Preparation, characterization and application of a new type of ion exchanger and solid acid zirconium sulfonated oligo-polystyrenylphosphonate-phosphate supported on ZrO$_2$

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Abstract

The new type of ion exchanger and solid acid zirconium sulfonated oligo-polystyrenylphosphonate-phosphate (ZSPSP) supported on ZrO$_2$ (ZSPSP/ZrO$_2$) was prepared and characterized by IR, SEM, TG and DSC. The thermal analysis indicated that the ZSPSP/ZrO$_2$ could be used safely below 200 °C. SEM micrographs demonstrated that ZSPSP/ZrO$_2$ with 1–100 μm of particle diameter was amorphous and microporous structure. Comparing with mineral acids such as H$_2$SO$_4$ and HCl or classical resins such as Amberlyst-15 and Nafion NR50 in the esterification reaction between acetic acid and 1-butanol, the order of catalytic activities was: H$_2$SO$_4$ > HCl > ZSPSP/ZrO$_2$ > Amberlyst-15 > Nafion NR50. ZSPSP/ZrO$_2$ exhibited higher ion exchange capacities and selectivity for Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions than for other ions.
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1. Introduction

As far as environmental and economic concern, there has been a strong interest in using solid acid catalysts to replace homogeneous catalysts such as HF, HCl, AlCl$_3$ and H$_2$SO$_4$ [1–6]. Although these traditional catalysts are very effective, they produce highly corrosive media with chemically reactive waste, which are difficult to handle especially in an industrial scale. The major challenge in this area is how to develop some cost effective, highly active, selective and stable solid acid replacements. It has been known that solid acid catalysts are easier to handle, simpler and cheaper to separate and purify, and safer to operate in the industrial process [6].

In the past few decades a lot of efforts have been made to search and develop the recoverable solid acid catalysts for minimizing pollution and reducing cost. These solid acid catalysts range from heteropolyacids [2], zeolites [3,7],

sulfated zirconias [1,8], zirconium phosphate–phosphonate [9–13], styrene-based sulfonic acids [14–18], perfluorinated resinsulfonic acids and the recently developed Nafion resin–silica nanocomposite [6,19,20]. Sulfonated polystyrene (SPS) strong acid cation exchange resin is a cheap multifunctional polymer and is widely used as solid acid catalyst in many organic reactions such as alkylation, isomerization, etherification, etherification, etc. [15,21], but all of these solid catalysts were limited to use at temperatures below 120 °C [14]. To be used in an industrial environment, polymer materials must possess some critical properties such as excellent chemical and mechanical resistance and especially high thermal stability. Many researchers have made great efforts to synthesize more thermally stable cation exchange polymer such as poly(arylsulfone) resins, polyimides and polyesters, etc. [16,22,23], but organic based materials still face thermal stability challenge. In the other hand, inorganic based acid catalysts such as zirconium layered sulfonated phenylphosphonates (ZSPP) or zirconium phosphate–phosphonates have been successfully used in many fields such as intercalation hosts [24], ionic conductivity and ion exchange

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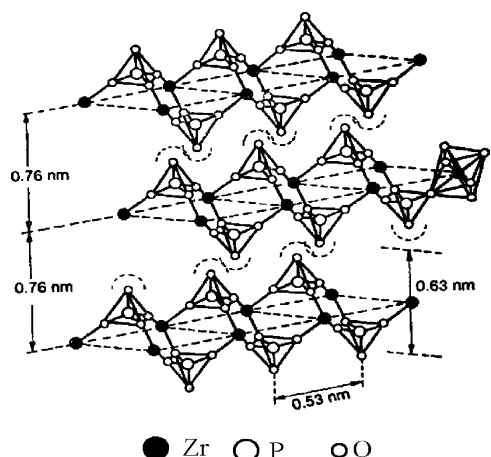*E-mail address:* chenlisy@swnu.edu.cn (X. Fu).

