

Catalytic Properties of Heteropoly Acid $H_3PW_{12}O_{40}$ Supported on Turkish Bentonite

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Catalysts based on tungstophosphoric acid on Turkish bentonite were obtained. The influence of the heteropoly acid content, in five different concentrations, was studied. The catalysts have been characterized using gas adsorption analysis (BET), thermogravimetry and surface acidity of samples were determined by pyridine adsorption using fourier transform infrared technique. The catalytic activity of these materials was tested for the esterification reactions of acetic acid with benzyl alcohol. The results showed that all catalysts have mesopores, thermal stability of samples higher than bulk heteropoly acid. According to FTIR results, the catalyst samples have medium Lewis acidity, but weak Brønsted acidity.

Key Words: Bentonite, Heteropoly acid, Catalyst, TGA.

INTRODUCTION

Industrially widely applied esterification reactions are commonly catalyzed using mineral liquid acids, such as sulfuric acid and *p*-toluene sulphonic acid. The catalytic activity of homogenous catalysts is high. They suffer, however, from several drawbacks, such as their corrosive nature, the existence of side reactions and the fact that the catalyst cannot be easily separated from the reaction mixture. The use of solid acid catalysts offers an alternative and has received a lot of attention in the past years. Solid acid catalysts are non-corrosive and coated onto a support, which can be easily reused¹.

12-Tungstophosphoric acid ($H_3PW_{12}O_{40}$), one of the strongest Brønsted solid acids, has high activity in demanding reactions, such as alkylation, esterification and alkane isomerization². Although there are many structural types of heteropoly acids, the majority of the catalytic applications use the common Keggin type heteropoly acids, especially for acid catalysis. The Keggin heteropoly acids comprise heteropoly anions of the formula $[XM_{12}O_{40}]^{n-}$ (α -isomer), where X is the heteroatom (P^{5+} , Si^{4+} , etc.) and M is the addenda atom (Mo^{6+} , W^{6+} , etc.). The structure of the Keggin anion is composed of a central tetrahedron XO_4 surrounded by 12 edge- and corner-sharing metal-oxygen octahedra MO_6 ³.

The catalytic function of heteropoly acids and related polyoxometallate compounds has attracted much attention particularly in the last two decades. It is a field of increasing importance in which new and promising developments are being carried out both at research and technological level. Heteropoly acids are widely used as model systems for fundamental research. They provide good basic for the molecular design of mixed oxide catalysts and have high capability in particular uses.

Heteropoly acids are good catalysts in homogeneous medium. They catalyze a wide variety of reactions in homogeneous phase offering strong option for efficient and cleaner processing compared to conventional mineral acids⁴. However, the useful solid heteropoly acids have low surface area (1-10 m²/g) and decompose at rather low temperatures. These drawbacks may limit the practical application of heteropoly acids. As a result, there are many attempts to obtain heteropoly acid catalysts that are thermally stable with a high surface area on different supports⁵.

Various supports like silica, titania, activated carbon, MCM-41, acidic ion exchange resins, neutral alumina have been used for supporting heteropoly acids⁶.

EXPERIMENTAL

The heteropoly acid sample, H₃PW₁₂O₄₀·xH₂O, was purchased from Riedel-De Haen Ag. Natural Turkish Bentonite was obtained from Resadiye-Tokat province of Turkey. For esterification procedure, acetic acid was obtained from Merck (cat. no: 100056) and benzyl alcohol was obtained from Synchemica.

Preparation of supporter material: Natural clay was purified in order to obtain pure clay. For that, 50 g natural clay was added onto 1.35 dm³ distilled water and vigorously stirred in a 2 dm³ beaker by a magnetic stirrer. At the end of this process, impurities like ferric oxide and the others were precipitated bottom of beaker. The suspension at the upper phase was separated from precipitate and then dried. At the last stage, obtained pure clay was grounded and sieved with 100 meshes.

