Oxidation of aldehydes using silica-supported Co(II)-substituted heteropolyacid

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Abstract

A supported Co(II)-substituted heteropolyacid salt, $Cs_6H_2P_2W_{17}O_{61}Co\cdot OH_2$, on silica was prepared and characterized by BET surface area measurements, thermal analysis (TGA/DTA) and infrared spectroscopy. The infrared spectroscopy and thermal analysis revealed that the supported heteropolyacid salt preserves Wells-Dawson structure and is stable upto $500°C$. The BET result shows that by supporting the above heteropolyacid salt on silica, surface area increases. The supported heteropolyacid was used as a heterogeneous catalyst for the oxidation of aldehydes to corresponding carboxylic acids with molecular oxygen. Silica-supported heteropolyacid is an effective catalyst for the oxidation of aldehydes to carboxylic acids. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Due to the environmental restriction on using harmful mineral acids, solid acid catalysts are becoming popular in chemical industry [1–5]. Among solid acid catalysts, heterpolyacids attracted considerable amount of interest owing to their reactivity, which can be fine-tuned by incorporating alkaline or transition metal ions [6,7]. Heteropoly molecules have diverse chemistry with well-defined composition; therefore, they are widely synthesized and characterized for catalytic applications [8–11]. On the basis of structure, heteropolyacids are classified to several types, which among them Keggin and Wells-Dawson structures have received the most attention.

Although, Keggin type polyoxoanions have widely been studied as homogeneous and heterogeneous catalyst for the oxidation of organic compounds [12–14], the application of Wells-Dawson type polyoxoanions is mostly limited to homogeneous [15–17] or gas phase application [18], and only few of them demonstrate catalytic activity in heterogeneous form [19]. Generally, Keggin structures show more acidity and catalytic activity among heteropolyacids [20,21], whereas Wells-Dawson heteropolyacids exhibit greater selectivity and activity in some acid catalyzed and oxidation reactions [19]. The Keggin anions offer a limited hydrolytic stability compared to the other types of heteropolyacids, especially, when they are supported on interacting substrates [12,22,23].

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Furthermore, acidity and oxidizing strength of a solid acid generally must be matched with its application. For instance, very strong isomerization catalysts can cause cracking [22,24]. Consequently, substitution of one or more addenda ions with transition metal ions in heteropolyacid catalysts will always lead to new catalyzed reactions or to those with (perhaps) greater reaction selectivity [9].

Ishii and coworkers reported a number of interesting reactions catalyzed by transition metal-substituted heteropolyacids, including oxidation of aldehydes to carboxylic acids [25]. Shimizu and coworkers showed [26] how product selectivity and activity depend on the composition of heteropolyanion and the type of counter cations as well as the support surface area. In addition they emphasize [26] that pore size distribution is very important. Mizuno and coworkers examined oxidation of octanal by O_2 with both nickel and iron containing heteropolyacids [27]. Zamaraev and coworkers reported the catalytic properties of several cobalt-containing heteropolyanions, viz. tetra-alkylammonium salts of $PW_{11}CoO_{39}{}^{-5}$ and $CoW_{12}O_{40}{}^{-6}$, in alkene epoxidation by dioxygen in the presence of iso-butyraldehyde, at ambient condition [28]. Apparently, the different transition metal-substituted heteropolyanions are active for aldehyde oxidation [9].

The mechanism and the catalytic activity of transition metal-substituted heteropolyacids have been speculated since 1970 [29] and later on the propensity of them to bind with molecular oxygen and the role of such dioxygen activated species in oxidation of organic substrate have been explored [30,31]. Since one transition metal ion can differ in chemistry from another quite dramatically, the reaction of each transition metal ion with oxygen offers distinctive features.

Oxidation of aldehydes are surface type reaction [32], and by considering the very low surface area of heteropolyacids and their activity in oxidation of aldehydes, supporting heteropolyacid on high surface area materials is necessary for increasing the activity of heteropolyacid in oxidation of aldehydes. High surface area silica has been reported as a suitable support for grafting heteropolyacids on the surface and thereby increasing surface area and thermal stability [33]. Alternatively, partial replacement of protons with large cations can enhance in thermal stability [34]. Due to the importance of cobalt in

chemical and biological systems, in the present work, our attention has been focused on cobalt-substituted heteropolyacid. We show that the silica-supported Co(II)-substituted Wells-Dawson heteropolyacid salt, $Cs_6H_2P_2W_{17}O_{61}Co\cdot OH_2$, in an organic solvent, renders effective aldehyde oxidation to carboxylic acid in the presence of molecular oxygen. This particular salt not only offers the characteristic acidic and oxidative properties of an heteropolyacid skeleton, but also, it exhibits the catalytic activity of transition metal cations.

