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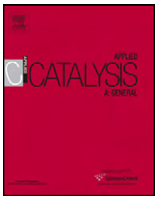

Isomerization of styrene oxide to phenylacetaldehyde over supported phosphotungstic heteropoly acid

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ABSTRACT

Silica-supported $H_3PW_{12}O_{40}$ (PW), the strongest heteropoly acid in the Keggin series, is an efficient, environmentally friendly heterogeneous catalyst for the liquid-phase isomerization of styrene oxide into phenylacetaldehyde, an industrially important intermediate for fine chemical synthesis. The reaction occurs in cyclohexane as a solvent under mild conditions at 25–70 °C with low catalyst loadings and without PW leaching in solution. At 60 °C, the yield of phenylacetaldehyde reaches 92% at 97% styrene oxide conversion, with a catalyst turnover number of 19 600. The catalyst can be recovered and reused.

1. Introduction

Epoxides are a versatile raw material used for the synthesis of various chemical products. For example, the isomerization of styrene oxide represents an industrial route to β-phenylacetaldehyde, which is practically useful for the production of drugs, perfumes, artificial sweeteners, and agricultural chemicals such as insecticides, fungicides and herbicides [1]. Epoxides are highly reactive compounds known to undergo easily ring opening giving alcohols, diols, aldehydes, ketones, etc. These reactions usually give a mixture of products and can be seriously complicated by substrate polymerization. The selective transformation of epoxides to aldehydes is a particularly problematic reaction due to a competitive aldolization of aldehyde products. The formation of high-boiling molecules in these systems often prejudices the catalyst performance and leads to catalyst deactivation by coke deposition.

Being a difficult industrial problem [1], the isomerization of styrene oxide into phenylacetaldehyde has been investigated by several research groups. Various solid acid materials, such as zeolites [2–6] and Nafion-H [7] have been applied as catalysts for this reaction. In most of these works, the reactions require very high catalyst to substrate ratios (10–60 wt%) to reach a reasonable yield. Although important advances have been made in the field, the development of alternative catalytic processes for the synthesis of phenylacetaldehyde from styrene oxide is still of interest in the fine chemistry.

Heterogeneous acid catalysis by heteropoly acids (HPAs) has attracted much interest because of its potential of great economic rewards and green benefits [8]. The majority of catalytic applications use the most stable and easy available Keggin HPAs comprising heteropoly anions of the formula $[XM_{12}O_{40}]^{n-}$, where X is the heteroatom (P^{5+}, Si^{4+}, etc.) and M the addendum atom (Mo^{6+}, W^{6+}, etc.). HPAs possess stronger acidity than conventional solid acid catalysts such as acidic ion exchange resins, oxides and zeolites. Due to their stronger acidity, HPAs often exhibit higher catalytic activities compared to the conventional catalysts. The acid strength of Keggin HPAs decreases in the order: $H_3PW_{12}O_{40} > H_4SiW_{12}O_{40} > H_3PMo_{12}O_{40} > H_4SiMo_{12}O_{40}$, and usually $H_3PW_{12}O_{40}$ is the catalyst of choice because of its stronger acidity [8]. Previously, we have reported HPAs to be versatile catalysts for isomerization of various compounds, e.g., α-pinene oxide [9,10].

In the present work, we report the application of silica-supported $H_3PW_{12}O_{40}$ (PW) as an efficient and recyclable solid acid catalyst for the rearrangement of styrene oxide into phenylacetaldehyde. To our knowledge, no attempt to use HPA catalysts for this reaction has been made so far.

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2. Experimental

All chemicals were purchased from commercial sources and used as received. $H_3PW_{12}O_{40}$ hydrate and styrene oxide were from Aldrich and Aerosil 300 silica from Degussa.

