



Catalytic synthesis of diphenolic acid from levulinic acid over cesium partly substituted Wells–Dawson type heteropolyacid

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ABSTRACT

A series of insoluble cesium partly substituted Wells–Dawson type heteropolyacids, $\text{Cs}_x\text{H}_{6-x}\text{P}_2\text{W}_{18}\text{O}_{62}$ ($x = 1.5\text{--}6.0$), were synthesized and characterized using the techniques including UV–vis/DRS, FT-IR, XRD, XPS, and N_2 porosimetry. As the unique and reusable solid acid catalysts, $\text{Cs}_x\text{H}_{6-x}\text{P}_2\text{W}_{18}\text{O}_{62}$ salts were applied to produce diphenolic acid by the condensation reaction of phenol with bio-platform molecule, levulinic acid. For comparison, cesium partly substituted Keggin type heteropolyacids ($\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$, $x = 1.0\text{--}3.0$), HCl, HZSM-5, and MCM-49 were also tested. Influences on the catalytic activity and selectivity were considered for factors including solvent, molar ratio of phenol to levulinic acid, amount of catalyst, reaction temperature, stirring speed, and reaction time. The experimental results demonstrated that both $\text{Cs}_{1.5}\text{H}_{4.5}\text{P}_2\text{W}_{18}\text{O}_{62}$ and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ exhibited excellent catalytic performance under solvent-free conditions. Furthermore, both selectivity and activity of $\text{Cs}_{1.5}\text{H}_{4.5}\text{P}_2\text{W}_{18}\text{O}_{62}$ were higher than those of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$. Reasons for the different catalytic behaviors between two types of cesium partly substituted heteropolyacids were investigated.

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1. Introduction

Diphenolic acid (DPA) is a structural analog of bisphenol A (BPA) and can serve in many of the same applications as BPA for the synthesis of industrially important epoxy resins and polycarbonates that are used in the production of reinforced plastics and other chemical materials [1,2]. DPA can be easily synthesized from the condensation reaction of levulinic acid (LA) with two moles of phenol in the presence of Brønsted acid [3,4]. The reactant LA is one of important biomass-derived platform molecules and can be obtained by treatment of 6-carbon sugar carbohydrates from starch or lignocelluloses with acid [5]. The biofine process offers LA at a much lower cost which will open up new opportunities for the cost-effective production of chemicals from the bio-renewable feed stocks. Therefore, DPA can serve as a replacement for BPA, whose development will provide new sustainable opportunities for the chemical industry. Traditionally, synthesis of DPA is catalyzed by strong mineral acids like concentrated HCl under the reaction conditions of the molar ratio of phenol to LA in the range of 2.25–4, reaction temperature up to 60 °C, and reaction time amounting to 60 h or more. Under these conditions, the maximum yield of total DPA can be up to 85% of the theoretical amount based on levulinic acid [4]. However, most of mineral acids are toxic, corrosive, and

produce many undesired side-products that are difficult to separate from the reaction media. Consequently, many efforts have been made to replace the conventional catalysts by the solid acid catalysts.

An ideal solid catalyst should be strong acidic and shape selective for the DPA synthesis reaction, where few by-products were formed. Zeolites have attracted considerable attentions as solid acids, but they present severe limitations when large reactant and/or product molecules are involved [6]. Heteropolyacids (HPAs) are useful solid acid catalysts for diverse reactions that require strong acidity. The acid strength of HPAs is stronger than that of the conventional solid acid catalysts (e.g. acidic oxides and zeolites). Therefore, they are generally active catalysts which allow efficient operation under mild conditions. The acid sites in HPAs are more uniform and easier to control than those in other solid acid catalysts. Owing to inherent advantages of HPAs, heterogeneous acid catalysis by them has the potential of a great economic reward and green benefits [7,8]. Although HPAs are themselves useful solid catalysts, they are highly soluble in, and difficult to separate from polar media [9]. Moreover, bulk HPAs show very small specific surface areas ($1\text{--}5\text{ m}^2\text{ g}^{-1}$) [7].

To overcome these shortcomings, many studies have put efforts into the immobilization of HPAs on high-surface-area solid supports including zeolite, silica, activated carbon, and zirconia. However, the high solubility of HPAs still makes such supported variants unsuitable for catalyzing polar chemistry if wet impregnation was used to prepare these materials [10–17]. More

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recently, we demonstrated a new route by combination of sol–gel chemistry, templating, and hydrothermal treatment to prepare $\text{H}_3\text{PW}_{12}\text{O}_{40}$ –silica composite catalysts with unique surface textural properties. As-prepared $\text{H}_3\text{PW}_{12}\text{O}_{40}$ –silica composites were catalytically active and stable to the synthesis reaction of DPA from LA, but the selectivity to *p,p'*-DPA isomer was not high enough [18]. Another way to enhance surface area of HPAs and decrease their solubility over the parent HPAs is to exchange them with large alkali cations such as Ag^+ , Cs^+ , or NH_4^+ to form insoluble salts. Especially, one of the partly substituted cesium salts of Keggin type dodecaheteropolyacids, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, has been reported to be the unique solid acid catalyst for many catalytic reactions such as isomerisation of butane and pentane, esterification of benzoic and acetic acids, and hydration of olefins [19,20]. The high catalytic activity of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ is ascribed to the hydrophobicity and bimodal pore structure as well as the strong acid strength [20]. It is found that the cesium salts consist of ultrafine crystallites formed by $\text{H}_3\text{PW}_{12}\text{O}_{40}$ epitaxially deposited on the surface of a core of $\text{Cs}_{3.0}\text{PW}_{12}\text{O}_{40}$ [21].

Although many successful acid-catalyzed reactions over cesium partly substituted HPAs have been reported, they are still promising candidates of the solid acids for the reactions with industrial interest. So far cesium partly substituted HPAs used in almost all experiments are of Keggin type, predominantly $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ with $x=1.0$ – 3.0 [22]. However, few of investigation have been done for the physicochemical and catalytic properties of Wells–Dawson type cesium salts. Recently, it was reported that Wells–Dawson type cesium salts $\text{Cs}_x\text{H}_{6-x}\text{P}_2\text{W}_{18}\text{O}_{62}$ ($\text{Cs}_{2.0}\text{H}_{4.0}\text{P}_2\text{W}_{18}\text{O}_{62}$, $\text{Cs}_{4.0}\text{H}_{2.0}\text{P}_2\text{W}_{18}\text{O}_{62}$, $\text{Cs}_{5.0}\text{HP}_2\text{W}_{18}\text{O}_{62}$, $\text{Cs}_{5.5}\text{H}_{0.5}\text{P}_2\text{W}_{18}\text{O}_{62}$, and $\text{Cs}_{6.0}\text{P}_2\text{W}_{18}\text{O}_{62}$) were active catalysts in gas phase synthesis of ethyl *tert*-butyl ether (ETBE) [23]. In fact, this type of HPA in its acid form possesses super acid strength and remarkable stability in both the solution and the solid state. For example, Maksimov and Kozhevnikov reported that a Wells–Dawson type HPA, $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$, was 2.7 times more active (per unit weight) than Keggin type HPA, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, in the homogeneous liquid-phase reaction of methanol and isobutylene to produce methyl *tert*-butyl ether (MTBE) [24]. Misono and coworkers reported that the activity of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ for the gas synthesis of MTBE was at least 13 times greater than that of Keggin type HPAs ($\text{H}_n\text{XW}_{12}\text{O}_{40}$, X = P, Si, Ge, B, and Co), and 170 times more than that of $\text{SO}_4^{2-}/\text{ZrO}_2$, H-ZSM-5, and $\text{SiO}_2\text{--Al}_2\text{O}_3$ [25]. They also found that the activity of $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ was greatly enhanced by supporting itself on silica matrix [26]. These properties make Wells–Dawson type cesium salts suitable catalytic materials in homogeneous and heterogeneous liquid-phase reactions, which are now the object of investigations in many laboratories.

Herein, we synthesized a series of cesium partly substituted Wells–Dawson type HPAs, $\text{Cs}_x\text{H}_{6-x}\text{P}_2\text{W}_{18}\text{O}_{62}$ ($x=1.5$ – 6.0), as water-tolerant catalysts for the DPA synthesis reaction. Furthermore, the catalytic performance of $\text{Cs}_x\text{H}_{6-x}\text{P}_2\text{W}_{18}\text{O}_{62}$ was compared with that of Keggin type acid cesium salts, $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ ($x=1.0$ – 3.0). The studied results demonstrate that both $\text{Cs}_{1.5}\text{H}_{4.5}\text{P}_2\text{W}_{18}\text{O}_{62}$ and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ exhibit excellent catalytic activity and selectivity to the DPA synthesis reaction.

2. Experimental

2.1. Catalyst preparation

Octadecadiphosphotungstic acid, $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$, was prepared according to the literature method [27] and purified through ether extraction and recrystallization. Commercial cesium carbonate Cs_2CO_3 (99%) and 12-tungstophosphoric acid (99.9%) were pur-

chased from Aldrich. The latter was recrystallized from deionized water solution before used.