2. Experimental

2.1. Materials

All reagents and solvents used in this work are available commercially and used as received, unless otherwise indicated. Previously reported methods were used to purify the aldehydes [35], and carboxylic acids used as standards. A Shimadzu GC-8APF gas chromatograph equipped with a flame ionization detector was employed to confirm their purity. The Cab-O-Sil silica powder (*ex* Cabot, USA) with mesh size of <325 and specific surface area of $178\,m^2/g$ was used as the catalyst support.

Randall's method [36] was followed for the preparation of potassium salt of the Wells-Dawson type heteropolyacid, $K_6P_2W_{18}O_{62}$, and then converted to pure α-form by a method described elsewhere [37]. For synthesise of cobalt-substituted heteropolyacid, first lacunary polyanion (α-$K_{10}P_2W_{17}O_{61}\cdot15H_2O$) was prepared from α-$K_6P_2W_{18}O_{62}\cdot14H_2O$ according to the procedure described by Lyon [37]. In a typical reaction, 67 g of (13.8 mmol) α-$K_6P_2W_{18}O_{62}\cdot14H_2O$ was dissolved in 150 ml of water in a 500 ml Erlenmeyer flask. To this solution during vigorous stirring 250 ml of 1 M $KHCO_3$ (0.25 mol) was added at the rate of 10 ml/min. A white precipitate was formed on addition of approximately half of the potassium bicarbonate solution. Stirring continued for 30 min after addition of the total volume and then the precipitate was filtered off and crystallized by dissolving it in 100 ml of boiling water and allowing the solution to cool to 5°C overnight. The resulting crystals were collected by filtration, washed with 50 ml of cold water and then dried overnight under vacuum at room

temperature. The recovered crystals weight 58 g representing an 87% yield. IR spectra: 740 (s), 805 (s), 880 (m), 905 (sh), 940 (s), 985 (m), 1022 (m), 1084 (s).

For the preparation of cobalt-substituted heteropolyacid, $K_8P_2W_{17}O_{61}Co \cdot OH_2$, 51 g (10.6 mmol) of the prepared lacunary polyanion, $K_{10}P_2W_{17}O_{61} \cdot 15H_2O$, was dissolved in 200 ml of water at 90°C. While stirring vigorously, 3.36 g of $Co(NO_3)_2 \cdot 6H_2O$ in 40 ml of water was added which resulted in formation of a dark-red solution. Stirring continued for 15 min and upon addition of 30 g powdered potassium chloride and cooling the solution to room temperature light-red crystals formed, which were collected and recrystallized from boiling water. Final compound was washed with cold water and dried as usual manner. The dried crystals weight 40.5 g representing 79% yield. IR spectra: 796 (s), 912 (s), 942 (s), 965 (sh), 1010 (m), 1082 (s).

Acid salt of cobalt-substituted heteropolyacid was synthesized from its potassium salt via ether extraction method. 10 g of $K_8P_2W_{17}O_{61}Co(H_2O) \cdot 16H_2O$ were dissolved in 150 ml of cold water. To this solution 70 ml concentrated (12 M) hydrochloric acid were added and then heteropolyacid was extracted with 100 ml of diethyl ether. The ether containing heteropolyacid was dried in desiccator over concentrated sulfuric acid. The heteropolyacid crystallized after approximately 2 days. The crystals were recovered as described above. The cesium salt of cobalt substituted heteropolyacid was prepared by addition of cesium carbonate to an aqueous solution of the heteropolyacid. The resulting precipitate was separated from the liquid and was washed and dried as described before.

For the preparation of silica-supported heteropolyacid, 2 g of silica was suspended in 25 ml of water and then to this suspension 1.5 g of heteropolyacid in 20 ml of water was added. To this suspension, stoichiometric amount of Cs_2CO_3 was added and the mixture was stirred at room temperature for 16 h. The supported catalyst was recovered by evaporation under vacuum and was calcined at 350°C just prior to its use.

2.2. Methods

Nitrogen gas adsorption, using ultra-high purity nitrogen gas (99.999%), adsorbed volumetrically by either the support or the catalyst and support, at −196°C, led to their specific surface area evaluation.

These measurements were obtained on a stainless-steel automatic volumetric adsorption apparatus [38]. The level of liquid nitrogen surrounding the sample is constant ±0.3 mm. The samples are degassed using liquid nitrogen, turbo-molecular and rotary mechanical pumps in tandem, producing a background pressure $<5 \times 10^{-6}$ mmHg. Prior to adsorption calculations, the sample weight was corrected for any weight loss due to degassing, or drying.