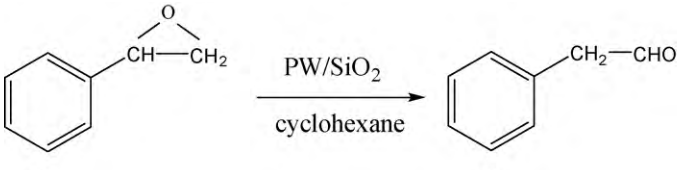
The catalyst, 20 wt% $H_3PW_{12}O_{40}/SiO_2$ (PW/SiO_2), was prepared by impregnating Aerosil 300 (S_{BET}, 300 $m^2\,g^{-1}$) with an aqueous PW solution and pre-treated under static vacuum at 0.2–0.3 Torr at 130 °C for 1.5 h, as described elsewhere [11]. Tungsten and phosphorus content was measured by inductively coupled plasma (ICP atomic emission spectroscopy, Spectro Ciros CCD). The BET surface area and porosity of the catalyst were obtained from nitrogen adsorption which was measured at −196 °C (Micromeritics ASAP 2000). ^{31}P MAS NMR spectra were measured on a Bruker Avance DSX 400 instrument at room temperature, 4 kHz spinning rate, using 85% H_3PO_4 as an external reference. XRD pattern of the catalyst was recorded on Rigaku Geigerflex-3034 diffractometer using CuK_α radiation.

In a typical reaction run, a mixture of styrene oxide (0.07–0.15 mol L^{-1}, 1.4–3.0 mmol), dodecane (0.10 mol L^{-1}, 2 mmol, internal standard), and PW/SiO_2 (1–13 mg, 0.08–0.006 wt%) in cyclohexane (20 mL) was intensely stirred in a glass reactor under air at a specified temperature. The reaction progress was followed by gas chromatography (GC, Shimadzu 17, Carbowax 20M). At appropriate time intervals, aliquots were taken and analyzed by GC. The GC mass balance was based on the substrate charged. Any difference in mass balance was attributed to oligomers, which were not GC determinable. Phenylacetaldehyde was identified by GC–MS (Shimadzu QP2010-PLUS, 70 eV) and also by GC co-injections with an authentic sample.

3. Results and discussion

3.1. Catalyst characterization

Silica-supported PW catalysts with different PW loadings have been characterized in detail previously (for a review see [8,12]). The catalyst, 20%PW/SiO_2, that was used in this work had a BET surface area of 200 $m^2\,g^{-1}$, a total pore volume of 0.53 $m^3\,g^{-1}$ and an average pore diameter of 107 Å. The integrity of PW Keggin structure was confirmed by ^{31}P MAS NMR. In agreement with the previous report [13], the catalyst showed a well-known peak at −15 ppm characteristic of $H_3PW_{12}O_{40}$. From XRD, the catalyst was amorphous; it did not exhibit PW crystalline phase, which also agrees with the previous study [13]. The PW crystalline phase on silica has been observed only at PW loadings above 20% [8,12]. The catalyst acidity under the conditions relevant to the present study has been characterized by microcalorimetry of pyridine adsorption [14]. It has been found that bulk PW, 20%PW/SiO_2 and pure SiO_2 possess initial heats of pyridine adsorption of 135, 58 and 28 kJ mol^{-1}, respectively, in cyclohexane at 50 °C [14]. Therefore, the 20%PW/SiO_2 catalyst has quite a strong acidity, although weaker than that of the bulk PW due to HPA interaction with the support [8,12]. However, the bulk PW has the drawback of a very low surface area (<5 $m^2\,g^{-1}$) [8,12].



1 **2**

Scheme 1. Acid-catalyzed isomerization of styrene oxide.

3.2. Isomerization of styrene oxide

The results on the isomerization of styrene oxide (**1**) in the presence of silica-supported PW are presented in Table 1. All experiments were performed using cyclohexane as a solvent. Due to a high tendency of styrene oxide toward polymerization under acidic conditions it was not possible to work in solvent-free systems. In a blank reaction, with no catalyst added, no conversion of the substrate was observed (run 1). On the other hand, styrene oxide is highly reactive in the presence of PW. With only 0.08 wt% of the PW/SiO_2 catalyst, a nearly complete conversion was achieved in 30 min at 25 °C resulting in the formation of only one GC detectable product identified as phenylacetaldehyde (**2**) (run 2, Scheme 1). However, the selectivity to phenylacetaldehyde was only 50%, with the rest attributed to oligomers, which were not detectable by GC.

