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Modification effects of magnetic supports and bimetallic structures on palladium nanocluster catalysts

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ABSTRACT

Palladium (Pd) and palladium–platinum (Pd–Pt) colloidal nanoclusters catalysts have been prepared and immobilized on a magnetic support. Modification effects of magnetic support Fe_3O_4 and bimetallic structure on the catalysts have been studied by catalytic experiments and computational simulation. The Fe_3O_4 support benefits to catalytic selectivity of the nanoclusters in the selective hydrogenation of *o*-chloronitrobenzene to *o*-chloroaniline. X-ray photoelectron spectroscopy analyses indicate that the interaction between Fe_3O_4 and Pd atoms modifies catalytic performances of the nanoclusters. Computational simulation gives the atom distribution, in which Pd atoms are enriched on the surface of the Pd–Pt bimetallic cluster, while Pt atoms on the subsurface. It is found that the inner Pt atoms present beneficial modification on catalytic selectivity. In conclusion, the magnetic metal nanocluster catalysts provide good catalytic properties and easy isolation by magnetic field for their reuse.

1. Introduction

Colloidal metal nanoclusters with size less than 10 nm have been attracted much attention because of their applications in catalysts [1–4], magnetism [5], and electronics [6] due to their distinct physical and chemical properties. As catalysts, they have been studied widely in various reactions [7]. Although the colloidal metal nanoclusters dispersing in liquid media have novel catalytic properties different from conventional catalysts, it is vital to immobilize them on different supports for their industrial applications. Up to now, there have been many kinds of inorganic supports such as Al_2O_3, MgO and many mesoporous materials. Liu's group [8–11] carried out many researches on immobilization and catalytic properties of polymer-stabilized metal colloids on various supports. In addition, magnetic materials Fe_3O_4 [12] and γ-Fe_2O_3 [13] can act as catalyst supports with the advantage of recycling the catalysts from the reaction system by applying magnetic field.

Haloaromatics amines are important intermediates in the chemistry of dyes, drugs, and pesticides. Selective hydrogenation of halonitroaromatic compounds to the corresponding haloamines over the metal catalysts is preferred [14]. Liu et al. [15] reported many researches on selective hydrogenation of chloronitrobenzene to chloroaniline over poly(*N*-vinyl-pyrrolidone) (PVP)-stabilized colloidal metal nanoclusters with predominant catalysis. Catalytic activities and selectivities of the colloidal metal nanoclusters can be improved obviously with the addition of some metal ions (Fe^{3+}, Co^{2+}, Ni^{2+}, etc.) or metal complexes [7] into the reaction system. Wang and coworkers [13] reported a Pt/γ-Fe_2O_3 nanocomposite catalyst and its novel catalytic properties for selective hydrogenation of *ortho*-chloronitrobenzene (*o*-CNB), which had fully suppression on hydrodechlorination of the hydrogenation product *ortho*-chloroaniline (*o*-CAN) at complete conversion of *o*-CNB.

As is well known, Pd is a good catalyst for hydrogenation reactions and much cheaper than Pt [16]. PVP-stabilized Pd colloidal nanoclusters have similar catalytic activity to the Pt nanoclusters in the selective hydrogenation of *o*-CNB, but the Pd catalysts present lower selectivity to *o*-CAN than the Pt catalysts [14]. So, efforts for the improvement of the catalytic selectivity of Pd catalysts are expected. Taking the promotion effect of the Fe^{3+} ions in the hydrogenation system into account, magnetic iron oxide can be selected as a support for the Pd nanoclusters. There may be two advantages with this support: one is the possibility of improving the catalytic selectivity, the other is magnetic isolation of the catalyst due to the presence of magnetic support. Moreover, PVP-stabilized colloidal bimetallic nanoclusters show better catalytic activity and selectivity than the monometallic clusters [14]. As a result, the presence of some amount of Pt would modify catalytic performances of the Pd nanoclusters. In this report, we describe catalytic properties of Fe_3O_4 supported Pd and Pd–Pt nanoclusters in the selective hydrogenation of *o*-CNB.

