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Creation of a Monomeric Ag Species on the Surface of γ-ZrP as an Efficient Heterogeneous Catalyst for the Selective Oxidation of Cycloolefins

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Abstract A hybrid complex $Zr(PO_4)(AgHPO_4)$ was prepared by ion-exchange and its activity was examined on the allylic oxidation of cycloolefins using *tert*-butylhydroperoxide (TBHP) as oxidant under argon atmosphere. Under these reaction conditions, attack of the activated C–H bond was preferred instead of the epoxidation of C=C bond, yielding enols as the main products, this is a novel highly active/selective and reusable heterogeneous catalyst.

Keywords Allylic oxidation · Cycloolefin · Enols · Silver · Zirconium phosphates

1 Introduction

The allylic oxidation of olefin into enone or enol under mild liquid phase condition is a subject of great interest from both academic and industrial points of view [1]. Due to the ease in separation, recovery and recycling for continuous processing, heterogeneous catalytic oxidation is a more acceptable pathway compared to homogeneous counterparts, so there has been an increasing interest in the development of heterogeneous catalysts for this reaction. Recent trends in this area fall into two broad categories: (i) development of new transition metal substituted/constituted redox molecular sieves [2, 3], and (ii) immobilization of known homogeneous oxidation catalysts on the surface and in the cavities of suitable hosts such as zeolites and structurally tailored sol–gel materials [4, 5]. However, the research in this area still is not enough and it is necessary to develop a better solid catalyst to achieve both high activity and high selectivity for enone or enol.

Layered materials, such as zirconium phosphates, are of considerable interest because of their practical applications mainly in the areas of ion-exchange, intercalation, catalysis and sorption [6]. Zirconium phosphates, mainly include $Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP), $Zr(HPO_4)_2$ (β-ZrP) and $Zr(PO_4)(H_2PO_4) \cdot 2H_2O$ (γ-ZrP), which respectively have interlayer spacing of 7.55, 9.4 and 12.2 Å. For γ-ZrP, their structure with zeolite type cages and their appropriate interlayer spacing provide potential usability as biomaterials, adsorbents, and ion exchangers [7]; however, only a few excellent applications as catalysts or catalyst precursors have emerged by far [8–10]. Herein, we present a new strategy for the design of high-performance heterogeneous catalyst utilizing the γ-ZrP as a macroligand for catalytically active centers, the introduction of transition metal cations Ag^+ into the γ-ZrP framework by ion-exchange could generate stable monomeric phosphate complex, which exhibits prominent catalytic performance for the allylic oxidation of cycloolefins to enols in an environmentally benign oxidation protocol involving aqueous *tert*-butyl hydroperoxide (TBHP) in argon atmosphere.

2 Experimental

2.1 Materials

All the materials were of commercial reagent grade. TBHP (70% in water), H_2O_2 (50% in water) and other reagents

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were all obtained from commercial sources without any further purification.

2.2 Catalyst Preparation

The precursor γ-ZrP was synthesized according to the literature [11], then the γ-ZrP (1.0 g) was stirred with 25 mL of a 5.6×10^{-2} M aqueous $AgNO_3$ solution at 25 °C for 24 h, the obtained slurry was filtered, washed sufficiently with deionized water, and dried overnight in a vacuum oven at 60 °C yielding the Ag–γ-ZrP white powder as catalyst.

