Highly active hydrogenation of 4-methoxyacetophenone by the novel carbon-supported ternary nanocatalyst palladium-vanadium-cobalt

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ABSTRACT

Multimetallic nanocatalysts have remarkably revealed activities in various catalytic applications. Herein, the ternary nanocatalysts based on palladium-vanadium-cobalt were successfully synthesized through the reduction of their salts with sodium borohydride including impregnating of activated carbon (AC) substrate with colloid solution of metallic nanoparticles (PdVCo/C). The immobile of trimetallic PdVCo on AC was evidenced by XRD, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and UV-VIS spectroscopy. TEM imaging showed that the PdVCo particles size is about 7 nm. The trimetallic nanocatalysts were characterized in transfer hydrogenation of carbonyl substrates to alcohol product which was defined by GC (FID detector). The obtained result is that the conversion of the carbonyl substrates is over 73% in the case of PdVCo nano-catalyst in the presence of potassium hydroxide.

1. Introduction

Since 1897, Knoevenagel and co-workers were discovered the transfer hydrogenation reaction [1,2]. In which the hydrogen was attached to the unsaturated π-bonds on the hydrocarbon structure. By now, transfer hydrogenation is still one of the powerful methods to synthesize from the organic compounds, pharma-ceutical to industrial applications [3,4]. Thus, there have been many reports on hydrogenation reactions using metallic catalysts gaining high activity, good selectivity, long-term stability, and facile recovery. Among them, nickel [9–11] and palladium [5–8] are two bright catalysts for hydrogenation. In recent years, the multimetallic catalysts [12] have been interested in various application such as hydrogen evolution [13,14], oxygen reduction [15,16], alcohol oxidation [12,17] and hydrogenation [18–21] as well. Thus, Ang and co-workers prepared carbon-supported palladium-vanadium nano-catalyst by wet chemical reduction and found that it has excellent catalytic activity and stability in oxygen reduction [22]. In addition, Zhao et al. have proved that V has lower electronegativity than that of palladium. Hence, by adding a metal such as V to the Pd alloy could change the electronic and geometrical structure of palladium and improve the catalytic efficiency [15]. On the other hand, Kumar and co-workers synthesized hollow carbon capsules supported PdCo and successfully used as catalyst for transfer hydrogenation of 4-chloroacetophenone [23]. However, the combination of ternary alloy Pd, V, and Co have not been found in the uses of transfer hydrogenation of carbonyl substrates. Therefore, in an attempt to explore the more application of multimetallic nanocatalysts based on palladium as well as to increase the yield of transfer hydrogenation of 4-methoxyacetophenone which is low conversion in the

common metallic catalysts [24]. Herein, this report focuses on the preparation of carbon-supported ternary nanocatalyst palladium-vanadium-cobalt as well as the evaluation the catalytic activity of the hydrogenation reaction of 4-methoxyacetophenone. The results will be described in this study.

2. Experimental

Analytical grade palladium chlorides 99% ($PdCl_2$), cobalt nitrate 99% ($Co(NO_3)_2.6H_2O$), vanadium oxide 99.5% (V_2O_5), $NaBH_4$, 98%, and EG 99% were purchased from Merck (USA) and used at receive. Ethanol and isopropyl alcohol (IPA) were supplied by Chemsol (Vietnam). Distilled water was used in the whole experiment. Nanocatalysts PdVCo was prepared by following method [12]: Palladium chloride (0.4425 g) was added to 50 mL 0.01 M solution of hydrochloric acid, vanadium pentoxide (0.4550 g) was dissolved in 50 mL 0.15 M solution of sodium hydroxide, and cobalt nitrate hexahydrate (0.4570 g) was dissolved in 50 mL distilled water. The combination reducing agents (ethylene glycol and 0.01 M $NaBH_4$) were dropwise added to the above mixture which was stirred for an hour at room temperature. The black powder of PdVCo/C at 20%wt were obtained by adding activated carbon powder (50 mg) to the mixture, then it was placed under supersonic instrument within 30 min. The black solution was then centrifured, rinsed with distilled water three times and put in vacuum oven at 85 °C for 3h.

The morphological features and particles size of catalysts were recorded by TEM method (transmission electron microscopy) using a 1400 JEOL microscope at 120 kV. The surface area (S_{BET}) was analyzed through N_2 adsorption technique (Micromeritic Flowsorb) under an out-gas process at 200 °C for 3 hours. The crystalline nature of catalysts was determined by XRD using a Brucker D8-Advanced diffractometer with Cu Kα radiation (λ = 1.540Å).

