



Characterizations of 12-tungstophosphoric acid metal salt nano particles synthesized by ultrasound

Elif Akbay^{1*}, Mert Can Ertaş²

¹Eskisehir Technical University, Dept. of Chemical Engineering, Eskişehir, 26470, Turkey, (ORCID ID 0000-0003-0323-7938), codes@eskisehir.edu.tr

²Eskisehir Technical University, Dept. of Chemical Engineering, Eskişehir, 26470, Turkey, (ORCID ID 0000-0003-0963-3173), mertcanertas@gmail.com

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Abstract

A set of nano metal exchanged 12-tungstophosphoric acid salt (M =Fe, Cr, Ni, Cu) was synthesized under ultrasonic irradiation in nanoscale. To thoroughly recognize the structure transformation induced by metal doping and morphologies of as-prepared M-TPA catalysts, a combination of XRF, XRD, SEM-EDX, N₂ adsorption-BET, were employed. These analyzes indicate that the chemical structure and crystallinity of nano M-TPA remained unchanged while its morphology was found a different particle size according to the exchange metal.

Keywords: Nano, 12-tungstophosphoric acid metal salt, ultrasonic irradiation.

Ultrason yardımı ile sentezlenen 12-tungstofosforik asit metal tuzu nanoparçacıklarının karakterizasyonları

Öz

Bir dizi nano metal değişimli 12-tungstofosforik asit tuzu (M =Fe, Cr, Ni, Cu) ultrasonik ışınlama altında nano ölçekte sentezlenmiştir. M-TPA katalizörlerinin metal dopingi ve morfolojilerinin neden olduğu yapı dönüşümünü tam olarak tanımak için XRF, XRD, SEM-EDX, N₂ adsorpsiyon-BET kombinasyonu ile karakterizasyon yapılmıştır. Bu analizler, nano M-TPA'nın kimyasal yapısının ve kristalliğinin değişmeden kaldığını, morfolojisinin metale göre farklı bir partikül boyutu bulunduğunu göstermektedir.

Anahtar Kelimeler: Nano, 12-tungstophosphoric asit metal tuzu, ultrasonik ışınlama.

* Sorumlu Yazar: codes@eskisehir.edu.tr

1. Introduction

Nowadays, researches have been started on some acid catalysts that can replace traditional mineral acid catalysts for current environmental and economic reasons. In this context, heteropoly acids are called super acids with stronger acidity than 100% sulfuric acid (H_2SO_4) (Misino, 2000). Heteropoly acids (HPAs), which possess ultra-strong acidity and unique Keggin-type structure, show unique properties such as high stability, excellent solubility, environmentally benign, and so on. However, HPAs are also disadvantaged by low surface area ($< 10 \text{ m}^2/\text{g}$) and difficulties in catalyst recovery, which largely limit their practical industrial applications (Cavani, 1998 and Okuhara et al, 1996). Today, it is possible to produce catalysts with a very large active surface area with nano-sized particles, which are products of nanotechnology. Because the active surface area of the catalysts synthesized by nanoparticles is much wider than the larger particles (Gallezot et al, 2017). Therefore nanocatalysts, as heterogeneous catalysts, have emerged as sustainable alternatives to conventional catalysts because of its stability and high surface area (Polshettiwar et al, 2017). Nanocatalyst shows both homogeneous catalyst properties, characterized by high activity and selectivity because of high surface area due to the nanoscale, and heterogeneous catalyst properties, characterized by the easy separation from the reaction mixture because of their very low-resolution feature. Therefore, nanocatalysts synthesis methods have gained importance. One of them is sonochemical synthesis, which is an effective method under the irradiation of ultrasound in a solution that has been used to prepare various nanomaterials (Martos et al, 2001, and Abbasi et al, 2010). The use of ultrasound irradiation offers versatility, rapidity, and high reaction yields while being eco-friendly by employing water as a solvent (Pinjaria et al, 2013).

