

## Thermal Stability and Acidity of Silica Supported Keggin Type Polyoxometalate $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$

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### Abstract

Silica supported polyoxometalate  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  was prepared systematically using tetraethyl ortho silicate by sol gel method to form  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$ . Compound  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  was characterized by diffraction, spectroscopic, and acidity analyses follow by thermal activity test at higher temperature up to 600 °C. Analysis of FTIR spectrum showed all unique vibration of polyoxometalate  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  was appeared at wavenumber 800-1000  $\text{cm}^{-1}$  before and after supporting process. Crystallinity of  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  and  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  were also similar without changing Keggin structure. Compound  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  showed higher acidity than  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  probably due to Lewis acidity species. Keggin structure of  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  was still retained up to 600 °C showing thermal stability of  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  at high temperature.

Keywords: *Keggin polyoxometalate, tetraethyl ortho silicate, thermal stability, acidity*

### Abstrak (Indonesian)

Senyawa polioksometalat  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  berpendukung silika telah dipreparasi secara sistematis menggunakan tetraetil orto silikat dengan metode sol gel membentuk senyawa  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$ . Senyawa  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  telah dikarakterisasi dengan difraksi, spektroskopi, dan analisis keasaman yang diikuti dengan uji stabilitas panas pada temperatur tinggi hingga 600 °C. Analisa spektrum FTIR menunjukkan semua vibrasi unik dari senyawa polioksometalat  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  muncul pada bilangan gelombang 800-1000  $\text{cm}^{-1}$  sebelum dan sesudah proses material berpendukung. Kristalinitas dari senyawa  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  dan  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  adalah sama tanpa merubah struktur Keggin. Senyawa  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  menunjukkan keasaman yang lebih tinggi daripada  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  yang diduga karena keasaman Lewis. Struktur Keggin  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  tetap bertahan hingga temperatur 600 °C menunjukkan bahwa senyawa  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  stabil terhadap temperatur tinggi.

Keywords: *Senyawa polioksometalat tipe Keggin, tetraetil orto silikat, stabilitas termal, keasaman*

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### INTRODUCTION

Polyoxometalates are anionic metal-oxygen clusters of the early transition metals.

Polyoxometalates have various physical chemical properties due to various kinds of oxidation states, structures, redox and acid bases properties. These

properties can be tuned by selection of addenda or heteroatoms in the polyoxometalates structures [1]. These materials are widely applied as catalysts for various organic reactions and transformations in homogeneous system. The bulk polyoxometalates has low surface area therefore its suitable for homogeneous catalysts system. In order to increase the surface area of polyoxometalates and number of acidic sites, modification of polyoxometalates is needed. A basic method to prepare modification of polyoxometalates is the immobilization of polyoxometalates onto various large surface area inorganic supports and also entrapping polyoxometalates into various matrixes. The successfully modifications of polyoxometalates is depending on these ways and usually achieved via a post synthesis such as grafting or impregnation [2].

Various matrixes are used for entrapping polyoxometalates i.e. mesoporous materials, zeolites, and metal oxides. Metal oxides are commonly used to support polyoxometalates exhibit distinctive functionalities due to large surface area and catalytic properties of polyoxometalates-metal oxides [3]. Furthermore, heterogeneity of catalysts is sharply increase and regeneration process in catalytic reaction can be achieved. On the other hand, other physical chemical properties such as thermal stability and acidity of polyoxometalates-metal oxides were stable [4].

Metal oxides such as silica, titanium, and alumina were extensively used as supported material for inorganic compounds including polyoxometalates. Lesbani et.al (2015) was used zirconium oxide for supporting Keggin type polyoxometalate  $H_4[\alpha-SiW_{12}O_{40}]$  as catalyst for desulfurization [5]. Supporting polyoxometalate with metal oxide also exhibit catalytic activity for desulfurization of benzothiophene [6]. Dawson type polyoxometalate also exhibit catalytic properties after supported with metal oxide such as tantalum [7]. These polyoxometalate was stable under high temperature although catalytic was performed under mild conditions.