$\text{Cs}_x\text{H}_{6-x}\text{P}_2\text{W}_{18}\text{O}_{62}$ samples ($x=1.5, 2.0, 2.5, 3.5, 4.5,$ and 6.0 , abbreviated as $\text{Cs}_x\text{H}_{6-x}\text{D}$) and $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ samples ($x=1.0, 1.5, 2.0, 2.5,$ and 3.0 , abbreviated as $\text{Cs}_x\text{H}_{3-x}\text{K}$) were prepared by adding slowly dropwise the predetermined amounts of Cs_2CO_3 (0.1 mol l^{-1}) to $\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ or $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (0.08 mol l^{-1}) solutions with vigorous stirring at room temperature. The precipitate obtained was aged in parent solution for 20 h at room temperature, evaporated in vacuum at 45 – 50°C , grinded into 60-mesh-pass particles, and finally calcined in air at 300°C for 1 h. The products were stored in air before analyzing and reaction testing.

2.2. Catalyst characterization

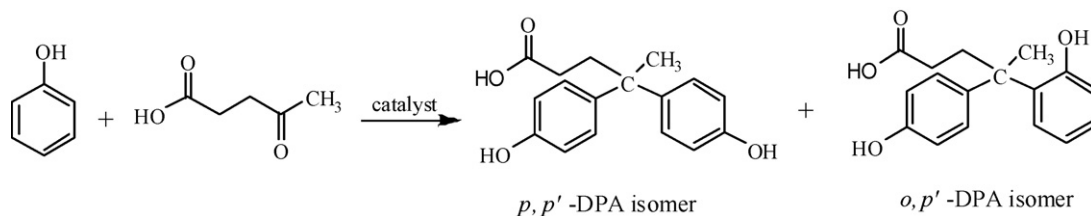
UV–vis diffuse reflectance spectra (UV–vis/DRS) were recorded on a Cary 500 UV–vis–NIR spectrophotometer. Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet Magna 560 IR spectrophotometer. Powder X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max-3c X-ray diffractometer using $\text{Cu K}\alpha$ ($\lambda=1.5418 \text{ \AA}$) radiation. X-ray photoelectron spectra (XPS) were performed on a VG-ADES 400 instrument with $\text{Mg K}\alpha$ -ADES source at a residual gas pressure of below 10^{-8} Pa. All the binding energies were referenced to the C1s peak at 284.6 eV of the surface adventitious carbon. The surface area of the composite catalyst was measured by BET method on an ASAP 2010M surface analyzer (the samples were outgassed under vacuum at 120°C overnight). Contents of P, W and Cs were determined by a Leeman Prodigy Spec inductively coupled plasma atomic emission spectrometer (ICP-AES) and Varian AA 220 FS atomic absorption spectrometer (AAS), respectively.

2.3. Catalytic test

LA (99.9%) and phenol (analytical grade) were purchased from Aldrich. DPA (99%) was purchased from BASF. All of the reagents were used as purchased without further purification.

A typical condensation of LA with phenol to produce DPA was performed in a sealed glass vessel at 100°C for 6 h. A typical experiment included a mixture of 0.99 g (10.2 mmol) of phenol, 0.40 g (3.4 mmol) of LA, and 50 mg of the catalyst. At each reaction interval, the concentration of LA and DPA were determined simultaneously. Before the determination, a measured amount of acetonitrile was added into the reaction system. Thereafter, the suspension was centrifuged, and the resulting solution was further diluted with the mixture of acetonitrile and water (1:1, v/v) and analyzed on an Applied Biosystem liquid chromatography (LC, C8 column)–Q-Trap triple quadrupole mass spectrometer (MS) equipped with electrospray ionization (EI) source. The instrument was interfaced to a computer running Applied Biosystems Analyst version 1.4 software, which was capable of recording ions up to m/z 1700. The analytical results of LC–MS show that the reaction results in the formation of two structural isomers of DPA, i.e., *p,p'*-DPA and *o,p'*-DPA (see Scheme 1).

The performance of the catalysts is characterized quantitatively by the conversion of LA (Conv%), the yield of DPA (Yield%), and the selectivity to *p,p'*-DPA or *o,p'*-DPA isomer (Sel%) obtained at the selected conditions. Conversion of LA is calculated as follows: $\text{Conv}\% = ([\text{LA}]_i - [\text{LA}]_t)/[\text{LA}]_i \times 100$, where $[\text{LA}]_i$ and $[\text{LA}]_t$ are the concentration of LA at initial and terminal reaction time, respectively. Yield of DPA is calculated as follows: $\text{Yield}\% = (M_y/M_E) \times 100$, where M_y is the number of moles of total DPA isomers yielded, M_E is the number of moles of total DPA expected. Selectivity is calculated as follows: $\text{Sel}\% = M_{p,p'\text{-DPA}} \text{ or } M_{o,p'\text{-DPA}} / (M_{p,p'\text{-DPA}} + M_{o,p'\text{-DPA}}) \times 100$,



Scheme 1.

where $M_{p,p'\text{-DPA}}$ or $M_{o,p'\text{-DPA}}$ is the number of moles of p,p' -DPA or o,p' -DPA.

3. Results and discussion

3.1. Catalyst characterization

Structures of $\text{Cs}_x\text{H}_{3-x}\text{K}$ and $\text{Cs}_x\text{H}_{6-x}\text{D}$ are firstly characterized by UV-vis/DRS in Fig. 1, which shows that both types of cesium partly substituted HPAs exhibit strong absorption at 195 nm regardless of the structures of HPAs. This absorption is originated from charge-transfer from O2p to W5d orbitals occurring at W=O terminal bonds. Another relatively weak absorption peak is closely related to the structure of HPA. This absorption is attributed to charge-transfer from O2p to W5d orbitals occurring at W–O–W bridge bonds. In the case of Keggin type $\text{Cs}_x\text{H}_{3-x}\text{K}$, the absorption peaks situate at 260 nm. While, as for Wells–Dawson type $\text{Cs}_x\text{H}_{6-x}\text{D}$, the weak absorption peaks appear at 250 and 305 nm, respectively. The above results are well consistent with those of the free acids H_3K and H_6D , demonstrating that the primary Keggin and Wells–Dawson structures remain intact after incorporation of Cs^+ ions [28].

It is well known that both Wells–Dawson structure of $\text{P}_2\text{W}_{18}\text{O}_{62}^{6-}$ and Keggin structure of $\text{PW}_{12}\text{O}_{40}^{3-}$ as heteropolyanions have W_3O_{13} triads and consist of four kinds of oxygen atoms. The first is P–O_a in which oxygen atom connects with heteroatom (here is P atom), the second is W–O_b–W oxygen bridges (corner-sharing oxygen bridges between different W_3O_{13} groups), the third is W–O_c–W oxygen bridges (edge-sharing oxygen bridges within W_3O_{13} groups), and the last is W=O_d terminal oxygen atoms [29]. The four kinds of oxygen atoms can be accurately identified by FT-IR. As shown in Fig. 2a, H_6D shows four vibrational absorption bands at $\nu_{\text{as}}(\text{P}-\text{O}_a) = 1090 \text{ cm}^{-1}$, $\nu_{\text{as}}(\text{W}=\text{O}_d) = 996 \text{ cm}^{-1}$, $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W}) = 915 \text{ cm}^{-1}$, and $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W}) = 786 \text{ cm}^{-1}$, respectively, which are characteristics of Wells–Dawson type HPAs [30]. Once the protons are partly substituted by Cs^+ ions, the vibration frequency of W=O_d bonds shifts from 996 to 963 cm^{-1} for the six $\text{Cs}_x\text{H}_{6-x}\text{D}$ salts with $x = 1.5, 2.0, 2.5, 3.5, 4.5,$ and 6.0 , respectively. However, the positions of the other three bonds remain intact. The shifts of the frequency of W=O_d bonds for $\text{Cs}_x\text{H}_{6-x}\text{D}$ are due to the incorporation of large Cs^+ ions as partial counteranions. In Fig. 2b, all $\text{Cs}_x\text{H}_{3-x}\text{K}$ ($x = 0\text{--}3.0$) exhibit the same characteristic IR absorption bands at $\nu_{\text{as}}(\text{P}-\text{O}_a) = 1080$, $\nu_{\text{as}}(\text{W}-\text{O}_d) = 983$, $\nu_{\text{as}}(\text{W}-\text{O}_b-\text{W}) = 887$, and $\nu_{\text{as}}(\text{W}-\text{O}_c-\text{W}) = 803 \text{ cm}^{-1}$, respectively, corresponding to those of the Keggin structure of $\text{PW}_{12}\text{O}_{40}^{3-}$ anions [31]. These results imply that exchange of Cs^+ ions with protons has little influence on the Keggin structure.

