available at www.sciencedirect.com



journal homepage: www.elsevier.com/locate/chnjc

Article Hydrogenation of 2-ethylanthraquinone with bimetallic monolithic catalysts: An experimental and DFT study

Yanyan Guo, Chengna Dai, Zhigang Lei *

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

ARTICLE INFO

Article history: Received 27 December 2017 Accepted 24 January 2018 Published 5 June 2018

Kevwords: Bimetallic monolithic catalyst Allov 2-Ethylanthraquinone hydrogenation DFT calculation Synergistic effect

ABSTRACT

We studied the hydrogenation of 2-ethylanthraquinone (eAQ) over Pd/SiO₂/COR (COR = cordierite) monometallic and Pd-M/SiO₂/COR (M = Ni, Fe, Mn, and Cu) bimetallic monolithic catalysts, which were prepared by the co-impregnation method. Detailed investigations showed that the particle sizes and structures of the Pd-M (M = Ni, Fe, Mn, and Cu) bimetallic monolithic catalysts were greatly affected by the second metal M and the mass ratio of Pd to the second metal M. By virtue of the small particle size and the strong interaction between Pd and Ni of Pd-Ni alloy, Pd-Ni bimetallic monolithic catalysts with the mass ratio of Pd/Ni = 2 achieved the highest H_2O_2 yield (7.5 g/L) and selectivity (95.3%). Moreover, density functional theory calculations were performed for eAQ adsorption to gain a better mechanistic understanding of the molecule-surface interactions between eAQ and the $Pd(1 \ 1 \ 1)$ or $PdM(1 \ 1 \ 1)$ (M = Ni, Fe, Mn, and Cu) surfaces. It was found that the high activity of the bimetallic Pd-Ni catalyst was a result of strong chemisorption between Pd₃Ni₁ (1 1 1) and the carbonyl group of eAQ.

> © 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen peroxide (H₂O₂) is an important green chemical raw material and an environment-friendly oxidant used for many industrial processes [1–8]. At present, more than 98% of H_2O_2 is produced by the anthraquinone process, in which 2-ethyl-9,10-anthraquinone (eAQ) is first hydrogenated to 2-ethyl-9,10-anthrahydroquinone (eAQH₂) and subsequent oxidation of eAQH₂ produces eAQ and H₂O₂. The catalytic hydrogenation of eAQ is the key step, in which the desired products (eAQH₂ and H₄eAQH₂) are produced (Scheme 1). Meanwhile, various other side reactions occur in this process and several degradation products (e.g., 2-ethylanthrone (eAN), 2-ethyloxoanthrone (OXO), 2-ethyl tetrahydroanthrone (H₄eAN), and octahydroanthrahydroquinone (H₈eAQH₂)), which cannot be oxidized to produce H₂O₂ in the anthraquinone process [9], are produced.

Currently, the most widely used catalysts in the anthroquinone process are Pd-based pellet catalysts. These show better activities when compared with other metal-based or metal-free pellet catalysts in the hydrogenation of eAQ. Interestingly, it has been shown that mass transfer is a key controlling factor in the catalytic hydrogenation of eAQ [10-15]. In contrast to the traditional Pd-based pellet catalysts, monolithic catalysts can decrease the internal and external diffusion resistances, and thus improve the overall reaction rate. Furthermore, supported Pd monolithic catalysts have been investigated by several researchers for the catalytic hydrogenation of eAQ. For example, the Pd/Al₂O₃/COR (cordierite) monolithic catalyst and Pd/Al₂O₃ pellet catalyst were used for the catalytic hydrogenation of eAQ. It was found that the monolithic catalyst gave a higher space time yield (STY) of H₂O₂ compared to the pellet





^{*} Corresponding author. Tel: +86-10-64433695; E-mail: leizhg@mail.buct.edu.cn

This work was supported by the National Natural Science Foundation of China (21476009, 21406007, U1462104).

DOI: 10.1016/S1872-2067(18)63035-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 6, June 2018



Scheme 1. Anthraquinone hydrogenation/oxidation process for manufacturing H_2O_2 [10].

catalyst, which was mainly attributed to the shorter diffusion distance in the case of the former leading to an improved diffusion process [16]. The Pd/SiO₂/COR (PSC) and Pd/Al₂O₃/COR (PAC) monolithic catalysts were also subjected to the 1000 h long stability tests in the catalytic hydrogenation of eAQ. The results showed that the durability of PSC was superior to that of PAC, which was attributed to the regular structure and weak acidity of the former monolithic catalysts [17].

Furthermore, it was evident that Pd-based bimetallic supported pellet catalysts exhibit superior performance in various hydrogenation reactions. For example, Pd-Ni/SiO₂ showed excellent activity in the catalytic hydrogenation of 5-hydroxymethyl-2-furaldehyde (HMF) and gave a higher yield of 2,5-bis(hydroxymethyl)tetrahydrofuran as compared to the commercial Pd/C catalyst and Raney Ni under the same operating conditions [18]. Similarly, Pd-Fe/SiO₂ and Pd/SiO₂ catalysts were tested in the liquid-phase hydrogenation of phenylacetylene and it was found that the former bimetallic catalyst exhibited better catalytic activity and selectivity than the latter monometallic catalyst [19]. In the selective hydrogenation of mixed C4 compounds with a high content of vinyl acetylene, Pd-Mn/Al₂O₃ catalyst with the mass ratio of Pd:Mn = 1:2, showed increased activity, selectivity, and yield of 1,3-butadiene as compared to the Pd-Ni/Al₂O₃ and Pd-Ag/Al₂O₃ catalysts [20]. A series of Pd, Cu, and Pd-Cu bimetallic catalysts with different metal loadings and supports were investigated for the aqueous phase hydrogenation of furfural to furfuryl alcohol. It was found that 5% Pd-5% Cu/MgO(Mg(OH)₂) as a catalyst led to complete conversion of furfural with high selectivity (>98%) toward furfuryl alcohol after 80 min [21]. Catalytic hydrogenation of eAQ was performed with (Co, Ag, Cu)-doped Pd/Al₂O₃ pellet catalysts and it was found that the

Pd-Co bimetallic catalyst with the mass ratio of Pd/Co = 4 demonstrated the highest activity and selectivity [22]. However, Pd-based bimetallic supported monolithic catalysts have not been studied as yet for the catalytic hydrogenation of eAQ.

Therefore, in the present work, we attempted to improve the catalytic performance in the hydrogenation of eAQ by adding Ni, Fe, Mn, or Cu into the Pd/SiO₂/COR monolithic catalyst. A series of Pd, Ni, Fe, Mn, and Cu monometallic, and Pd-M (M = Ni, Fe, Mn, Cu) bimetallic catalysts were prepared via the co-impregnation method for the catalytic hydrogenation of eAQ. The monometallic and bimetallic monolithic catalysts were characterized by scanning electron microscopy (SEM) with energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), H₂-temperature programmed reduction (H₂-TPR), X-ray photoelectron spectroscopy (XPS), and H₂-O₂ titrations. Finally, DFT calculations were performed to gain a deep mechanistic understanding of the hydrogenation of eAQ over different monometallic and bimetallic monolithic catalysts.

