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ORIGINAL ARTICLE

Comparative catalytic evaluation of nickel and cobalt substituted phosphomolybdic acid catalyst supported on silica for hydrodesulfurization of thiophene

Nabil Al-zaqri^a, Ali Alsalmeh^a, Syed F. Adil^a, Ahmad Alsaleh^a,
Saad G. Alshammari^a, Saud I. Alresayes^a, Raja Alotaibi^b,
Mohammed Al-Kinany^b, Mohammed Rafiq H. Siddiqui^{a,*}

^a Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

^b King Abdulaziz City for Science and Technology (KACST), Riyadh, Saudi Arabia

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Brønsted/Lewis acidity

Abstract Phosphomolybdic acid supported on silica (PMoA), and phosphomolybdic acid supported on silica substituted with nickel (Ni-PMoA), cobalt (Co-PMoA), are prepared with different loadings. All catalysts have been characterized using thermogravimetric analysis (TGA), BET surface area, Solid-state ³¹P NMR spectra, FT-IR, Diffuse Reflectance Infrared Fourier Transform (DRIFT) and Powder X-ray diffraction analysis (XRD). The surface areas of the catalysts are slightly lower than the surface area of the silica used in making these catalysts, while the XRD studies indicated the amorphous nature of the prepared catalysts. All catalysts are tested for their activity in the hydrodesulfurization of thiophene in the temperature range of 300–500 °C. Under similar conditions the silica supported catalyst i.e. PMoA, showed lower hydrodesulfurization activity, compared to the nickel and cobalt substituted heteropoly acids, i.e. Ni-PMoA and Co-PMoA, indicating enhancement of catalytic activity with substitution of nickel and cobalt. Moreover, the nickel-substituted catalyst, Ni-PMoA, showed slightly higher activity than the cobalt-substituted ones, Co-PMoA. At 500 °C, Ni-PMoA gave a 99.6% HDS conversion of thiophene whereas the Co-PMoA yielded a 98.3% HDS conversion of thiophene. Brønsted/Lewis acidity of the catalyst precursor appear to be essential for the catalytic hydrodesulfurization.

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* Corresponding author.

E-mail address: rafiks@ksu.edu.sa (M.R.H. Siddiqui).

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1. Introduction

Sulfur dioxide (SO₂) is a very serious environmental pollutant which causes a series of environmental and health issues. For instance, when it combines with water and air, it forms sulfuric acid, which is the main component of acid rain that leads to

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acidified soils, lakes, streams, accelerated corrosion of buildings and monuments, and also reduce visibility. High concentrations of SO_2 in air may result in serious breathing problems, respiratory illnesses and various other health related ailments [1,2]. Particularly, sulfur based compounds that are largely found as impurities in various petroleum fractions are the major cause of these problems. Notably, among various impurities, the major refractive sulfur species in diesel are dibenzothiophenes and 4, 6-substituted dibenzothiophenes (DBTs) [3]. The presence of sulfur compounds in crude oil and heavy fractions is an undesirable issue. It can lead to corrosion in oils and lubricants and poisonous emissions such as SO_2 and H_2S when the fuel is burned. Several processes have been proposed to deal with the problem of removing these compounds [4].

Recently, awareness about environmental protection has increased and consequently legislation to limit sulfur contents in fuels has been strictly applied throughout the world [5]. Nowadays, high quality of petroleum products is required to reduce environmental problems induced by the SO_x emissions to the environment. For this purpose, more active and selective catalysts for the hydro-treatment processes have been proposed. In order to reach ultra-low sulfur levels (< 15 ppm), the development of a new generation of catalysts with very high hydrodesulfurization (HDS) activity is highly desirable.