Fig. 3 displays XRD patterns of $\text{Cs}_x\text{H}_{6-x}\text{D}$ (Fig. 3a) and $\text{Cs}_x\text{H}_{3-x}\text{K}$ (Fig. 3b), respectively. From Fig. 3a, it is found that difference of XRD patterns of $\text{Cs}_x\text{H}_{6-x}\text{D}$ with various Cs contents are mainly observed at low 2θ values ($2\theta \leq 10^\circ$). The free acid H_6D shows diffraction peaks at $4.71^\circ, 6.15^\circ, 6.87^\circ, 7.99^\circ,$ and 8.84° , respectively. The $\text{Cs}_{6,0}\text{D}$ salt shows diffraction peaks at 8.79° and 9.30° , respectively. As for $\text{Cs}_x\text{H}_{6-x}\text{D}$ salts, with low Cs contents ($x = 1.5$ and 2.0), the peaks originated from both H_6D ($2\theta = 4.71^\circ$ and 6.15°) and $\text{Cs}_{6,0}\text{D}$

($2\theta = 8.79^\circ$ and 9.30°) appear simultaneously, implying that there are two coexisting phases (one is similar to the structure of H_6D and the other is similar to the structure of $\text{Cs}_{6,0}\text{D}$). However, the crystallinity decreases compared with H_6D or $\text{Cs}_{6,0}\text{D}$. Additionally, the peak at $2\theta = 7.60^\circ$ is observed neither in H_6D nor $\text{Cs}_{6,0}\text{D}$. Further increasing x to 3.5, most of the peaks originated from H_6D disappear. At $x = 4.5$, all H_6D diffraction peaks disappear, and the sample

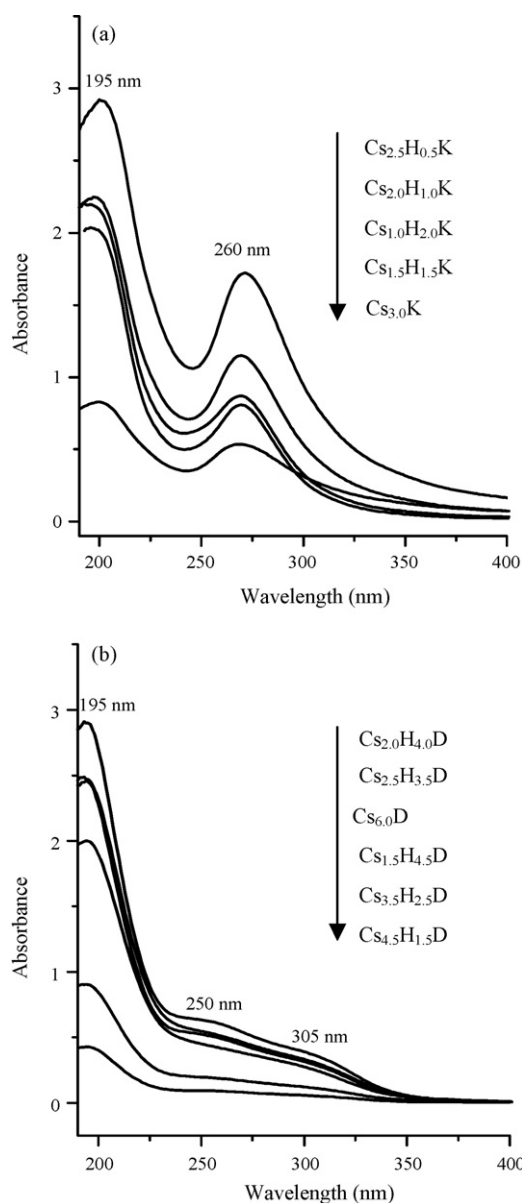


Fig. 1. UV/DRS of cesium partly substituted Keggin (a) or Dawson type HPA samples (b) with different cesium contents.

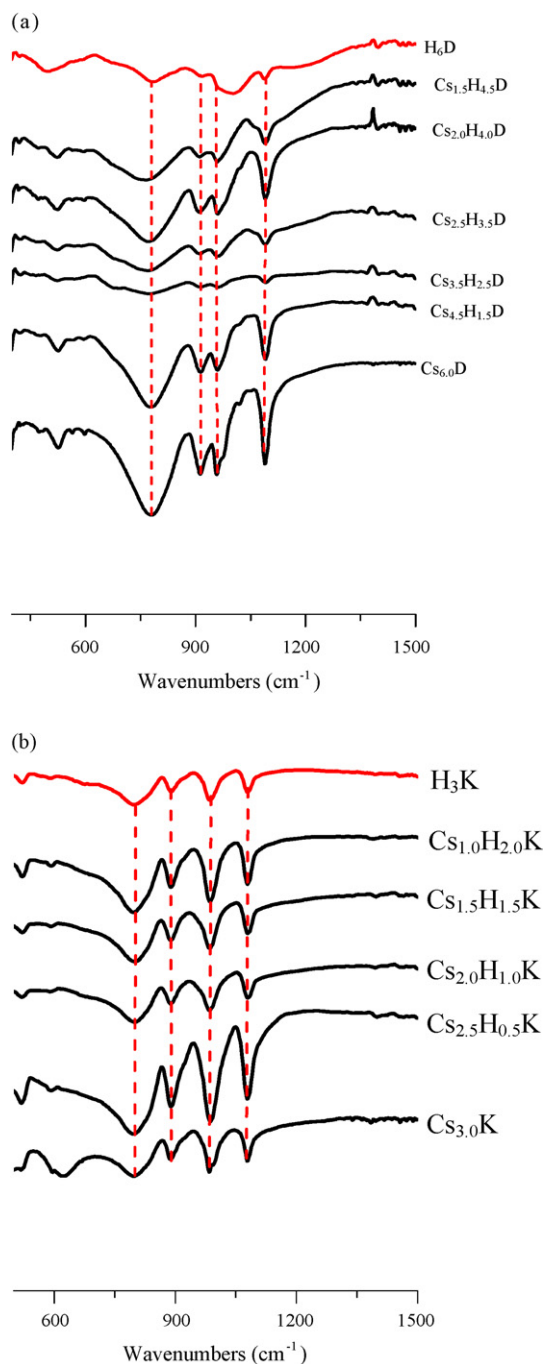


Fig. 2. FT-IR spectra of cesium partly substituted Dawson (a) or Keggin type HPA samples (b) with different cesium contents.

exhibits $\text{Cs}_{6.0}\text{D}$ phase characteristics. These results demonstrate the most probable substitution of Cs cations to the structure occurs for samples containing not less than 4.5 Cs cations per Dawson anion [23]. As for $\text{Cs}_x\text{H}_{3-x}\text{K}$ (Fig. 3b), the free acid H_3K shows the main diffraction peaks at 10.35° , 14.60° , 17.85° , 20.68° , 23.11° , 25.44° , 29.40° , 31.22° , and 34.67° , respectively. $\text{Cs}_{3.0}\text{K}$ salt shows the main diffraction peaks at 10.54° , 18.45° , 23.82° , 26.15° , 30.31° , and 35.58° , respectively. At low Cs content ($x=1.0$ – 2.0), the peaks originated from both H_3K ($2\theta=14.60^\circ$, 20.68° , and 31.22°) and $\text{Cs}_{3.0}\text{K}$ (10.54° , 18.45° , 23.82° , 26.15° , 30.31° , and 35.58°) appear simultaneously. At $x=2.5$, all H_3K diffraction peaks disappear, and the sample exhibits a unique crystalline $\text{Cs}_{3.0}\text{K}$ phase characteristics [21,32]. The above

XRD and IR results indicate that the effect of partial substitution of protons by Cs^+ cations is more obvious for Dawson type HPAs than for Keggin type ones. Moreover, the structure difference between the free Dawson acid (H_6D) and its Cs salt ($\text{Cs}_{6.0}\text{D}$) are only due to an arrangement of anions and cations in the secondary structure of HPA. However, the primary structures of both types of HPAs still remain intact [23,32].

To study the surface properties of $\text{Cs}_x\text{H}_{6-x}\text{D}$, we have carried out XPS analysis of $\text{Cs}_{1.5}\text{H}_{4.5}\text{D}$, $\text{Cs}_{4.5}\text{H}_{1.5}\text{D}$, and $\text{Cs}_{6.0}\text{D}$. The XPS spectra of Cs3d state of $\text{Cs}_x\text{H}_{6-x}\text{D}$ are fitted with the nonlinear least-squares fit program using Gauss-Lorentzian peak shapes, and two Cs3d $_{5/2}$ peaks in the $\text{Cs}_{4.5}\text{H}_{1.5}\text{D}$ and $\text{Cs}_{6.0}\text{D}$ samples are found after deconvolution (Fig. 4). The results indicate that two different Cs environments exist in the $\text{Cs}_x\text{H}_{6-x}\text{D}$ samples. Moreover, the Cs3d $_{5/2}$ peak becomes broad with increasing Cs content. As for the low loading sample, $\text{Cs}_{1.5}\text{H}_{4.5}\text{D}$ exhibits a single characteristic peak of Cs^+ ion at 724.8 eV. For high loading samples, $\text{Cs}_{4.5}\text{H}_{1.5}\text{D}$ and $\text{Cs}_{6.0}\text{D}$, a second low binding energy state evolves at 724.3 eV. This observation reveals that there are two Cs^+ coordination environments. The results are analogous to previous studied results of XPS for cesium partly substituted Keggin type HPAs, in which two Cs3d $_{5/2}$ binding energy states are found with Cs content of $x=2.3$ – 3.0 . The low and high binding energy components are attributed to the terminal and bridge sites of surface-terminating layer, respectively [32].