Fig. 1. The construction sketch map of ideal α-Zr(HPO$_4$)$_2$.

[25,26], photochemical reactions [27] and reaction catalysts [13,28–30]. Although these solid acid catalysts for example of ZSPP, can be used over 200 °C with good catalytic activities, but they suffer the disadvantages due to the complicated preparation procedure and high cost. In this paper, we report a new preparation method. If phosphonic or phosphorous acid moiety is introduced into SPS, and react with ZrOCl$_2$ to form mixed zirconium phosphate–phosphonate Zr(HPO$_4$)$_{2-x}$(O$_3$PG)$_x$ (x = 0–2, G: organic groups), a new type of ion exchanger and solid acid could be easily prepared. The ideal structure of α-Zr(HPO$_4$)$_2$ is shown in Fig. 1. Similarly to α-Zr(HPO$_4$)$_2$, the structure of this new ion exchanger and solid acid may be considered that phosphoric acid groups are partly substituted by sulfonated polystyrenylphosphonic acid to form layered zirconium (oligo-polystyrenylphosphonate-phosphate) (ZSPSP) with different inorganic/organic ratio. For this new ion exchanger and solid acid, we believe that it has some very good feathers due to (1) the interlayer distance of zirconium (sulfonated oligo-polystyrenylphosphonate-phosphate) is wider

than that of ZSPP and α-Zr(HPO$_4$)$_2$ due to the bulky volume of sulfonated oligo-polystyrene group. This is helpful to effectively increase the catalytic acid sites; (2) the ratio of phosphonate and phosphate in the catalyst can be rationally designed to meet different needs; (3) the starting materials are available and cheap, the reaction conditions are mild.

In this paper, in order to obtain larger surface area, ZSPSP was supported on ZrO$_2$ to form ZSPSP/ZrO$_2$; the preparation was outlined in Scheme 1.

## 2. Experimental

2.1. Materials and methods

Styrene (fresh distilled prior to use), nitric acid, hydrated sodium orthophosphate, hydrated zirconyl chloride, zirconium dioxide (with average particle diameter 4.71 μm) were analytic grade. Amberlyst-15 and Nafion NR50 was purchased from Aldrich. Oligo-polystyrenylphosphonous acid (PSPUA) was synthesized according to literature [31].

Infrared spectra were recorded on Spectrum GX using polystyrene as a standard (KBr pellet). TG and DSC analysis were performed on NETZSCH STA449C thermal analysis instrument (heating rate of 20 °C min^{-1}). GC analysis was carried out using SP 3400 GAS chromatograph equipped with a flame ionization detector. ^{1}H NMR was recorded at 298 K in CDCl$_3$ on AV-300 spectrum using TMS as internal reference. Atom adsorption analysis was conducted on Zeeman 180–80 atom adsorption analyzer.