Thermal analysis of the heteropolyacids and silica-supported heteropolyacids were made using a Rheometric Scientific STA-1500. Sample heating rates were 10°C/min. The sample mass of ≈15 mg was accurately defined prior to heating with a precision of ±5 µg.

An infrared spectrum of each salt was recorded on a Bio-Rad FTS-65 computer operated spectrometer with a wave number resolution of 4 cm^{-1}. Prior to recording the spectra, we dried each sample and a batch of KBr in a vacuum oven at 100°C. Solid solutions of either the catalyst and support or the support were prepared by mixing thoroughly then pressing as a pellet with a Carver press at ≈10 tonnes per square inch (≈154 MPa).

Atomic absorption spectroscopy was used to determine the cesium content of the heteropolyacid salt. The amount of cesium was calculated against an absorbance calibration curve prepared from several CsCl solutions.

2.3. Catalytic tests

Prior to use, catalyst and its support were calcined at 350°C in a furnace for 4 h. The catalytic activity was examined by suspending 80 mg of the catalyst in a thermostate batch-reactor containing 30 ml of dichloromethane and 5 mmol of a pre-selected aldehyde. High purity oxygen gas (99.999%) was introduced to the stirred reaction mixture via an immersed sintered-glass fitting at a flow rate of 0.25 l/min. The mixture was refluxed for 30 h. For the efficient condensation of vapor during this period the vapor in the system was cooled to −30°C. Volume of fluid was maintained constant by adding CH_2Cl_2 via a securely fitted dropping funnel.

The extent of aldehyde conversion was monitored by sampling 1 ml of aliquots of reaction mixture every 5 h. The reaction mixture was filtered to
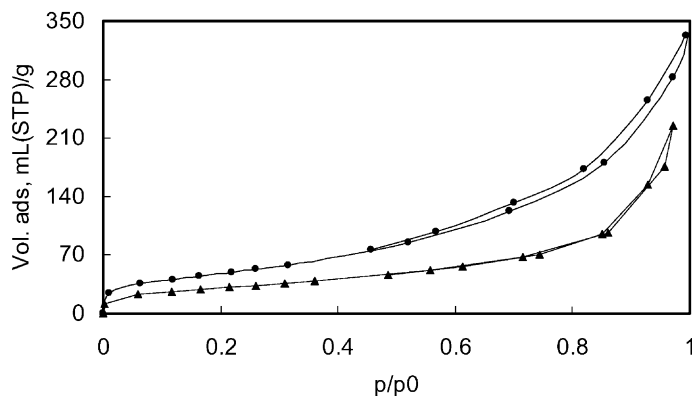
Fig. 1. BET plot of silica before (●) and after (▲) introducing of heteropolyacid catalyst.

remove any suspended material and analyzed via gas chromatography.

3. Results and discussion

3.1. Characterization of silica-supported Co-substituted heteropolyacid

Fig. 1 shows nitrogen adsorption isotherms for silica before and after introducing heteropolyacid. The decrease in specific surface area, from 178 to 112 m^2/g is attributed to 43 wt.% decrease of silica in the mixture since silica is the principal contributor to the total specific surface area. By assuming 2.2 nm^2 cross section for each heteropoly molecule, only monolayer of heteropoly acid covered the support. Moreover, after supporting the heteropolyacid on silica the mesopore volume decreased, Fig. 2, and the maximum of pore width of silica reduced from 100 to 48 nm.

Fig. 3 shows the DTA and TGA curves of silica-supported heteropolyacid. The endothermic peak between 75 and 200°C in DSC curve with slight weight loss in TGA curve is associated with elimination of physically absorbed water and some hydration water. The distinct weight loss that starts at 500°C and continues upto 800°C is due to the decomposition of heteropolyacid. This type of thermal
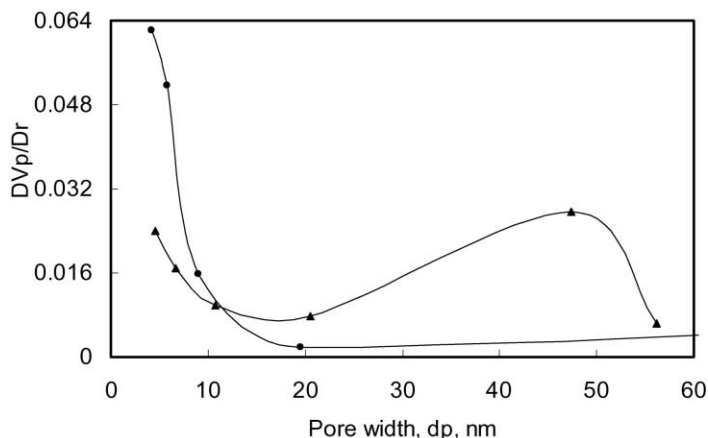