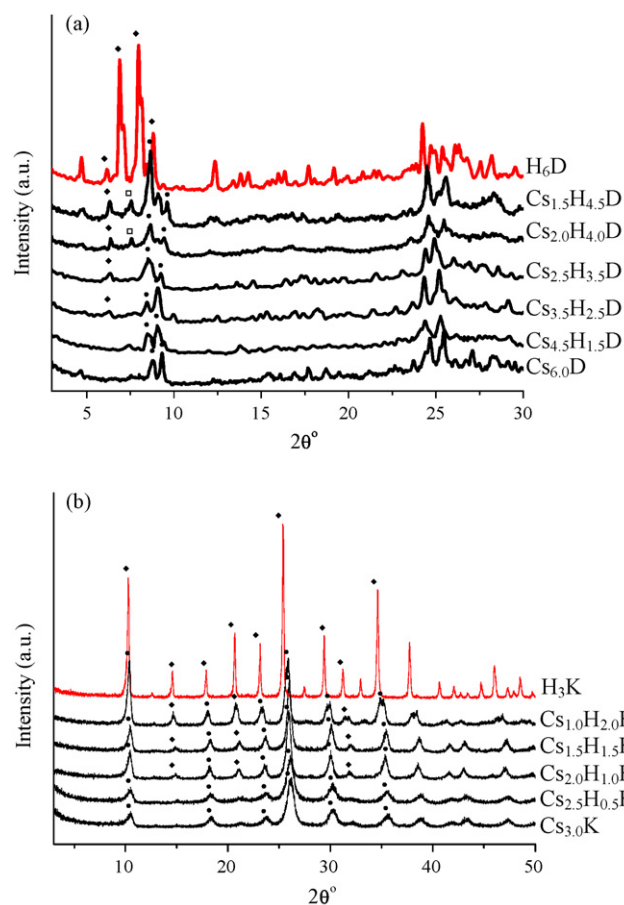


Fig. 3. XRD patterns of (a) cesium partly substituted Dawson type HPA samples ($\text{Cs}_x\text{H}_{6-x}\text{D}$), where signs (♦) and (●) mark the main reflexes characteristic for H_6D and $\text{Cs}_{6.0}\text{D}$, respectively; sign (□) is marked reflexes of $\text{Cs}_{1.5}\text{H}_{4.5}\text{D}$ and $\text{Cs}_{2.0}\text{H}_{4.0}\text{D}$ which are not found in H_6D or $\text{Cs}_{6.0}\text{D}$ patterns; (b) Cesium partly substituted Keggin type HPA samples ($\text{Cs}_x\text{H}_{3-x}\text{K}$), where signs (♦) and (●) mark the main reflexes characteristic for H_3K and $\text{Cs}_{3.0}\text{K}$, respectively.

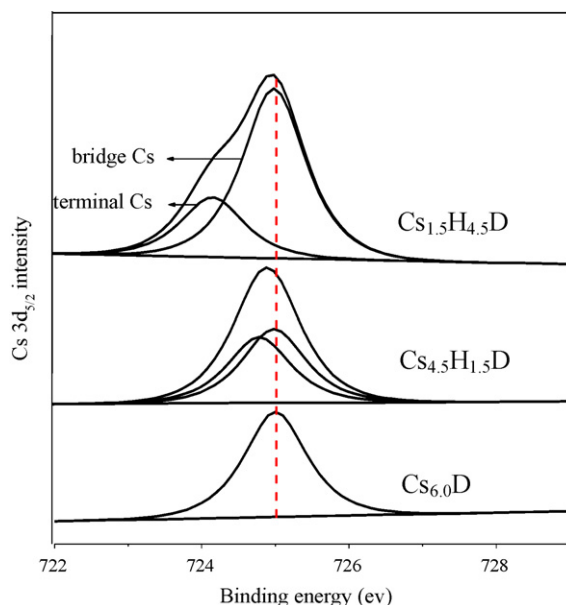


Fig. 4. High-resolution XPS spectra of $\text{Cs}_{1.5}\text{H}_{4.5}\text{D}$, $\text{Cs}_{4.5}\text{H}_{1.5}\text{D}$, and $\text{Cs}_{6.0}\text{D}$ in the $\text{Cs}3d_{5/2}$ region.

The BET surface areas and average pore diameters of $\text{Cs}_x\text{H}_{3-x}\text{K}$ samples are listed in Table 1. As the Cs content exceeds 2.0, the surface areas increase sharply and reach maximum ($150 \text{ m}^2 \text{ g}^{-1}$) at $x=3.0$. In addition, study on porosity exhibits that average pore diameter increases significantly from 3.2 to 11.9 nm for Cs content beyond $x=2.0$. The above results are consistent with those reported by the literatures [8,32], suggesting that $\text{Cs}_x\text{H}_{3-x}\text{K}$ have dense porous network and higher surface areas than the free acid H_3K . For the Wells–Dawson type $\text{Cs}_x\text{H}_{6-x}\text{D}$, according to measurement of their BET surface areas in the literature, all samples remain low BET surface areas (of order of $1 \text{ m}^2 \text{ g}^{-1}$) [23].

3.2. Catalyst activity

The insoluble nature and high acid-catalytic activity of Dawson type $\text{Cs}_x\text{H}_{6-x}\text{D}$ ($x > 1.5$) in polar media make this HPA attractive for use in the condensation reaction pertinent to DPA synthesis. For comparison, Keggin type $\text{Cs}_x\text{H}_{3-x}\text{K}$ ($x \geq 1.5$), free H_6D and H_3K , HCl, HZSM-5, and MCM-49 are also tested. The acid catalytic activities of above catalysts are summarized in Table 2 and Fig. 5. Additionally, the adsorption behaviors of $\text{Cs}_x\text{H}_{6-x}\text{D}$ and $\text{Cs}_x\text{H}_{3-x}\text{K}$, and influence factors including solvents, molar ratios of phenol to LA, catalyst amount, reaction temperatures, reactor stirring speed, and reaction time are also considered during the DPA synthesis procedure (Table 3 and Figs. 6–11).

3.2.1. Effect of the catalyst

As shown in Table 2, the catalyst activities for the condensation reaction increase gradually in the order of $\text{HZSM-5} < \text{MCM-49}$

Table 1
BET surface area and average pore diameter of cesium partly substituted Keggin type HPAs

Sample	BET surface area ($\text{m}^2 \text{ g}^{-1}$)	Average pore diameter (nm)
$\text{Cs}_{1.0}\text{H}_{2.0}\text{K}$	2.0	–
$\text{Cs}_{1.5}\text{H}_{1.5}\text{K}$	3.1	–
$\text{Cs}_{2.0}\text{H}_{1.0}\text{K}$	36.4	3.2
$\text{Cs}_{2.5}\text{H}_{0.5}\text{K}$	125.8	8.6
$\text{Cs}_{3.0}\text{K}$	150.0	11.9

Table 2

Comparison of the conversion of LA, the yield of DPA, and the selectivity to *p,p*-DPA or *o,p*-DPA isomer for different catalysts in condensation of phenol with LA reaction

Catalyst	Conv%	Yield%	Sel%	
			<i>p,p</i> -DPA	<i>o,p</i> -DPA
$\text{Cs}_{1.5}\text{H}_{4.5}\text{D}$	35.9	34.6	88.0	12.0
$\text{Cs}_{2.0}\text{H}_{4.0}\text{D}$	35.1	33.7	87.8	12.2
$\text{Cs}_{2.5}\text{H}_{3.5}\text{D}$	32.3	30.4	87.8	12.2
$\text{Cs}_{3.5}\text{H}_{2.5}\text{D}$	29.5	27.6	86.7	13.3
$\text{Cs}_{4.5}\text{H}_{1.5}\text{D}$	27.2	25.6	85.3	14.7
$\text{Cs}_{6.0}\text{D}$	0.6	0.2	82.8	17.2
H_6D	39.2	36.8	77.8	22.2
$\text{Cs}_{1.0}\text{H}_{2.0}\text{K}$	20.5	17.7	71.4	28.6
$\text{Cs}_{1.5}\text{H}_{1.5}\text{K}$	22.3	20.5	77.8	22.2
$\text{Cs}_{2.0}\text{H}_{1.0}\text{K}$	27.1	25.3	80.8	19.2
$\text{Cs}_{2.5}\text{H}_{0.5}\text{K}$	28.3	26.5	80.4	19.6
$\text{Cs}_{3.0}\text{K}$	0.7	0.2	77.8	22.2
H_3K	33.3	30.0	60.0	40.0
HZSM-5	0.9	0.3	60.0	40.0
MCM-49	19.7	14.0	51.9	48.1
HCl	45.8	27.5	68.8	31.2

3.4 mmol LA, 10.2 mmol phenol, catalyst 50 mg, 100°C , stirring speed 1200 rpm, 6 h.