Here, polyoxometalate  $K_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O$  was supported with silica from tetra ethyl ortho silicate to form  $K_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O/Si$ . Silica was obtained after reducing process of tetra ethyl ortho silicate using sol gel method with sodium bis-(2-ethylhexyl) succosufinate. The objectives of this research were to prepare  $K_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O/Si$  and to identify the thermal stability of  $K_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O/Si$  at various high temperatures. Characterization was conducted using FTIR spectroscopy and X-Ray

powder analysis. Acidity of compound was also carried out using potentiometric titration.

## EXPERIMENTAL SECTION

### Materials

All chemicals were used directly after purchased without further purification such as sodium tungstate (Merck), sodium metasilicate (Merck), potassium chloride (Merck), sodium bis-(2-ethylhexyl)succosufinate (Aldrich), cyclohexane (Merck), tetra ethyl ortho silicate (Aldrich), and hydrochloric acid (Merck).

### Synthesis Silica Supported Keggin Polyoxometalate $K_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O$

Polyoxometalate  $K_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O$  was synthesized according to literature [8] while silica supported  $K_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O$  was synthesized according to Kim *et.al* [9] with slightly modification as follows: sodium bis-(2-ethylhexyl)succosufinate (1.5 g) was dissolved into 1 mL of cyclohexane (solution A). Polyoxometalate  $K_4[\alpha-SiW_{12}O_{40}] \cdot nH_2O$  (0.76 g) was dissolve with 1 mL water (solution B). Solution B was added into solution A in 250 mL of Beaker glass with slow stirring for 30 min follow with addition of 11.2 mL tetra ethyl ortho silicate. The mixtures were stirred 2 hours at 60 °C. Temperature of reaction was increased to 100 °C to form white hydrogel in intermediate phase and white crystals after cooling at room temperature to form  $K_4[\alpha-SiW_{12}O_{40}]/SiO_2$ . The white crystals stored in a desiccator.

### Characterization

FTIR spectrum was recorded using Shimadzu Prestige-21 using KBr disc at scanning wave number range of 300-4000  $cm^{-1}$ . X-ray diffraction patterns were recorded on Shimadzu Lab X type 6000. Data were collected over a  $2\theta$  range 0-80° at scanning speed 1°  $min^{-1}$ .

The acid properties of polyoxometalates were quantitative and qualitative determined. Ammonia was used as a probe for quantitative analysis. Samples were exposed using ammonia for 24 h at room temperature under oxygen atmospheric conditions. The acidity of polyoxometalates was determined using FTIR measurement at range 1000-2000  $cm^{-1}$ . Quantitative acid properties were analyzed using potentiometric titration using 0.05 M n-butylamine as titrant. Structure stability of supported polyoxometalate was conducted by calcination at 300-600 °C under atmospheric conditions and materials were analyzed using X-ray diffraction analysis.

## RESULT AND DISCUSSION

FTIR spectrum of  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  and  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  was presented in Figure 1. Compound  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  in Figure 1A has specific vibration at  $925.8\text{ cm}^{-1}$  ( $\nu$  Si-O),  $979.8\text{ cm}^{-1}$  ( $\nu$  W=O),  $779.2\text{ cm}^{-1}$  ( $\nu$  W-Oc-W), and  $879.5\text{ cm}^{-1}$  ( $\nu$  W-Oe-W). Waveumber at  $3448.7\text{ cm}^{-1}$  was assigned as vibration of O-H from water [10]. Compound  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  was supported with silica from tetra ethyl ortho silicate which was prepared using sol gel method with sodium bis(2-ethyl hexyl)sulfosuccinate to form  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$ . Compound  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  was also characterized using FTIR as shown in Figure 1B. Specific vibration of polyoxometalate with Keggin structure  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  was appeared in Figure 1 B at wavenumber in the range  $779\text{-}979\text{ cm}^{-1}$ . Additional vibration was appeared in Figure 1 B at  $1095.6\text{ cm}^{-1}$  as vibration of Si-O-Si from silica support. This data showed that silica successfully supported onto Keggin structure of polyoxometalate.

