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Catalytic deoxygenation of benzaldehyde on cobalt and cooper tungstates

Rafael Oliveira Paes de Lima, Marcelo da Silva Batista

Chemical Engineering Department, Federal University of São João Del Rei, Campus Alto Paraopeba,
Rodovia MG 443, Km 5, Pobox 131, Cep 36420-000, Ouro Branco MG, Brazil.

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Abstract
Hydrodeoxygenation reaction (HDO) has been used to remove oxygen of substances in bio-oil and improve the quality of this biofuel. In this work were prepared copper and cobalt tungstates to be evaluated as catalysts for HDO of benzaldehyde. The benzaldehyde was used as model of bio-oil in HDO. Copper and cobalt tungstates ($Cu_{1-x}Co_xWO_4$ where x=0; 0.5; 1) were prepared by co-precipitation method and characterized by XRD and H_2-TPR. The XRD results showed presence of tungstates ($CuWO_4$, $CoWO_4$, $Cu_{0.5}Co_{0.5}WO_4$) and also copper oxide. The H_2-TPR profile showed that copper and cobalt in tungstate and copper oxide were reduced at temperature different. $CoWO_4$ showed the highest catalytic activity and the high selective to toluene and benzyl alcohol. $CuWO_4$ and $Cu_{0.5}Co_{0.5}WO_4$ showed lower selectivity to benzyl alcohol, and consequently, the highest selective to HDO.

Keywords: Hydrodeoxygenation; Benzaldehyde; Catalyst; Tungstates.

1. Introduction

In recent years, strategies for the production and use of new energy sources are required for keep sustainable development safe. Biomass is the only current sustainable source of organic carbon for liquid bio-fuels production. The first generation bio-fuels (bio-ethanol and biodiesel) have been implemented but the energy efficiency per unit land is relatively low. For this reason new research focuses on developing second generation bio-fuels, which can be produced from other biomass sources such as agricultural waste, wood and others [1-3].

The fast pyrolysis of biomass technology is an economical and advantageous method of obtaining liquid fuels and it can continuously change biomass to bio-oil in large scale. The bio-oil has high energy density and it is considered clean energy with very low content of sulfur and nitrogen compounds [4]. However, the bio-oil has a large amount of oxygenates (10-40 wt%) and water (10-30 wt%), acidity (pH=2-4), which conflicts with the standards of fuels from oil, as gasoline and diesel. The low quality of the bio-oil is mainly caused by the large amount of oxygenates, which required the development of technologies upgrade. The catalytic process of hydrodeoxygenation (HDO) is the most efficient for the removal of oxygenated compounds from bio-oil, but the great diversity of these compounds makes it difficult to study catalysts for this process [5].

However, some authors have used: benzaldehyde, anisole, cresol and phenol as model compound for evaluation of catalysts in the process of HDO [6-8]. Benzaldehyde stands out mainly because of its simple structure has been used as model in the study of catalysts for HDO [9]. Catalysts containing noble metals (Ru, Rh, Pd, Pt) supported are active and most studied for HDO, but the high cost of these metals makes these unattractive catalysts. As alternative, the copper and cobalt tungstates, which have much lower cost and it cold to be evaluated in the HDO of benzaldehyde. Recently, tungstates have been used as catalyst for photodegradation, production of hydrogen and selective oxidation of alcohols [10-12]. The co-precipitation method is considered a versatile and effective route for the preparation of tungstates, due to the low cost, simplicity, efficiency and good potential for large scale production [13].

In this way, the purpose of this paper is the study of benzaldehyde hydrodeoxygenation on copper and cobalt tungstates ($Cu_{1-x}Co_xWO_4$ x=0; 0.5; 1) in batch reactor. For this, $CuWO_4$, $CoWO_4$ and $Cu_{0.5}Co_{0.5}WO_4$ catalysts were prepared by co-precipitation method and characterized by X-ray diffraction (XRD) and temperature programmed reduction with hydrogen (H_2-TPR). The catalytic activity and selectivity of copper and cobalt tungstates were evaluated in the HDO of benzaldehyde.

