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Preparation and catalytic properties of cobalt salts of Keggin type heteropolyacids supported on mesoporous silica

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ABSTRACT

Some heteropoly salts – mesoporous silica composites were prepared from Co salt of molybdophosphoric acid CoHPMo₁₂O₄₀ (CoHPM) by supporting on mesoporous silica in different concentrations (20–40 wt% CoHPM) of active phase. The acidity of composites was studied by the adsorption of ammonia and its temperature programmed desorption – TPD using thermogravimetry. The evolved gases during the adsorption–desorption of ammonia on CoPM–silica composites were identified by online mass spectrometry coupled with thermal gravimetry technique. The elemental concentrations based on the relative area of XPS spectra components for Co 2p, Mo 3d, Si 2p and O 1s were obtained for the surface of CoHPM/silica. The dehydration of ethanol was used to probe the catalytic properties of the CoHPM samples incorporated on the silica matrix. The main reaction products obtained on acid (dehydration) catalytic centres were ethylene and diethyl ether, besides acetaldehyde which was obtained on redox (dehydrogenation) catalytic centres. It is shown that silica – supported catalysts, appeared to be more active than bulk CoHPM catalyst in dehydration and dehydrogenation reactions. The higher values of dehydration and reaction products formation are obtained with the lowest loading (20 wt% CoHPM) and as a consequence the highest dispersion of active phase. The ethanol conversion and the carbon selectivity to the primary compounds were investigated during time on stream in order to study the stability and regenerability of supported catalysts.

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1. Introduction

Polyoxometalates (POMs) which also include heteropolyacids (HPAs), are a large class of molecular metal-oxygen anions with a remarkable structural variety which can be applied in areas such as catalysis [1], magnetism [2], photochemistry [3], medicine and biology [4,5].

Polyoxomolybdates of the Keggin structure, H_{3+x}PV_xMo_{12-x}O₄₀ (especially x = 0–2), have been attracting considerable interest over recent years as oxidation catalysts for both gas phase and liquid oxidation reactions. In the area of liquid-phase oxidation, Neumann and co-workers studied various catalytic oxidations of halides, alcohols, ketones and amines, phenols, (alkyl)aromatics, dienes and alkanes [6–9].

In gas phase reactions, heteropolyacids (HPAs) especially Keggin type HPAs have been used extensively both in acid and redox catalysed reactions. On the one hand, tungstophosphoric acid (HPW),

the strongest one in the Keggin series, have well performed in a variety of acid-catalyzed reactions, on the other hand heteropoly-molybdates are used as oxidation catalysts due to the relatively high oxidation ability of molybdenum ions [10,11].

However, bulk HPAs have the own disadvantages, such as, low porosity, low specific surface area which results in few active sites on their surface and relatively weak thermal stability. Therefore, for effective utilization of HPAs in catalytic reactors, these compounds should be deposited or incorporated on suitable porous supports with high surface area and/or by replacement of protons with different cations [12,13].

In the literature very few references have been reported concerning the cobalt salts of molybdophosphoric acid (HPM) and their composites with mesoporous supports. Majority of the studies have been focused on investigation of other HPAs salts (Cs, Ag, NH₄, K) [14–23].

The catalytic properties of some 12-heteropolytungstates (Co_{1.5}PW₁₂O₄₀, Fe_{1.5}PW₁₂O₄₀) and 12-heteropolymolybdates (Co_{1.5}PMo₁₂O₄₀, and Fe_{1.5}PMo₁₂O₄₀) were investigated for direct synthesis of dimethyl carbonate (DMC) from methanol and CO₂ [24].

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It was found that $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ was the most active and selective catalyst for the direct synthesis of DMC from methanol and CO_2 . The methanol conversion activity was drastically increased whereas the DMC selectivity was decreased if $\text{Co}_{1.5}\text{PW}_{12}\text{O}_{40}$ was supported on an acidic or a weak basic support. Thus, the direct conversion of the methanol in DMC can be enhanced if the 12-tungstophosphate cobalt salt is impregnated on a support that is adequately basic.

Romero-Galarza et al. have studied a series of Mo catalysts promoted by Co and supported on Al_2O_3 which were prepared from a reduced Co Keggin salt ($\text{Co}_{7/2}\text{PMo}_{12}\text{O}_{40}$) as active phase precursors [25]. It was observed that the production of highly active hydrodesulphurization catalysts depends to a greater extent on the level of promotion reached during the catalyst preparation. To increase the number of promoted Co (Ni) – Mo–S sites, it is desirable for the Co (Ni) and Mo atoms to be as close as possible during the activation (sulfidation) of the catalyst. The preparation utilizes a solution of a commercial heteropolyacid such as HPM to which Co or Ni are added in the form of nitrates in the necessary amount to reach a $\text{Co}(\text{Ni})/\text{Co}(\text{Ni}) + \text{Mo}$ ratio around 0.33, which is reported as optimum for conventionally prepared HDS catalysts.

Some $\text{CoMo}/\text{Al}_2\text{O}_3$ catalysts were synthesised from the ammonium and Co salts of $[\text{CoMo}_6\text{O}_{24}\text{H}_6]^{3-}$ and $[\text{Co}_2\text{Mo}_{10}\text{O}_{38}\text{H}_4]^{6-}$ anions as well as Co–chelate complexes with nitrilotriacetic, ethylenediaminetetraacetic, citric and tartaric acids [26]. The catalysts were tested in the hydrotreating (HDT) of a mixture containing thiophene and **hexene-1**, the hydrodesulphurisation (HDS) of dibenzothiophene and 4,6-dimethyldibenzothiophene and the HDT of diesel. The catalytic activity, selectivity and turnover frequency during the HDS and hydrogenation reactions depend on the number and location of CoMoS sites, as well as the shape of the active phase crystallites.

