

# Highly Active and Reusable Catalyst for Fries Rearrangement of Phenyl Acetate<sup>1</sup>

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Received December 2, 2010

**Abstract**—Silica-12-tungstophosphoric acid core-shell nanoparticles were prepared by sol-gel method followed by steaming. The catalytic activity of fresh and steamed catalysts was studied in Fries rearrangement of phenyl acetate. The reaction parameters, such as catalyst loading and reaction temperature, were optimized. The structural properties of the prepared catalysts were analyzed by X-ray diffraction and transmission electron microscopy techniques. The nature and strength of acid sites in the catalysts were analyzed by pyridine adsorption followed by infrared spectroscopy and differential scanning calorimetry measurements. The XRD and TEM analyses confirm the formation of silica-12-tungstophosphoric acid core-shell nanoparticles during steaming process. Acidity measurement indicates that both fresh and steamed catalyst samples carry weak acid sites and Brønsted acid sites. In addition, the steaming of heteropoly acid contained silica enhances the strength of Brønsted acid sites. The catalytic activity of fresh as well as steamed catalysts in liquid-phase Fries rearrangement showed that the steam treated sample exhibits higher conversion and selectivity to the desired product compared to the fresh catalyst sample. The higher activity of steam treated catalysts has been explained in terms of surface acidity of the catalysts. Reusability of the steamed catalyst shows that there is no appreciable change either in the conversion rate or product selectivity.

**DOI:** 10.1134/S002315841106019X

The Fries rearrangement of phenyl acetate leads to hydroxyacetophenones, which are valuable precursors in the pharmaceutical industry [1]. Traditionally, the Fries rearrangement is conducted with stoichiometric amounts of Lewis acid (e.g.,  $\text{AlCl}_3$ ) or mineral acid (e.g.,  $\text{H}_2\text{SO}_4$  or HF) and generates large amounts of inorganic salts as by-products. Therefore, the environmental impact of these processes makes highly desirable the development of new technologies that employ heterogeneous, reusable catalyst, and of reactants that generate more environmentally friendly co-products [2]. Consequently a variety of solid acids, particularly zeolites, have been studied in the Fries rearrangement both in the liquid and vapor phases [3–5]. As found recently, Keggin-type heteropoly acids (HPAs) are highly active solid acid catalysts for Fries rearrangement in liquid phase [6–8]. These catalysts are much more active than zeolites and can be separated and reused. However, the conversion is still poor. Thus, there still exists scope to develop better catalysts which would catalyze the Fries rearrangement with excellent conversion and selectivity at comparatively low temperatures.

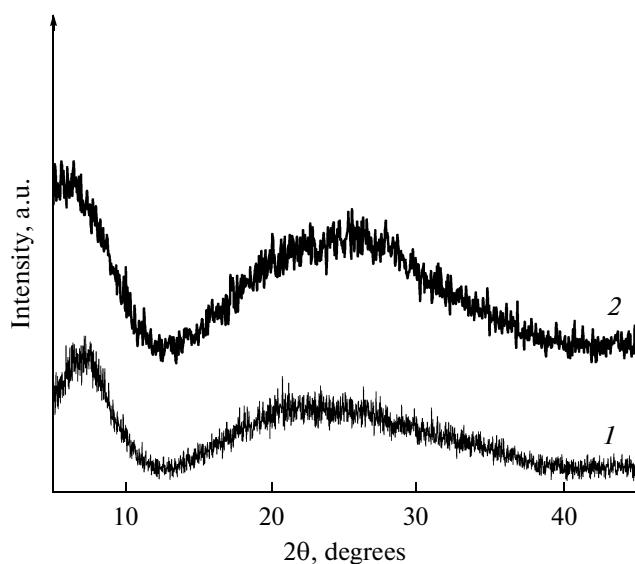
This paper reports an efficient catalytic Fries rearrangement of phenyl acetate using 12-tungstophosphoric acid included in silica nanoparticles. The effects of steam treatment, the amount of catalyst and the temperature on the conversion rate were investigated.