2. Experimental

2.1 Catalysts preparation

Copper and cobalt tungstates were prepared by co-precipitation method. For samples preparation were added 50 mL of aqueous solution of copper chloride and/or cobalt nitrate, concentration 0.2 mol L^{-1} solution of sodium tungstate (Na_2WO_4) and the pH adjusted previously (pH= 9.0) with NaOH solution of 1 mol L^{-1}. The stoichiometric mixture ($M^{+2}/WO_4^{-2}=1$) was homogenized with magnetic stirring and pH controlled. After one hour, the copper and cobalt tungstates precipitated was separated by filtration and washed with distilled water to remove sodium salts. The solid was dried at 110 °C for 2 h and calcined at 750 °C (rate of 10 °C min^{-1}) for 5 h, for obtain the $CuWO_4$, $CoWO_4$ and $Cu_{0.5}Co_{0.5}WO_4$.

2.2 Catalysts characterization

The copper and cobalt tungstates were characterized by XRD (X-ray diffraction) and H_2-TPR (temperature programmed of reduction by hydrogen).

XRD analyzes were performed by the powder method on a Shimadzu diffractometer (XRD 6000) with Cu tube, Ni-filtered, operating at 30 KV, 15 mA and CuKα radiation ($\lambda = 0.1542$). The speed of the goniometer used was 2°(2θ)/min, the angle ranging between 15 and 60°(2θ). Crystallite phases were determined by correlating the diffraction patterns with those in the standard powder XRD files (X´pert database) [14]. H_2-TPR analyses were performed on a SAMP3 equipment (Termolab Equipment, Brazil) with 100 mg of catalyst and flow of 30 ml/min from a mixture of 2 % H_2/Ar, heating rate 10 °C/min in which hydrogen consumption was monitored by a thermal conductivity detector. The decomposition of the Gaussian peaks was performed with settings using computer software.

2.3 Catalytic tests

The hydrodeoxygenation reaction was carried out in a batch reactor of stainless steel 280 ml, operated at 220 °C and 12 atm of H_2, under magnetic stirring for 6 h. Before of start, only the catalysts were reduced with H_2/Argon flow from ambient temperature to 950 °C. In each reaction was used 100 mg of catalyst, 15.00 g of dodecane and 4.00 g benzaldehyde. After the reaction, the liquid products were analyzed by gas chromatography (Agilent 7820A GC) using a DB-1 capillary column (30 m × 0.32 mm) with flame ionization detector.

The catalytic activity was measured as a function of benzaldehyde conversion (Equation 1). The equations (2), (3), (4) and (5) were used to calculating the selectivity to toluene, benzene and cyclohexane, benzyl alcohol and HDO reaction, respectively.

$$X(\%) = \frac{\sum \text{products mols}}{\sum \text{benzaldehyde mols} + \sum \text{products mols}} \text{x100} \qquad (1)$$

$$Selectivity\ to\ toluene = \frac{\sum \text{toluene mols}}{\sum \text{products mols}} \text{x100} \qquad (2)$$

$$Selectivity\ to\ benzene + cyclohexane = \frac{\sum \text{benzene mols +cyclohexane mols}}{\sum \text{products mols}}\ x\ 100 \quad (3)$$

$$Selectivity\ to\ benzyl\ alcohol = \frac{\sum benzyl\ alcohol\ mols}{\sum \text{products mols}}\ x\ 100 \quad (4)$$

$$Selectivity\ to\ HDO = \frac{\sum toluente+benzene+cyclohexane\ mols}{\sum \text{products mols}}\ x\ 100 \quad (5)$$

3. Results and discussion

Figure 1 shows the XRD patterns of $CoWO_4$, $CuWO_4$ and $Cu_{0.5}Co_{0.5}WO_4$. The XRD patterns showed the characteristic reflections of tungstates, $MW0_4$ (M =Co and Cu; PDF 72-0479 and 73-1823, respectively) and also $Cu_{0.5}Co_{0.5}WO_4$ [13]. The diffractogram of $CoWO_4$ no shows evidence of cobalt oxide formation. On the other hand, the diffractogram of $CuWO_4$ catalyst shows the formation of copper tungstate, but the intensity of the peak in 2θ = 35.6°, 38.7° and 48.6° in the diffraction pattern also suggest the formation of copper oxide (CuO). In the $Cu_{0.5}Co_{0.5}WO_4$ sample also was observed peaks attributed to copper oxide both with tungstate.