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Modification effects of the magnetic supports and the structures of the bimetallic clusters on the metal catalysts are discussed with regard to catalytic properties and the interaction between metal and support from experimental and computational analyses.

2. Experimental

2.1. Preparation of the magnetic catalysts

Magnetic support Fe_3O_4 was prepared as following method. Aqueous solutions of $FeCl_2{\cdot}4H_2O$ (8.4 mmol) and $FeC1_3{\cdot}6H_2O$ (1.5 mmol) were mixed and stirred in water-bath at 65 °C. Sodium hydroxide solution was added into the mixture till its pH reached 12. After remaining for 30 min, the pH value of the mixture decreased to 7 and black fluid magnetic Fe_3O_4 was then obtained. The PVP-stabilized Pd and Pd–Pt colloidal nanoclusters were synthesized as reported in a previous paper [17]. For example, in a 100 mL flask, palladium chloride $PdCl_2$ (0.04 mmol) was dissolved in 30 mL methanol by stirring for 10 h, resulting in a light turbid yellow solution. Hexachloroplatinic acid $H_2PtCl_6{\cdot}6H_2O$ (0.02 mmol, only used in the preparation of the Pd–Pt colloid) and amount of PVP (1.5 mmol as monomeric unit) as a stabilizer were dissolved in 30 mL water. The above two solutions were mixed and stirred at room temperature for 0.5 h and then refluxed for 1.5 h. Finally, a dark-brown homogeneous dispersion was obtained, which shows the formation of PVP-stabilized colloidal Pd or Pd–Pt nanoclusters with the average diameter of 2.7 nm or 2.3 nm, respectively [14]. The obtained colloidal metal nanoclusters and the black fluid magnetic Fe_3O_4 were mixed and stirred for four days at room temperature. After being washed by water for several times, the final obtained powders were dried in air and were designated as Pd–Fe_3O_4 and Pd–Pt–Fe_3O_4 catalysts.

2.2. Characterizations of the magnetic catalysts

Element analyses of the metal catalysts on the Fe_3O_4 support were carried out on the ULTIMA (France JY Inc.) inductively coupled plasma spectrometry (ICP). Transmission electron microscopy (TEM) photographs were taken by using the JEOL JEM-3010 instrument. X-ray photoelectron spectra (XPS) were recorded on the ESCALAB 250 (Thermo Inc.) photoelectron spectrometer using the Al Kα X-ray source. All binding energy values were referred to carbon (C 1s = 285.0 eV). For the XPS measurement of the PVP–Pd–Pt colloidal sample, the solvent (the ethanol–water mixture) was removed by rotated evaporator and the as-prepared solid residues were used for the XPS measurement. Magnetic measurements of the catalysts were carried out on the JDM-13 vibrating sample magnetometer (VSM).

2.3. Selective hydrogenation of *o*-CNB over the magnetic catalysts

Selective hydrogenation of *o*-CNB was carried out in a 30-mL flat bottom flask. Reactions were conducted at constant temperature 303 K and 0.1 MPa. The catalyst containing 4.8×10^{-6} mol Pd or Pd–Pt was mixed with 1 mmol *o*-CNB or/and metal salt solution. The metal salt solution is methanol solution of $FeCl_3$, $CoCl_2$ or $NiCl_2$ with 1 mmol metal cations. Methanol was used as the solvent and the total reaction volume was 15 mL. Chemical analyses of the products were performed by gas chromatography (Beifen TP-2080) equipped with a FID detector and DC-710 column. Decanol was used as an internal standard for the analyses.