Herein, we carried our the hydrogenation reaction of 4-methoxyacetophenone in alkaline solution with hydrogen atmosphere using 2 mol% of the catalysts. Indeed, to the 20 cc multireactors, the substrates, the solvent and alkaline solution (5% KOH in isopropanol), and catalysts with suitable amount were added with stirring at 60 °C under reflux condensation. After which, H_2 is fed by Schlenk- line to the solution mixture at ambient pressure in 60 min. The conversion of 4-methoxyaceto-phenone and selectivity of products was determined by gas-chromatography and gas-chromatography/mass spectroscopy (column with 30 m

x 0.25 mm, FID detector). Experiment was repeated at least three times to reduce the experimental errors.

3. Results and discussion

As shown in Fig 1, the specific XRD patterns of ternary alloy palladium-vanadium-cobalt nano catalysts with the metal loading of 20 wt%. The peaks located at 40.02°, 46.71° and 67.62°, which corresponds to (111), (200), and (220) lattice planes as per the JCPDS Card 00-005-0681 emphasizing the face-centered cubic phase of Pd particles suggesting the single-phase structure for all nanocatalysts, respectively.
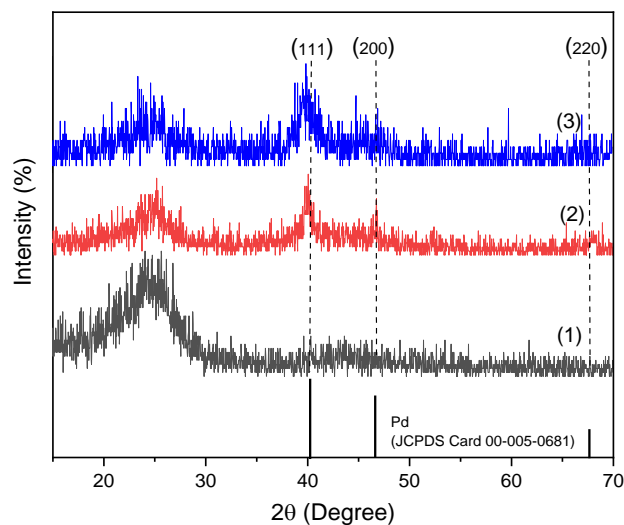

Fig 1: XRD patterns of nanocatalysts: (1) PdV/C; (2) PdCo/C; (3) PdVCo/C

From the initial phase palladium (a = 3.897 Å), the typical peaks of palladium-vanadium-cobalt shifts slightly towards higher 2θ, which reflects the combination of Co and V into the palladium lattice to create tertiary alloy phase palladium-vanadium-cobalt. In addition, the cubic-lattice parameter of palladium-vanadium-cobalt was slightly reduced based on the smaller atomic radii of V and Co. The broadened diffraction peaks is regarded as the nano-crystalline characteristic of ternary palladium-vanadium-cobalt nanocatalysts. The average crystallite size is made from FWHM (full width of the half maximum) of most strength peak (111) by the Scherrer's equation [25,26] as showed below:

$$d = \frac{K\lambda}{\beta\cos\theta}$$

Where d = the average size of crystallite, K = 0.94 Scherrer constant depending on the crystallite shape; λ = 1.541 Å, wavelength of Cu Kα X-ray radiation; β = FWHM of the most intense peak and determined by Highscroce+ software; θ = diffraction angle in radians. It is that the crystallite sizes of as prepared PdVCo

nanocatalysts was found to be around 7 nm. Despite no diffraction peaks of vanadium and cobalt nanoparticles in different phases are observed.

Moreover, the EDX spectrum of nano catalysts clearly indicates that both Co and V are present in the trimetallic sample, the mass ratio of Pd/Co/V were illustrated in Table 1. In particular, the vanadium-weight and cobalt-weigth in catalytic samples were low based on AAS analysis and EDX spectra as shown in Figure 2, the atomic ratios between of Pd/Co/V in ternary metallic catalysts are 1/0.57/0.45. The results revealed the reason why Co and V disappeared on the XRD patterns.
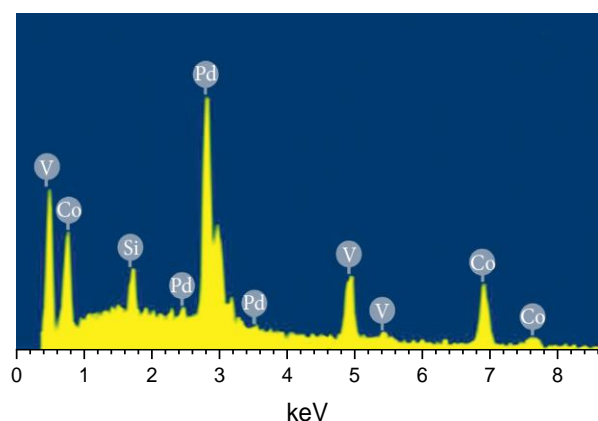