2.2. Preparation of the ZSPSP/ZrO$_2$

2.2.1. Synthesis of oligo-polystyrenylphosphonic acid (PSPNA)

Ten percent aq. nitric acid (6.3 g, 10 mmol) was added dropwise into PSPUA (12.1 g, 10 mmol) within a 0.5 h, the
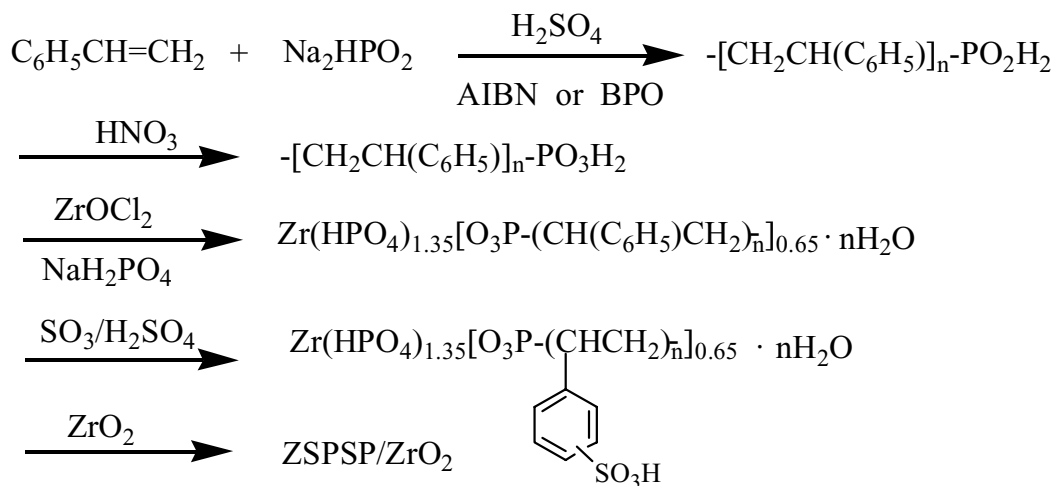
Scheme 1.

mixture was then heated to 85 °C and stayed 2 h. After cooling to room temperature, the pale yellow viscous material was filtered and solid was washed three times with 100 ml of deionized water and dried in vacuo. White solid of PSPNA (11.7 g, 95.3%) was obtained. IR (KBr, ν, cm^{-1}): 3030, 2920 (CH), 2365, 1180 (PO$_3$H$_2$), 1600, 1585, 1495, 1450, 755, 695 (–C$_6$H$_5$), 1365, 1385(P=O), 999 (P=O).

2.2.2. Synthesis of zirconium oligo-polystyrenylphosphonate–phosphate (Zr(HPO$_4$)$_{1.35}$(O$_3$P-PS)$_{0.65}$·H$_2$O)

PSPNA (8.0 g, 6.5 mmol) was dissolved in 30 ml of warm ethanol solution and added into 200 ml of water. In the solution hydrated zirconyl chloride (3.2 g, 10 mmol) and hydrated sodium orthophosphate (2.1 g, 13.5 mmol) aqueous solution was slowly added respectively with vigorously stirring to give white precipitates immediately, then hydrochloride acid (2 mol l^{-1}) was used to adjust the pH in the range of 2–3 and kept at 70 °C for 24 h, filtered, washed with deionized water until chloride ion could not be detected and dried in vacuo. White solid of Zr(HPO$_4$)$_{1.35}$(O$_3$P-PS)$_{0.65}$·H$_2$O was obtained in 91–95% yields. IR (KBr, ν, cm^{-1}): 3397 (Zr–O), 3027, 2925 (CH), 2370 (O=P–OH), 1603, 1494, 1453, 699, 754 (–C$_6$H$_5$), 1267 (P=O), 1067, 1013 (PO$_3^{2-}$).

2.2.3. Synthesis of zirconium sulfonated oligo-polystyrenylphosphonic-phosphate supported on zirconium dioxide (Zr(HPO$_4$)$_{1.35}$(O$_3$P-SPS)$_{0.65}$·nH$_2$O)/ZrO$_2$, (ZSPSP/ZrO$_2$)

Thirteen milliliter of H$_2$SO$_4$ containing ca. 10% SO$_3$ was added dropwise into Zr(HPO$_4$)$_{1.35}$(O$_3$P-PS)$_{0.65}$·H$_2$O (5.2 g, 5 mmol), heated at 60 °C for 2 h with vigorously stirring. After cooling, the solution was poured into 100 g ice-water. Zirconium dioxide (3.5 g, 0.028 mmol) was added into the mixture, kept at 80 °C for 24 h, filtered, washed, and dried at 120 °C for 3 h. White solid of ZSPSP/ZrO$_2$ was obtained with a yield of 85.2%. IR (KBr, ν, cm^{-1}): 2933, 2852 (CH), 1340 (–SO$_2$OH), 1072, 1022 (PO$_3^2$).