2. Experimental

2.1. Materials

Cordierite was purchased from Nanning Yilaite Environmental Protection Technology Co. FeCl₃·6H₂O was procured from Tianjin Damao Reagent Factory. PdCl₂, NiCl₂·6H₂O, and Mn(CH₃COO)₂·4H₂O were sourced from Tianjin Guangfu Fine Chemical Research Institute. C₄H₆CuSO₄·H₂O was obtained from Shanghai Aladdin Chemistry Co. and SiO₂ sol was purchased from Sigma Aldrich (Shanghai) Trading Co., Ltd.

2.2. Catalyst preparation

The monolithic catalysts were prepared according to the following three procedures.

(i) Pretreatment of monolithic honeycomb cordierite: Cylindrical cordierites (ϕ 101.6 × 127 mm, and 400 channels per square inch (cpsi)) were cut into pieces of monolithic supports (ϕ 20 × 10 mm) and then treated with 15 wt% nitric acid at 80 °C for 4 h. Subsequently, the pretreated cordierite monolithic samples were washed using deionized water until they were neutral, dried at 100 °C for 4 h, and calcined in a muffle furnace at 550 °C for 4 h.

(ii) Preparation of SiO₂/cordierite. The pretreated monolithic supports were immersed into the SiO₂ sol solution for 5 min and the coated support was then dried at 100 °C. This procedure was repeated several times until the desired loading was obtained. The coated supports were subsequently calcined in a muffle furnace at 550 °C for 4 h.

(iii) Formation of Pd-M/SiO₂/COR precursors and PdO $(M_xO_y)/SiO_2/COR$ (M = Ni, Fe, Mn, and Cu). For the preparation of bimetallic monolithic catalysts, PdCl₂ powder was dissolved in HCl solution. The second metal precursors were then added to the PdCl₂ aqueous solution. This mixed solution was stirred using an agitator for 1 h. Subsequently, the coated supports were placed into the above solution and heated at 100 °C for 18

h. After impregnation, the supports were dried at 100 °C for 4 h, followed by calcination in a muffle furnace at 550 °C for 4 h. For the preparation of monometallic monolithic catalysts, PdCl₂ powder was first dissolved in the HCl solution. The coated supports were then placed into the above solution and heated at 100 °C for 18 h. After impregnation, the supports were dried at 100 °C for 4 h and later calcined in a muffle furnace at 550 °C for 4 h.

Herein, the SiO₂ loading amount was calculated based on the total catalyst mass consisting of COR and SiO₂. The metal (Pd or the second metal) loading, which was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES), was calculated based on the mass of SiO₂.

2.3. Catalyst characterization

The SEM micrographs and the EDS spectra of the monolithic catalysts were examined on a JEOL JSM-6701F microscope operating at an accelerating voltage of 5.0 kV. Before observation, the samples were sputter-coated with a thin gold film by an ion sputtering instrument to make the samples conductive.

The catalysts were also characterized by TEM (JEM-2000 EX, JEOL, Japan). The electron microscope was operated at an accelerating voltage of 120 kV. Before analysis, the catalyst samples were ground into powder and dispersed in ethanol by ultrasonication. Drops of these suspensions were applied onto a copper grid-supported transparent carbon foil and dried in air.

The reducibilities of the monolithic catalysts were measured by H₂-TPR experiments with a Thermo Electron TPD/R/O 1100 series instrument equipped with a thermal conductivity detector (TCD).

The XPS files were obtained with an ESCALAB 250 photoelectron spectrometer (ThermoFisher Scientific, USA) using monochromated Al K_{α} excitation at pass energies of 200 eV for survey and 30 eV for high-resolution scans. The binding energy calibration of all spectra was referenced to the adventitious carbon (C 1*s*) signal at 284.6 eV to reduce the charging effect of the samples.

The actual Pd contents of the monolithic catalysts were measured by ICP-AES with a Shimadzu Corporation ICP-7500 spectrometer. The degree of Pd dispersion and the Pd surface area of Pd/SiO₂/COR and Pd-M/SiO₂/COR (M = Ni, Fe, Mn, and Cu) monolithic catalysts were measured by H₂-O₂ titration on a Thermo Electron TPD/R/O 1100 series instrument equipped with a TCD. The catalyst (100 mg) was placed in a quartz tube reactor, pretreated with 50 mL/min of high-purity He at 450 °C for 0.5 h, and then cooled to 50 °C. Next, the catalyst was reduced with 50 mL/min of 5% H₂/Ar at 120 °C for 2 h, followed by treatment with 50 mL/min of high-purity He for 2 h. Subsequently, pulses of oxygen were introduced until the catalyst was fully saturated. The chemisorbed oxygen was titrated with hydrogen, and this titration was repeated twice to ensure the accuracy of the volume of H_2 . The Pd dispersion (D_{Pd}) and Pd metal surface area (SPd) were calculated using the following equations [23]:

$$D_{\rm Pd} (\%) = \frac{2 \times V_{\rm H} \times M \times 10^{-3}}{3 \times 22.4 \times W \times P} \times 100$$
(1)

$$S_{\rm Pd} \left({\rm m}^2 / {\rm g} \right) = \frac{2 \times V_{\rm H} \times N \times \sigma \times 10^{-3}}{3 \times 22.4 \times W \times P} \times 100$$
⁽²⁾

where $V_{\rm H}$ is the volume of H₂ used for the titration with O₂ (mL), *M* is the relative molecular mass of Pd (g/mol), *W* is the catalyst mass (g), *P* is the mass fraction of Pd, *N* (6.023 × 10²³) is Avogadro's constant, and σ is the cross-sectional area of a Pd atom (8.97 × 10⁻²⁰ m²).

2.4. Catalytic activity test

The catalytic hydrogenation of eAQ was performed in a stainless steel fixed-bed reactor (20 mm in inner diameter and 450 mm in height) with a central thermocouple to measure the temperature of the reaction zone at atmospheric pressure. Before the reaction, the monolithic catalysts were reduced under H₂ gas at a certain temperature for 3 h in the fixed-bed reactor. After reduction, the reactor was cooled to 80 °C and 45 mL of the working solution, consisting of a mixture of industrial grade C9 aromatics and trioctyl phosphate in the volume ratio of 3:1, along with 2.7 g eAQ (60 g/L) were pumped into the fixed-bed reactor at a flow rate of 0.7 mL/min. Meanwhile, H₂ gas was fed into the fixed-bed reactor by a mass flowmeter (MFC/MFM 007-7, Sevenstar, China) at a rate of 10 mL/min. The operating parameters were chosen according to the results of the catalytic activity test of the Pd/SiO₂/COR monolithic catalyst as described in our previous work [24].