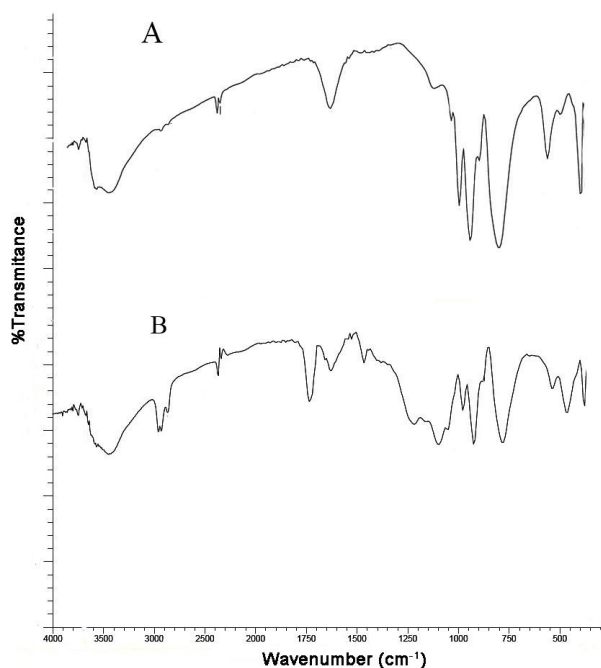


Fig 1. FTIR spectrum of  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  (A) and  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  (B)

XRD powder pattern of  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  and  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  was shown in Figure 2. Diffraction of  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  was appeared in specific range in  $2\theta$  value of 10 deg and 27-32 deg with high crystallinity [11]. After addition of silica support, diffraction of polyoxometalate was still remained and

another diffraction at  $2\theta$  value 24-26 deg was appeared. That phenomena probably due to diffraction of support which was identical with silica in oxide form. Thus supporting process was successfully carried out on polyoxometalate with Keggin structure.

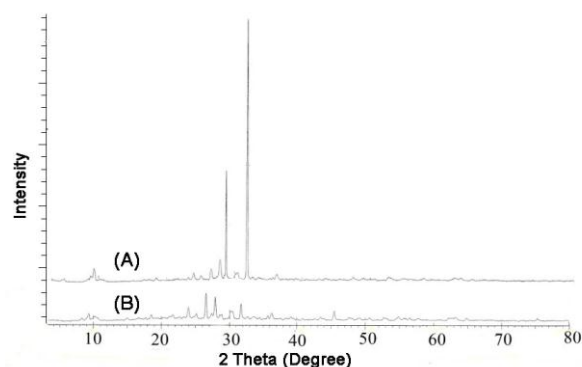


Fig 2. XRD powder pattern of  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  (A) and  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  (B)

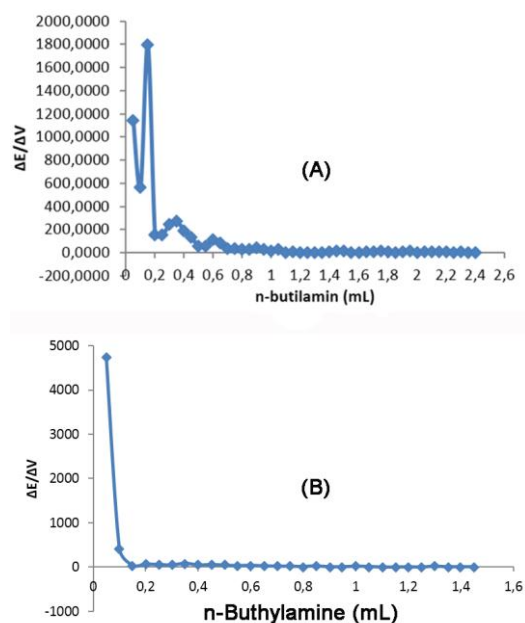


Fig 3. Potentiometric 1<sup>st</sup> derivative curve of  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  (A) and  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  (B)

Acidity of  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  and  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  was determined using potentiometric titration. First derivative titration curve of  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  and  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$  was shown in Figure 3. The initial potential of  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}$  and  $K_4[\alpha\text{-SiW}_{12}\text{O}_{40}]\cdot n\text{H}_2\text{O}/\text{Si}$

$\text{SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$  was 57.3 mV and 78.4mV. According to Reddy et.al (2006) , compound  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$  has higher acidity than  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$  . There was an effect of silica support as Lewis acid in this case. Another acid species such as Bronsted acid probably give only a little contribution to increase the acidity species. Figure 3A and 3B shows the totally differences pattern titration curve of  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$  and  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$  due to acidity level.