Heteropoly acids catalysts constitute an alternative for reactions, as they are characterized by well-defined structure, Bronsted acidity, high proton mobility, the ability to exchange electrons (Wang et al, 2017, Silva et al, 2020). As a heteropoly acid, 12-tungstophosphoric acid, $H_3PW_{12}O_{40}$, is known as strong acid and it is considered within the class of superacid (Misino, 2000). One of the strategies to circumvent the above drawbacks is to by modifying HPAs with metal cations (e.g., Ag, Cs, Fe, Mn, Fe, Co, Ni, Cu) Lewis acid centers will be formed in addition to the Brønsted acid sites (Patel et al, 2014).

Herein, a series of metal ion-exchanged phosphotungstic acid (M-TPA) have been synthesized with the adopted metals included (M = Fe, Cr, Cu, Ni). The physicochemical properties of the as-synthesized M-TPA catalysts were characterized by a variety of different analytical and spectroscopic techniques such as XRD, XRF, SEM-EDX, and N_2 adsorption.

2. Material and Method

All nano metal salts of 12-tungstophosphoric acid (M-TPA) were prepared according to the following method. To synthesize the catalysts, 0.05 M aqueous solution containing a stoichiometric amount of metal salt was slowly added at a rate of about $1 \text{ ml} \cdot \text{min}^{-1}$ controlled by a flow meter to an aqueous solution of 0.04 M heteropolyacid $H_3PW_{12}O_{40} \cdot nH_2O$ (20 ml) at room temperature, under ultrasonic irradiation for 3h. The resultant suspension was dried at 333 K for 1 day and the solid was centrifuged and washed three times with methanol.

A multiwave ultrasonic generator (Bandelin Sonopuls Ultrasonic Homogenizers HD 3100; equipped with a generator, converter, converter cable, and ultrasound horn) was used at a frequency of 20 kHz for the ultrasound irradiation.

The crystallinity and the phase purity of the synthesized samples were analyzed by X-ray diffraction (XRD) patterns using X-ray diffractometer (Rigaku Rind XRD MiniFlex 300/600), and Cu-K α (1.54 \AA) radiation (40kV-15mA). The scanning was done from $2\Theta=70^\circ$ to $2\Theta=5^\circ$ at a rate of 2° min^{-1} .

The results from scanning electron microscopy (SEM) were obtained on an SEM-Benchtop tabletop microscope with 15 kV accelerating voltage. X-ray fluorescence (XRF) analysis was carried out by using Rigaku ZSX Primus II.

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. Before measurement, samples were degassed at 100°C for about 2 hr.

3. Results and Discussion

In this work, ultrasonic irradiation was used in the synthesis of M-TPA (M: Fe, Cr, Cu, Ni) to achieve a unique catalyst in nanoscale. M-TPA was synthesized. The structure and morphology of all synthesized nanocatalysts were studied by XRD, XRF, BET, SEM, and N_2 adsorption.

The results of the XRF analysis showed that W/Metal and P/Metal ratios. The results are given in Table 1.

Table 1. The result of XRF analysis of nano M-TPA

Catalyst	Stoichiometric ratio		Stoichiometric ratio(calculated)	
	W/M	P/M	W/M	P/M
$FePW_{12}O_{40}$	12	1	12.20	0.95
$CrPW_{12}O_{40}$	12	1	12.05	1.03
$Ni_3(PW_{12}O_{40})_2$	8	0.66	8.5	0.9
$Cu_3(PW_{12}O_{40})_2$	8	0.66	7	0.75

As seen in Table 1, all synthesized nano-M-TPA were in agreement with the stoichiometric ratios of the M-TPA structure, indicating a successful formation of catalyst.

XRD analysis was performed for all synthesized M-TPAs given in Fig 1.