Fig. 2. Pore width plot of silica before (●) and after (▲) introducing of heteropolyacid catalyst.
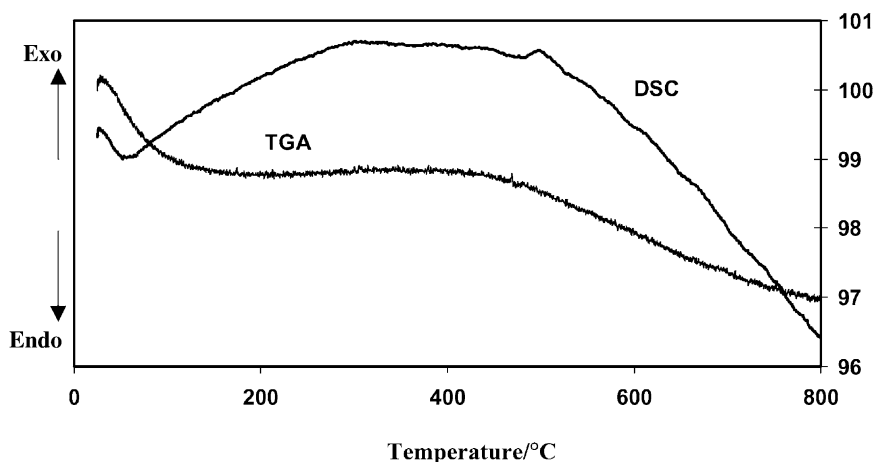
Fig. 3. TGA and DTA of $Cs_6H_2P_2W_{17}O_{61}Co \cdot OH_2/SiO_2$.

behavior previously has been observed in zeolites and other transition metal-substituted heteopolyacids with Wells-Dawson structure [18,39]. The high thermal stability of silica-supported heteropolyacid salt also disclosed by infrared spectrum with the appearance of Wells-Dawson characteristic peaks, as shown for bulk cesium salt in Fig. 4, after calcination at 350°C. Therefore, from infrared spectrum and thermal analysis data, it may be concluded that the Co-substituted

heteroploy acid preserves its Wells-Dawson structure after supporting on silica. Apparently, the high stability of Co-substituted heteropoly arises by replacement of protons with cesium and further stability enhanced by grafting it on silica. The high thermal stability of cesium salt of heteropolyacid is not unusual [40]; increase in thermal stability has been correlated to the number of protons in heteropolyacid [34].
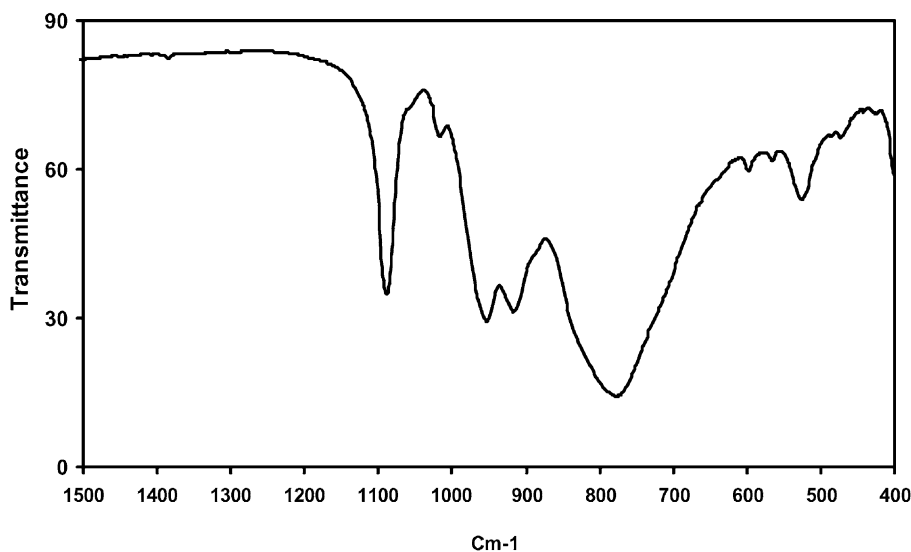

Fig. 4. Infrared spectra of $Cs_6H_2P_2W_{17}O_{61}Co \cdot OH_2$.