2.3 Catalyst Characterization

The morphologies of obtained γ-ZrP and Ag–γ-ZrP particles were examined by transmission electron microscope (TEM) (JEM-1200EX), scanning electron microscope (SEM) (JSM-5600 LV). The crystals of the catalysts were studied by X-ray diffraction (XRD), the XRD data were collected on X' Pert PRO X-ray diffraction, patterns were recorded using a X'Celerator Discover, with Cu–$K\alpha$ radiation ($\lambda = 0.154$ nm) and a graphite monochromator in the range 10–80 °C. Surface composition was determined by X-ray photoelectron spectroscopy (XPS), using an ESCALAB 210 XPS System with a Mg–$K\alpha$ source. Simultaneous thermogravimetry-differential scanning calorimetry (TG-DSC) was carried out using a NETZSCH STA 409 PG/PC thermal analysis system under a flow of dry air, the temperature was raised from room temperature to 1273 K using a linear programmer at a heating rate of 10 K min^{-1}. The fourier transformed-infrared spectroscopy (FT-IR) spectra of samples were obtained on a Bruker IFS 120 HR FT-IR spectrometer. Mass spectrometric measurements were performed on a VG ZAB-HS instrument (VG analytical Ltd.) operating in fast atom bombardment (FAB) conditions. Elemental analysis was determined by X-ray fluorescence spectrometry (XRF) (Magix PW 2403 XRF), using PAN analytical X radial tube with a Rh–$K\alpha$ source.

2.4 Cycloolefin Oxidation

The allylic oxidations of cycloolefins were carried out in a 25 mL round-bottom flask equipped with a condenser. In a typical run, a mixture of catalyst (0.05 g), cyclohexene (10 mmol) and acetonitrile (5 mL) was stirred under argon atmosphere in a 25 mL round-bottom flask equipped with a condenser at room temperature for 30 min, after the addition of TBHP (5 mL), the reactor was placed into the oil bath preheated to 82 °C to start the reaction, then carried out with vigorous stirring under argon atmosphere for a certain time. After filtration and extraction, the filtrate was concentrated by rotary evaporator then analyzed by GC using a GC 201 gas chromatograph equipped with a SE-54 capillary column (30 m), the nature of the products was also determined by GC-MS. The conversion, product selectivity were calculated as follows: conversion (%) = [(moles of reactant converted) × 100]/[moles of reactant in feed], product selectivity (%) = [(moles of product formed) × 100]/[moles of reactant converted].

3 Results and Discussion

3.1 The determination of Ag–γ-ZrP Complex

By exchanging one of protons for the ammonium, Poojary and Clearfield obtained a new γ-ZrP phase, signed $Zr(PO_4)(NH_4HPO_4)$ [11], the formation of the fully NH_4^+ exchanged phase did not occur in the synthesis procedure of γ-ZrP, because it was energetically unfavorable due to the crowding about the P–O^- groups and the lattice expansion to 13.5 Å, which was required to alleviate this crowding [7]. Since only one NH_4^+ could be introduced into the γ-ZrP, and the radius of NH_4^+ (1.48 Å) was close to that of Ag^+ (1.26 Å), so we have introduced one Ag^+ into the γ-ZrP framework by ion-exchange with one ammonium ion, could generate stable monomeric $Zr(PO_4)(AgHPO_4)$ complex.

The newly formed complex is approved by characterization. Figure 1 illustrates the XRD patterns of the γ-ZrP and silver-exchanged ones, the peak positions of Ag–γ-ZrP are similar to those of a parent γ-ZrP, the original characteristic peaks of host decrease slightly when ammonium ions are exchanged by the silver ones. No new peaks appear for Ag–γ-ZrP solid, which means that no change in crystal and interlayer spacing [12]. The TG and DSC curves of the Ag–γ-ZrP solid measured in air are shown in Fig. 2. TGA curves