Fig 2: EDX spectra of PdVCo/C

Besides, the TEM images of Pd alloy nanocatalysts and their particles-size distribution are described in Fig 3. The prepared nanoparticles PdV (3a) possess a small spherical size and are well dispersed on the C-support surface as well as into the pores with a low particle size distribution from 3 - 8 nm, and the average particle diameter are found to be 6.8 nm. Similarly, in the case of PdCo (3b), the average particles diameter was found to be 6 nm, in which the particles larger 6 nm were filled more than 50% on the catalytic sample. Furthermore, different from the two above, the ternary PdVCo nanocatalysts (3c) possess the larger spherical nanoparticles, most of the particle sizes are distributed in the range of 3-9 nm and the major particles diameter is found to be 7 nm.

This could be explained in terms of the reduction process using the combination reducing agent (EG and NaBH$_4$), that leads to a rather larger spherical nanoparticles. Besides, the incorporation of cobalt and vanadium also bring to increase the particles size of the catalyst and leads to a change in the surface morphology of Pd resulted in an increase in the adsorbed species of the catalysts which highly contributes to the transfer hydrogenation on the Pd nanoparticles site [27].
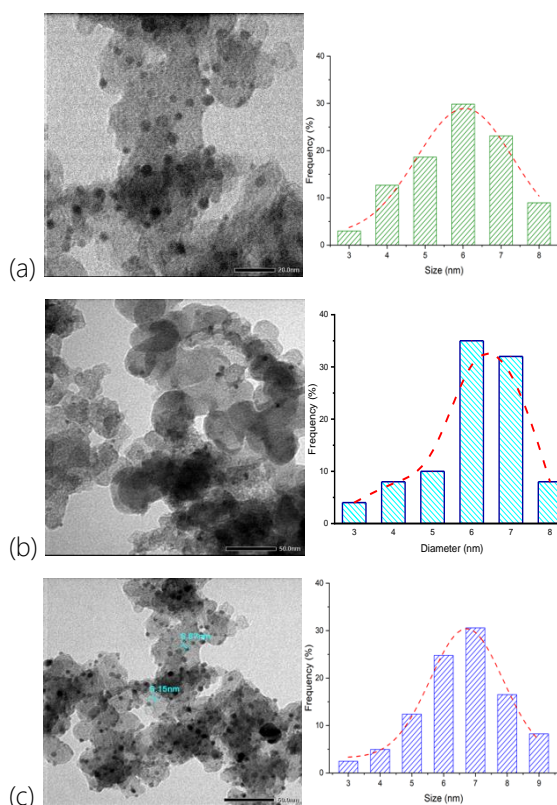

Fig 3: TEM emages of of nanocatalysts: (a) PdV/C; (b) PdCo/C; (c) PdVCo/C

Table 1 described the specific surface area (S$_{BET}$) of nano-catalysts which is determined by nitrogen absorption after being out-gas under 200 °C within 2h. The surface area's increasing which was caused by the slower addition of reduction agent and decreased of nanoparticles diameter. The smaller nanoparticles size could be more suitable for the surface adsorption and catalytic activities in transfer hydrogenation reaction. Although the nanoparticle size increased but not significantly in the case of PdVCo (Fig 3).

Table 1: Surface area and molar ratio of catalysts

Samples	S$_{BET}$ (m^2/g)	Molar ratio
C	318.4	
PdV	103.2	1 : 0.27
PdCo	132.7	1 : 0.24
PdVCo	127.4	1 : 0.45 : 0.57

Meanwhile, the surface area of the PdV decreased quite sharply, even though the PdV nanoparticle size was the lowest. This could be explained in terms of the nano-particles deeply loaded into the pores of the support, leading to reducing the surface area significantly.

The catalytic activities were tested by the transfer hydrogenation of 4-methoxyacetophenone, in which