After hydrogenation, the hydrogenated working solution was oxidized with air produced by an oil-free air generator (GC-ready SPB-5000 Automatic Air Source, China) at 25 °C and 101 kPa for 30 min. The H_2O_2 produced in the oxidized working solution was extracted with deionized water several times to obtain its aqueous solution. Finally, 10 mL of 25.2 wt% sulfuric acid solution was added to the H_2O_2 solution, and the amount of H_2O_2 was determined by titration with the standard potassium permanganate solution.

The catalyst selectivity (*S*), H_2O_2 yield (*B*), and turnover frequency (TOF) were calculated as follows.

$$S(\%) = \frac{n_{eAQ} + n_{H_4 eAQ}}{n_0 (eAQ)} \times 100$$
 (3)

$$B = \frac{5C_{\text{KMen}_4} \times V_{\text{KMen}_4} \times M_{\text{H}_2\text{O}_2}}{2V}$$
(4)

$$TOF = \frac{n_0 C}{n_{cat} t}$$
(5)

$$n_{\rm cat} = \frac{WP}{M_{\rm Pd}} D_{\rm Pd}$$
(6)

where *S* is the selectivity toward active quinones (eAQ and H₄eAQ), n_0 and *n* are the molar concentrations of the components in the initial working solution and oxidized solution (mol/L), respectively, $C_{\rm KMn04}$ is the concentration of the KMn0₄ solution (mol/L), and $V_{\rm KMn04}$ and *V* represent the volumes of the KMnO₄ solution and H₂O₂ solution (mL), respectively. In Equation (5), *C* refers to the conversion of eAQ at reaction time *t* and $n_{\rm cat}$ is the mole number of the exposed Pd atoms, given by Equation (6), where $M_{\rm Pd}$ is the molar mass of Pd, *W* is the catalyst mass (g), *P* is the mass fraction of Pd, and $D_{\rm Pd}$ is the degree

of Pd dispersion.

2.5. Computational method

The first-principles calculations based on density functional theory (DFT) with a plane wave basis set were carried out to investigate the mechanism of the hydrogenation of eAQ over different monometallic and bimetallic monolithic catalysts [25,26]. In this work, all DFT calculations were carried out with the Vienna ab initio simulation package (VASP) to obtain the optimized Pd/Pd-M surfaces and the corresponding adsorption energies of eAQ. The exchange-correlation functional was described by the GGA-PBE functional [27] and all-electron plane-wave basis set was used with an energy cutoff of 400 eV. In addition, a projector augmented wave (PAW) method was adopted to improve the computational efficiency [28]. A Brillouin-zone of p(3 × 2) lateral supercell was sampled by 1×1×1 k-points with the Monkhorst Pack scheme. Forces blow 0.05 $eV\cdot Å^{-1}$ and the energy differences less than 4 × 10⁻⁶ eV were used as the criterion for convergence.

Pd and the second metal (Ni, Fe, Mn, or Cu) were reduced to their metallic state (zero valence) at 700 °C. In the calculation, Pd₃M₁ and pure Pd were used to model the Pd-M alloys and Pd metal. The lattice constants of the optimized structures were a = b = c = 3.94 Å for Pd, a = b = c = 3.87 Å for Pd₃Ni₁, a = b = c = c3.85 Å for Pd₃Fe₁, a = b = c = 3.86 Å for Pd₃Mn₁, and a = b = c = c3.88 Å for Pd₃Cu₁, which are close to the values reported in the literature [29–32]. The Pd(1 1 1) and Pd₃M₁(1 1 1) (M = Ni, Fe, Mn, Cu) surfaces were modeled by a supercell (3×2) consisting of a three-layer Pd slab. For structural optimizations, the atoms in the bottom two layers were fixed and the atoms in the uppermost layer along with the adsorbed eAQ molecule were relaxed. The two successive slabs were separated by a 10 Å vacuum region to ensure that the adsorbate (eAQ) and the subsequent slab would not interact. The adsorption energy of eAQ was defined as follows:

$$E_{ads} = -\left(E_{Pd(111)/Pd_{3}M_{1}(111)-eAQ} - E_{Pd(111)/Pd_{3}M_{1}(111)} - E_{eAQ}\right)$$
(7)

where $E_{Pd(111)/Pd_3M_1(111)-eAQ}$, $E_{Pd(111)/Pd_3M_1(111)}$, and E_{eAQ} are the total energy for eAQ adsorbed on either the Pd(1 1 1) or Pd₃M₁(1 1 1) surface, the energy of either free Pd(1 1 1) or Pd₃M₁(1 1 1), and the energy of free eAQ, respectively.

3. Results and discussion

3.1. SEM, TEM, HRTEM, and EDS results

SEM was used to observe the microscopic changes of the surface of the monolithic catalyst. TEM, HRTEM, and EDS were used to investigate the alloying effect of the second metal (Ni, Fe, Mn, Cu) on Pd. The results are shown in Figs. 1 and 2. The SEM images show that the walls of the Pd-Ni/SiO₂/COR monolithic catalyst were covered with a thin layer of active washcoat [33,34]. The black spherical particles observed in the TEM images were identified as the Pd and Pd-M species, indicating that the PdO and Pd-M oxide species disappeared to some extent after H₂ reduction.

The HRTEM images of the Pd-M/SiO₂/COR monolithic catalyst show that the metal particles were dispersed uniformly without aggregation after H₂ reduction. In Fig. 2(a), the lattice fringes of Pd with a distance of 0.227 nm corresponded to the Pd(1 1 1) plane. Meanwhile, the lattice fringes in Fig. 2(b)-(e) with distances of 0.224, 0.214, 0.216, and 0.225 nm, indicated the formation of PdNi, PdFe, PdMn, and PdCu nanoalloys, respectively. The particle size distribution measurements show that the mean particle sizes of Pd/SiO₂/COR, Pd-Ni/SiO₂/COR, Pd-Fe/SiO₂/COR, Pd-Mn/SiO₂/COR, and Pd-Cu/SiO₂/COR were 7.5, 4.0, 4.6, 5.1, and 6.0 nm, respectively, as calculated from 50 metal particles selected from different regions [35,36]. It was evident that the mean particle sizes of Pd-M/SiO₂/COR (M = Ni, Fe, Mn, and Cu) were smaller than that of Pd/SiO₂/COR. The addition of the second metal reduced the aggregation of Pd particles, which led to the better dispersion and smaller particle sizes of Pd. The interaction of Pd and the second metal M in the Pd-M alloys also inhibited metal sintering because of the



Fig. 1. SEM images of Pd-Ni/SiO₂/COR catalyst (a) and (b); TEM images of Pd/SiO₂/COR (c), Pd-Ni/SiO₂/COR (d), Pd-Fe/SiO₂/COR (e), Pd-Mn/SiO₂/COR (f), and Pd-Cu/SiO₂/COR (g).