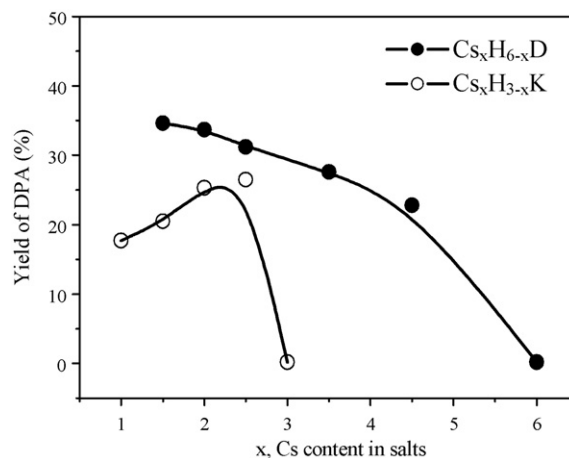


Fig. 5. Correlation between the yield of DPA and cesium content in $\text{Cs}_x\text{H}_{6-x}\text{D}$ and $\text{Cs}_x\text{H}_{3-x}\text{K}$ samples. 3.4 mmol LA, 10.2 mmol phenol, catalyst 50 mg, 100°C , stirring speed 1200 rpm, 6 h.

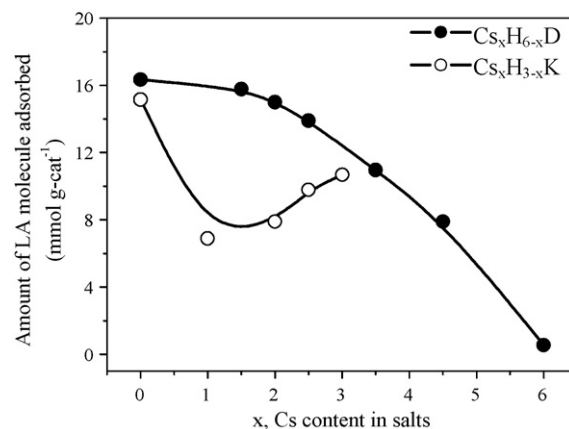


Fig. 6. Adsorption study of LA molecule by the bulk of $\text{Cs}_x\text{H}_{6-x}\text{D}$ and $\text{Cs}_x\text{H}_{3-x}\text{K}$. Catalyst 50 mg, stirring speed 1200 rpm, LA 0.4 g, 35°C , 1 h. Adsorption ability of $\text{Cs}_x\text{H}_{6-x}\text{D}$ or $\text{Cs}_x\text{H}_{3-x}\text{K}$ to LA is represented by the amount of LA molecule adsorbed on per gram catalyst ($\text{mmol g}^{-1} \text{ cat}^{-1}$).

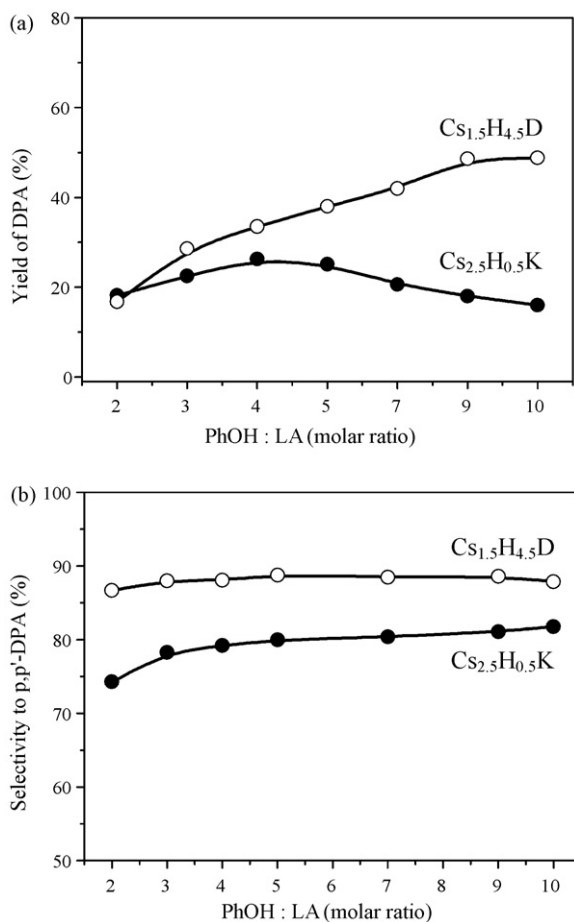


Fig. 7. Effects of the molar ratio of phenol to LA on the yield of DPA and selectivity to *p,p'*-DPA. Catalyst 50 mg, 100 °C, stirring speed 1200 rpm, 6 h.

49 < HCl < Cs_xH_{3-x}K < Cs_xH_{6-x}D. As for Cs_xH_{6-x}D or Cs_xH_{3-x}K, the correlation between the yield of DPA and Cs content in the cesium partly substituted HPAs are shown in Fig. 5. In the Cs_xH_{6-x}D systems, the yield of DPA decreases monotonically with the order of H₆D > Cs_{1.5}H_{4.5}D > Cs_{2.0}H_{4.0}D > Cs_{2.5}H_{3.5}D > Cs_{3.5}H_{2.5}D > Cs_{4.5}H_{1.5}D > Cs_{6.0}D. Moreover, the activity decreases slowly with increasing Cs content from $x=1.5$ to $x=3.5$ in the Cs_xH_{6-x}D and then decreases sharply with x beyond 4.5. However, in the Cs_xH_{3-x}K systems, the order of the catalyst activity is H₃K > Cs_{2.5}H_{0.5}K > Cs_{2.0}H_{1.0}K > Cs_{1.5}H_{1.5}K > Cs_{1.0}H_{2.0}K > Cs_{3.0}K. That is, the activity of Cs_xH_{3-x}K increases from $x=1.0$ to $x=2.5$, and then decreases greatly at $x=3.0$. As for the most active Cs_{1.5}H_{4.5}D and Cs_{2.5}H_{0.5}K, their selectivities to *p,p'*-DPA isomer are also the highest among all tested samples, where the selectivity to *p,p'*-DPA

Table 3

Effects of solvent on the yield of DPA and the selectivity to *p,p*-DPA or *o,p*-DPA isomer for Cs_xH_{6-x}D or Cs_{2.5}H_{0.5}K in condensation of phenol with LA

Solvent	Cs _{1.5} H _{4.5} D		Cs _{2.5} H _{0.5} K			
	Yield%	Sel%		Yield%		
		<i>p,p'</i> -DPA	<i>o,p'</i> -DPA		<i>p,p'</i> -DPA	<i>o,p'</i> -DPA
–	34.6	88.0	12.0	26.5	80.1	19.9
C ₆ H ₆	1.8	–	–	0.7	–	–
PhCH ₃	2.5	83.0	17.0	0.9	–	–
H ₂ O	1.1	–	–	0.5	–	–
EtOH	1.3	–	–	0.6	–	–

3.4 mmol LA, 10.2 mmol phenol, catalyst 50 mg, 100 °C, stirring speed 1200 rpm, 6 h.

isomer is higher for Cs_{1.5}H_{4.5}D system (88.0%) compared with Cs_{2.5}H_{0.5}K system (80.4%) under the same conditions (Table 2).

3.2.2. Adsorption behavior of the catalyst

Fig. 6 shows LA adsorption by the bulk of Cs_xH_{6-x}D ($x=0, 1.5, 2.5, 3.5, 4.5,$ and 6.0) and Cs_xH_{3-x}K ($x=0, 1.0, 2.0, 2.5,$ and 3.0) after adsorption–desorption reaches equilibrium. The results indicate that substitution of protons by cesium ions can change the adsorption ability of Cs_xH_{6-x}D to LA, which is closely related to the content of cesium in Cs_xH_{6-x}D compounds. With increasing the content of cesium in Cs_xH_{6-x}D from 0 to 6, the adsorption ability of Cs_xH_{6-x}D to LA decreases from 16.3 to 0.6 mmol g cat⁻¹. The amount of LA molecule adsorbed on Cs_{1.5}H_{4.5}D is the strongest among all tested Cs_xH_{6-x}D. In the case of Cs_xH_{3-x}K, its adsorption ability to LA increases with increasing the content of cesium from 1 to 3, implying that the adsorption ability of Cs_xH_{3-x}K is determined by its specific surface area.

3.2.3. Effect of the solvent

The results in Table 3 reveal that the condensation reaction of phenol with LA to produce DPA has the best performance under solvent-free condition. The yield of DPA in both apolar (benzene and toluene) and polar media (H₂O and ethanol) is very low, which is probably ascribed to the competitive adsorption between the solvent molecules and reaction molecules on the catalyst [26].