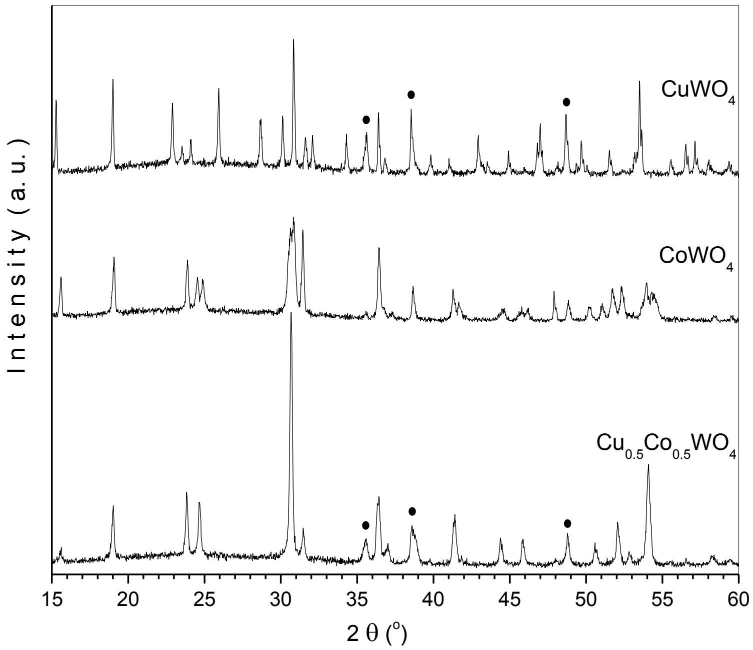


Figure 1. XRD patterns of $CoWO_4$, $CuWO_4$ and $Cu_{0.5}Co_{0.5}WO_4$. Peaks relating to copper oxide (●).

Figure 2 shows the H_2-TPR profiles of $CuWO_4$, $CoWO_4$ and $Cu_{0.5}Co_{0.5}WO_4$ and also a sample of sodium tungstate (Na_2WO_4) used as reference. Note that Na_2WO_4 only starts reduction at temperatures above 850 °C and this reduction can be assigned to the reduction of W(VI) to W(IV). Consequently, peaks observed below this temperature were attributed to reduction of different species of copper and cobalt. $CuWO_4$ exhibits peak at 350 °C corresponding to reduction of CuO to Cu° [15], and new reduction peaks appear at 532, 584 and 690 °C, indicating the reduction of copper-forming part of $CuWO_4$. CuO reduction is easier than the reduction of $CuWO_4$, further reduction of copper in Cu-WO_x requires higher temperature and apparent activation energy. Copper oxide is formed during the calcination of samples at 750 °C after the co-precipitation process and it was detected by XRD (Figure 1).

Figure 2 shows peaks of H_2 consumption between 500 and 800 ºC for $CoWO_4$. Note that no cobalt oxide peak was observed below at 500 ºC [16,17]. In agreement with the XRD data, TPR indicates that a high degree of Co-WO_x interaction is observed for $CoWO_4$. Thus, the reduction peaks observed at 625, 660 and 725 °C indicate the reduction of cobalt in Co-WO_x interaction, consequently more difficult to reduce. These peaks can be assigned to the reduction of Co^{2+} to Co^o for which there exists a range of degrees of interaction between the Co-WO_x [17].