Fig. 2. HRTEM images of Pd/SiO₂/COR (a), Pd-Ni/SiO₂/COR (b), Pd-Fe/SiO₂/COR (c), Pd-Mn/SiO₂/COR (d), and Pd-Cu/SiO₂/COR (e); and Pd particle size distributions of Pd/SiO₂/COR (f), Pd-Ni/SiO₂/COR (g), Pd-Fe/SiO₂/COR (h), Pd-Mn/SiO₂/COR (i), and Pd-Cu/SiO₂/COR (j).



Fig. 3. H₂-TPR spectra of different monolithic catalysts. (a) Pd-Ni/SiO₂/COR. (1) 0.4% Ni/SiO₂/COR; (2) 0.8%Pd-2% Ni/SiO₂/COR; (3) 0.8% Pd-0.4% Ni/SiO₂/COR; (4) 0.8% Pd/SiO₂/COR; (b) Pd-Fe/SiO₂/COR. (1) 0.4% Fe/SiO₂/COR; (2) 0.8% Pd-2% Fe/SiO₂/COR; (3) 0.8% Pd-0.4% Fe/SiO₂/COR; (4) 0.8% Pd/SiO₂/COR. (c) Pd-Mn/SiO₂/COR. (1) 0.4% Mn/SiO₂/COR; (2) 0.8% Pd-2% Mn/SiO₂/COR; (3) 0.8% Pd-0.4% Mn/SiO₂/COR; (4) 0.8% Pd/SiO₂/COR. (d) Pd-Cu/SiO₂/COR. (1) 0.8% Pd-2% Cu/SiO₂/COR; (2) 0.8% Pd-0.4% Cu/SiO₂/COR; (3) 0.8% Pd/SiO₂/COR. (d) Pd-Cu/SiO₂/COR. (h) Pd-2% Cu/SiO₂/COR; (2) 0.8% Pd-0.4% Cu/SiO₂/COR; (3) 0.8% Pd/SiO₂/COR. (h) Pd-Cu/SiO₂/COR; (h) Pd-2% Cu/SiO₂/COR; (h) Pd-Cu/SiO₂/COR; (h) Pd-2% Cu/SiO₂/COR; (h) Pd-Cu/SiO₂/COR. (h) Pd-Cu/SiO₂/COR; (h) Pd-2% Cu/SiO₂/COR; (h) Pd-Cu/SiO₂/COR. (h) Pd-Cu/SiO₂/COR; (h) P

stabilizing effect of the two metals [30].

The EDS results of the monolithic catalysts confirmed the presence of different metals (Pd, Ni, Fe, Mn, and Cu). Neither Pd nor the second metals existed in regions far away from the investigated metal particles, indicating that the second metal is located nearby the Pd particles, forming Pd-M alloys [30] (see

Fig. S1 in Supporting Information).

3.2. H₂-TPR results

 H_2 -TPR measurements were used to analyze the reducibilities of the different monometallic and bimetallic monolithic catalysts, and the results are shown in Fig. 3. In the case of Pd/SiO₂/COR, no reduction peak was found because the PdO species on the surface of the monolithic catalyst was reduced readily and even at a low temperature with relative ease [37,38]. For the Ni/SiO₂/COR monolithic catalyst, there was one reduction peak at 412 °C, which was assigned to the NiO species on the catalyst surface. In contrast, there were three reduction peaks at 566–633, 457, and 416 °C for Fe/SiO₂/COR. The first peak was assigned to the reduction of FeO to Fe, the second corresponded to the reduction of Fe₂O₃ to Fe₂O₄. In the case of the Mn/SiO₂/COR monolithic catalyst, there were four reduction peaks at 554, 423, 356, and 300 °C, which were assigned to the reduction of MnO to Mn, Mn₃O₄ to MnO, Mn₂O₃ to Mn₃O₄, and MnO₂ to Mn₂O₃, respectively.

For 0.8% Pd-2% M/SiO₂/COR (M = Ni, Fe, Mn, Cu) bimetallic monolithic catalysts, the number of reduction peaks were the same as that of the M/SiO₂/COR monometallic monolithic catalysts, although the reduction temperatures were lower [39]. However, one peak in the H2-TPR plots of the Pd-M/SiO2/COR bimetallic monolithic catalysts decreased remarkably, indicating the formation of Pd-M alloys [40]. Compared to the reduction peaks of the 0.8% Pd-2% M/SiO₂/COR monolithic catalyst, those of the 0.8% Pd-0.4% M/SiO2/COR catalysts were shifted to lower temperatures because of the lower content of the second metal in the latter catalysts. It is worth noting that the reduction temperatures decreased with the addition of the second metal and the increasing Pd/M mass ratio, implying that Pd seemingly promoted the reduction of the second metal oxides in a hydrogenation spillover from Pd to the second metal M [41].

It is noted that a negative peak was observed at 100 °C for several monolithic catalysts, which corresponded to the decomposition of the PdH species that was formed during the initial hydrogenation stage of Pd [42,43]. It has been reported that the formation of alloys upon the addition of the second metal (Bi, Cu, Ag) in bimetallic catalysts suppresses the formation of PdH [41,44–46]. For all the bimetallic monolithic catalysts investigated in this work, the PdH peaks either decreased in intensity or even completely disappeared when the second metal (M = Ni, Fe, Mn, Cu) was added, which further confirmed the formation of alloy catalysts

3.3. XPS results

To investigate the surface properties and chemical states of Pd in Pd-M bimetallic monolithic catalysts, XPS analysis was performed. The binding energies of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ in pure Pd (Fig. 4) were 335.5 and 340.7 eV, respectively, which is consistent with previous reports [47,48]. In the case of Pd-M alloys, i.e., after doping Pd with the second metal, new peaks appeared for the binding energies of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ at 336.3±0.1 and 341.4 ±0.1 eV, respectively. The increase in the binding energy for Pd did not exceed 1.0 eV as compared to pure Pd, which is consistent with the previous work [22]. The shift in the binding energies originates from the decrease in the density of states at the Fermi level because of the *d*-band hy-



Fig. 4. XPS spectrum of different monolithic catalysts. (1) 0.8% Pd/SiO₂/COR; (2) 0.8% Pd-0.4% Ni/SiO₂/COR; (3) 0.8% Pd-0.4% Fe/SiO₂/COR; (4) 0.8% Pd-0.4% Mn/SiO₂/COR; (5) 0.8% Pd-0.4% Cu/SiO₂/COR.

bridization between Pd and the second metal upon alloying [49,50]. It can be seen that the overall intensity of the Pd peaks decreased upon addition of the second metal, which suggested a lower degree of exposure of the Pd atoms in the Pd-M bime-tallic monolithic catalysts.