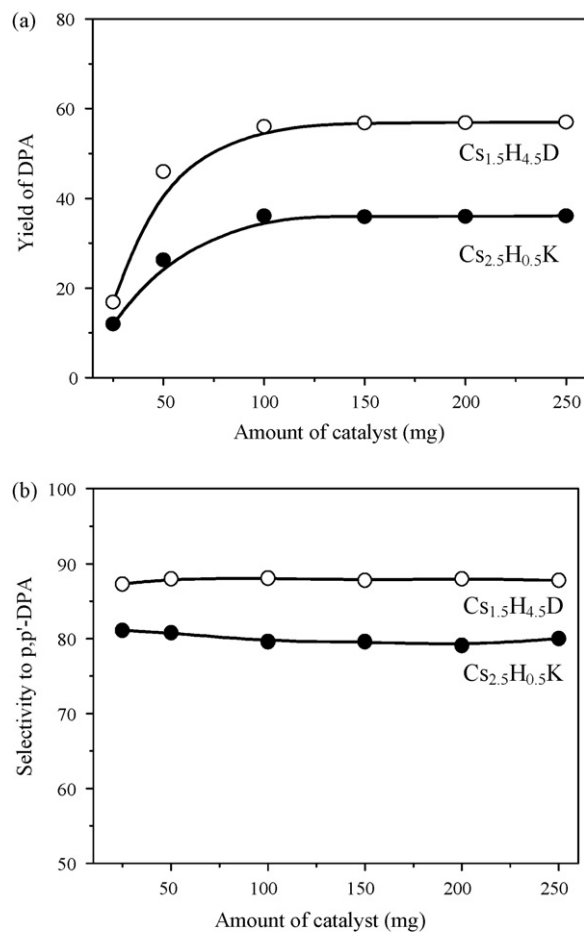


Fig. 8. Effects of catalyst amount on the yield of DPA and the selectivity to *p,p'*-DPA. Cs_{1.5}H_{4.5}D system: LA 3.4 mmol, phenol 30.6 mmol, 100 °C, stirring speed 1200 rpm, 6 h; Cs_{2.5}H_{0.5}K system: LA 3.4 mmol, phenol 13.6 mmol, 100 °C, stirring speed 1200 rpm, 6 h.

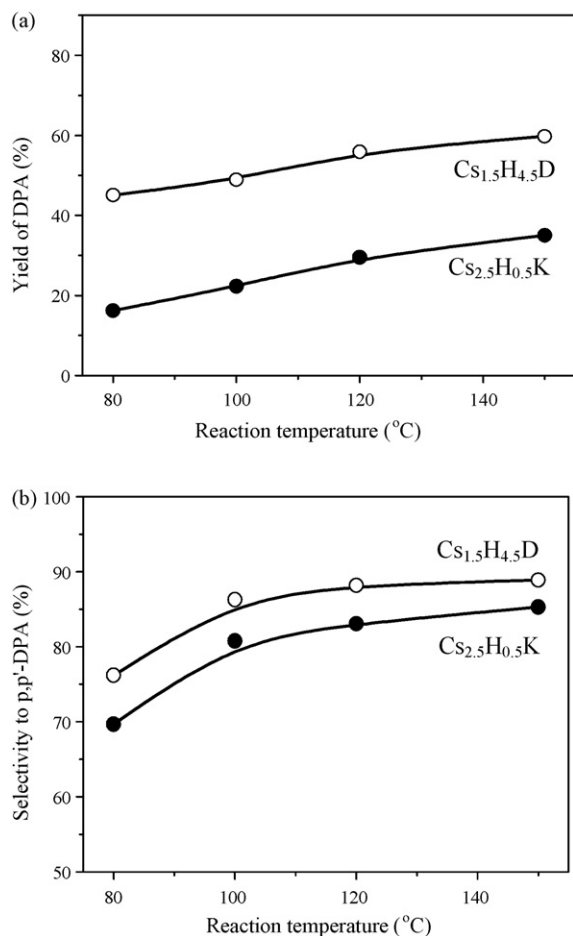


Fig. 9. Effects of the reaction temperature on the yield of DPA and selectivity to *p,p'*-DPA. Cs_{1.5}H_{4.5}D as a catalyst (50 mg), LA 3.4 mmol, phenol 30.6 mmol, stirring speed 1200 rpm, 6 h; Cs_{2.5}H_{0.5}K as a catalyst (50 mg), LA 3.4 mmol, phenol 13.6 mmol, stirring speed 1200 rpm, 6 h.

3.2.4. Effect of the molar ratio

The molar ratio of phenol to LA is one of the important factors that affect the yield of DPA and selectivity to *p,p'*-DPA isomer. Herein, the molar ratio of phenol to LA is varied from 2:1 to 10:1. As shown in Fig. 7a, the yield of DPA increases with increasing molar ratio over Cs_{1.5}H_{4.5}D and reaches maximum yield (48.6%) at 9:1.

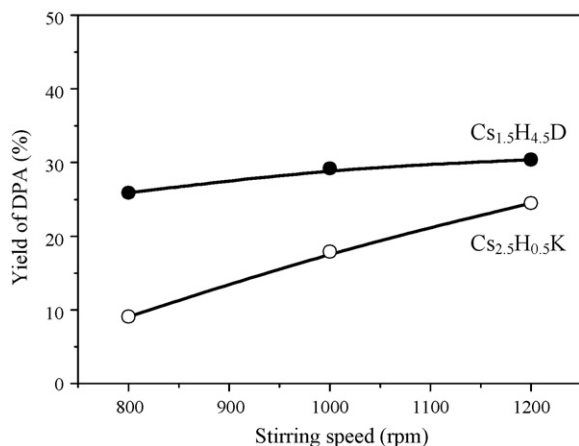


Fig. 10. Effects of the stirring speed on the yield of DPA. 3.4 mmol LA, 10.2 mmol phenol, catalyst 50 mg, 100 °C, 6 h.

However, the selectivity of Cs_{1.5}H_{4.5}D to *p,p'*-DPA isomer is almost unchanged with molar ratio changes. As for Cs_{2.5}H_{0.5}K, the yield of DPA increases with increasing molar ratio and reaches the maximum yield (26.3%) at 4:1, and further increasing the molar ratio results in the decrease of the yield of DPA (Fig. 7b). However, the selectivity of Cs_{2.5}H_{0.5}K to *p,p'*-DPA isomer increases from 74.4% to 81.8% as the molar ratio increases from 2:1 to 10:1.

3.2.5. Effect of the catalyst amount

Fig. 8 shows the effect of catalyst amount on the yield of DPA and selectivity to *p,p'*-DPA isomer. The experiments are carried out with varying catalyst amount between 25 and 250 mg using Cs_{1.5}H_{4.5}D or Cs_{2.5}H_{0.5}K catalyst. The yield of DPA increases as the amount of Cs_{1.5}H_{4.5}D or Cs_{2.5}H_{0.5}K increases. The maximum yield is attained at 100 mg of the catalyst amount, and then the yield almost remains unchangeable with further increasing catalyst amount. However, the effect of catalyst amount on the selectivity to *p,p'*-DPA isomer is negligible.

3.2.6. Effect of the reaction temperature

For evaluating the effect of the reaction temperature on the condensation reaction catalyzed by Cs_xH_{6-x}D or Cs_xH_{3-x}K, the reaction is carried out at 80, 100, 120, and 150 °C, respectively. It is observed that the yield of DPA increases slowly with increasing the reaction temperature from 80 to 150 °C in the presence of

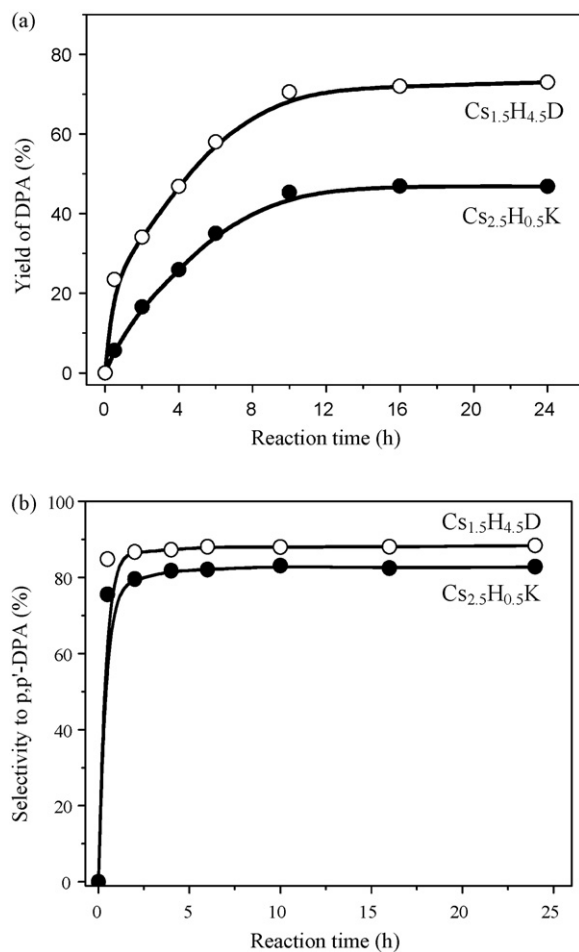


Fig. 11. Time courses of condensation of phenol with LA catalyzed over Cs_{1.5}H_{4.5}D and Cs_{2.5}H_{0.5}K. (a) changes of the yield of DPA and (b) changes of the selectivity to *p,p'*-DPA. Catalyst 100 mg, stirring speed 1200 rpm, molar ratio of phenol to LA 4:1 for Cs_{2.5}H_{0.5}K and 9:1 for Cs_{1.5}H_{4.5}D system, 150 °C.

Cs_{1.5}H_{4.5}D or Cs_{2.5}H_{0.5}K catalyst (Fig. 9a). At 80 and 150 °C, the yield of DPA reaches 16.2% and 35.0%, respectively, for the reaction catalyzed by Cs_{2.5}H_{0.5}K. Under the same conditions, the yield of DPA reaches 45.1% and 59.8%, respectively, for the reaction catalyzed by Cs_{1.5}H_{4.5}D. As for the selectivity of Cs_{1.5}H_{4.5}D or Cs_{2.5}H_{0.5}K to *p,p'*-DPA isomer, it increases obviously as increasing the reaction temperature from 80 to 150 °C (Fig. 9b). At 80 and 150 °C, the selectivity of Cs_{2.5}H_{0.5}K to *p,p'*-DPA isomer is 69.7% and 85.3%, while the selectivity of Cs_{1.5}H_{4.5}D to *p,p'*-DPA isomer is 76.2% and 88.9%, respectively.