2.3. General procedure for acid catalytic reactions

A three-neck round-bottom flask (150 ml) equipped with a Teflon-covered magnetic stirring bar, thermometer, reflux condenser and Dean-Stark trap was charged with acid (or aldehyde or ketone) 0.2 mol, a proper molar ratio of alcohol and 2 g of ZSPSP/ZrO$_2$. The mixture was allowed to reflux in the range of 120–170 °C until no water globules in Dean-Stark trap appeared and cooled to room temperature. The catalysts were recovered by filtration, washed by petroleum ether, dried and reused. The filtrate was washed successively with 5% aq. Na$_2$CO$_3$ (20 ml × 2), 20 ml of water, dried by anhydrous sodium sulfate, and distilled under reduced pressure. The products were analyzed by gas chromatograph, and characterized by IR and ^{1}H NMR.

Sulfuric acid, concentrated hydrochloric acid, Amberlyst-15 and Nafion NR50 were used to catalyze the esterification reaction of acetic acid with 1-butanol at 80 °C, without Dean-Stark trap and at equimolar initial concentration, respectively, to assess the activities of different catalysts by the same steps.

2.4. General procedure for ion exchange reactions

ZSPSP/ZrO$_2$ (1.0000 g) was placed in an Erlenmeyer flask (250 ml) containing exactly 200 ml of 0.10 mol l^{-1} metallic chloride aqueous solution and allowed to stand for 24 h. The content of each metal element in the solution was quantitatively analyzed by using Zeeman 180–80 atom adsorption analyzer.

To assess the selective adsorption abilities of metal ions, 0.5000 g of ZSPSP/ZrO$_2$ was added to 100 ml of a mixed metal aqueous solution containing 0.10 mol l^{-1} of Na$^+$, K$^+$, Mg^{2+} and Ca^{2+} and allowed to stand for 24 h. Then the ZSPSP/ZrO$_2$ was filtered, washed three times with distilled water and dried. The relative adsorption amounts of metal ions were carried out in Zeeman 180–80 atom adsorption analyzer.

3. Results and discussion

3.1. The preparation of ZSPSP

Due to hydrophobic property of oligo-polystyrenylphosphonous acid, PSPUA was difficult to react with aq. ZrOCl$_2$. Instead oligo-polystyrenylphosphonic acid has stronger hydrophic property than PSPUA, PSPNA was easier to react with aq. ZrOCl$_2$ to obtain zirconium phosphate–phosphonate. Obviously, the oxidization of PSPUA to PSPNA was one of the key steps for the preparation of this new type of ion exchanger solid acid—ZSPSP/ZrO$_2$. To avoid introducing impurities and side reactions, we selected hydrogen peroxide as oxidizing reagent, but unfortunately, it was found that hydrogen peroxide was not strong enough to completely oxidize PSPUA. IR analysis revealed that P–H (2240–2350 cm^{-1}) adsorption peak still remained although the intensity decreased. When diluted nitric acid was used as oxidizing reagent, best results had been achieved. After reaction, no P–H peak could be detected from IR analysis.

To zirconium (sulfonated oligo-polystyrenylphosphonate-phosphate), the molar ratio of PSPNA and NaH$_2$PO$_4$ could be adjusted to meet different needs. In our experiments, the optimized result was found that the molar ratio of PSPNA and NaH$_2$PO$_4$ was 0.65/1.35 for preparation of esters, which is very well agreed with our previous reports [32].