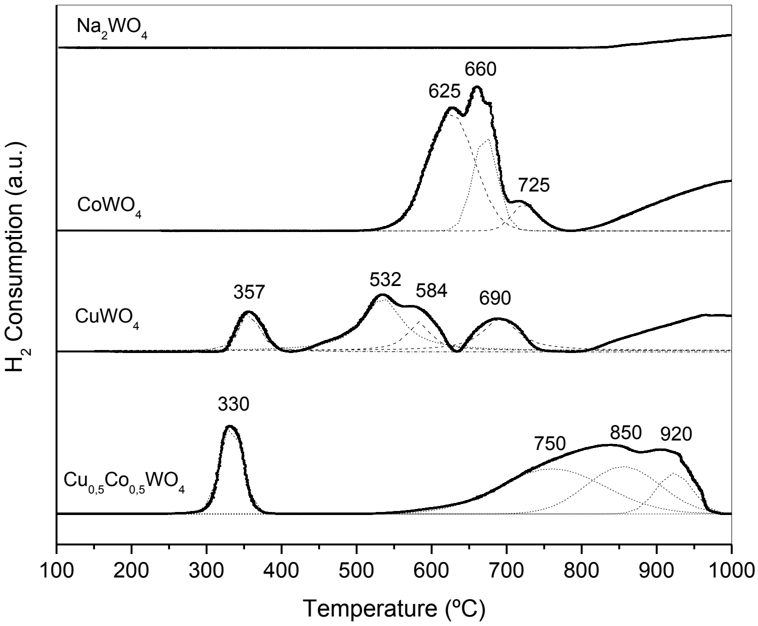


Figure 2. H_2-TPR profiles of tungstate samples.

In the TPR profiles of $Cu_{0.5}Co_{0.5}WO_4$ the peak at 330 °C was attribued to reduction of CuO to Cu°, as also observed in $CuWO_4$. Note that others reduction peaks appear at 750, 850 and 920 °C, indicating the reduction of copper and cobalt tungstate and together the reduction of own tungstate. These peaks were displaced to higher temperature compared to $CuWO_4$ and $CoWO_4$ probably due to interactions forces, causing the oxides require a higher temperature to reduce.

The results of benzaldehyde conversion and selectivity to products obtained in HDO of benzaldehyde on $CuWO_4$, $CoWO_4$ and $Cu_{0.5}Co_{0.5}WO_4$ catalysts are summarized in Table 1. Note that $CoWO_4$ (55.8%) had the highest conversion, followed by $Cu_{0.5}Co_{0.5}WO_4$ (41.3%) and $CuWO_4$ (34.8%). This higher activity of cobalt catalyst in HDO reactions was also observed in the literature [7,8,18-19]. Consequently, adding cobalt in tungstate promove improvement of catalytic activity in HDO of benzaldehyde [8]. Thus, $Cu_{0.5}Co_{0.5}WO_4$ showed intermediate activity (41.3%) between the activity of $CoWO_4$ and $CuWO_4$.

As seen in Table 1, the products over tungstate in HDO of benzaldehyde at 220 °C and 12 atm were toluene, benzene, cyclohexane, and benzyl alcohol. Repeated experiments in batch reactor showed that the conversion and selectivity values to vary within ±5 percentage units, indicating good reproducibility of experimental data.

Table 1. HDO of benzaldehyde on $CuWO_4$, $CoWO_4$ and $Cu_{0.5}Co_{0.5}WO_4$.

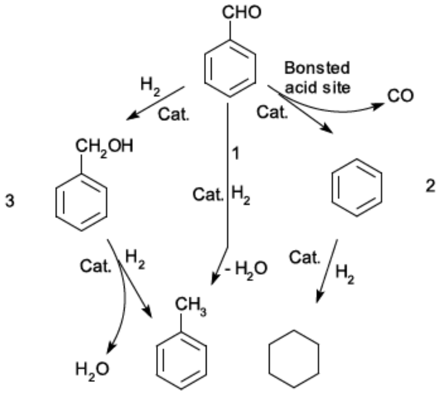
Catalyst	$CuWO_4$	$CoWO_4$	$Cu_{0.5}Co_{0.5}WO_4$
Conversion (%)	34.8	55.8	41.3
Toluene	65.1	76.4	59.5
Benzene + Cyclohexane	31.8	13.2	36.5
Benzyl alcohol	3.1	10.4	4.0
Deoxygenation rate (%)	96.9	89.6	96.1

