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Preparation and characterization of transition metal-modified lacunary Keggin 11-tungstophosphates supported on carbon

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Abstract

Transition metal-modified lacunary Keggin heteropolycompounds $[PW_{11}O_{39}M]^{5-}$, with M=Ni^{2+}, Co^{2+}, Cu^{2+}, or Zn^{2+}, were synthesized and characterized. These heteropolycompounds were used to prepare the carbon-supported catalysts. Both the heteropolycompounds and the carbon-supported catalysts showed FT-IR spectra with the characteristic bands of these compounds and provided an indirect measure of the interaction strength between M and the oxygen of the central tetrahedron group of the Keggin structure. The anion decomposition of the modified compounds takes place at equal or lower temperature than that of the bulk and supported parent lacunary $[PW_{11}O_{39}]^{7-}$ anion. The species present on the support surface may be highly dispersed as a non-crystalline form, as a result of the interaction with the support surface groups. The activity of the synthesized catalysts in isopropanol dehydration, reflecting their acidity, increases as the reduction temperature of the decomposition products of the heteropolycompounds decreases. It may be assumed that the generation of acid sites is a result of the interaction of hydrogen, donated by isopropanol during its decomposition, with the M cation, leading to M reduction and protons.

Keywords: Lacunary Keggin anions; Preparation; Characterization; Isopropanol dehydration

1. Introduction

The catalytic properties of heteropolycompounds have drawn much attention in the last decades owing to the versatility of these compounds as catalysts, which has been demonstrated both by successful large-scale applications and by promising laboratory results.

Keggin heteropolycompounds have special properties that are of great value in catalysis, such as strong Brönsted acidity, ability to catalyze reversible redox reactions under mild conditions, high solubility in water and oxygenated solvents, and fairly high stability in the solid state [1]. They may be used as homogeneous catalysts, as well as in phase-transfer catalysis and in liquid–solid or gas–solid heterogeneous reactions [2].

Acid and oxidation reactions catalyzed by solid heteropolycompounds (gas–solid and liquid–solid systems) can proceed via three main ways of reaction named surface, bulk type I (pseudoliquid) and bulk type II catalysis [2,3].

In surface type catalysis, the reactions take place on the external and internal pore surfaces of solid catalysts. The reaction rate is proportional to the catalyst surface area.

Supported catalysts based on Keggin heteropolyacids are important because bulk compounds have a low specific surface area [4]. When supporting this type of heteropolycompound, it is necessary to pay attention to the changes in the acid strength, the structures of aggregates, and the possibility of decomposition. The catalytic activity of these supported catalysts is related to the type of carrier, the precursor loading, and the pretreatment conditions [5]. Basic solids such as Al_2O_3 and MgO tend to decompose the heteropolycompounds [6–9]. Acidic or neutral substances such as SiO_2 [10], active carbon [11], or acidic ion-exchange resin [12] are suitable as supports.

Activated carbon has been found to be able to efficiently entrap Keggin heteropolyacids [13]. The compounds thus entrapped are hardly removed even by extraction with water or hot

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methanol [14]. Entrapped catalysts have proved to be convenient for liquid-phase and vapor-phase reactions.

Transition metal-modified lacunary heteropolycompounds of the general formula $[XW_{11}O_{39}M]^{n-}$, where X=P or Si and M=first row transition metal, have recently attracted considerable attention [5]. This is because of their thermal and chemical stability, and the range of possibilities for their modification without affecting the Keggin-type primary structure [15]. These metal-modified lacunary heteropolycompounds display many characteristics of metalloporphyrins. The robust nature of the polyoxometalate ligand and their resistance to oxidation are added advantages that allow the use of these species in both polar and nonpolar solvents [16] as homogeneous catalysts [17].

Advantages to be highlighted about using supported transition metal-modified lacunary heteropolycompounds as catalysts are their easiness of recovery and recycling after carrying out liquid-phase reactions, and the easier product isolation, when they are compared to that of the homogeneously catalyzed reactions.

The aim of this paper is to study the preparation and characterization of carbon-supported transition metal-modified lacunary heteropolycompounds to be used as catalysts in the epoxidation of alkenes.