3.2. Thermal analysis of ZrO$_2$ and ZSPSP/ZrO$_2$

ZrO$_2$ and ZSPSP/ZrO$_2$ were characterized by TG and DSC and shown in Figs. 2 and 3. DSC curve for ZrO$_2$ did not show obvious phase transition between 30 and 1000 °C,
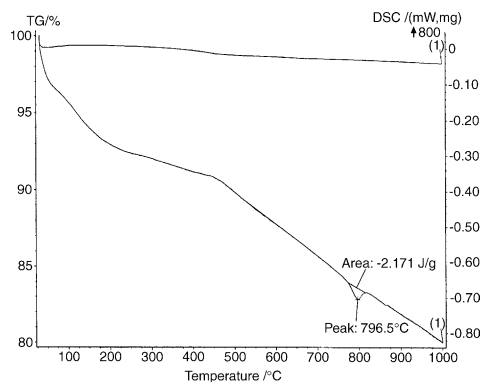
Fig. 2. The TG and DSC analysis of supporter ZrO_2.

Fig. 4. SEM micrographs of ZSPSP/ZrO_2 (500 times).

but ZSPSP/ZrO_2 presented two endothermic peaks at the temperature of 117.7 and 388.5 °C, which could be due to losing the crystalline water and decomposing of sulfonic acid groups from ZSPSP/ZrO_2 complex, respectively. Correspondingly, TG showed 4.0 and 17.1% weight loss of ZSPSP/ZrO_2 in the range of 30–200 °C and 200–700 °C, which we believe are attributed to the loss of crystal water and organic groups, respectively. These results indicate that ZSPSP/ZrO_2 can be used safely below 200 °C.

3.3. Morphological characterization of ZSPSP/ZrO_2

The SEM micrographs of ZSPSP/ZrO_2 were shown in Figs. 4–6. From the SEM micrographs, we found that ZSPSP/ZrO_2 with particle diameter 1–100 μm was amorphous and microporous structure greatly increased the surface area and the accessibility for substrates to the acid sites. The irregular and amorphous α-$Zr(HPO_4)_2$ have more surface area than that of crystalline α-$Zr (HPO_4)_2$ [30].

3.4. The results of acid catalytic reactions

To assess the catalytic activities of this novel catalyst, the esterification and acetalization (ketal) reactions using ZSPSP/ZrO_2 as solid acid catalysts were investigated. The results were shown in Table 1.
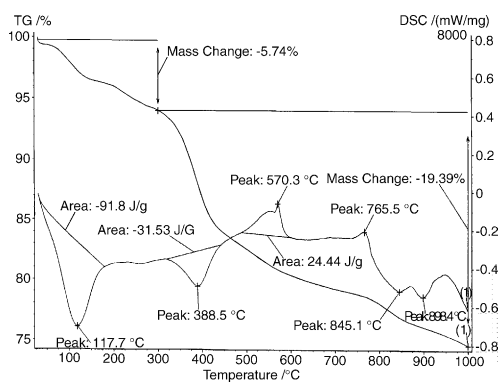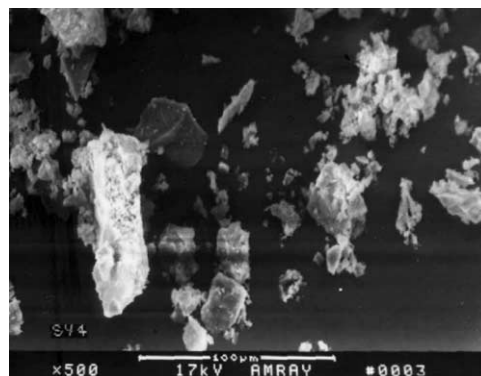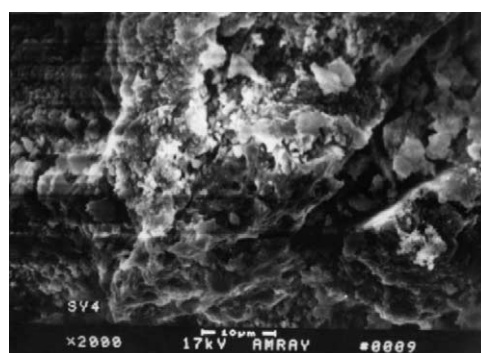

Fig. 5. SEM micrographs of ZSPSP/ZrO_2 (2000 times).