Further, our main effort was aimed to control the substrate oligomerization by choosing appropriate reaction conditions and to improve the yield of the aldehyde. Decreasing the catalyst amount to 0.025 wt%, which corresponded to a substrate to PW molar ratio of nearly 10 000, did not result in a better selectivity (run 3). The reaction was nearly complete in 1 h; however, a half of the substrate was again transformed into high-boiling products. On the other hand, with a decrease in the initial concentration of the substrate, the selectivity for **2** increased to nearly 60% (cf. runs 4 and 3). This can be explained by a higher reaction order in substrate for oligomerization compared to the desired isomerization of styrene oxide. We did not observe significant changes in selectivity in the course of these runs, at least after ca. 60% conversion of the substrate. The reactions were too fast to be monitored by GC at lower conversions.

Table 1
Isomerization of styrene oxide (**1**) into phenylacetaldehyde (**2**) catalyzed by 20 wt% $H_3PW_{12}O_{40}/SiO_2$ in cyclohexane.

Run	[**1**] (mol L^{-1})	Catalyst ($\times 10^2$ wt%)	*T* (°C)	Time (min)	Conversion (%)	Selectivity for **2** (%)	TON[a]
1	0.15	None	25	240	0	0	–
2	0.15	8.0	25	30	98	50	3300
3	0.15	2.5	25	60	98	50	10 600
4	0.07	2.5	25	60	99	59	5000
5	0.07	2.5	15	200	95	37	4800
6	0.07	0.6	25	300	90	50	18 200
7	0.07	0.6	40	300	81	70	16 300
8	0.07	0.6	60	180	83	85	16 800
9	0.07	0.6	70	120	80	87	16 100
10[b]	0.07	0.6	60	90	97	95	19 600
11[b,c]	0.07	0.6	60	90	95	95	19 200

[a] Turnover number: the number of substrate molecules converted per molecule of PW.

[b] The substrate was charged in two equal portions: the first one at the beginning of the reaction and the second one 30 min later, after the first portion had been almost completely consumed.

[c] After run 10, the catalyst was separated by centrifugation, washed with hexane and reused in run 11.

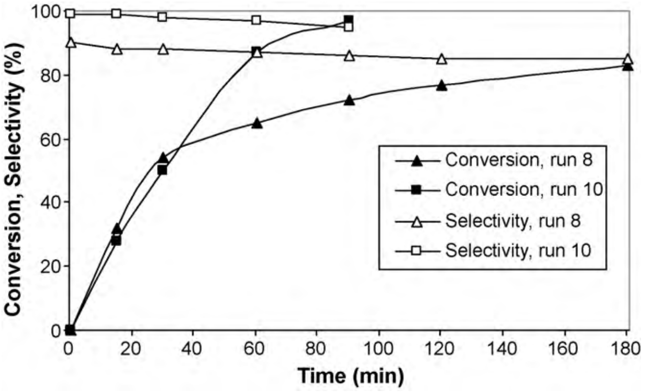


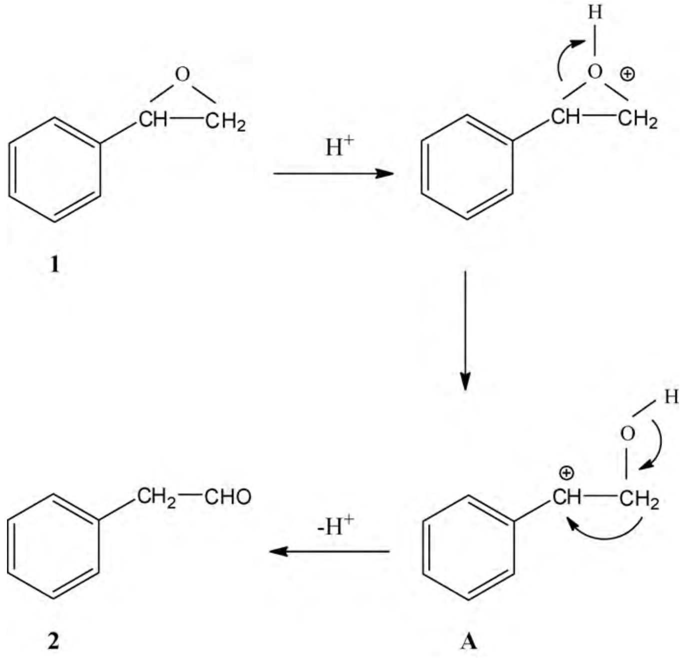
Fig. 1. Isomerization of styrene oxide into phenylacetaldehyde on 20 wt% $H_3PW_{12}O_{40}/SiO_2$ in cyclohexane (Table 1, runs 8 and 10). Both runs were performed under the same conditions except that in run 10 the substrate was charged in two equal portions.