3.4. H₂-O₂ titration

 H_2-O_2 titrations were performed to determine the degrees of Pd dispersion and specific surface areas of the monometallic and bimetallic monolithic catalysts, which were affected remarkably by the addition of the second metal [23]. The detailed data are listed in Table 1. It can be seen that the Pd dispersion and specific surface area in the Pd-Ni/SiO₂/COR were higher than those of other bimetallic monolithic catalysts, even though the Pd loadings were identical. These results confirmed that there were strong interactions between Pd and Ni, as the addition of the second metal, i.e., nickel, improved the Pd dispersion and prevented the migration and aggregation of Pd particles. Thus, the results of H₂-O₂ titrations were consistent with the HRTEM, H₂-TPR, and XPS characterizations.

3.5. Catalytic hydrogenation of eAQ

The hydrogenation of eAQ over monometallic and bimetallic monolithic catalysts was performed in a stainless steel fixed-bed reactor. In this experiment, Pd loading was fixed at 0.8 wt%. The effect of loading of the second metal on the selectivity and H₂O₂ yield in the hydrogenation of eAQ was investigated, as shown in Fig. 5 and Table 1. It can be seen that the H₂O₂ yield achieved by using Ni/SiO₂/COR was lower than that obtained with Pd/SiO₂/COR. Furthermore, the Pd-Ni/SiO₂/COR bimetallic monolithic catalyst demonstrated higher selectivity and gave better H₂O₂ yields than the Pd/SiO₂/COR and Ni/SiO₂/COR monometallic monolithic and other bimetallic

Table 1

Catalytic performance and textural	parameters of different monolithic catalysts for	or the hydrogenation of eAQ to $eAQH_2$.
------------------------------------	--------------------------------------------------	---------------------------------------------

Sample	Weekset	Washcoat	Pd loading	Second metal	Selectivity	Yield of H ₂ O ₂	Pd efficiency	$D_{\rm Pd}{}^{\rm a}$	$S_{ m Pd}$	TOF
	washcoat	loading (wt%)	(wt%)	loading (wt%)	(%)	(g/L)	(g/(g·h))	(%)	(m²/g)	(s ⁻¹)
Pd/SiO ₂ /COR	SiO ₂	30	0.8	_	42.2	3.82	793	16	81	0.69
Ni/SiO ₂ /COR	SiO ₂	30	0.8	_	35.0	2.84	_	_	_	0.49
Pd-Ni/SiO ₂ /COR	SiO ₂	30	0.8	0.4	95.3	7.5	1349	45	228	1.21
Pd-Fe/SiO ₂ /COR	SiO ₂	30	0.8	0.4	80.6	5.5	1141	36	183	0.99
Pd-Mn/SiO ₂ /COR	SiO ₂	30	0.8	0.4	63.7	4.35	902	32	162	0.78
Pd-Cu/SiO ₂ /COR	SiO ₂	30	0.8	0.4	40.4	3.1	643	26	132	0.56

 $^{a}D_{Pd}$ was determined by H₂-O₂ titration analysis.



Fig. 5. Effect of the second metal loading on selectivity (a) and H_2O_2 yield (b). Reaction conditions: pressure = 101 kPa, temperature = 80 °C, concentration of eAQ solution = 60 g/L, flow rate of eAQ solution = 0.7 mL/min, and flow rate of H_2 gas = 10 mL/min. (A) Pd/SiO₂/COR; (B) 0.8% Pd-0.2% M/SiO₂/COR; (C) 0.8% Pd-0.4% M/SiO₂/COR; (D) 0.8% Pd-0.8% M/SiO₂/COR; (E) 0.8% Pd-1% M/SiO₂/COR; (F) 0.8% Pd-2% M/SiO₂/COR.

monolithic catalysts. One reason for these results is that the formation of Pd-Ni alloys led to the better catalytic performance, as proven by XPS, TEM, and TPR results. The other reason is the strong interaction between the carbonyl bond of eAQ and the Pd-Ni alloys, as confirmed by DFT calculations.

Since H₂O₂ yield is strongly influenced by the metal loading, a series of catalysts with different Pd/M (M = Ni, Fe, Mn, Cu) ratios and at a fixed Pd loading of 0.8 wt% were prepared and their catalytic activities in the hydrogenation of eAQ were investigated (Fig. 5). It was found that the bimetallic Pd-Ni/SiO₂/COR, Pd-Fe/SiO₂/COR, Pd-Mn/SiO₂/COR, and Pd-Cu/SiO₂/COR monolithic catalysts reduced at 700 °C achieved the highest selectivity and H₂O₂ yield at the mass ratio of Pd/M = 2. The selectivity and H₂O₂ yield increased with the increasing loading amounts of the second metal (i.e., Ni, Fe, Mn, and Cu) below a final amount of 0.4 wt%. However, the trend was reversed at loading amounts above 0.4 wt%.

In addition, the TOFs of 0.8% Pd-0.4% M/SiO₂/COR (M = Ni, Fe, Mn) bimetallic monolithic catalysts were higher than that of the 0.8% Pd/SiO₂/COR monometallic monolithic catalyst (Table 1), which was attributed to the improved Pd dispersion after the addition of the second metal. However, while the Pd dispersion and specific surface area in the case of the 0.8% Pd-0.4% Cu/SiO₂/COR catalyst were higher than those of the 0.8% Pd/SiO₂/COR monometallic monolithic catalyst, the TOF of the former was lower than that of the latter monometallic monolithic catalyst. The lower TOF of the bimetallic catalyst was attributed to the inhibition adsorption of eAQ on the Pd-Cu nanoalloy surface [22].

3.6. DFT calculations on $Pd(1 \ 1 \ 1)$ and $Pd_3M_1(1 \ 1 \ 1)$ (M = Ni, Fe, Mn, and Cu) surfaces

It is generally believed that the hydrogenation of eAQ on monometallic Pd and bimetallic Pd-M pellet catalysts follows the Langmuir-Hinshelwood (L-H) mechanism, in which H₂ is preferentially adsorbed on the top of a Pd atom and then dissociated with a low overall activation barrier (3.9 kcal/mol) [22,51]. This implies that the adsorption of eAQ on the surfaces of Pd or Pd-M (M = Ni, Fe, Mn, and Cu) monolithic catalysts was crucial for the hydrogenation of eAQ.

In this work, DFT calculations were conducted to compare the adsorption energetics for eAQ on both Pd and Pd-M (M = Ni, Fe, Mn, and Cu) surfaces to explain the differences in the catalytic activity of monometallic Pd and bimetallic Pd-M monolithic catalysts. Thus, the four crystal structures of Pd₃-Ni₁, Pd₃-Fe₁, Pd₃-Mn₁, and Pd₃-Cu₁, along with that of pure Pd, were used to model the Pd-M alloy (Fig. 6).