In Table 1, this catalyst showed very good catalytic activities at 95–172 °C for 1–4 h. Importantly, the catalysts ZSPSP/ZrO_2 could suffer 50 °C higher in our experiments than SPS [14].

The reusability of ZSPSP/ZrO_2 was also investigated by selecting the esterification reaction of $HOOC(CH_2)_4COOH$ with $CH_3(CH_2)_7OH$ (entry 13, Table 1). This catalyst could be used for eight times continuously at 170–172 °C without obvious decrease in catalytic activities. After that catalytic activity begin to fall down slowly. This might be due to the gradual decomposing of sulfo-groups in ZSPSP/ZrO_2 at higher temperature for longer time.
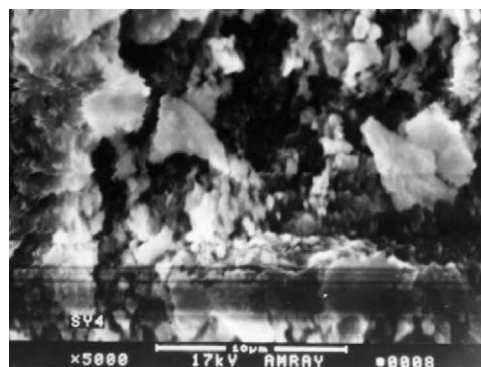

Fig. 3. The TG and DSC analysis of ZSPSP/ZrO_2.

Fig. 6. SEM micrographs of ZSPSP/ZrO_2 (5000 times).

Table 1
Acid catalytic reactions using ZSPP/ZrO$_2$ as catalyst

Entry	Substrate (A)	Substrate (B)	Temperature (°C)	Time (h)	Conversion (%)	Yield (%)
1	CH$_3$COOH	CH$_3$(CH$_2$)$_3$OH	117–120	2.0	100.0	92.0
2	CH$_3$CH$_2$COOH	CH$_3$(CH$_2$)$_3$OH	115–120	1.5	100.0	93.5
3	CH$_3$CH$_2$COOH	CH$_3$(CH$_2$)$_4$OH	125–130	2.0	100.0	95.0
4	CH$_3$CH$_2$COOH	CH$_3$(CH$_2$)$_2$CH(CH$_3$)OH	120–128	2.0	99.9	92.6
5	C$_6$H$_5$COOH	CH$_3$(CH$_2$)$_3$OH	115–120	4.5	99.2	91.5
6	C$_6$H$_5$COOH	CH$_3$(CH$_2$)$_4$OH	138–142	3.5	98.4	91.6
7	C$_6$H$_5$COOH	CH$_3$(CH$_2$)$_2$CH(CH$_3$)OH	135–140	4.0	98.0	85.5
8	HOOC(CH$_2$)$_8$COOH	CH$_3$(CH$_2$)$_3$OH	115–118	2.0	99.4	93.4
9	HOOC(CH$_2$)$_8$COOH	CH$_3$(CH$_2$)$_4$OH	130–135	2.0	99.2	92.1
10	HOOC(CH$_2$)$_4$COOH	CH$_3$(CH$_2$)$_3$OH	115–118	2.0	100.0	93.1
11	HOOC(CH$_2$)$_4$COOH	CH$_3$(CH$_2$)$_4$OH	135–140	2.0	100.0	93.4
12	HOOC(CH$_2$)$_4$COOH	CH$_3$(CH$_2$)$_2$CH(CH$_3$)OH	135–140	2.0	99.8	93.0
13	HOOC(CH$_2$)$_4$COOH	CH$_3$(CH$_2$)$_7$OH	170–172	2.0	100.0	94.5
14	HOOC(CH$_2$)$_4$COOH	CH$_3$(CH$_2$)$_5$CH(CH$_3$)OH	170–172	2.0	99.7	94.2
15	C$_6$H$_5$CHO	HOCH$_2$CH$_2$OH	95–100	1.0	93.5	90.0
16	(CH$_2$)$_5$CO	HOCH$_2$CH$_2$OH	95–98	1.0	93.8	92.0

Measured by chromatography integral ratio.