Preparation of catalysts: The impregnation of the clays was carried out as follows. The heteropoly acid was dried 24 h at 393 K. 23.82 g dried heteropoly acid was dissolved into 2 dm³ of distilled water. 50 mL of this solution was added drop wise to 5 g of support that was previously dispersed into 50 cm³ of water. After 2 h under stirring at room temperature, mixture was exposure to aging overnight. Latest, the solid was collected by evaporating the solvent. The solid was then dried overnight at 393 K and grounded.

In order to study the effect of the impregnation level on the support, the same procedure was used with different volumes (100, 150, 200, 250 cm³) of HPA solution. The samples were designated as HPW-1, HPW-2, HPW-3, HPW-4 and HPW-5. All this process was summarized in Table-1.

TABLE-1
PREPARATION PARAMETERS OF CATALYSTS

Samples	Amount of support (g)	Volume of water (mL)	Volume of HPA solution (mL)	Amount of HPA per support ($\mu\text{mol g}^{-1}$)
HPW-1	5	75	50	36.7
HPW-2	5	75	100	73.4
HPW-3	5	75	150	110.1
HPW-4	5	75	200	146.8
HPW-5	5	75	250	183.5

HPA = Heteropoly acid.

Characterization: The thermal analyses were carried out by non-isothermal thermogravimetry using Shimadzu TGA-50 analyzer. Thermal gravimetric experimental procedure involves placing the sample (max. amount 20 mg) into a platinum crucible and then heating ambient to 800 °C at a linear heating rate of 10 °C min⁻¹ and with a nitrogen flow rate of 15 mL min⁻¹. The weight losses occurring in correspondence to the temperature rises were continuously recorded with a computer working in coordination with the furnace and the control unit of the analyzer.

The surface area and pore size distribution of the samples were determined by nitrogen adsorption/desorption technique using Quantachrome Autosorb Automated Gas Adsorption System equipment. The catalysts were first pre-treated at 200 °C under vacuum for 2 h to desorb contaminating materials from the catalyst surface.

The different types of acidity in the samples were evaluated by recording vibrational IR spectra of adsorbed pyridine. A special IR cell fitted with greaseless stopcocks and NaCl windows was used. Self-supported samples of the catalysts were outgassed about 10⁻⁴ mm Hg at 473 K for 1 h. After cooling to room temperature, the catalyst samples were exposed to pyridine for 1 h and physically adsorbed pyridine was removed by outgassing at room temperature for 0.5 h.

Esterification procedure: The catalytic activity of samples was carried out in esterification reaction between acetic acid and benzyl alcohol. The experiments were studied in a stirred batch reflux system at 303 K. A three-necked flask equipped with a condenser and stirrer was used. First, 6 mL acetic acid and 12 mL benzyl alcohol (molar ratio 1:1) was added to reactor, then upon 0.25 g catalyst was added, the reaction was started. For following the reaction, samples were taken periodically and analyzed by gas chromatograph (Shimadzu GC 14A). All catalysts were employed under same conditions.

RESULTS AND DISCUSSION

The thermogravimetric analysis result of pure heteropoly acid shows 6.1 % weight loss between room temperature and 220 °C. The analysis followed up to 800 °C, but it wasn't seen any weight loss. On the other hand, TG/DTG data of purified bentonite was demonstrated two stages of weight loss. First stage called dehydration in the range of room temperature to 300 °C and second stage called dehydroxylation region⁷ is in the range of 300-800 °C. The amount of total weight loss was 8 %. The TGA of supported heteropoly acid onto Turkish bentonite showed 5.7-7.8 % weight loss in the range of room temperature to 800 °C according to impregnation level. That weight loss was also two stages. The first stage within room temperature to 300 °C was mainly due to a loss of adsorbed water molecule and dehydration of bentonite. On the other hand, the second stage within 300-800 °C was due to dehydroxylation of bentonite. That scene shows the increase in the stability of heteropoly acid after supporting onto Turkish bentonite. This may be due to the formation of intermolecular hydrogen bonding between support and heteropoly acid^{4,6}.

A typical isotherm of the N₂ adsorption-desorption for catalyst samples is shown in Fig. 1. All catalyst samples showed type V isotherm, in which hysteresis of desorption branch was observed, indicating the presence of mesopores. Mesopores are defined⁸ as pores having width of 20-500 Å.