## Experimental Chemicals

Tetraethoxysilane (TEOS), dodecatungstophosphoric acid (DTP), dodecane and phenyl acetate were commercial samples from “Merck” and were used without further purification.

The silica-12-tungstophosphoric acid core-shell nanoparticles catalyst (25 wt % DTP/ $\text{SiO}_2$ ) was prepared by sol-gel method followed by steaming. In a typical procedure, DTP (2.5 g) was dissolved in deionized water (10 ml). TEOS mixed with ethanol (26 g TEOS and 10 g EtOH) was dropped into the above solution under vigorous stirring. Upon addition of TEOS and ethanol mixture, the sol was subjected evaporation at 70°C under vacuum and during concentration the sol turned into a transparent viscous gum-like liquid. After continuous heating this became a transparent sticky solid, which finally transformed into transparent sugar-like cubes. The transparency of

<sup>1</sup> The article is published in the original.



**Fig. 1.** XRD patterns of 25 wt % DTP/SiO<sub>2</sub> samples before (1) and after (2) steaming at 150°C for 6h.

the solid implies that they were composed of nanometer-sized particles. The solid powder was dried in an air oven at 120°C for 6 h. The dried solid powder was then steamed at 150°C for 6 h.

#### Characterization

Powder X-ray diffraction (**XRD**) patterns were recorded on a Rigaku 2000 diffractometer using CuK<sub>α</sub> a radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the range 2θ from 5 to 45° at a scan rate of 2°/min with a step size of 0.04°.

Morphological observations of the silica-12-tungstophosphoric acid core-shell nanoparticles were carried out using transmission electron microscope (**TEM**) JEM-2010 at 200 kV.

Vapor phase adsorption of pyridine as probe molecule [9] was adopted to find out the acidity of catalyst samples. The nature of acid sites was characterized on

the basis of IR spectral data. The nature and strength of acidic sites were determined by differential scanning calorimetric (**DSC**) measurements.

#### Catalytic Activity Measurements

The rearrangement of phenyl acetate was carried out in liquid phase over the silica-12-tungstophosphoric acid core-shell nanoparticles at 150°C under nitrogen atmosphere in a 100 ml glass reactor equipped with a condenser and a magnetic stirrer. In typical experiment, the reaction mixture consisted of phenyl acetate (50 mmol) in dodecane was taken with a total liquid volume of 30 ml. The freshly activated catalyst (0.5 g) was then added to the flask, which is heated at constant temperature of 150°C in oil bath and stirred magnetically. This operation was conducted under nitrogen atmosphere for 2 h. The progress of the reaction was monitored by gas chromatographic analysis using SE-30 columns and flame ionization detector. The composition of products was confirmed by gas chromatography-mass spectroscopy method.

