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., AlCl₃) or mineral acid (e.g., H₂SO₄ 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.

1 The article is published in the original.

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/SiO₂) 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...
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 CuKα a radiation (λ = 1.5418 Å) 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/SiO2 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/SiO2 sample before and after steaming are presented in Fig. 2.