3.2.7. Effect of the stirring speed

To estimate possible diffusion limitation in the Cs_xH_{3-x}K- or Cs_xH_{6-x}D-catalyzed DPA synthesis system, the effect of stirring speed on the yield of DPA is studied (Fig. 10). By changing the stirring speed from 800 to 1200 rpm, the yield of DPA increases for both Cs_{2.5}H_{0.5}K and Cs_{1.5}H_{4.5}D. However, the influence of stirring speed on the yield of DPA is different for the above two systems. In the Cs_{2.5}H_{0.5}K system, the yield of DPA increases obviously with increase of the stirring speed. As for the Cs_{1.5}H_{4.5}D system, the yield of DPA increases slowly. The results imply that the effect of external diffusion limitation on the reaction catalyzed by Cs_{2.5}H_{0.5}K is more obvious compared with Cs_{1.5}H_{4.5}D-catalyzed DPA synthesis reaction.

The above results are consistent with those of the studies on catalyst amount and reaction temperature, which shows the presence of external diffusion limitations in current catalytic systems. Therefore, the increase of DPA yield is not proportional to the catalyst amount. Moreover, the maximum conversion of LA at every temperature is limited and rises slowly with increase of temperature.

3.2.8. Effect of the reaction time

Under the optimal conditions (catalyst 100 mg, stirring speed 1200 rpm, molar ratio of phenol to LA 4:1 for Cs_{2.5}H_{0.5}K and 9:1 for Cs_{1.5}H_{4.5}D system, 150 °C), the time courses of the condensation reaction in Cs_{1.5}H_{4.5}D and Cs_{2.5}H_{0.5}K systems are studied (Fig. 11). For both of the catalysts, the activity and selectivity increase rapidly at the beginning of the reaction. After the reaction proceeds for 10 h, DPA yield is 70.5% and 45.3% for Cs_{1.5}H_{4.5}D and Cs_{2.5}H_{0.5}K, respectively, and the selectivity of Cs_{1.5}H_{4.5}D and Cs_{2.5}H_{0.5}K to *p,p'*-DPA isomer is 88% and 83.1%, respectively. When the reaction time increases further to 24 h changes of both activity and selectivity are negligible.

3.2.9. The recycle tests of the catalyst

The catalyst reuse is one of the most valuable and attractive properties for heterogeneous catalysts. Herein, the stability and reusability of the catalyst (Cs_{1.5}H_{4.5}D or Cs_{2.5}H_{0.5}K) are examined by repetitive use of the catalysts (Fig. 12). The results indicate that the catalyst activity does not change significantly after three repetitive runs. After the reaction finishes, the catalyst is easily separated from the production mixture because it settles at the bottom of the reactor. For the next catalytic cycle, the recovered catalyst is washed with ethanol and then calcined at 100 °C in vacuum for 60 min. The catalyst-free reaction liquor is examined by ICP-AES analysis. It is found that the leakage of Cs_{1.5}H_{4.5}D and Cs_{2.5}H_{0.5}K is 4.5%, 2.1%, 1.8% and 3.1%, 1.8%, 1.0%, respectively, for the three catalytic runs.

To further test the leaching of the catalyst (Cs_{2.5}H_{0.5}K or Cs_{1.5}H_{4.5}D) during the reaction process, the following experiment is carried out under the same reaction conditions showed in Fig. 11. The reaction is stopped after 2 h and the yield of DPA is 16.5% or 33.1% by using Cs_{2.5}H_{0.5}K or Cs_{1.5}H_{4.5}D catalyst. The separated filtrate is allowed to react for another 8 h under the same reaction conditions, but the yield of DPA maintains unchangeable. Thus the

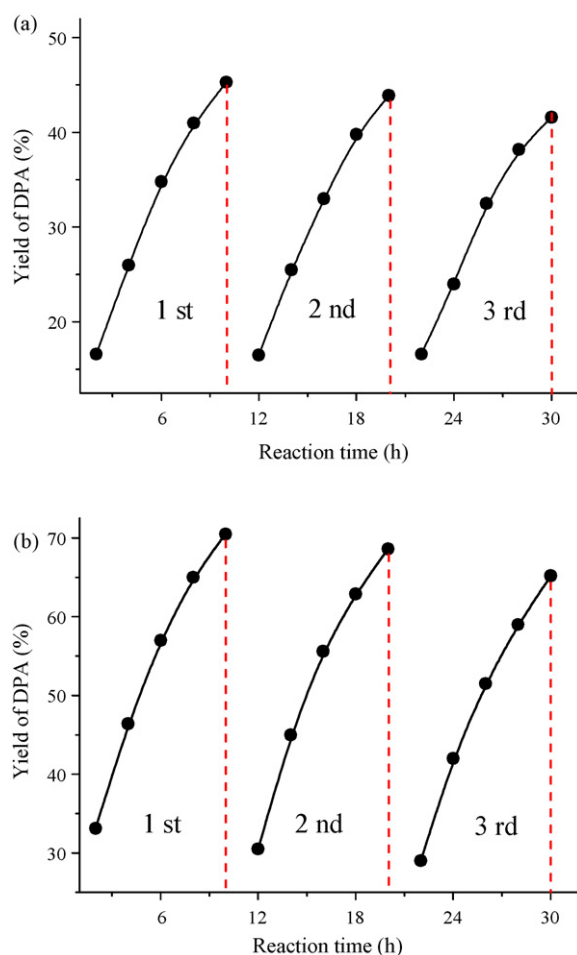


Fig. 12. Catalyst recycles for the DPA synthesis reaction over Cs_{2.5}H_{0.5}K (a) and Cs_{1.5}H_{4.5}D (b). Catalyst 100 mg, 150 °C, stirring speed 1200 rpm, 10 h. Molar ratio of phenol to LA 4:1 for Cs_{2.5}H_{0.5}K and 9:1 for Cs_{1.5}H_{4.5}D system.

catalysts (Cs_{2.5}H_{0.5}K and Cs_{1.5}H_{4.5}D) are considerably stable under the present conditions.

3.3. Discussion

The above catalytic test results show that both activity and selectivity of cesium partly substituted Dawson type HPAs are higher than those of cesium partly substituted Keggin type HPAs for the DPA synthesis reaction. Among all tested catalysts, the catalytic activity of Cs_{1.5}H_{4.5}D or Cs_{2.5}H_{0.5}K is the highest. Considering that the physicochemical surface properties and catalytic behaviors of Cs_xH_{6-x}D are obviously different from those of Cs_xH_{3-x}K, we reasonably infer that the Cs_xH_{6-x}D and Cs_xH_{3-x}K-catalyzed DPA synthesis reaction proceeds in different mechanisms. From XRD results it can be seen that the crystallinity of Well-Dawson type HPAs (Cs_xH_{6-x}D) is low due to the ellipsoidal shape of polyanions which is not suitable for the formation of stable crystalline structure. However, Keggin type polyanions (Cs_xH_{3-x}K) with spherical shape favor the crystalline structure. In addition, BET surface areas of all Cs_xH_{6-x}D remain low (ca. 1 m² g⁻¹), so that their catalytic activity is independent of the specific surface area. On the other hand, the adsorption behavior of Cs_xH_{6-x}D to LA molecule is different from that of Cs_xH_{3-x}K. For the Cs_xH_{6-x}D, its adsorption ability is closely related to the content of cesium. For example, Cs_{1.5}H_{4.5}D and H₆D have the same adsorption ability, but the adsorption ability of Cs_xH_{6-x}D decreases gradually with Cs content further increased. As

for the $Cs_xH_{3-x}K$, its adsorption ability is determined by its specific surface area.

The above properties suggest that $Cs_xH_{6-x}D$ -catalyzed DPA synthesis reaction proceeds in the type of pseudo-liquid phase. Hence, polar molecules (e.g. LA) are rapidly adsorbed into the $Cs_xH_{6-x}D$ lattice and react there, where the solid catalyst behaves in a sense like a concentrated solution [33]. This behavior often brings about high catalytic activity and unique selectivity. For various tested $Cs_xH_{6-x}D$ ($x=0-6.0$) samples, their activity for DPA synthesis reaction strongly depends on their acid strength. Thus, the activity is the highest in the case of free acid (H_6D) and decreases monotonically with increasing Cs content in $Cs_xH_{6-x}D$ salts. These results demonstrate that the catalytic activity of cesium partly substituted Dawson type HPAs can be designed by controlling their acid strength in this manner. As for $Cs_xH_{3-x}K$ -catalyzed DPA synthesis reaction, it takes place on the surface of $Cs_xH_{3-x}K$ (surface type reaction) and the catalyst activity is controlled largely by the relative number of available surface acid sites (determined by both surface area and acid strength) [33]. It has been reported that the acid strength of $Cs_xH_{3-x}K$ materials are weakly perturbed during exchange of proton with doping Cs up to loadings of $Cs_{2.3}H_{0.7}K$ [32]. However, the acid strength of heavily substituted ($>Cs_{2.4}H_{0.6}K$) samples is significantly low. Considering the factors of BET surface areas and acid strength, the available number of surface acid sites is the most for $Cs_{2.5}H_{0.5}K$ and the least for $Cs_{3.0}K$ in cesium partly substituted Keggin type HPAs. Therefore, $Cs_{2.5}H_{0.5}K$ and Cs_3K exhibit the highest and lowest activity to this reaction, respectively. Although $Cs_{2.5}H_{0.5}K$ has more surface sites, the number of its surface acid sites is about half of the total number of protons contained in the free acid H_3K [19]. Thus, the activity of $Cs_{2.5}H_{0.5}K$ is lower than that of H_3K . Similar results have been attained by many reactions using $Cs_xH_{3-x}K$ materials as catalysts [34–37].