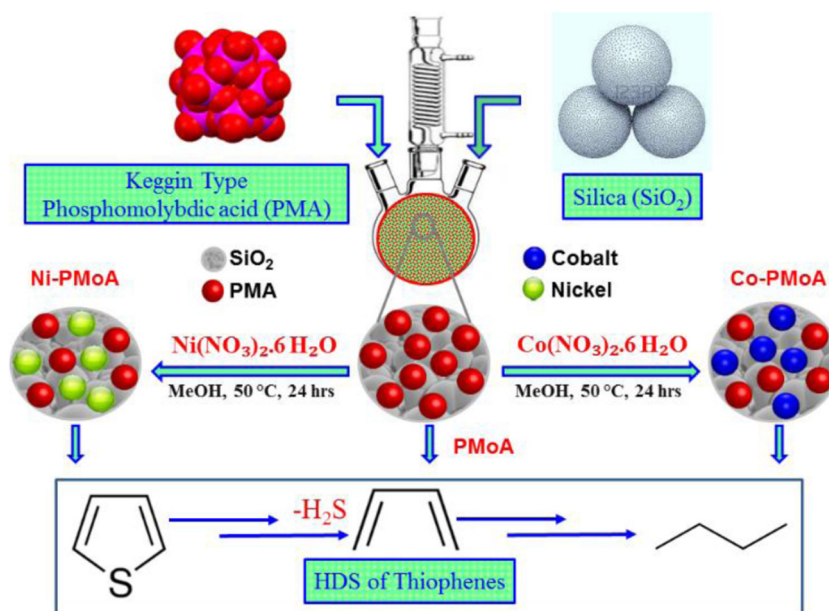
At present, the hydrodesulfurization (HDS) process is an efficient method for sulfur removal from gasoline and diesel of high sulfur content [6]. In this process organic sulfur compounds in the liquid fuels are broken down to H_2S using catalysts [7], followed by the removal of H_2S . Using this process the sulfur content in fuels can be reduced to about 10 ppm [8]. For this process several mixed transition metals and metal oxides based catalysts have been reportedly employed. For example, various HDS reactions are reported to be catalyzed by using CoMo [9], NiW [10], or the trimetallic NiMoW catalysts supported mainly on $\gamma\text{-Al}_2\text{O}_3$ [11] and many other

supports containing the active acidic or basic sites such as SiO_2 [12–15], ZrO_2 [16], TiO_2 [17], MgO [18].

In a recent study, molybdenum catalysts supported on alumina were investigated for the effect of nickel and phosphorus on activity of hydrodesulfurization (HDS) of thiophene and hydrodenitrogenation (HDN) of pyridine [19]. The presence of nickel into molybdenum-containing catalysts strongly promoted HDS activity. In another study, a weak promoting effect of phosphorus was observed, in the case of $\text{NiMo-Al}_2\text{O}_3$ catalyst modified with phosphorus [20].

Recently, the popularity of the heteropoly acids as catalysts for various organic transformations has grown [21–24], especially, the Keggin type heteropoly acids (HPAs) have been proved to be excellent catalysts for various reactions [25–28] due to their simple synthesis, relatively high thermal stability [29] and very strong acidity and redox properties [30]. Although, several new industrial processes based on HPA catalysis have been developed and commercialized in the last two decades [31]. One of the most important properties of heteropoly anions is that they can be isolated as solids when coupled with an appropriate counter cation, e.g. H^+ , NH_4^+ . Heteropoly acids (HPA) are the hydrogen (acidic) forms and are utilized primarily as catalysts, and is reflected in the statistic that 80–85% of patent applications concerning the polyoxometalates are related to catalysis [32]. Nevertheless, there are few scientific reports available on the application of HPAs with respect to the hydrodesulfurization reaction.

In our earlier studies we have demonstrated the excellent ability of heteropoly acid to act as catalyst precursors in the hydrodesulfurization reactions, where these catalysts have performed better than the commercial catalysts [33]. With our continued interest in heteropoly acids and hydrodesulfurization, this study was carried out to gain further insight into the mechanism of supported heteropoly acids in the presence of nickel and cobalt (cf. Scheme 1). Additionally, the aim of this study is also to get an insight into the role of Brønsted and Lewis acidity and its relation to HDS activity Scheme 2.



Scheme 1 Graphical representation of the synthesis of PMoA, Ni-PMoA, Co-PMoA catalysts and their evaluation as hydrodesulfurization catalyst.

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