In Table 1, note that toluene was the principal product in HDO of benzaldehyde for all catalysts. However, $CoWO_4$ showed highest selectivity to toluene (76.4%). According to Procházková et al. [9], toluene is the major product in hydrodeoxygenation reaction of benzaldehyde. Copper and cobalt catalysts are highly active in HDO reactions and the products formed indicate the occurrence of decarbonylation, hydrogenation and hydrogenolysis [20]. Thus, copper and cobalt tungstates reduced by H_2 appears as active phase Cu^0 and Co^0, and also H_xWO_3-z (x=0.9-1.3), which are important for vacancies formation and Brønsted acid sites [6]. This new heterogeneous catalysts for benzaldehyde HDO has a mechanism similar to Mars-van Krevelen cycle [21]. According to the products observed in Table 1, in the temperature and pressure conditions used in this work, can be proposed the mechanism of reactions shown in Scheme 1. In this scheme, benzaldehyde HDO were divided into three routes. In route 1, benzaldehyde is adsorbed on the catalyst vacancy forming a metal-oxygen bond, then occurs the breakdown of carbon-oxygen bond and leads to toluene direct formation.

In route 2, benzene is produced by direct decarbonylation over Brønsted acid sites. This benzene may also react with H_2 to form cyclohexane. In route 3, benzaldehyde is hydrogenationed for benzyl alcohol formation. Subsequently, benzyl alcohol reacts again with H_2 and finally, toluene is produced with eliminating water.

Note that benzene is produced by direct decarbonylation over Brønsted acid sites. Toluene is produced by direct hydrogenolysis of C=O bond or hydrogenation-hydrogenolysis route with benzyl alcohol as an intermediate, over catalyst bifunction (metallic function for hydrogenation and the presence of acidic protons for dehydration). HDO of benzaldehyde can theoretically also proceed via transformation of carbonyl group into methane (dealkylation of toluene) or CO (decarbonylation). However, dealkylation reaction to the formation of benzene is negligible compared to decarbonylation [20].

In general, $CuWO_4$ and $Cu_{0.5}Co_{0.5}WO_4$ catalysts present high selectivity to HDO, 96.9% and 96.1%, respectively. Thus, these catalysts are most favor the formation of non-oxygenated compounds. These results show that copper and cobalt tungstates can contribute to deoxygenation of the bio-oil and enable the upgrading of biofuels.



Scheme 1. Main reaction pathways of benzaldehyde HDO.

4. Conclusion

According to results obtained was observed formation of copper oxide together with copper and cobalt tungstate. H_2-TPR profiles showed the presence of different interactions of Cu-WO_x and Co-WO_x that require higher temperature to reduce compared to copper and cobalt oxides pure. The results showed that copper and cobalt tungstates have activity in HDO reaction of benzaldehyde. Benzene is produced by direct decarbonylation over Brønsted acid sites. Toluene is formed by direct hydrogenolysis or hydrogenation-hydrogenolysis route over catalyst bifunction and benzyl alcohol was an intermediate. $CoWO_4$ showed the highest catalytic activity and higher selectivity to toluene and benzyl alcohol. On the other hand, $CuWO_4$ and $Cu_{0.5}Co_{0.5}WO_4$ showed lower selectivity to benzyl alcohol, and consequently higher HDO selectivity.

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Rafael Oliveira Paes de Lima was a student in The Hague University of Applied Sciences and trainee in the department of Machine Dish Wash - Home Care, in Unilever, Vlaardingen, Netherland, in 2016. He is a chemical engineering student at the Federal University of São João del Rey, Brazil. He is currently researching about biofuel.
E-mail address: rafael.oliveira.paes.lima@gmail.com

Marcelo S. Batista received the Chemical Engineer degree from the Federal University Rural of Rio de Janeiro, Brazil, in 1994 and MSc. and PhD in Chemical Engineering from the Federal University of São Carlos, São Paulo, Brazil, in 2002. He holds a post PhD from the University of São Paulo (IQSC/USP), São Carlos, Brazil, in 2004 in the field of production of H2 coupled to Fuel Cell. Currently, he is a professor at the Federal University of São João del Rey. Dr. Batista is teaching in postgraduate course of the same institution and leader of the Nucleus of Research in Chemical Engineering. His research in the field of fuels and environmental catalysis has more than 30 international journal publication and 100 publications in conferences.
E-mail address: marcelobatista@ufsj.edu.br