The calculations for the adsorption of eAQ on the Pd(1 1 1) and $Pd_3M_1(1 \ 1 \ 1)$ surfaces were somewhat complicated because of the numerous possible configurations. In terms of previous work [51], the most relevant structures of eAQ on these surfaces were chosen for calculations. The possible structures are shown in Fig. S2 (see Supporting Information), and the



Fig. 6. Bulk monometallic Pd and bimetallic Pd-M (M = Ni, Fe, Mn, and Cu) alloy structures.

most stable structures are shown in Fig. 7. The adsorption energies (E_{ads}) and bond lengths are listed in Table 2 (for more details, see Table S1 in the Supporting Information).

The adsorption of eAQ on the optimized Pd(1 1 1) surface was such that the two benzene rings and carbonyl oxygen atoms of eAQ were located at the bridge sites, while the carbonyl bond was elongated (0.048 Å), which was likely due to the interaction of the carbonyl π bond with the Pd(1 1 1) surface (i.e.,

electron back-donation), as reported in literature [38,51]. The adsorption energy of eAQ on Pd(1 1 1) was calculated as 61.4 kcal/mol. The aromatic ring of eAQ played an important role in promoting a flat adsorption on the Pd(1 1 1) surface. This was similar to the adsorption of furan on Pd(1 1 1) described by Bradley et al. [52] on the basis of DFT calculations. This result showed that the preferred adsorption structure was one with the aromatic ring essentially parallel to the metal surface.

The addition of the second metal (i.e., Ni, Fe, Mn, and Cu) weakened the adsorption of the benzene rings, which was explained by the strong affinity of the aromatic rings toward Pd and not for the second metals [40]. As a result, the adsorption energies of eAQ on Pd₃Ni₁(1 1 1), Pd₃Fe₁(1 1 1), Pd₃Mn₁(1 1 1), and Pd₃Cu₁(1 1 1) decreased to 59.8, 50.7, 44.5, and 35.5 kcal/mol, respectively. However, the adsorption energies of eAQ on Pd_3M_1 (M = Ni, Fe, and Mn) did not change as much as that on Pd(111), because of the strong bonding of the carbonyl group with the second metal atoms, as shown in Fig. 7. At the same time, the strong binding of the carbonyl group on the Pd-M (M = Ni, Fe and Mn) alloy surface facilitated the hydrogenation of eAQ to eAQH₂ [30]. This was in good agreement with the experimental results of enhanced catalytic activity of the Pd-M (M = Ni, Fe, and Mn) alloys. However, the adsorption energy of eAQ on Pd₃Cu₁(1 1 1) changed a little more as opposed to that on Pd(1 1 1), which was attributed to the inhibition of adsorption of eAQ on $Pd_3Cu_1(1\ 1\ 1)$ [22]. This proved to be unfavorable for the hydrogenation of C=O groups and led to lower catalytic activity.

The benzene rings greatly enhanced this interaction on pure Pd. However, when the second metals were added, the stability of eAQ on $Pd_3M_1(1\ 1\ 1)$ decreased dramatically. Compared to



Fig. 7. DFT optimized structures of eAQ (a) and eAQ adsorbed on Pd(1 1 1) (b), $Pd_3Ni_1(1 1 1)$ (c), $Pd_3Fe_1(1 1 1)$ (d), $Pd_3Mn_1(1 1 1)$ (e), and $Pd_3Cu_1(1 1 1)$ (f).

Table 2

Adsorption energies and optimized bond lengths of eAQ on Pd(1 1 1) and on $Pd_3M_1(1 1 1)$ (M = Ni, Fe, Mn, and Cu) slabs.						
Model	Eads (kcal/mol)	C-0 (Å)	Pd–C a (Å)	Pd-0 ^b (Å)	M–C ° (Å)	М-О ^d (Å)
eAQ	_	1.237	—	_	_	_
eAQ/Pd(111)	61.4	1.285/1.286	2.276/2.268	2.382/2.372	_	_
eAQ/Pd3Ni1(111)	59.8	1.313/1.286	2.235/2.270	2.579	_	2.035
eAQ/Pd3Fe1(111)	53.3	1.291/1.331	2.271/2.243	2.459	_	2.007
eAQ/Pd3Mn1(111)	44.5	1.275/1.341	2.362/2.267	2.536	_	1.948
eAQ/Pd3Cu1(111)	35.5	1.284/1.288	2.325	2.516/2.492	2.379	_

^aPd-C: the distance between C and the nearest Pd atom, as shown in Fig. 7.

^bPd-O: the distance between O and the nearest Pd atom, as shown in Fig. 7.

^cM–C: the distance between C and the nearest second metal atom, as shown in Fig. 7.

^dM-0: the distance between 0 and the nearest second metal atom, as shown in Fig. 7.

eAQ on Pd (1 1 1), the bonds (C=O, Pd-C/M-C, and Pd-O) (M = Ni, Fe, and Mn) were elongated, which indicated a strongly binding carbonyl group and weakly binding benzene rings (Table 2 and Table S1). At the same time, the M-O (M = Ni, Fe, and Mn) bond lengths were shortened as compared to Pd-O. Therefore, the stronger adsorption between the Pd-M (M = Ni, Fe, and Mn) alloy surface and the carbonyl group led to higher catalytic activity in comparison with the monometallic Pd monolithic catalysts.

4 Conclusions

In this work, a series of Pd-M/SiO₂/COR (M = Ni, Fe, Mn, and Cu) bimetallic and Pd/SiO₂/COR monolithic catalysts were prepared, characterized, and evaluated for the hydrogenation of eAQ. The bimetallic 0.8% Pd-0.4% Ni/SiO₂/COR monolithic catalyst gave the highest H₂O₂ yield (7.5 g/L) and selectivity (95.3%) among all the monolithic catalysts investigated. The higher activity of this catalyst was attributed to the formation of PdNi alloys. The results of the different catalyst characterization methods (e.g., SEM, EDS, TEM, H2-TPR, XPS, and H2-O2 titration) were consistent with the activity test. To the best of our knowledge, this is the first work to study the catalytic performance on Pd-M/SiO₂/COR (M = Ni, Fe, Mn, and Cu) bimetallic monolithic catalysts for the hydrogenation of eAQ.

DFT calculations revealed that the strong adsorption between the Pd-M (M = Ni, Fe, and Mn) alloy surface and the carbonyl group of eAQ was responsible for the higher catalytic activity. For example, Pd-Cu inhibited the adsorption of eAQ on the PdCu surface and this proved to be unfavorable for the hydrogenation of the C=O moiety. For the different Pd-M (M = Ni, Fe, and Mn) alloys, a stronger adsorption between the Pd-M alloy surface and the carbonyl group implied higher adsorption energy for the eAQ chemisorption on Pd-M, which explained the higher catalytic activity. Furthermore, theoretical insights were also gained into the reaction performance of the monometallic Pd and Pd-M bimetallic monolithic catalysts for the hydrogenation of eAQ.