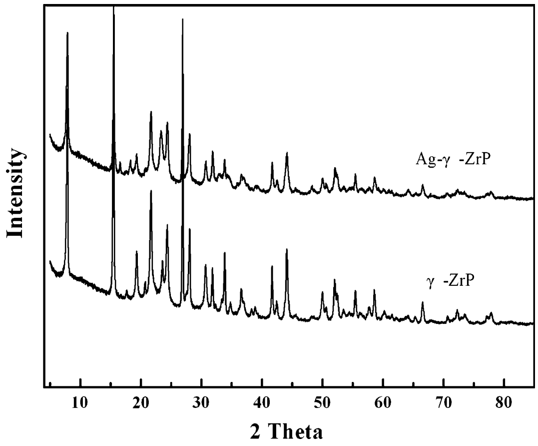


Fig. 1 XRD patterns of γ-ZrP precursor and Ag–γ-ZrP catalyst

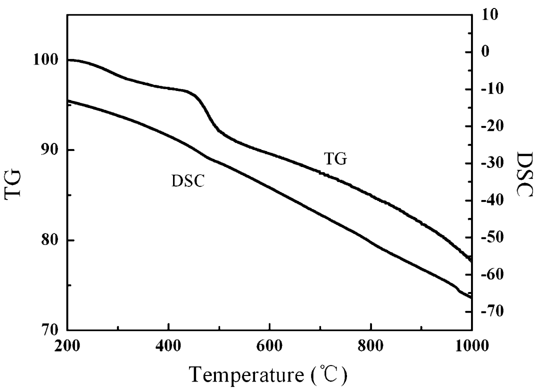


Fig. 2 TG-DSC curve for the Ag–γ-ZrP catalyst

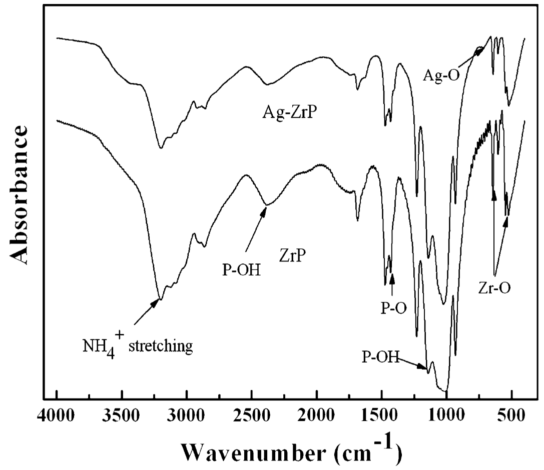


Fig. 3 FT-IR spectra of γ-ZrP precusor and Ag–γ-ZrP catalyst

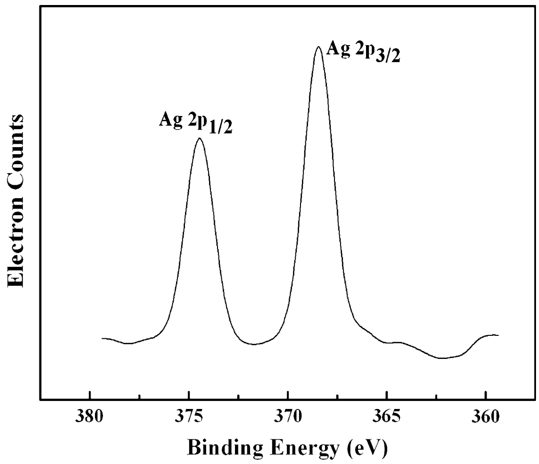


Fig. 4 XPS of Ag 2p region of Ag–γ-ZrP catalyst

exhibit two weight-loss stages, the first weight loss at 300 °C is mainly resulted from the decomposition of the AgO(H), while 3.5% weight loss from 469 °C to 485 °C is attributed to the formation of $Zr_2P_2O_7$.

Figure 3 presents the FT-IR spectra for the γ-ZrP before and after silver-exchanges, typical peaks for γ-ZrP are found at ca.615 cm^{-1} (P=O bending), 930 cm^{-1} (PO_4^{3-}, P–O stretching), 1098 cm^{-1} (PO_4^{3-}, P–O streching), 1141 cm^{-1} (P–OH bending), 2380 cm^{-1} (P–OH streching), 3437 cm^{-1} (hydrogen bonded OH) [13–14]. Also, the characteristic peak for NH_4^+ (3197 cm^{-1}) is detected in the both before and after silver-exchanged γ-ZrP , this means that the silver-exchanges only occur at the surface of the γ-ZrP. While the bands of Ag–O is not clear, this confirms the weak linkages for silver in the $Zr(PO_4)(AgHPO_4)$ complex. The presence of ion-exchanged Ag^+ was confirmed by XPS