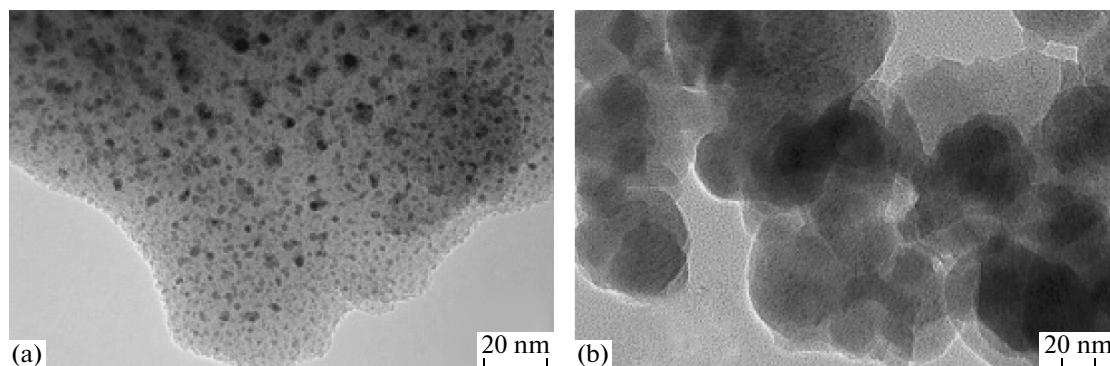
## RESULTS AND DISCUSSION

#### XRD

The XRD patterns of 25 wt % DTP/SiO<sub>2</sub> sample before and after steaming are shown in Fig. 1. It is clear that XRD pattern of the sample is very similar to that of pure silica except presence of a broad peak located at 2θ range of 3°–8°. This broad peak located at very low angles can be attributed to the scattering effects due to the presence of very fine particles, i.e. at the nanoscale. The XRD result confirms the absence of free DTP particles before and after steaming.

#### TEM

The TEM micrographs of 25 wt % DTP/SiO<sub>2</sub> sample before and after steaming are presented in Fig. 2.

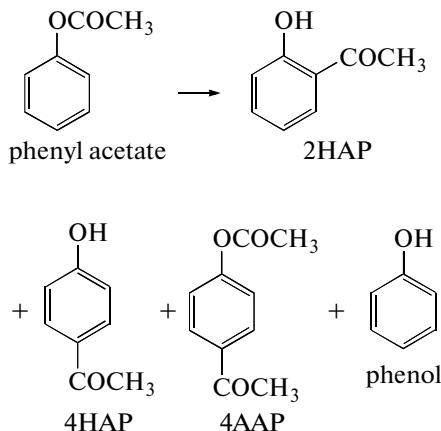


**Fig. 2.** TEM images of 25 wt % DTP/SiO<sub>2</sub> samples before (a) and after (b) steaming at 150°C for 6 h.

As seen in the micrographs, steaming leads to an increase of the DTP average particle's size: during steaming, the DTP particles were dissolved in the steam and then coated on the surface of the silica nanoparticles, therefore forming  $\text{SiO}_2$ –DTP core-shell nanoparticles as final product.

### Catalyst Activity

Fries rearrangement of phenyl acetate was studied using  $\text{SiO}_2$ –DTP core-shell nanoparticles. The products of the rearrangement were found to be 2- and 4-hydroxyacetophenones (**2HAP** and **4HAP**, respectively), 4-acetoxyacetophenone (**4AAP**) and phenol (**PhOH**):



Freese et al. [10] have suggested the mechanism of Fries rearrangement of phenyl acetate over H-form of Y- and ZSM-5 zeolites catalysts. It was deduced that the *para*-product is formed via an ionic species (benzylum ion) by an intermolecular reaction whereas the *ortho*-product is formed by an intramolecular mechanism.

The influence of steam treatment on the conversion of phenyl acetate and the product selectivity is presented in Table 1. The fresh 25 wt % DTP/ $\text{SiO}_2$  catalyst is not much active in Fries rearrangement of phenyl acetate (<5% conversion). However, steam treatment of 25 wt % DTP/ $\text{SiO}_2$  (150°C, 6 h) tremendously increased its catalytic activity (59.8% conversion). In addition, the selectivity of HAPs has also been found to be increased. This can be explained by surface acidity of both catalysts. Silica contained heteropoly acid carries weak acid sites and Brønsted acid sites (Table 2). Steaming of heteropoly acid contained silica enhanced the strength of Brønsted acid sites and increased the heat of desorption of pyridine from 300 to 708 J/g. It is supported by the IR analysis of the pyridine adsorbed samples, where 2 absorption bands located at 1639 and 1644  $\text{cm}^{-1}$  are observed (Fig. 3), which indicate the presence of strong Brønsted acid sites. The increase in activity of the catalyst after steaming can also be explained on the basis of the

**Table 1.** Conversion and product selectivity in Fries rearrangement of phenyl acetate over fresh and steamed 25 wt % DTP/ $\text{SiO}_2$

