZrP [24, 25] the two peaks centred at –9 and –14 ppm were assigned to $\mathrm{O_2P(OH)_2}$ groups in several different environments, while the peak at –28 ppm was due to inner PO_4 groups of γ-ZrP. The resonance with peak at –22.8 ppm can be assigned to $\mathrm{O_3{-}P{-}OH}$ groups of α-ZrP, while the other peak at –29.7 ppm and also the smaller peak at about –39 ppm can be assigned to acid pyrophosphate groups of lamellar zirconium phosphate are in different environment.

The relative percentages of the phosphate species estimated from the intensities of above peaks were: $\mathrm{O_3P{-}OH}$ (21%), $\mathrm{O_2P(OH)_2}$ (19%), $\mathrm{O_2(OH)P{-}O{-}P(OH)O_2}$ (20%) and PO_4 (40%). Based on these data may be concluded that during the process of insertion of γ-ZrP lamellae in the silica, about 20% of the original γ-$\mathrm{ZrPO_4.O_2P(OH)_2}$ crystalline form is transformed into α-$\mathrm{Zr(O_3P{-}OH)_2}$. Furthermore, the ratio (~1:1) between $\mathrm{O_2P(OH)_2}$ and $\mathrm{O_2(OH)P{-}O{-}P(OH)O_2}$ groups strongly indicated that γ-ZrP is essentially dispersed in silica as bilamellar packets of composition $\mathrm{ZrPO_4[O_2P(OH)_2]_{0.5}[O_2(OH)P{-}O{-}P(OH)O_2]_{0.35}}$. Comparing the above data and the results of acidity measurements can be assumed that the acidic surface P–OH groups of the lamellar species (~1.0 meq g^{-1}) do not destroyed up to temperature of 1030 K.

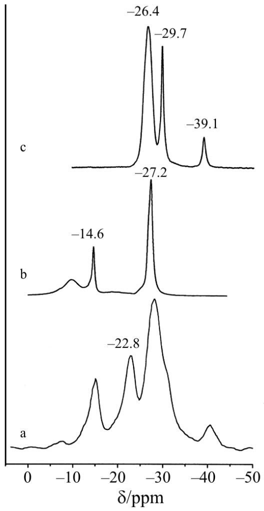

Fig. 2 ^{31}P MAS NMR spectra of the investigated samples; a – γ-ZrP\SiO$_2$ composite, b – γ-ZrP and c – γ-ZrP$_{\text{calc.}}$

The specific surface areas of 1.7, 7.1, 11.8 and 421 m^2 g^{-1} were found for α-ZrP, γ-ZrP, γ-ZrP$_{\text{calc.}}$ and γ-ZrP/SiO$_2$ composite, respectively. Taking into consideration the surface area and NMR data it is possible to estimate the specific surface attributable to the bilamellar γ-ZrP and monolamellar α-ZrP contained in 1 g of composite. They are 112 and 79 m^2 g^{-1}, respectively. Further we conclude, that the difference between them and the experimentally measured value (421 m^2 g^{-1}) is attributable to the surface of silica. If taking into account that 1 g of composite contains 0.6 g of silica, then 1 g of silica dispersed in composite have a surface of 387 m^2. Since, the specific surface area of silica 170 m^2 g^{-1}, in the composite both silica and γ-ZrP increased their surface because it can be estimated that in the bilamellar compound, (the lamellar γ-ZrP and the silica) have reciprocal effect. The specific surface area of lamellar compound is increased because the silica prevents the lamellar aggregation of exfoliated lamellae, while the specific surface area of silica is also increased because the dispersed γ-ZrP prevent the aggregation of nano-particles of silica.

The thermal behaviour of γ-ZrP/SiO$_2$ composite was investigated in comparison with that of the α-ZrP, γ-ZrP and γ-ZrP$_{\text{calc}}$, respectively.