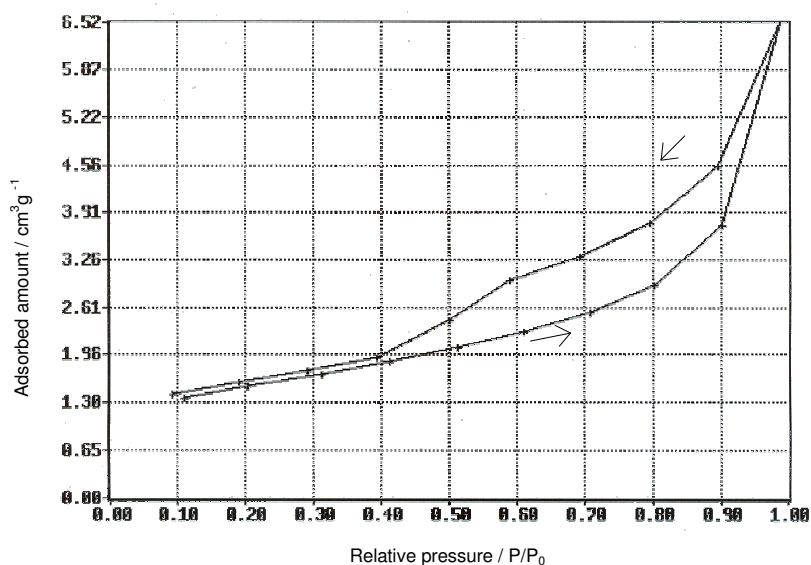


Fig. 1. Typical N₂ adsorption-desorption isotherm of a catalyst sample (HPW-1) at 77 K. → = adsorption branch, ← = desorption branch

Catalytic and adsorption properties of catalysts depend on porosity and energetic heterogeneity of the surface⁹. The surface properties of catalyst samples determined from N₂ adsorption-desorption isotherm are presented in Table-2. Increase in the concentration of heteropoly acid in the sample mass results in decreasing BET surface area (SBET) in the range of 49.7-17.1 m² g⁻¹. Increasing concentration of heteropoly acid results in pore volume and insignificant changes of pore radius.

TABLE-2
ADSORPTION AND STRUCTURAL PARAMETERS OF
CATALYST SAMPLES

Samples	S _{BET} (m ² g ⁻¹)	S _{MESO} (m ² g ⁻¹)	V _{ADS-1} (cm ³ g ⁻¹)	V _{MES-1} (cm ³ g ⁻¹)	D _{AV} (Å)
HPW-1	49.7	36.5	12.3	26.9	40.6
HPW-2	35.6	24.6	8.3	18.8	38.4
HPW-3	32.4	22.2	7.4	18.4	38.7
HPW-4	23.8	17.7	6.3	13.1	40.5
HPW-5	17.1	11.5	4.4	7.8	39.7

S_{BET} = BET surface area, S_{MESO} = mesopore area, V = pore volume,
D_{AV} = average pore diameter.

Adsorption of bases such as pyridine is generally used for the determination of the acidity of catalysts. The criterion for determination of the acid sites on the catalyst surfaces is the formation of pyridinium for Brønsted centers and coordination of pyridine on Lewis centers. The IR bands appeared in both regions characteristic of the Brønsted and Lewis acidities at 1580-1550 and 1455-1440 cm⁻¹, respectively. The band generally appearing at 1490 cm⁻¹ is characteristic both of the Brønsted and Lewis acidity.

IR spectra of pyridine coordinated compounds are clearly distinct from pyridinium ion and H-bonded pyridine can easily be distinguished. The ring vibration modes 19b and 8a are the most sensitive vibrations with regard to the nature of intermolecular interactions *via* nitrogen lone pair electrons. These two modes are observed at 1447 to 1440 and at 1600 to 1580 cm⁻¹, respectively, for H-bonded pyridine, at 1550 to 1535 and around 1640 cm⁻¹ for pyridinium ion and at 1464 to 1447 and 1634 to 1600 cm⁻¹ for coordination compounds^{10,11}.