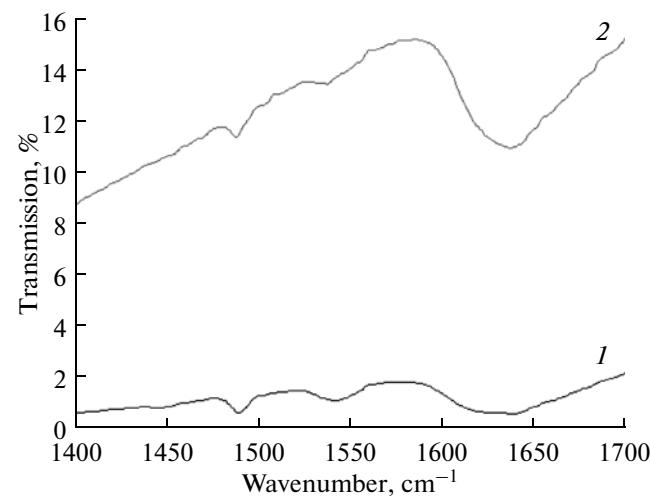
Catalyst	Conversion, %	Selectivity, %			
		PhOH	2HAP	4HAP	4AAP
Fresh	<5	64.0	7.9	7.1	21.0
Steamed	59.8	51.1	21.0	12.3	15.6

Note: Catalyst weight 0.5 g, temperature 150°C, phenyl acetate 50 mmol, reaction time 2 h.

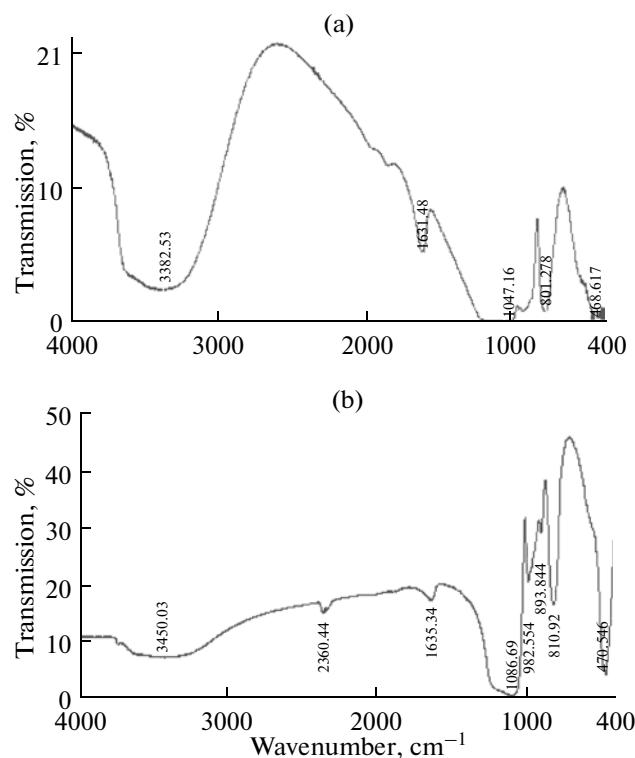
**Table 2.** DSC and FT-IR data for pyridine adsorption on catalysts

Catalyst	IR frequency, $\text{cm}^{-1}$		$\Delta H$ , J/g
	weak acid sites	Brønsted sites	
HPA before steaming	1490	1639 1543	300
HPA after steaming	1487	1644 1556	708.6

FT-IR data. The broad peak observed about 3382  $\text{cm}^{-1}$  corresponding to silanol groups (Fig. 4a) was decreased after steaming at 150°C (Fig. 4b). The sharp absorption bands at 1047 and 468  $\text{cm}^{-1}$  assigned to the  $\text{SiO}-\text{Si}$  framework are well resolved after steaming. Kunkeler et al. [11] have reported that the presence of water during activation at 450 and 550°C has a profound influence on the catalytic activity of the zeolite Beta and leads to a drastic increase of the catalytic activity. The combination of a high temperature and



**Fig. 3.** FT-IR spectra of pyridine adsorbed on 25 wt % DTP/ $\text{SiO}_2$  samples before (1) and after (2) steaming at 150°C for 6 h.