2. Experimental

2.1. Transition metal-modified lacunary heteropolycompound synthesis

The lacunary heteropolycompounds modified with transition metal ions $[PW_{11}O_{39}M]^{5-}$, M=Ni^{2+}, Co^{2+}, Cu^{2+}, or Zn^{2+}, were prepared according to the literature data [18–20]. Their synthesis involves the alkalization of an aqueous solution of $H_3PW_{12}O_{40}\cdot 23H_2O$ (Fluka p.a.) with aqueous $NaHCO_3$ (Fluka p.a.) solution up to a pH value of 5.0–5.5, which results in the formation of the lacunary heteropolyanion $[PW_{11}O_{39}]^{7-}$. In order to introduce the transition metal ion into the octahedral lacuna, the obtained solution of $[PW_{11}O_{39}]^{7-}$ and an aqueous solution of the transition metal salt were mixed and stirred at 60–90 °C. The sodium salts of the lacunary heteropolycompounds were obtained by solvent evaporation, and recrystallization from water. They were dried at 70 °C before their characterization by thermal and physico-chemical techniques.

2.2. Catalyst synthesis

Commercial activated carbon, previously washed with 0.1 N solutions of NaOH and HCl, and then treated with a HNO_3 30% solution under heating to reflux for 2 h was used as support. It has a surface area of 806 m^2/g, and a mean pore diameter below 2 nm. The carbon was impregnated using the incipient wetness method, with $[PW_{11}O_{39}M]^{5-}$ water solutions (0.14 M), in order to add 1.0 10^{-4} mol of the lacunary heteropolycompounds per gram of carbon. The catalysts were kept at room temperature till dryness and then thermally treated at 70 °C for 24 h. The catalysts will be named PW_{11}MC.

A fraction of the solids thus obtained was washed with acetonitrile, chloroform, or toluene for two 24-hour periods. For this leaching experiment, 1 g of solids was placed in contact with 4 ml of solvent at 20 °C under constant stirring for a selected time.

The tungsten concentration in the solutions, after leaching, was determined by atomic absorption spectrometry. The calibration curve method was used, with standards prepared in the laboratory. An IL Model 457 spectrophotometer, with single channel and double beam and monochromator with a 330 mm focal distance, was used. The light source was a hollow monocathode lamp. The analysis was carried out at wavelength 254.9 nm, bandwidth 0.3 nm, lamp current 15 mA, phototube amplification 800 V, burner height 4 mm, and acetylene–nitrous oxide flame (11:14).

2.3. Catalyst characterization

2.3.1. Fourier transform infrared spectroscopy (FT-IR)

Spectra of $[PW_{11}O_{39}M]^{5-}$ sodium salts and catalysts dried at 70 °C for 24 h were recorded. For this characterization, Bruker IFS 66 FT-IR equipment, pellets in BrK and a measuring range of 400–1500 cm^{-1} were used.

2.3.2. X-ray diffraction (XRD)

Powder XRD patterns were recorded on the same samples that have been analyzed by FT-IR. The equipment used to this end was a Philips PW-1732 with built-in recorder, using Cu Kα radiation, nickel filter, 30 mA and 40 kV in the high voltage source, and scanning angle between 5 and 60° of 2θ at a scanning rate of 1° per minute.

2.3.3. Scanning electron microscopy

The distribution of $[PW_{11}O_{39}M]^{5-}$ anions along the width of the carbon granules was measured with a Philips Model 505 scanning electron microscope with an energy dispersive X-ray analysis (EDAX) system, following a technique previously reported [21,22].

2.3.4. Thermogravimetric and differential thermal analysis (TG–DTA)

The TG–DTA measurements of the solid samples were carried out using a Shimadzu DT 50 thermal analyzer. The thermogravimetry and differential thermal analysis experiments were performed under argon and nitrogen respectively, using 25–50 mg samples and a heating rate of 10 °C/min. Quartz cells were used as sample holders with α-Al_2O_3 as reference. The studied temperature range was 20–700 °C.

2.3.5. Temperature programmed reduction (TPR)

Samples dried at 70 °C (100 mg) were screened (60 to 100 mesh) and were subjected to TPR using a mixture of H_2 (5%) in Ar flowing at 90 cm^3/min. The heating rate was kept at 10 °C/min until reaching a temperature of 1000 °C. The amount of H_2 consumed during reduction was determined using a thermal conductivity detector.

2.3.6. Isopropanol decomposition

The isopropanol dehydration test reaction was carried out in a conventional flow fixed bed reactor at atmospheric pressure and