Owing to different reaction types between $Cs_xH_{6-x}D$ and $Cs_xH_{3-x}K$ catalysts, higher catalytic activity and selectivity are brought about by $Cs_xH_{6-x}D$ due to its pseudo-liquid phase behavior. Therefore, the reactions take place at the surface and solid bulk of the polyanions and the adsorption–desorption is rapid. As for $Cs_xH_{3-x}K$, the catalytic reaction takes place on the solid surface due to its surface-type reaction, and adsorption is excessive and slow [38]. Influence of molar ratio on the DPA yield over different types of HPAs can also be explained by the different types of catalysis. As for $Cs_{1.5}H_{4.5}D$ sample, the high molar ratio of phenol to LA makes the reactant molecules approach active sites of the catalyst easily, which facilitates the DPA formation [39]. However, the high molar ratio is unfavorable to the DPA production if the reaction is catalyzed by $Cs_{2.5}H_{0.5}K$. This is due to the reaction takes place in the pores of catalyst. As the molar ratio increases, excessive reactant molecules may slow down the reaction process [20]. Finally, although the free acid H_6D and H_3K exhibit excellent activity for DPA synthesis, their selectivity to p,p' -DPA isomer is lower than that of the corresponding cesium partly substituted salts. Significantly, they are completely soluble in the reaction media and thus unable to compete with many process advantages offered by their heterogeneous counterparts.

Considering potential industrial application, the selectivity to p,p' -DPA isomer is expected to be improved further. This can be obtained by using $Cs_{1.5}H_{4.5}D$ rather than $Cs_{2.5}H_{0.5}K$ catalyst under the optimal experimental conditions including suitable molar ratio of phenol to LA and reaction temperature. However, relatively low yield of DPA under current reaction system is still a problem, and the study will be extended to mend the performance of cesium partly substituted Wells–Dawson type HPAs for increasing the reactivity of DPA synthesis.

4. Conclusions

Cesium partly substituted Wells–Dawson type HPAs, $Cs_xH_{6-x}D$ ($x=1.5-6.0$), have been investigated for the DPA synthesis reaction from the important bio-platform molecule (LA). With $x=1.5$, the sample exhibits the highest activity and selectivity. For studying the catalytic behaviors of $Cs_xH_{6-x}D$, cesium partly substituted Keggin type HPAs, $Cs_xH_{3-x}K$ ($x=1.0-3.0$), are also tested under the same experimental reactions. The most active and selective compound in all tested $Cs_xH_{3-x}K$ samples is $Cs_{2.5}H_{0.5}K$. However, both activity and selectivity of $Cs_{1.5}H_{4.5}D$ exceed those of $Cs_{2.5}H_{0.5}K$ owing to their different reaction types. For $Cs_xH_{6-x}D$ samples, pseudo-liquid behavior should be considered as the governing factor of high catalytic activity and selectivity. Besides that, changes of acid strength with Cs content need to be examined. In the case of $Cs_xH_{3-x}K$ samples, surface type reaction is followed, in which the activity is determined by the relative number of available surface acid sites.

Acknowledgements

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References

- [1] J. Bozell, L. Moens, D. Elliott, Y. Wang, G. Neuenschwander, S. Fitzpatrick, R. Bilski, J. Jarnefeld, *Resour. Conserv. Recy.* 28 (2000) 227–239.
- [2] G.M. Campbell, C. Webb, S.L. McKee, *Proceedings of an International Conference on Cereals: Novel Uses and Processes*, Manchester, United Kingdom, 1996, pp. 49–55.
- [3] Y. Isoda, M. Azuma, Japanese Patent 08053390, Honshu Chemical Ind., 1996.
- [4] S.C. Johnson, US Patent 790373, Wikipatents, 1958.
- [5] Y. Cha, M.A. Hanna, *Ind. Crops Prod.* 16 (2002) 109–118.
- [6] M.E. Davis, *Acc. Chem. Res.* 26 (1993) 111–115.
- [7] I.V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171–198.
- [8] N. Mizuno, M. Misono, *Chem. Rev.* 98 (1998) 199–217.
- [9] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1996) 113–116.
- [10] Y. Izumi, M. Ono, M. Kitagawa, M. Yoshida, K. Urabe, *Microporous Mater.* 5 (1995) 255–262.
- [11] Y. Guo, Y. Wang, C. Hu, E. Wang, *Chem. Mater.* 12 (2000) 3501–3508.
- [12] Y. Guo, C. Hu, C. Jiang, Y. Yang, S. Jiang, X. Li, E. Wang, *J. Catal.* 217 (2003) 141–151.
- [13] P. Vázquez, L. Pizzio, G. Romanelli, J. Autino, C. Cáceres, M. Blanco, *Appl. Catal. A: Gen.* 235 (2002) 233–240.
- [14] Q.Y. Liu, W.L. Wu, J. Wang, X.Q. Ren, Y.R. Wang, *Microporous Mesoporous Mater.* 76 (2004) 51–60.
- [15] I.V. Kozhevnikov, K.R. Kloetstra, A. Sinnema, H.W. Zandbergen, H. Bekkum, *J. Mol. Catal. A: Chem.* 114 (1996) 287–298.
- [16] D.P. Sawant, A. Vinu, N.E. Jacob, F. Lefebvre, S.B. Halligudi, *J. Catal.* 235 (2005) 341–352.
- [17] M. Misono, *Catal. Rev. Sci. Eng.* 29 (1987) 269–321.
- [18] Y. Guo, K. Li, J. Clark, *Green Chem.* 9 (2007) 839–841.
- [19] M. Misono, *Chem. Commun.* (2001) 1141–1152.
- [20] T. Okuhara, *Catal. Today* 73 (2002) 167–176.
- [21] T. Okuhara, H. Watanabe, T. Nishimura, K. Inumaru, M. Misono, *Chem. Mater.* 12 (2000) 2230–2238.
- [22] B.B. Bardin, R.J. Davis, *Top. Catal.* 6 (1998) 77–86.
- [23] J. Poźniczek, A. Lubńska, D. Mucha, A. Bielanski, *J. Mol. Catal. A: Chem.* 257 (2006) 99–104.
- [24] G.M. Maksimov, I.V. Kozhevnikov, *React. Kinet. Catal. Lett.* 39 (1989) 317–322.
- [25] S. Shikata, T. Okuhara, M. Misono, *J. Mol. Catal. A: Chem.* 100 (1995) 49–59.
- [26] S. Shikata, S. Nakata, T. Okuhara, M. Misono, *J. Catal.* 166 (1997) 263–271.
- [27] J. Poźniczek, A.M. Ilinicka, A. Lubańska, A. Bielański, *Appl. Catal. A: Gen.* 286 (2005) 52–60.
- [28] A. Hiskia, A. Mylonas, E. Papaconstantinou, *Chem. Soc. Rev.* 30 (2001) 62–69.
- [29] M.T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer Verlag, Berlin, 1983.
- [30] G. Baronetti, H. Thomas, C.A. Querini, *Appl. Catal. A: Gen.* 217 (2001) 131–141.
- [31] L. Li, Q. Wu, Y. Guo, C. Hu, *Microporous Mesoporous Mater.* 87 (2005) 1–9.

- [32] K. Narashimharao, D.R. Brown, A.F. Lee, A.D. Newman, P.F. Siril, S.J. Tavener, K. Wilson, *J. Catal.* 248 (2007) 226–234.
- [33] G. Li, Y. Ding, J. Wang, X. Wang, J. Suo, *J. Mol. Catal. A: Chem.* 262 (2007) 67–76.
- [34] M. Kimura, T. Nakato, T. Okuhara, *Appl. Catal. A: Gen.* 165 (1997) 227–240.
- [35] T. Nakato, Y. Toyoshi, Y. Toyoshi, M. Kimura, T. Okuhara, *Catal. Today* 52 (1999) 23–28.
- [36] T. Nakato, M. Kimura, S. Nakata, T. Okuhara, *Langmuir* 14 (1998) 319–325.
- [37] Y. Sun, Y. Yue, Z. Gao, *React. Kinet. Catal. Lett.* 63 (1998) 349–354.
- [38] S. Shikata, M. Misono, *Chem. Commun.* (1998) 1293–1294.
- [39] K. Jeřábek, L. Hanková, Z. Prokop, E.G. Lundquist, *Appl. Catal. A: Gen.* 232 (2002) 181–188.