Long et al. have studied a catalytic system consisting of HPW/C and Co (II) which has been used to oxidize m-xylene (MX) to isophthalic acid (IPA) [27]. The experimental results prove that the HPW/C and Co catalytic system is capable of catalyzing the oxidation of MX to IPA, which can obtain a higher MX conversion and IPA concentration than the homogeneous $\text{HPW}/\text{Co}(\text{OAc})_2/\text{Mn}(\text{OAc})_2$ catalytic system. The heterogeneous catalytic system is also advantageous over the homogeneous catalytic system in the inhibition of the oxidation of acetic acid and IPA. The amount of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ immobilized on carbon is an important factor determining the catalytic capability of HPW/C . The best amount of HPW loaded on carbon is 7.5% (wt). Co (II) also plays an important role in this catalytic system. The optimum Co (II) concentration for IPA production is 0.064 wt.%.

The synthesis of ordered mesoporous silica materials can be performed using various cationic and non-ionic surfactants and silica sources. Toufaily et al. [28] used different types of non-ionic and ionic surfactants. These materials exhibit structures with uniform channel diameters over a range comparable with the MCM-41 type materials. They prepared a solid catalyst by direct incorporation of HPW into organized mesoporous silica. The structure of inorganic species was controlled either by a mixture of non-ionic and cationic surfactant or only by a non-ionic one.

In a previous work, we studied the direct incorporation of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ into mesoporous silica during the synthesis [29]. The synthesis of mesoporous silica containing HPAs was carried out in acidic media by using a mixture of cationic and non-ionic surfactants, such as cetyltrimethylammonium bromide ($\text{C}_{16}\text{TMABr}$) and Triton (TX-100) or Tween 100. In the study a comparison between direct incorporation of HPAs into mesoporous silica and impregnation of HPAs on mesoporous silica was done. After incorporation or impregnation, the HPAs anions preserved their Keggin structure on the surface of mesoporous silica–heteropolyacid composites and form finely dispersed HPAs

species. The favourable effects of HPAs incorporation on mesoporous silica is the increasing of pore volume and specific surface area, which renders the silica–heteropolyacid composites appropriate for heterogeneous catalysis. The mesoporous silica–HPAs composites are thermally more stable than the parent acids, due to the strong anion-support interaction.

Although different HPAs salts (especially of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ acid) based on only one type of cation or mixed salts have been extensively reported, the influence of surface coverage of Co salts of 12-molybdophosphoric supported on different supports in reference to the bulk solids have not been significantly explored in the literature.

The aim of this work was to synthesize and characterize the $\text{CoHPMo}_{12}\text{O}_{40}$ – silica composites of different concentration of active phase and to test their catalytic activity in reference to the corresponding bulk CoHPM . The synthesis of mesoporous silica was carried out in acidic media by using a non – ionic surfactants Tween 60. In order to obtain highly dispersed heteropolyacid species, the Co salt of molybdophosphoric acid $\text{Co}_1\text{HPMo}_{12}\text{O}_{40}$ (CoHPM) was supported on mesoporous silica with Tween 60 in different concentration of active phase. The dehydration of ethanol was used to probe the catalytic properties of the CoHPM samples impregnated on the mesoporous silica.

2. MATERIALS and METHODS

2.1. Samples preparation

Molybdophosphoric acid, $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 12\text{H}_2\text{O}$ was purchased from Merck. The silicon source was tetraethoxysilane (TEOS) from Fluka. Polyethylene sorbitan-monostearate (Tween 60) from Merck was used as non-ionic surfactant. Sodium fluoride NaF, from Fluka, was employed as mineralizing agent.

The bulk CoHPM with Co/Keggin unit ratio of 1 was prepared by adding slowly drop wise the required amount of aqueous cobalt nitrate $\text{Co}(\text{NO}_3)_2$ to aqueous solution of HPM with vigorous stirring at room temperature. The precipitate obtained was aged in parent solution for 24 h at room temperature, followed by evaporation in vacuum at 323 K. For comparison one group of samples was calcinated at 523 K for 4 h.

Organized mesoporous silica with Tween 60 was prepared by the hydrolysis of tetraethyl orthosilicate using non-ionic surfactants. The procedure was described in our previous work [29]. The synthesis was performed by sol-gel technique with the following molar composition: $1\text{SiO}_2:0.067\text{ Tween }60:0.04\text{ NaF}:148\text{ H}_2\text{O}$. In the first step, 5.24 g of Tween 60 was dissolved in 150 ml distilled water containing 4 ml of hydrochloric acid (HCl 37 wt.%). Then, after a clear solution was obtained, 12.5 g of TEOS was added and stirred until complete dissolution. The solution was aged for 24 h at room temperature without stirring. A small amount of sodium fluoride (0.1 g) was added then in order to promote the hydrolysis of TEOS. The solution was furthermore aged at 333 K for 48 h. The solid product was filtered, washed with distilled water and dried in air for 6 h. Calcination for template surfactants removal was carried out under air by increasing temperature from 298 to 823 K with a rate of $2^\circ\text{C}/\text{min}$ and heating at 823 K for 4 h.

The mesoporous silica-supported HPAs were prepared by impregnation of active phase (CoHPM) on mesoporous silica with Tween 60 by two-step sequential impregnation method: first cobalt nitrate was impregnated by aqueous incipient wetness onto mesoporous silica with Tween 60, dried and calcined at 573 K and finally 12 – molybdophosphoric acid was impregnated by a similar aqueous impregnation route. CoHPM is deposited by impregnation on the calcined samples of mesoporous silica with Tween 60 in the

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