Supporting Information

Supporting Information associated with this article can be found in the online version.

References

- [1] C. Samanta, Appl. Catal. A, 2008, 350, 133–149.
- E. Santacesaria, M. D. Serio, R. Velotti, U. Leone, Ind. Eng. Chem. Res., 1994, 33, 277-284.
- H. Shang, H. J. Zhou, Z. H. Zhu, W. H. Zhang, J. Ind. Eng. Chem., 2012, [3] 18, 1851-1857.
- [4] J. M. Campos-Martin, G. Blanco-Brieva, J. L. G. Fierro, Angew. Chem. Int. Ed., 2006, 45, 6962-6984.
- [5] V. Paunovic, V. Ordomsky, M. F. N. D'Angelo, J. C. Schouten, T. A. Nijhuis, J. Catal., 2014, 309, 325-332.
- [6] L. K. Ouyang, G. J. Da, P. F. Tian, T. Y. Chen, G. D. Liang, J. Xu, Y. F. Han, J. Catal., 2014, 311, 129-136.



- [7] R. Ciriminna, L. Albanese, F. Meneguzzo, M. Pagliaro, *ChemSusChem*, 2016, 9, 3374–3374.
- [8] R. B. Rankin, J. Greeley, ACS Catal., 2012, 2, 2664–2672.
- H. M. Chen, D. P. Huang, X. Y. Su, J. L. Huang, X. L. Jing, M. M. Du, D.
 H. Sun, L. S. Jia, Q. B. Li, *Chem. Eng. J.*, **2015**, 262, 356–363.
- [10] Y. Y. Guo, C. N. Dai, Z. G. Lei, *Chem. Eng. Sci.*, **2017**, 172, 370–384.
- [11] A. Drelinkiewicz, A. Waksmundzka-Góra, J. Mol. Catal. A, 2006, 258, 1–9.
- [12] R. Kosydar, A. Linkiewicz, E. Lalik, J. Gurgul, Appl. Catal. A, 2011, 402, 121–131.
- [13] C. Shen, Y. J. Wang, J. H. Xu, Y. C. Lu, G. S. Luo, *Chem. Eng. J.*, 2011, 173, 226–232.
- [14] Y. C. Zhu, L. Y. Yu, X. F. Wang, Y. H. Zhou, H. Q. Ye, *Catal. Commun.*, 2013, 40, 98–102.
- [15] A. Drelinkiewicz, M. Hasik, J. Mol. Catal. A, 2001, 177, 149–164.
- [16] J. G. Zhang, D. F. Li, Y. J. Zhao, Q. D. Kong, S. D. Wang, *Catal. Commun.*, **2008**, 9, 2565–2569.
- [17] X. T. Li, H. J. Su, G. Y. Ren, S. D. Wang, *RSC Adv.*, **2015**, 5, 100968–100977.
- [18] Y. Nakagawa, K. Tomishige, Catal. Commun., 2010, 12, 154–156.
- [19] A. A. Shesterkina, O. A. Kirichenko, L. M. Kozlova, G. I. Kapustin, I. V. Mishin, A. A. Strelkova, L. M. Kustov, *Mendeleev Commun.*, 2016, 26, 228–230.
- [20] P. Insorn, B. Kitiyanan, Catal. Today, 2015, 256, 223–230.
- [21] K. Fulajtárova, T. Soták, M. Hronec, I. Vohra, E. Dobrocka, M. Omastová, *Appl. Catal. A*, **2015**, 502, 78–85.
- [22] E. X. Yuan, C. Wu, X. Hou, M. B. Dou, G. Z. Liu, G. Z. Li, L. Wang, J. Catal., 2017, 347, 79–88.
- [23] J. T. Feng, H. Y. Wang, D. G. Evans, X. Duan, D. Q. Li, *Appl. Catal. A*, 2010, 382, 240–245.
- [24] Y. Y. Guo, C. N. Dai, Z. G. Lei, B. H. Chen, X. C. Fang, *Catal. Today*, 2016, 276, 36–45.
- [25] R. Car, M. Parrinello, Phys. Rev. Lett., 1985, 55, 2471–2474.
- [26] M. C. Payne, J. D. Joannopoulos, D. C. Allan, M. P. Teter, D. H. Vanderbilt, *Phys. Rev. Lett.*, **1986**, 56, 2656.
- [27] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865–3868.
- [28] G. Kresse, D. Joubert, Phys. Rev. B, 1999, 59, 1758-1775.
- [29] F. Cinquini, F. Delbecq, P. Sautet, Phys. Chem. Chem. Phys., 2009, 11, 11546–11556.
- [30] N. Pino, S. Sitthisa, Q. H. Tan, T. Souza, D. López, D. E. Resasco, J. Catal., 2017, 350, 30–40.
- [31] E. Povoden-Karadeniz, P. Lang, F. Moszner, S. Pogatscher, A. V.

Ruban, P. J. Uggowitzer, E. Kozeschnik, *Calphad*, **2015**, 51, 314–333.