According to aforementioned explanations, surface acidity of catalyst samples was justified by pyridine adsorption experiments. A typical IR spectrum obtained from pyridine adsorption on catalyst sample HPW-2 is presented in Fig. 2. In the spectra of pyridine on catalyst samples showed similar patterns. As spectra show the (bands at between 1575 and 1500 cm⁻¹) weak bands characteristic of Brønsted acid sites is prevailing. In the spectral

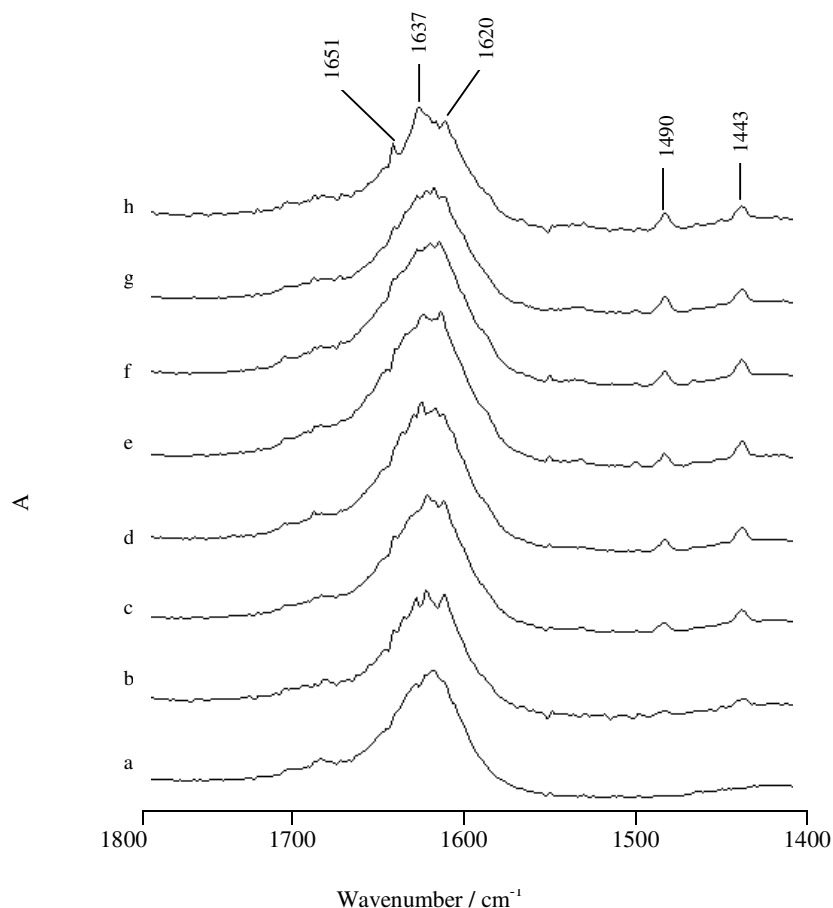


Fig. 2. FTIR spectra of pyridine adsorbed on HPW-2 catalyst. (a) reference, (b) initial adsorption, (c) 15 min adsorption, (d) 30 min adsorption, (e) 60 min adsorption, (f) initial desorption, (g) 15 min desorption, (h) 30 min desorption

range where pyridine is adsorbed on Lewis acid sites, the most intense band appeared to be at 1443-1442 cm^{-1} . The spectra of pyridine adsorbed on samples show the bands at 1652-1614 cm^{-1} associated with pyridine coordinated over Lewis acid sites.

The use of the bentonite-supported heteropoly acid catalysts in the esterification of acetic acid and benzyl alcohol showed similar results. The percentage yield of benzyl acetate has been listed in Table-3. It is seen from Table-3, that HPW-4 and HPW-5 are the best ones among all. Because of the medium Lewis acidity and weak Brønsted acidity and increase in the concentration of heteropoly acid in the sample mass results in decreasing BET surface area (SBET), the percentage yields were relatively low.

TABLE-3
PERCENTAGE OF BENZYL ACETATE

Samples	Yield (%)
HPW-1	8.4
HPW-2	4.6
HPW-3	6.0
HPW-4	10.4
HPW-5	10.4

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