In case of α-ZrP (Fig. 3) four, well defined processes were distinguished, in the temperature range of 383–501 K, 501–527, 813–1008 and 1173–1373 K, respectively. From them the first three were endothermic (the second without mass loss), while the last one is exothermic.

The above enlisted processes can be interpreted as follows: the first endothermic process can be ascribed to the loss of crystal water (it was calculated one mole H$_2$O per molecule unit), the second endothermic process, without mass loss, concerned to the conversion of ξ-ZrP phase to η-ZrP phase (with interlayer distance of 0.720 nm). The third endothermic process can be assigned to the loss of structural water, originated from the decomposition of phosphate groups. The last, exothermic process belongs to the change of ZrO$_2$ structure from monoclinic to orthorhombic. Based on the above interpretation the thermal decomposition of α-ZrP can be described as follows:

$$\mathrm{Zr(O_3P{-}OH)_2{\cdot}H_2O \xrightarrow{-H_2O} Zr(O_3P{-}OH)}$$
$$\mathrm{\xrightarrow{\text{phase transition}} Zr(HPO_4)_2 \xrightarrow{-H_2O} ZrP_2O_7}$$
$$\mathrm{\xrightarrow{\text{decomposition}} ZrO_2.P_2O_5}$$
$$\xrightarrow{\qquad} \text{phase transition of } \mathrm{ZrO_2}$$

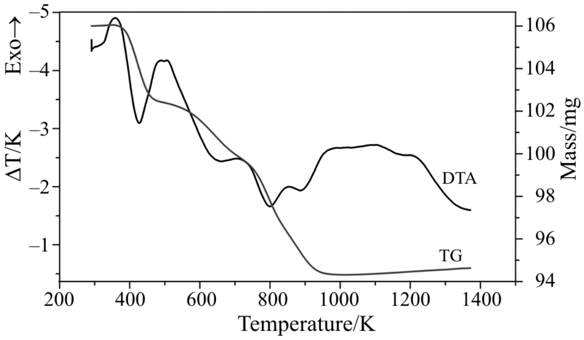

Fig. 3 DTA and TG curves of α-Zr(HPO$_4$)$_2$·H$_2$O

In case of γ-ZrP (Fig. 4), in the temperature range of 320–445, 445–555, 735–910 and 910–1200 K there were found five well distinguished processes. From them the first two endothermic processes can be assigned to the loss of crystal water (it was calculated two mole of H$_2$O per molecule unit). The third one due to the loss of one mole of water, originated from the process of resulting acidic pyrophosphate group, while the fourth endothermic process can be described the following process going between the temperature range of 910–1200 K:

$$\mathrm{ZrPO_4{\cdot}O_2P(OH)_2 \rightarrow}$$
$$\mathrm{ZrPO_4[O_2(OH)P{-}O{-}P(OH)O_2]{\cdot}0.5H_2O}$$

After 1200 K the γ-zirconium phosphate acid pyrophosphate (interlayer distance is 0.82 nm) is then immediately transformed into cubic ZrP$_2$O$_7$. Based on

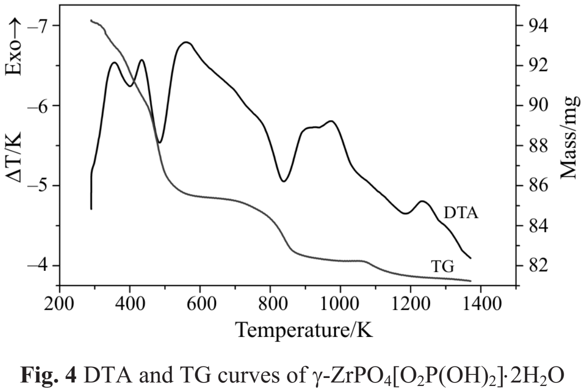

Fig. 4 DTA and TG curves of γ-ZrPO$_4$[O$_2$P(OH)$_2$]·2H$_2$O

the above interpretation the thermal decomposition of γ-ZrP can be described as follows:

$$\mathrm{ZrPO_4[O_2P(OH)_2]\cdot 2H_2O} \xrightarrow{-\mathrm{H_2O}} \mathrm{ZrPO_4[O_2P(OH)]\cdot H_2O}$$
$$\xrightarrow{-\mathrm{H_2O}} \mathrm{ZrPO_4[O_2P(OH)_2]}$$
$$\xrightarrow{-\mathrm{H_2O}} \mathrm{ZrPO_4[O_2(OH)P{-}O{-}P(OH)O_2]_{0.5}\cdot 0.5H_2O}$$
$$\xrightarrow{-0.5\mathrm{H_2O}} \mathrm{ZrP_2O_7} \xrightarrow{\text{decomposition}} \mathrm{ZrO_2\cdot P_2O_5}$$

The γ-ZrP calcined at 923 K for 24 h showed the same thermal behaviour as γ-ZrP/SiO$_2$; i.e. in this case were found only the processes exist at about 900 K and higher. In case of γ-ZrP/SiO$_2$ composite (Fig. 5) one endothermic process was found in temperature range of 310–440 K with mass loss. It was followed a continuous mass loss, and in parallel the DTA curve do not showed any other endotherm processes. At least, an exotherm process at about 1250 K, was checked. Knowing the composition of the γ-ZrP\SiO$_2$ composite we assigned the found process to the water loss. The total mass loss to 7.79% was found. Making the appropriate calculations this value corresponds to 0.42 mole of H_2O per molecule unit; this is in correlation, inside the error of measurement, with theoretically existing value. As we found the main part of this crystal water is lost at higher temperature, than that of usual for such process. The remained trace of this water is lost very slow until a high temperature. The fact can be connected with the difficult composition of the composite. Such nature of the mass loss process can be in correlation with the structure of the investigated material; namely, with the position of lamellar species of γ-ZrP in the composition.

At least, the checked exotherm process between 1200–1260 K can be assigned to the crystalline transfer of ZrO$_2$ from monoclinic to orthorhombic.

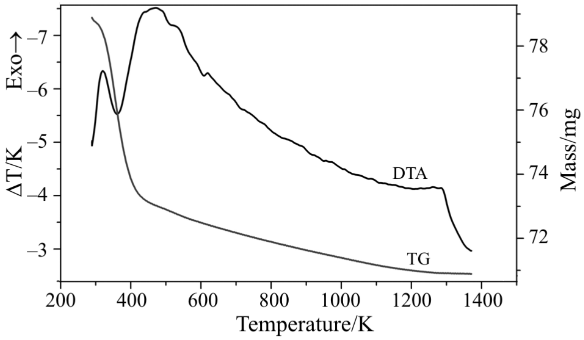

Fig. 5 DTA and TG curves of γ-ZrP\SiO$_2$ composite

Conclusions

On the basis of the above results, the following conclusions can be done:

- the amorphous γ-ZrP\SiO$_2$ composite have a complicated composition
- the composite have much more higher specific surface area (421 m^2 g^{-1}) in comparison with that of its constituent parts of γ-ZrP and SiO$_2$, because of the reciprocal effect of the latter materials (the silica prevents the lamellar aggregation, while the dispersed lamella of γ-ZrP prevent the aggregation of nano particles of silica)
- in comparison with α- and γ-crystalline form zirconium phosphates the γ-ZrP\SiO$_2$ composite showed higher stability during the thermal treatment till temperature of 1030 K

Taking into consideration the quantity of surface acidic P–OH groups (there are ≈1 meq g^{-1}) and the fact that acidic protons easily can be replaced by a large variety of metal ions, we could conclude that this material can deserve attention as catalyst first of all in reactions going at relatively high temperature and using acid catalyst.

Acknowledgements

The authors express one's thanks to Prof. G. Alberti to giving the material for investigations.

The support from Hungarian OTKA Fund (M-027367) is greatly appreciated.

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Received: May 3, 2005
Accepted: April 24, 2006

DOI: 10.1007/s10973-005-6862-x