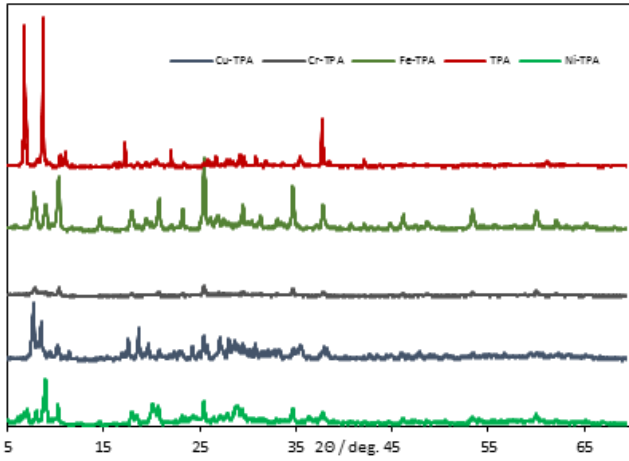


Fig. 1. XRD diagrams of nano M-TPA catalyst

As seen in Figure 1, the characteristic peaks of the Keggin anions in $H_3PW_{12}O_{40}$ were observed at 8. 10 and 37°. The same characteristic peaks of the Keggin structure were also observed in the synthesized $FePW_{12}O_{40}$, $CrPW_{12}O_{40}$, $Cu_3(PW_{12}O_{40})_2$, and $Ni_3(PW_{12}O_{40})_2$, with a slight shift toward higher 2θ values was observed. These shifts show the interaction of metal on the structure of Keggin. Additionally, the characteristic peaks of the exchanged metal (Fe, Cr, Cu, Ni) cations were also observed in the XRD patterns of the samples. In addition, there was a decrease in peak intensity due to metal interaction.

Table 2. Crystal sizes of nano M-TPA catalysts

Catalysts	Peak Degree 2θ (°)	FWHM B_{size} (°)	Dp (nm)
$CrPW_{12}O_{40}$	25.48	0.218	39.05
$FePW_{12}O_{40}$	25.48	0.244	34.89
$Cu_3(PW_{12}O_{40})_2$	7.74	0.261	31.89
$Ni_3(PW_{12}O_{40})_2$	8.96	0.320	26.03

The crystal sizes of all synthesized nano M-TPAs were calculated using XRD data and the results are given in Table 2. Given in Table 2, the metal salts presented ranged from 26 (i.e., CuTPA) to 39 nm (i.e., FeTPA).

The morphology of the metal-exchanged TPA catalysts was also investigated by SEM shown in Fig. 3.