Comparing with mineral acids such as sulfuric acid and concentrated hydrochloric acid or classical resins supported solid acid such as Amberlyst-15, Nafion NR50 in the esterification reaction between acetic acid and 1-butanol, the order of catalytic activities is: sulfuric acid > concentrated hydrochloric acid > ZSPSP/ZrO$_2$ > Amberlyst-15 > Nafion NR50 (Table 2). The acid strength (H_0) of Amberlyst-15, Nafion NR50 and ZSPSP/ZrO$_2$ are about -3, -12 and -10 respectively. The acid amount of Nafion NR50, Amberlyst-15 and ZSPSP/ZrO$_2$ are 0.89, 4.4 and 6.82 meqH$^+$ g^{-1}, respectively, which are consistent with their catalytic activities. Nafion NR50 is stronger acid but with lower catalytic activities. This is due to its low surface area (0.02 m^2 g^{-1}) and poor accessibility. Recent report indicated that Nafion resin–silica nanocomposite could significantly increase the effective surface area and catalytic activity [6]. ZrO$_2$ could still be a good choice to offer because its easier preparation procedure.

3.5. The properties of ion exchange

The ion exchange capability of ZSPSP/ZrO$_2$ for different metal ions such as Na$^+$, K$^+$ and Mg^{2+} was investigated in aqueous solution (Table 3). In general, the electric attraction between exchange groups and ions, the ion exchange capacity increased with the increasing charge and the number of the metal ions with the same charge. An interesting result was that the metal ion exchange capacities of ZSPSP/ZrO$_2$ for Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions were obviously higher than for others. One possible reason might be ascribed to the fact that these ions have the similar outermost electronic structures whose 3d orbital were not fully filled. Because the acid active sites of ZSPSP/ZrO$_2$ could result from several resources such as sulfonic acid groups, phosphoric or phosphonic acids, the relationship between acid content and ion exchange capacity for ZSPSP/ZrO$_2$ and the detailed mechanism still need further investigation.

It was shown in Table 4, that the relative amount of adsorbed metal ions in mixed metal solution increased with increasing atomic number. The metal ions with two positive charges were adsorbed much more rapidly than metal ions with one positive charge, and the metal ions with the same valence ions were more rapidly adsorbed with the increase of the atomic number.

In summary, in this paper a new type of ion exchangers and solid acids had been prepared and their acid catalytic and ion exchange properties had been investigated. This new type

Table 2
Activity of different catalysts

Catalyst	Conversion at 2 h
	0.070
Sulfuric acid	0.702
Concentrated hydrochloric acid	0.690
Amberlyst-15	0.512
Nafion NR50	0.305
ZSPSP/ZrO$_2$	0.546

Table 3
Ion exchange capability of ZSPSP/ZrO$_2$ in aqueous solution at room temperature

Element	mmol/g
Na$^+$	3.85
K$^+$	3.91
Mg^{2+}	3.90
Ca^{2+}	3.94
Fe^{3+}	4.55
Co^{2+}	4.25
Ni^{2+}	4.21
Cu^{2+}	4.28
Zn^{2+}	3.72
Pb^{2+}	2.10
Hg^{2+}	2.35

Table 4
Relative adsorption of metal ions for ZSPSP/ZrO$_2$ in aqueous at room temperature

Element	mmol/g
Na$^+$	0.51
K$^+$	0.59
Mg^{2+}	1.30
Ca^{2+}	1.65
Total	4.05

of the mixed zirconium phosphate–phosphonate possessed higher thermal stability than SPS and exhibited higher ion exchange capacities and selectivity for Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions than for other metal ions.

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