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# Impregnation of 12-tungstophosphoric acid on tonsil: An effective catalyst for esterification of formic acid with n-butyl alcohol and kinetic modeling

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ABSTRACT

Esterification of formic acid with n-butanol was catalyzed by dodecatungstophosphoric acid, $H_3PW_{12}O_{40}$ (DTP) impregnated on tonsil earth. A series of catalysts containing 10%, 20% and 30% of DTP on tonsil earth were synthesized. The samples were characterized by FT-IR, XRD, BET and TG. The 20% DTP loaded on tonsil showed the highest catalytic activity among the samples prepared in this study. Therefore the kinetics of esterification of formic acid with butanol has been studied in the presence of 20% DTP/T. The kinetic behavior of the reaction has been found to follow the Eley–Rideal model.

## 1. Introduction

Heteropoly acids (HPAs) have been widely used in numerous acid-catalyzed reactions due to their strong Bronsted acidity [1,2]. In homogeneous liquid-phase catalysis, the advantages of the HPAs are more distinctive due to their low volatility, low corrosiveness, high acidity, activity and flexibility. The major disadvantages of HPAs, as catalyst lies in their low thermal stability, low surface area (1–10 $m^2/g$) and separation problem from reaction mixture [3]. HPAs on suitable supports are expected to overcome the above mentioned problems. A number of porous supports with high surface areas, such as silica [4,5] titania [5,6] alumina [5] active carbon [6,7], MCM-41 [8,9], acidic ion exchange resins [10], clay [11,12], have been used for supporting HPAs. Acid modified clay minerals can also be used as an efficient supports [13] because they exhibit higher surface area, pore volume, pore diameter and higher surface acidity [14] which results in its improved adsorption and catalytic properties. In particular, the acid treated clay catalysts have received considerable attention in different organic synthesis as a catalyst or as a support because of their environmental compatibility, low cost and operational simplicity. Using clay catalysts, one can conduct environmentally benign green chemistry both at industrial level and on laboratory scale. The acid strength of HPA supported on some of the materials mentioned above is lower than that of bulk HPA, due to the interaction of HPA with surface functional groups of supports. In cases of composite material, there is an influence of support on the acidity function of HPA and vice versa [15,16].

In the present work, synthesis of 12-tungstosilicicacid (DTS) and 12-tungstoposphoric acid supported with tonsil earth. A series of catalysts, which have high conversion, containing different percent heteropoly acid included were synthesized. The support and new amorphous catalysts have been characterized by FT-IR, XRD, particle size distribution and surface area measurement (BET method) and thermo gravimetric analyses (TGA). Their catalytic properties were evaluated for the esterification of formic acid with butanol.

## 2. Experimental

### 2.1. Materials

Tonsil earth was supplied from Ravin Company in Turkey. It is a fine, yellowish-grey powder and used for bleaching of vegetable and animal oil since it has a highly porous inner structure. Tonsil earth oxide composition is $SiO_2$: 66.8%; $Al_2O_3$:14.2%; $Fe_2O_3$:

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**Table 1**
Physical and chemical properties of tonsil earth obtained from Ravin Company.

| Physical/chemical characteristics | Value |
|---|---|
| Apparent bulk density g/l | 550 |
| Free moisture (2 h, 110 °C) % | ~10 |
| Loss on ignition (predried, 2 h, 1.000 °C) | 8.0 |
| pH (10% suspension, filtered) | 2.2–4.8 |
| Acidity mg KOH/g | 4.5 |

3.07%; MgO: 2.3%; CaO: 1.1%; $Na_2O$:08%, $K_2O$:2.2%. Other physical and chemical properties of tonsil earth are also given in Table 1.

The Merck quality of 12-tungstophosphoric acid (DTP) and 12-tungstosilicic acid (DTS) were used as the HPA. The other catalyst, Amberlyst-15, was purchased from Aldrich. Butyl alcohol (>99.5%) was obtained from Fluka. Formic acid (>99.5%) and dioxane, as the solvent, were supplied by Merck.

### *2.2. Catalyst preparation*

Loading of 20% DTP and DTS on tonsil earth was realized first. After finding that the catalyst containing DTP, between them, has higher activity the catalyst having 10%, 20% and 30% of DTP on tonsil earth were prepared by the incipient wetness impregnation method [17]. In this method, a known amount of tonsil earth was dried in an oven at 120 °C for 1 h. The measured heteropoly acid (HPA) was dissolved in methanol forming a homogeneous solution. The methanolic HPA solution was slowly added to the tonsil earth with constant stirring with the help of glass rod. Initially, supports were in powdered form; however, upon subsequent addition of methanolic HPA solution on them they form a paste or wet cake. Further kneading of the paste for 10 min yielded a dry free flowing powder. The preformed catalyst was dried in an oven at 120 °C for 1 h and then calcined at 275 °C for 3 h. The prepared catalysts were kept in desiccators for experiments.