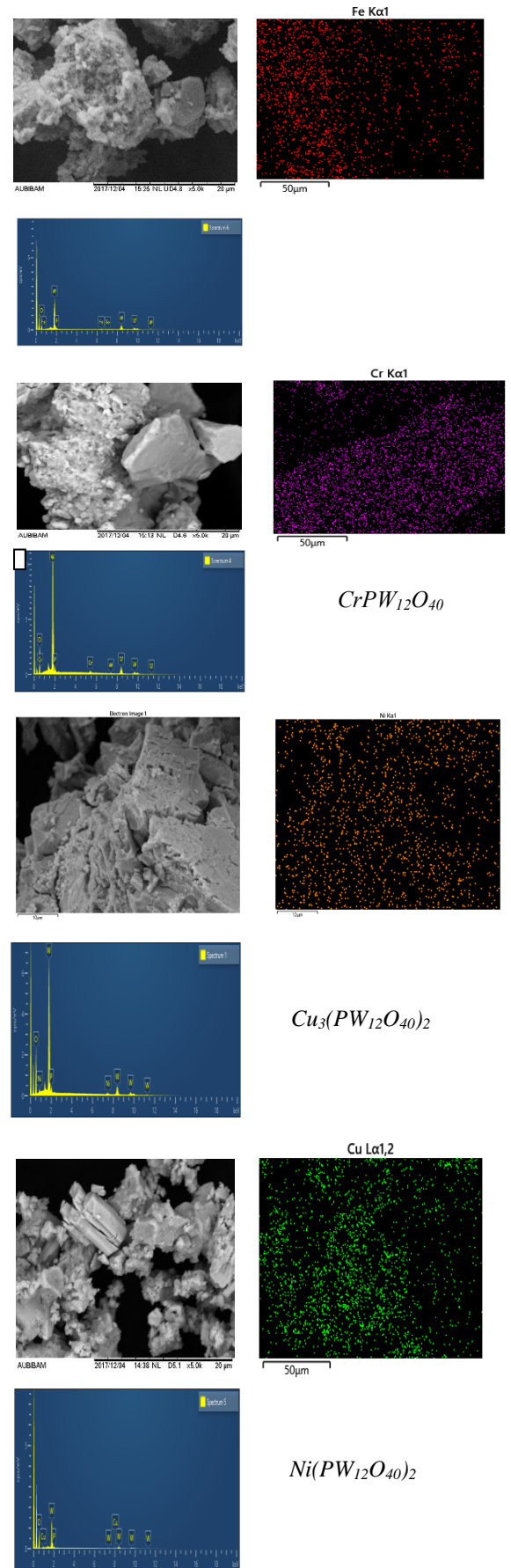


Fig 3. SEM, SEM-EDX mapping, and EDX spectra of nano M-TPA

M-TPA are well-defined crystalline particles with the irregular shapes which is consistent with the literature.

The textural properties of pure TPA and metal exchanged TPA catalysts were investigated using N₂ adsorption desorption analysis (Fig.4).

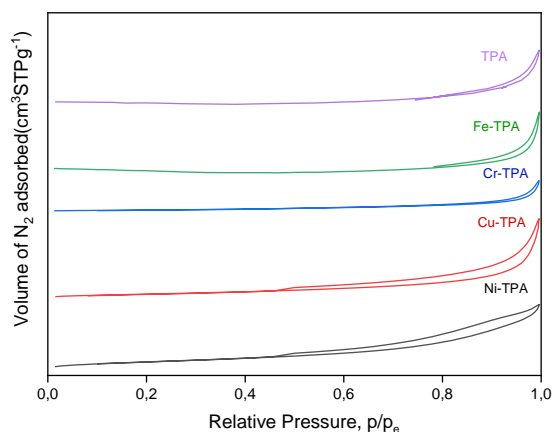


Fig.4. N₂ adsorption isotherms of TPA and metal exchanged TPA

Average pore diameter, pore volume and BET surface area of these materials based on N₂ adsorption analysis are given in Table 3.

Table 3. BET surface area, average pore diameter, pore volume of M-TPA catalysts on N₂ adsorption analysis

	BET Surface Area (m ² /g)	Pore Diameter (Å)	Pore Volume (cm ³ /g)	Pore Volume (Meso) (cm ³ /g)	Pore Volume (Macro) (cm ³ /g)
TPA	5.91	57.27	0.102	0.0081	0.00
Fe ₃ (PW ₁₂ O ₄₀) ₃	2.92	54.72	0.111	0.0031	0.0025
Cr ₃ (PW ₁₂ O ₄₀) ₃	0.91	53.8	0.029	0.0017	0.0014
Cu ₃ (PW ₁₂ O ₄₀) ₂	0.40	104.12	0.0022	0.0013	0.0009
Ni ₃ (PW ₁₂ O ₄₀) ₂	0.04	72.24	0.0045	0.0025	0.0020

According to IUPAC recommendations, the isotherms of the synthesized catalysts can be classified as type II as shown in Fig. 4. It is usually observed for non-porous or macroporous materials (Kong et al, 2016). The pore distribution of M-TPAs synthesized in nanoparticles has wide ranges. As can be seen from the pore volumes in the table. The macropore percentages of nano M-TPAs are high so, they have a highly nonporous structure and therefore their surface area is lower than TPA.

4. Conclusions and Recommendations

Nano metal exchanged 12-tungstophosphoric acid salt (M = Fe, Cr, Ni, Cu) were synthesized with ultrasonic and hydrothermal methods, one of the nanomaterial synthesis methods, in this work. All synthesized catalysts were characterized by XRF, XRD, SEM-EDX, and N₂ adsorption

analyzes. The characterization results show that the structure of M-TPA salts is synthesized as nanoparticles without deterioration.

5. Acknowledge

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