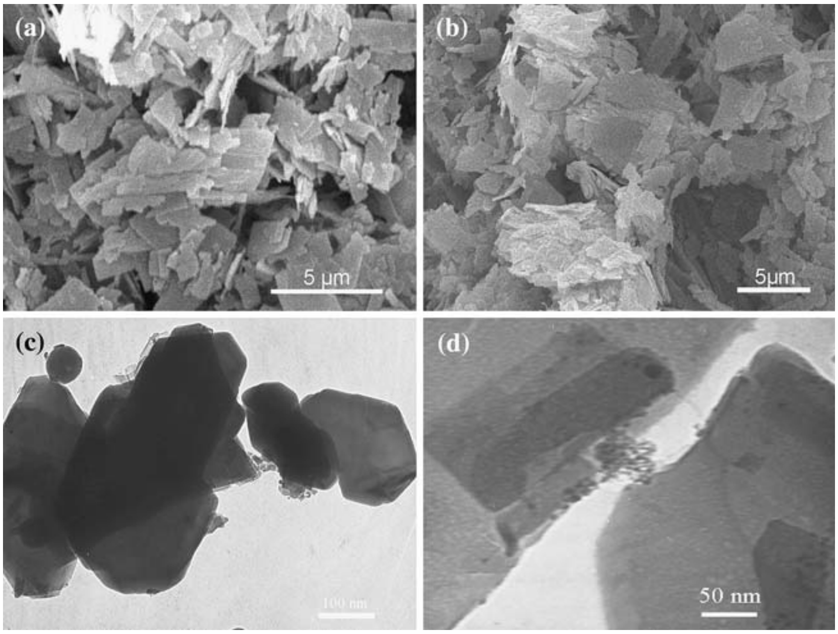


Fig. 5 SEM images of (**a**) γ-ZrP, (**b**) Ag–γ-ZrP and TEM images of (**c**) γ-ZrP, (**d**) Ag–γ-ZrP

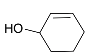
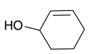
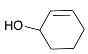
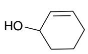
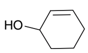
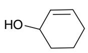
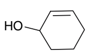
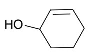
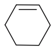
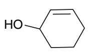
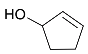
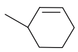
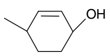
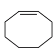
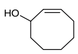
(368.4 eV, Fig. 4) and EDS, the (Ag+N)/P ratio of Ag–γ-ZrP was 1:2, which was in agreement with N/P ratio of γ-ZrP. Also, the molecular weight was determined as 390.2 by mass spectrum, which was in agreement with that of $Zr(PO_4)(AgHPO_4)$ compound. On the basis of XRD, elemental analysis, TGA data and mass spectrum studies, compound Ag–γ-ZrP is formulated as $Zr(PO_4)(AgHPO_4)$.

The platelike morphologies of γ-ZrP and Ag–γ-ZrP are observed by SEM and TEM (Fig. 5). Parent γ-ZrP and Ag–γ-ZrP solids are almost the same in the shape of crystallites, the size of these crystallites is 3–5 μm in diameter and 50–100 nm in thickness (Fig. 5a, b). Also, no silver particles are found from TEM, this means no dissociative Ag^+ particles except exchanged ones (Fig. 5c, d) at the surface of Ag–γ-ZrP. XRF gave the concentration of Ag^+ was 0.37 mmol g^{-1}. The present simple preparation method using the ion-exchange ability of γ-ZrP can allow a strong protocol to create a monomeric metal species on the solid surface as a hybrid heterogeneous catalyst.

3.2 Catalytic Activity

The oxidations of cycloolefins to corresponding enols over Ag–γ-ZrP catalyst at different conditions were investigated, the results are shown in Table 1.