### *2.3. Catalyst characterization*

The crystallinity and the phase purity of synthesized samples were analyzed by X-ray diffraction (XRD) patterns by using X-ray diffractometer (Rigaku Rind 2000, Japan), and Cu-K$\alpha$ (1.54 Å) radiation. XRD was performed within $2\theta$ range of 10°–70°.

The BET (Brunauer–Emmett–Taller) specific surface area was obtained from $N_2$ adsorption–desorption isotherm measured at 77 K in an automatic adsorption apparatus (ASAP2010; micrometritics). $N_2$ vapor adsorption data was obtained at the vapor pressure range ($P/P_0$) of 0.03–0.3. The specific surface area was calculated by using multipoint BET method. The pore size distributions were also determined by the BJH (Barret–Joyner–Halenda) method using the $N_2$ desorption isotherm. Prior to measurement, samples were degassed at 275 °C for 2 h.

FTIR studies of the catalysts were conducted by using a Bruker IFS-66 single channel Fourier transform spectrophotometer. Thin wafers were prepared by mixing 0.004 g of the catalysts with 0.196 g of KBr.

Thermal analysis was carried out using a NETZSCH STA 409 PC/PG thermal analyzer. The samples with mass of about 10 mg were placed in alumina crucible .The measurements were performed in dynamic nitrogen atmosphere with the flow rate of 50 mL min$^{-1}$, in the temperature range of 20–750 °C with a heating rate of 10 °C min$^{-1}$.

### *2.4. Esterification reactions*

The catalytic experiments were carried out in a stirred batch reactor at reflux conditions. In a typical experiment, dioxane as the solvent and one of the reactant were placed in the reactor. A known amount of catalyst was added and the reactor contents were well mixed. After a steady value of desired temperature was attained, the second reactant was added and this was taken as zero time for the run. Two milliliters of liquid sample was withdrawn from the reactor at regular intervals for analysis and immediately transferred to a crucible in an ice bath in order to ensure that no further reaction took place.

Formic acid, in the reaction mixture, was determined by titration with 0.1 N standard sodium hydroxide solutions with phenolphthalein as an indicator.

## 3. Results and discussion

### *3.1. Characterization of catalysts*

#### *3.1.1. FTIR*

The primary structures of supported HPAs (Proton form) were identified by comparing their FT-IR absorbance bands to those of bulk DTP, DTS and tonsil (Fig. 1). Bulk DTP in Fig. 1(d) shows the characteristic IR bands at ca. 1080 cm$^{-1}$ (P–O in central tetrahedral), 983 cm$^{-1}$ (terminal $W=O$), and 890 and 797 cm$^{-1}$ (W–O–W) associated with the asymmetric vibrations in the Keggin polyanion (Fig. 1(d and e)) which matches very well with that of the finding of

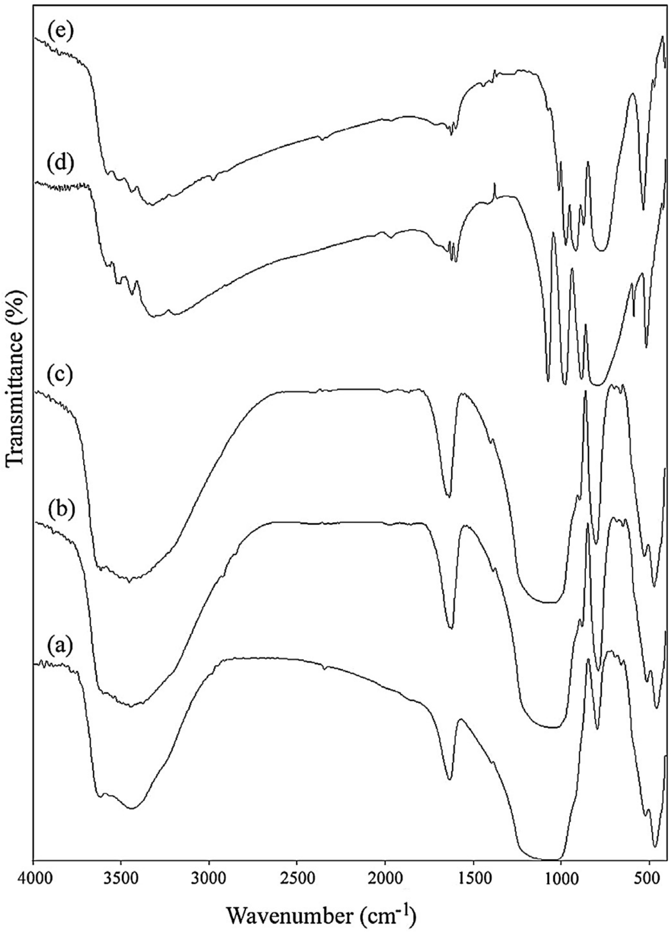

**Fig. 1.** FITR spectra of (a) pure tonsil, (b) 20% DTP/T, (c) 20% DTS/T, (d) pure DTP (e) pure DTS.