**Fig. 4.** FT-IR spectra of 25 wt % DTP/SiO<sub>2</sub> samples before (a) and after (b) steaming at 150°C for 6 h.

the presence of water results in very active Beta samples. We observed the similar influence of catalyst activation conditions at relatively lower steaming temperature 150°C. It is evident from the literature that supported HPAs are more active and sol-gel PW catalysts show only a negligible activity in the Fries reaction of phenyl acetate [7].

The effect of catalyst amount (0.25–1.0 g) on the conversion rate and selectivity was studied. It was observed that with increasing in the catalyst loading, the conversion of phenyl acetate increases, and then becomes less significant beyond 0.5 g (Table 3). This increase of conversion is due to proportional increase

in the number of active sites. Beyond 0.5 g, the additional active sites do not increase further the adsorption of reactants at given concentration; therefore the conversion of phenyl acetate becomes almost steady. Hence all further experiments were carried out using 0.5 g of catalysts.

The effect of temperature on the conversion of phenyl acetate was studied over a temperature range of 90–180°C (Table 4). The conversion was found to increase significantly with increasing temperature till 150°C and thereafter remains constant. In addition, the effect of temperature is more pronounced on the product selectivity than that of the catalyst loading

**Table 3.** Effect of catalyst quantity on conversion and product selectivity in Fries rearrangement of phenyl acetate over steamed 25 wt % DTP/SiO<sub>2</sub>

Catalyst amount, g	Conversion, %	Selectivity, %			
		PhOH	2HAP	4HAP	4AAP
0.25	23.6	54.0	20.0	11.8	14.2
0.50	59.8	51.1	21.0	12.3	15.6
0.75	63.9	53.0	23.1	14.0	9.9
1.0	65.3	50.1	21.7	15.4	12.8

Note: Temperature 150°C, phenyl acetate 50 mmol, reaction time 2 h.

**Table 4.** Effect of temperature on conversion and product selectivity in Fries rearrangement of phenyl acetate over steamed 25 wt % DTP/SiO<sub>2</sub>

Reaction temperature, °C	Conversion, %	Selectivity, %			
		PhOH	2HAP	4HAP	4AAP
90	23.6	59.0	10.7	2.0	28.3
120	47.9	54.8	15.7	6.5	23.0
150	59.8	51.1	21.0	12.3	15.6
180	63.9	50.9	23.7	13	12.4

Note: Catalyst weight 0.5 g, phenyl acetate 50 mmol, reaction time 2 h.

**Table 5.** Reusability of the steamed 25 wt % DTP/SiO<sub>2</sub>

Catalyst	Conversion, %	Selectivity, %			
		PhOH	2HAP	4HAP	4AAP
Fresh used	59.8	51.1	21.0	12.3	15.6
First reused	59.0	51.5	21.1	12.0	15.4
Second reused	59.0	51.0	20.7	12.3	16.0

Note: Catalyst weight 0.5 g, phenyl acetate 50 mmol, temperature 150°C, reaction time 2 h.

amount, as reported earlier. The formation of HAPs increased with the increase of temperature.

#### *Reusability of the Catalyst*

In order to confirm catalyst reusability it was recycled for three times in the same reaction under similar reaction conditions. The catalyst was centrifuged, washed with ethylene dichloride and subsequently dried at 120°C for 3 h before being reused in subsequent batches. It is important to note that no appreciable changes were observed either in the conversion rate or product selectivity (Table 5).

Thus, the present study demonstrated that SiO<sub>2</sub>—DTP core-shell nanoparticles are active and environmentally friendly catalyst for the Fries rearrangement of phenyl acetate. The fresh nanoparticles are less active (<5% conversion), however, steam treatment of SiO<sub>2</sub>—DTP core-shell nanoparticles (150°C, 6 h) tremendously enhanced its catalytic activity (to 59.8% conversion) in Fries rearrangement of phenyl acetate. The higher activity of steamed catalyst is due to enhanced strength of Brønsted acid sites. The catalyst is reusable.

The authors gratefully acknowledge the financial support from the National Science Council, Taiwan (NSC) (98-222-E-262-002).

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