In this heteropolyanion, cobalt(II) is located partially outside of the lacunary hole and, thus, the cation exhibits characteristics both of free cobalt ions and of cobalt-containing heteropolyacids. Interestingly, in one stage of the preparation of this catalyst, when attempt was made to convert this heteropolyanion to a heteropolyacid by ion exchange method, the cobalt(II) cation was simply extracted from the heteropolyacid skeleton. This ease of exchange occurs only for cobalt(II)-containing heteropolyacids. It is not a general feature, for example, it will not occur for Mn(III)-containing heteropolyacids. This subtle exchange capability is due to the size of these metal ions. Zonnevijlle showed [41] that lacunary heteropolyacids can exchange only metal ions of diameter approximately <90 pm. Since cobalt(II) is larger than this critical dimension, as an ionic sieve effect, it must remain partially outside the lacunary hole and should be extracted relatively easily by strong ion exchange resins. Regardless of this fact, the cobalt(II) substituted heteropolyacid in this work is stable upto 500°C as shown by DTA and also by IR spectroscopy.

3.2. Catalytic activity

Table 1 summarizes aldehyde oxidation efficiency and selectivity by this Co(II) heteropolyacid. Clearly, this catalytic system favors aliphatic aldehyde oxidation over that of aromatic aldehydes. It is also interesting to compare selectivity and conversion of benzaldehyde to hydroxyl substituted benzaldehyde. Apparently, by hydroxyl substitution, conversion and selectivity increase and increase is in order of substitution in *ortho*, *meta* and *para* positions. Such trend

Table 1
Oxidation of different aldehydes with molecular oxygen catalyzed by silica-supported Co(II)-substituted heteropolyacid

Aldehyde	% Conversion	% Selectivity[a]
Isobutyraldehyde	88	86
n-Butyraldehyde	83	92
n-Propanaldehyde	79	88
Benzaldehyde	19	81
4-Hydroxy benzaldehyde	46	72
3-Hydroxy benzaldehyde	40	65
2-Hydroxy benzaldehyde	37	63
2-Phenyl acetaldehyde	54	76

[a] Selectivity for corresponding carboxylic acids.

previously have been reported in oxidation of hydroxyl benzaldehyde, when cobalt(II) chloride was used as catalyst for oxidation to the corresponding carboxylic acid [42]. In addition, present heterogeneous catalytic system shows higher yield in oxidation of aliphatic aldehydes in respect to homogeneous cobalt(II) chloride system. The reason for the higher efficiency in oxidation of aliphatic aldehydes by silica-supported heteropolyacid in present study is not clear at this time. However, the extensive mechanistic studies on the oxidation of aldehyde by cobalt-containing catalyst using various source of oxygen including acylperoxy radicals [43,44] or peroxy acids coordinated to transition center [45], high valent metal oxo-species [46], hydroperoxo and peroxo complexes [44], and singlet oxygen species [47] have been carried out. The activation of dioxygen and/or aldehyde via coordination on the metal center has also been suggested [45]. The exact mechanism still is controversial, but it seems that oxidation of aldehydes proceed via radical chain mechanism as it proved by inhibition of catalytic oxidation after introducing radical scavengers such as hydroquinone to the reaction media [9]. It seems that in the present work also the high activity of silica-supported heteropolyacid arise from cobalt's ability to form complexes with dioxygen and oxidize aliphatic aldehydes through a chain mechanism [44,45]. However, presence of appropriate ligands such as heteropolyanions that could stabilizes the higher oxidation states of transition metals must be realized [48]. Apparently, the mechanism by which oxidation of aldehydes governs by cobalt(II)-substituted heteropolyacid system is quite different from cobalt(II) chloride in homogeneous system.

Unfortunately, insolubility and phase separation of cobalt-substituted heteropolyacid in CH_2Cl_2 did not allow us to compare its catalytic activity in oxidation of aldehydes for homogeneous and heterogeneous systems. However, if we realize the idea of activation of two oxygen atoms by two metal center [49], higher activity is expected in heterogeneous system by bringing two metal moieties close together in heterogeneous system.

In conclusion, although the silica-supported Wells-Dawson heteropolyacid is a suitable catalyst for the oxidation of aldehydes, in comparison to similar catalysts in the literature; the effectiveness of catalyst should not be understated from aliphatic or aromatic

type of aldehydes point of view. However, further mechanistic information is needed before reaching a solid conclusion.

Acknowledgements

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