- [32] S. Sitthisa, T. Pham, T. Prasomsri, T. Sooknoi, R. G. Mallinson, D. E. Resasco, J. Catal., 2011, 280, 17–27.
- [33] O. Sanz, F. J. Echave, M. Sánchez, A. Monzon, M. Montes, *Appl. Catal. A*, **2008**, 340, 125–132.
- [34] B. Yuan, B. Zhang, Z. L. Wang, S. M. Liu, J. Li, Y. Liu, C. Li, Chin. J. Catal., 2017, 38, 440–446.
- [35] M. Q. Chai, X. Y. Liu, L. Li, G. X. Pei, Y. J. Ren, Y. Su, H. K. Cheng, A. Q. Wang, T. Zhang, *Chin. J. Catal.*, **2017**, 38, 1338–1346.
- [36] B. Y. Bai, Q. Qiao, J. H. Li, J. M. Hao, Chin. J. Catal., 2016, 37, 102–122.
- [37] G. Agostini, C. Lamberti, R. Pellegrini, G. Leofanti, F. Giannici, A. Longo, E. Groppo, ACS Catal., 2014, 4, 187–194.
- [38] E. Groppo, G. Agostini, A. Piovano, N. B. Muddada, G. Leofanti, R. Pellegrini, G. Portale, A. Longo, C. Lamberti, J. Catal., 2012, 287, 44–54.
- [39] G. X. Pei, X. Y. Liu, M. Q. Chai, A. Q. Wang, T. Zhang, Chin. J. Catal., 2017, 38, 1540–1548.
- [40] S. Sitthisa, T. Pham, T. Prasomsri, T. Sooknoi, R. G. Mallinson, D. E. Resasco, J. Catal., 2011, 280, 17–27.
- [41] R. R. Hong, Y. F. He, J. T. Feng, D. Q. Li. AlChE J., 2017, 63, 3955–3965.
- [42] Y. N. Liu, Y. F. He, D. R. Zhou, J. T. Feng, D. Q. Li, *Catal. Sci. Technol.*, 2016, 6, 3027–3037.
- [43] J. Sá, G. D. Arteaga, R. A. Daley, J. Bernardi, J.A. Anderson, J. Phys. Chem. B, 2006, 110, 17090–17095.
- [44] S. Karski, I. Witońska, J. Rogowski, J. Gołuchowska. J. Mol. Catal. A, 2005, 240, 155–163.
- [45] S. Karski, I. Witońska. J. Mol. Catal. A, **2003**, 191, 87–92.
- [46] Q. Zhang, J. Li, X. X. Liu, Q. M. Zhu. Appl. Catal. A, 2000, 197, 221–228.
- [47] A. S. Ivanova, E. M. Slavinskaya, R. V. Gulyaev, V. I. Zaikovskii, O. A. Stonkus, I. G. Danilova, L. M. Plyasova, I. A. Polukhina, A. I. Boronin, *Appl. Catal. B*, **2010**, 97, 57–71.
- [48] V. Johánek, I. Stará, V. Matolín, Surf. Sci., 2002, 507-510, 92-98.
- [49] S. Maheswari, S. Karthikeyan, P. Murugan, P. Sridhar, S. Pitchumani, *Phys. Chem. Chem. Phys.*, **2012**, 14, 9683–9695.
- [50] N. Lopez, J. K. Nørskov, *Surf. Sci.*, **2001**, 477, 59–75.
- [51] T. Kamachi, T. Ogata, E. Mori, K. Iura, N. Okuda, M. Nagata, K. Yoshizawa, J. Phys. Chem. C, 2015, 119, 8748–8754.
- [52] M. K. Bradley, J. bin Roson, D. P. Woodruff, Surf. Sci., 2010, 604, 920–925.

2-乙基蒽醌在双金属整体式催化剂上的氢化反应: 实验和 DFT 研究

郭燕燕,代成娜,雷志刚*

北京化工大学化工资源有效利用国家重点实验室,北京100029

摘要: 过氧化氢(H₂O₂)是一种绿色化工原料和环境友好氧化剂.目前,超过 98%的H₂O₂是通过蒽醌法生产. 蒽醌法主要包括 2-乙基蒽醌氢化生成 2-乙基氢蒽醌和 2-乙基氢蒽醌氧化生成 2-乙基蒽醌和H₂O₂的过程.其中, 2-乙基蒽醌氢化是关键步骤.在氢化过程中,生成的 2-乙基氢蒽醌和四氢-2-乙基氢蒽醌是目标产物,同时生成许多副产物.目前,Pd 颗粒催化剂 是广泛使用的催化剂,但是蒽醌氢化过程中,质量传递是主要的控制因素.与颗粒催化剂对比,整体式催化剂可以减弱整 个反应的内外扩散,提高反应速率.很多研究结果显示,整体式催化剂的传质优于颗粒催化剂,可以提高催化效率.近期许 多研究显示,双金属颗粒催化剂在很多氢化反应中体现出优异的催化性能.本工作制备了双金属整体式催化剂,考察了其 在蒽醌氢化过程中的催化性能.

首先, 通过浸渍法制备了4 种双金属整体式催化剂 Pd-M/SiO₂/COR (M = Ni, Fe, Mn 和 Cu)以及 Pd/SiO₂/COR 和 Ni/SiO₂/COR 两种单金属整体式催化剂. 催化活性结果显示, Ni/SiO₂/COR的H₂O₂产量低于 Pd/SiO₂/COR, 而且在 700 ℃还

原的 Pd-Ni/SiO₂/COR 整体式催化剂在 Pd/M = 2 时取得了最高选择性 (95.3%) 和H₂O₂产量 (7.5 g/L). 然后,考察了金属负载量的影响. 结果显示,在金属负载量低于 0.4% 时,随着金属负载量增加,选择性和H₂O₂产量增加,在金属负载量高于 0.4% 时,随着金属负载量增加,选择性和H₂O₂产量降低.

TEM结果表明, 添加第二种金属后, 双金属整体式催化剂颗粒尺寸变小, 分布更均匀. EDS结果显示, 双金属形成了合金. H₂-TPR结果显示, 随着Pd/M比率增加, 还原温度降低, 说明Pd有助于第二种金属氧化物的还原. 这可能是由于 Pd 表面的氢溢流到第二种金属 (Ni, Fe, Mn和 Cu) 表面. 此外, 文献结果表明, 合金的形成能够抑制 PdH 的形成. 本工作表明添加第二种金属 (Ni, Fe, Mn和Cu) 后, PdH 的峰强度减弱或者峰消失, 也说明形成了合金. XPS 结果显示, 添加第二种金属后, 在 336.3 ± 0.1 和 341.4 ± 0.1 eV 出现了新的 Pd 3d_{5/2}和 Pd 3d_{3/2}峰, 说明形成了合金. H₂-O₂ 滴定结果表明, Pd-Ni/SiO₂/COR的Pd分散度和Pd比表面积都高于其他双金属催化剂, 说明第二种金属 Ni 更有利于促进 Pd 的分散, 减弱颗粒集聚, 揭示了 Pd 和 Ni 之间强烈的相互作用.

DFT 计算结果显示, Pd₃M₁ (M = Ni, Fe, Mn和Cu) 双金属整体式催化剂和 2-乙基蒽醌之间的结合能低于 Pd/SiO₂/COR 和 2-乙基蒽醌之间的结合能, 但是 Pd₃M₁ (M = Ni, Fe和Mn) 双金属催化剂和 2-乙基氢蒽醌之间的结合能减小得很少, 这可能是由于 2-乙基蒽醌的 C=O 和第二种金属之间具有强烈相互作用的缘故. Pd₃Cu₁ 双金属催化剂和 2-乙基氢蒽醌之间的结合能减小得多, 主要是由于 Pd₃Cu₁ 表面不利于 2-乙基氢蒽醌的吸附.

因此, Pd-Ni/SiO₂/COR 比 Pd/SiO₂/COR, Ni/SiO₂/COR 和其他的双金属整体式催化剂具有更高的选择性和H₂O₂产量, 主要是由于合金的形成以及 2-乙基氢蒽醌的 C=O 双键和 2-乙基氢蒽醌强烈的相互作用. 关键词:双金属整体式催化剂; 合金; 2-乙基氢蒽醌; DFT 计算; 协同作用

收稿日期: 2017-12-27. 接受日期: 2018-01-24. 出版日期: 2018-06-05.

*通讯联系人. 电话: (010)64433695; 电子信箱: leizhg@mail.buct.edu.cn

基金来源:国家自然科学基金 (21476009, 21406007, U1462104).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(http://www.sciencedirect.com/science/journal/18722067).