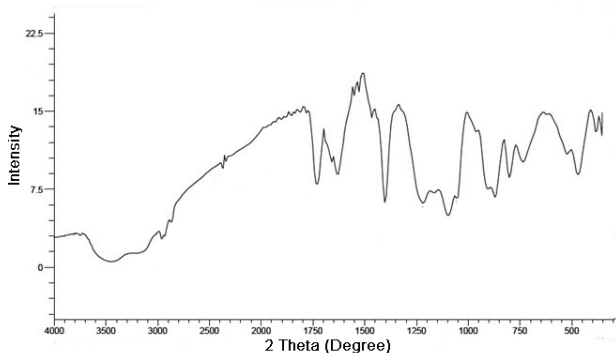


Fig 4. FTIR spectrum of  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$  exposed ammonia

Qualitative analysis of FTIR spectrum of  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$  exposed ammonia as shown in Figure 4C indicated that contribution of acidity in  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$ . According Seo et.al (1988), ammonia can be absorbed on acidity sites from polyoxometalate or metal cation from metal support [12]. Thus vibration at  $1400\text{-}1440\text{ cm}^{-1}$  was attributed from ammonium ion ( $\text{NH}_4^+$ ) which was related with vibration at  $3217\text{ cm}^{-1}$  ( $\nu\text{ N-H}$ ).

Analysis thermal stability test of  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$  using XRD powder analysis at various temperatures was shown in Figure 5. Crystallinity of  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$  in all temperature range was stable but unique diffraction pattern of polyoxometalate at  $2\theta$  value about 8-10 deg was shifted to 12 deg. Probably polyhedra of Keggin in  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$  was reoriented without changing all composition of polyhedra. In general term, compound  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$  was stable under high temperature.

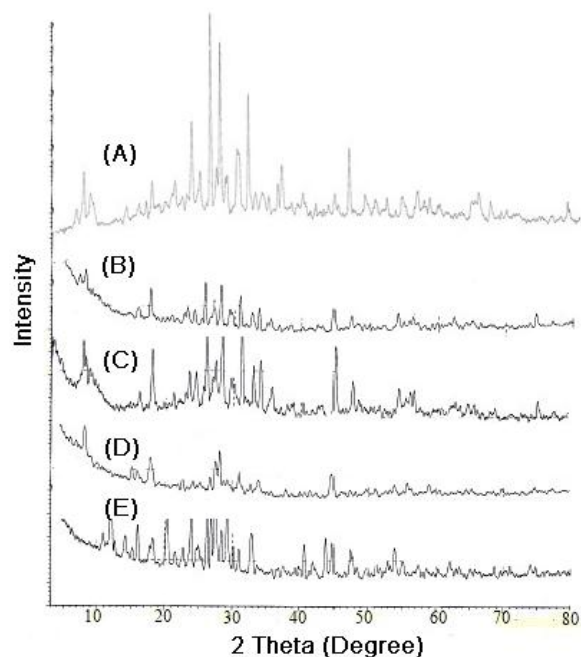


Fig 5. XRD powder pattern of and  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$  under thermal treatment (A = rt; B= 300 °C; C= 400 °C; D= 500 °C; E=600 °C).

## CONCLUSION

Silica supported polyoxometalate  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$  was successfully prepared using tetraethyl ortho silicate by sol gel method. Characterization showed that crystallinity of  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$  was retained with functional groups identity. Acidity of  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$  was increased systematically after supported  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}$  with silica. Compound  $\text{K}_4[\alpha\text{-SiW}_{12}\text{O}_{40}] \cdot n\text{H}_2\text{O}/\text{Si}$  showing thermal stability at high temperature with retaining Keggin structure.

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