the substrates was hydrogenated in alkaline solution (5% KOH in IPA) within 90 min. All the experiments were performed at 60 °C under hydrogen atmosphere and results are described in Fig 4. Therein, in the case of PdVCo catalyst, the best conversion of 4-methoxyacetophenone was obtained at 73.5%, it could be explained partly by the large surface area of the catalyst, and partly by the wider distribution of active sites (Pd), due to the presence of both V and Co [15], based on AAS analysis of the catalysts as showed in the Table 1, namely surface area of PdVCo was over 127 m^2g^{-1}, eventhough, the particles size are rather bigger than the others (particles diameter 7-8 nm).
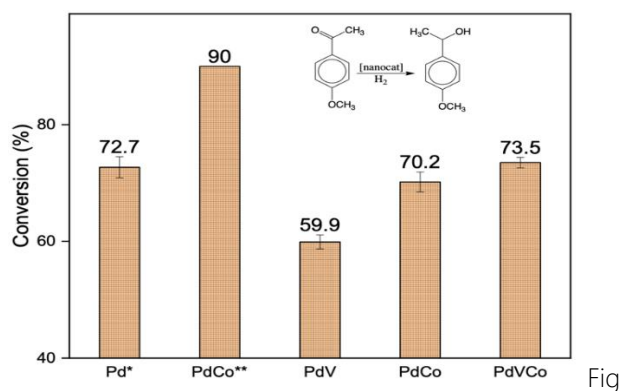

Fig 4: Activity of nanocatalysts on the hydrogenation of 4-methoxyacetophenone; *[28] reaction in KOH at 90 °C for 3h over Pd/zeolite catalyst; **[23] reaction in KOH at 90 °C for 16h over PdCo/HCC catalyst (hollow carbon capsules) with 4-chloroacetophenone

Furthermore, as mentioned in the previous section, the incorporation of V and Co increases the nanoparticle size of the catalyst, which changes the surface structure of Pd leading to more active sites in the catalyst which highly contributes to the transfer hydrogenation on the Pd nanoparticles site. Likewise, in the case of PdCo catalyst, significant activity in the transfer hydrogenation of 4-methoxyacetophenone was obtained at 70.2% conversion within 60 min reaction. Thus, as compared to Kumar and co-workers [23], the hydrogenation conversion are quite lower, in this case, they replaced the methoxy group by chloride on the ketone substrate and use hollow carbon capsules as support instead of activated carbon. This demonstrates the efficiency and important role of support's shape and structure.

However, in the case of PdV/C, the catalytic activities of ketone substrate are significantly decreased to 59.9%, the catalytic activity of carbon-supported palladium-vanadium alloy on the transfer hydrogenation reaction is not better than Pd/C. The reason is explained that the lower surface area of the catalyst, the lower substrate adsorption is obtained. Interestingly, in our previous

report [28], the hydrogenation conversion of the same substrate was 72.7% in the case of pure palladium nanoparticles supported on zeolite, loading 2 mol% of the catalyst. This conversion is almost the same to the PdVCo catalyst, eventhough the palladium loading lower as an half weight%. It is significant lower the cost of catalyst as well as demonstrates the highly catalytic activity.
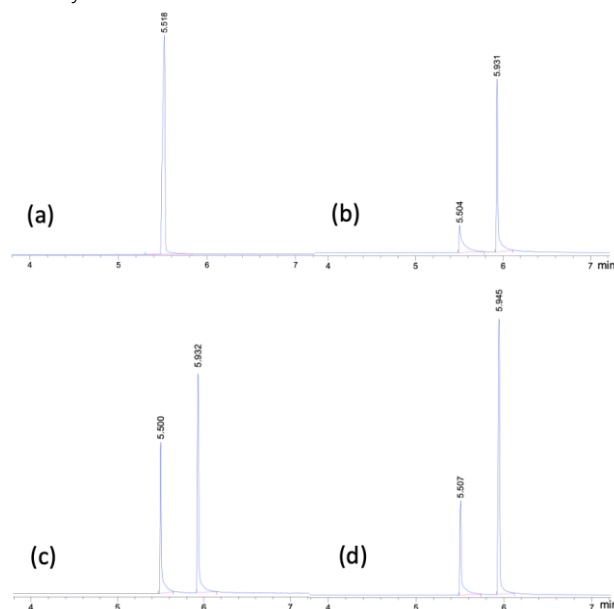

Fig 5: GC analysis of substrate 4-methoxyacetophenone (a) and product mixture of hydrogenation reaction with PdV (b); PdCo (c); PdVCo (d) as catalysts; the ketone substrate gives the retension time of 5.5 min while the alcohol product gives at 5.9 min

Conclusion

In summary, the multimetallic nanocatalysts based on palladium were successfully prepared by the reduction of salt precursors. All the physio-chemical characteristics were performed, in which TEM method demonstrated the size of PdVCo nanoparticles is around 7 nm and well loading on the support. Besides, this study exhibited that trimetallic nano-particles are the excellent catalysts for transfer hydrogenation of ketone substrates in the flexible condition as well. Namely, the conversion was over 73% within 60 min in the hydrogenation of 4-methoxyacetophenone in the case of ternary PdVCo/C nanocatalyst.

Acknowledgments

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