Table 1 Ag–γ-ZrP catalyzed allylic oxidation of cycloolefins[a]

Entry	Substrate	Product	Time	Conv.[b](%)	Sel.[b] (%)	TON[c]
1			8	87.5	95.0	449
			12	96.4	94.1	490
2[d]			8	46.7	96.1	242
3[e]			8	12.6	92	62
4[f]			8	91.2	85.7	422
5[g]			8	40.3	94.2	205
6[h]			8	17.9	82.5	80
7[i]			10	92.7	93.7	470
8[j]			8	17.1	–	–
9[k]			8	–	–	–
10			8	92.4	96.2	480
11			8	86.7	94.1	440
12			8	81.5	94.2	415

[a] Conditions: catalyst (0.05 g), substrate (10 mmol), CH_3CN (5 ml), 82 °C, TBHP (70% in water, 5 ml), argon atmosphere. [b] Conv.: conversion; Sel.: selectivity, all determined by GC. [c] TON = moles of products/moles of silver in the catalyst. [d] H_2O_2 (50% in water, 2 ml) as oxidant. [e] Air atmosphere, TBHP (70% in water) as oxidant. [f] anhydrous TBHP as oxidant. [g] $ClCH_2CH_2Cl$ as solvent. [h] CH_3OH as solvent. [i] Recycled test. [j] γ-ZrP as catalyst. [k] Blank experiment, without any catalyst

The result of allylic oxidation of cycloolefins over Ag–γ-ZrP catalysts using TBHP (70% in water) as oxidant under argon atmosphere has been compared with that in the presence of air, other oxidants such as hydrogen peroxide and anhydrous TBHP, various solvents (Table 1, entries 1–7). A highly efficient allylic oxidation of cyclohexene could be accomplished at 82 °C over Ag–γ-ZrP catalyst in acetonitrile solvent using TBHP (70% in water) under argon atmosphere (entry 1), TON as high as 490 could be achieved, which was better than many of the heterogeneous catalytic systems reported earlier. Using hydrogen peroxide (50% in water) as oxidant, when the mole ratio of oxidant versus reactant was the same as entry 1, the reaction showed good selectivity for enol but low conversion of cyclohexene (entry 2), the reaction was much slower in the presence of air, only gave a trace of product (entry 3). Also, a comparative experiment was carried out using anhydrous TBHP as oxidant, the reaction showed a slightly higher conversion but lower enol selectivity than hydrous TBHP (entry 4), in view of economic and facile reasons, the TBHP (70% in water) should be optimal oxidant. 1,2-dichloroethane also was found to be a favorable solvent for the allylic oxidation (entry 5), but the conversion of cyclohexene was lower than that in acetonitrile. The reaction, however, showed low activity and badly enol selectivity in methanol (entry 6). The catalyst recycled was used to allylic oxidation of cyclohexene for the second time, also gave 92.7% conversion and 97% selectivity for enol (entry 7). It was confirmed by induced coupled plasma techniques (ICP) that the silver content of recycled Ag–γ-ZrP catalyst was the same as that of the fresh ones and no Ag^+ species were detected in the filtrate, meanwhile, the catalyst was filtered off after ca. 50% conversion at the reaction temperature, further treatment of the filtrate under similar reaction conditions did not afford to any products. Meanwhile, using γ-ZrP precursor as catalyst (without silver), the reaction gave low conversion but no enol selectivity (main product was cyclohex-2-enone), which showed that the silver component increased the cyclohexene conversion and enol selectivity (entry 8). A blank experiment also has been done and no product was detected (entry 9). After optimal conditions had been discerned for cyclohexene, the generality of oxidative reaction was investigated by variation of cyclic alkene substrates, such as cyclopentene, cyclooctene and 3-methylcyclohexene, these reactions also gave high conversion and excellent selectivity (entries 10–12).

4 Conclusions

In this work, a compound of newly synthesized by ion-exchange, $Zr(PO_4)(AgHPO_4)$ as catalyst, *t*-butylhydroperoxide as terminal oxidant, when stirred in CH_3CN at 82 °C under argon atmosphere shows a very pronounced efficiency for allylic oxidation of cycloolefins. Due to the simple preparation method of Ag–γ-ZrP catalyst and possibility to separate and re-use the catalyst after the reaction, we conclude that this complex is a promising heterogeneous catalyst for the oxidation of cycloolefins and should be studied in more detail.

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