At 15 °C, the reaction occurred much slower; however, the selectivity for phenylacetaldehyde dropped to 37% (cf. runs 5 and 4). This result could imply that the activation energy for the isomerization is higher than that for oligomerization. Thus, we suggested that the increase in temperature could favor the reaction selectivity. To be able to monitor the reaction, we decreased the amount of catalyst to 0.006 wt%, which corresponds to a substrate to PW molar ratio of about 20 000 (run 6). To our surprise, the PW/SiO_2 catalyst even in such a small amount converted styrene oxide almost completely in 5 h with a phenylacetaldehyde selectivity of 50%. Then the same reaction was run at 40, 60 and 70 °C (runs 7–10). The reaction rate increased significantly with temperature; however, the most encouraging was a remarkable improvement in selectivity, which increased from 50% at 25 °C to nearly 90% at 70 °C.

It should be mentioned that in runs 6–9, where very small amounts of the catalyst were used, the reaction became stagnated after 85–90% conversion and could be completed only by addition of fresh catalyst. A possible reason for that could be catalyst deactivation due to styrene oxide polymer deposited on the catalyst surface. In order to control the polymerization and prevent the catalyst deactivation, we decided to charge the substrate into the reactor in portions. In run 10, a half of the substrate was added at the beginning of the reaction and the second half 30 min later after the first portion had been almost completely consumed. An excellent selectivity of 95% was obtained at almost complete conversion matching the best results on the reaction yield reported so far.

The time courses for runs 8 and 10 performed at 60 °C (Table 1) are shown in Fig. 1 to illustrate the advantage of maintaining a low concentration of the substrate during the reaction. It is important that almost 100% selectivity was observed in run 10 up to near 90% conversion, with selectivity being decrease to 95% only at the very end of the reaction. Thus, the formation of polymers was reduced significantly, which benefited the catalysts stability—the rates of the substrate conversion during the second half of the reaction, i.e., after ca. 50% conversion, were much higher in the run with the portioned charge of the substrate (Fig. 1).

It is also important that the PW/SiO_2 catalyst is active at a very low catalyst/substrate weight ratio of 1:150. Most of solid acid catalysts reported for this reaction so far are used in much higher catalyst/substrate ratios, e.g., 1:0.6 or 1:7.5 for zeolite [6,4] and 1:4.8 for Nafion-H [7]. The result presented in run 10 corresponds to a turnover number (the number of substrate molecules converted per molecule of PW) of ca. 20 000 and average turnover frequency (the number of substrate molecules converted per molecule of PW per min) of ca. 220 min^{-1}. Furthermore, a real catalyst activity may be higher, because only a part of proton sites are accessible for the substrate.



Scheme 2. Mechanism of the acid-catalyzed isomerization of styrene oxide.

The acid-catalyzed transformation of styrene oxide is likely to occur via a carbenium-ion mechanism, which may be represented in Scheme 2. Protonation of the oxygen atom in the substrate induces the epoxy ring opening to form carbocation **A**, followed by 1,2-shift of a hydrogen atom and proton loss to give phenylacetaldehyde. The selectivity of reaction depends on the direction of ring cleavage. The neighboring aryl group favors the formation of carbocation **A** by stabilizing positive charge on α-carbon atom.

Because the HPA is insoluble in non-polar solvents, such as cyclohexane, neither HPA leaching nor any contribution of homogeneous catalysis was expected. To prove this, the catalyst was filtered off after reaction completion. Then a fresh portion of substrate was added to the supernatant and the reaction was allowed to proceed further. No activity was observed in this experiment, which indicated that PW did not leach from silica into the reaction medium under the conditions used. The catalyst can be recycled. After run 10, the catalyst was reused after washing with hexane without any loss in its activity and selectivity (run 11).

4. Conclusions

We have found an efficient and environment-friendly solid acid catalyst, $H_3PW_{12}O_{40}/SiO_2$, for the liquid-phase isomerization of styrene oxide into the industrially important compound, phenylacetaldehyde. The catalyst is easy to prepare; it is very active and selective in small amounts exhibiting high turnover numbers (up to 20 000), stable to leaching under reaction conditions, and can be recovered and reused.

Acknowledgments

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