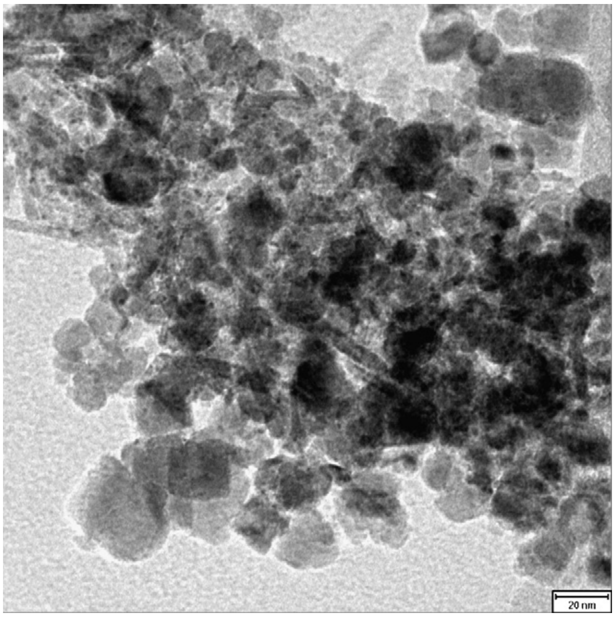

Fig. 1. TEM photograph of the Pd–Pt–Fe_3O_4 catalyst.

3. Results and discussion

3.1. Characterizations of the Pd–Fe_3O_4 and Pd–Pt–Fe_3O_4 catalysts

PVP-stabilized colloidal Pd and Pd–Pt nanoclusters were immobilized on the magnetic supports Fe_3O_4. ICP measurements indicate that the metal loading is 0.92% (weight percentage) and 1.04% for the Pd and Pd–Pt nanoclusters, respectively. In the Pd–Pt–Fe_3O_4 catalyst, the metal loading of Pd is 0.72% and the loading of Pt is 0.32%. A TEM photograph of the Pd–Pt–Fe_3O_4 catalyst is given in Fig. 1. It can be seen that small Pd–Pt nanoclusters are immobilized on the Fe_3O_4 support. Because the same magnetic supports were used for the preparation of Pd–Fe_3O_4 and Pd–Pt–Fe_3O_4 catalysts, magnetic measurement was carried out only for the Pd–Pt–Fe_3O_4 catalyst. Fig. 2 is the magnetization curve of the Pd–Pt–Fe_3O_4 catalyst. It can be seen that the Pd–Pt–Fe_3O_4 catalyst has high magnetism and its saturated magnetization is 51.7 emu/g, which implies that the catalyst can be easily separated from the reaction system by magnetic field. Fig. 2 indicates that the Pd–Pt–Fe_3O_4 catalyst is ferromagnetic with small coercivity 150 Oe and remanence 7.19 emu/g, which means that the catalysts will agglomerate after

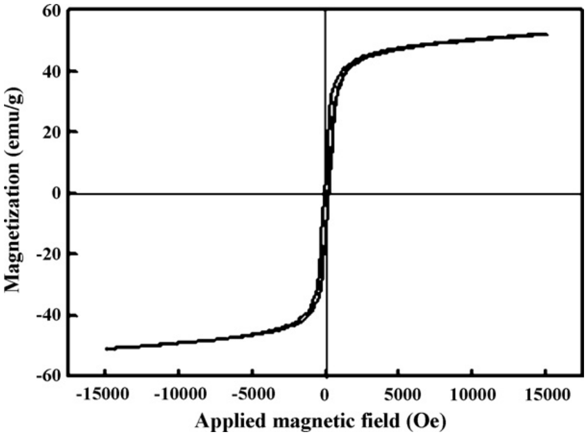

Fig. 2. Magnetization curve of Pd–Pt–Fe_3O_4 catalyst at room temperature.

magnetic separation for recycling uses. In our experiments, a magnetic stirrer was placed to separate the catalyst from the reaction system. In the recycling catalytic reactions, most of the catalysts can be re-dispersed in the reaction system through the magnetic stirring.

3.2. Catalytic properties of the Pd–Fe_3O_4 and Pd–Pt–Fe_3O_4 catalysts

Selective hydrogenation reactions of *o*-CNB were carried out over the Pd–Fe_3O_4 and Pd–Pt–Fe_3O_4 catalysts. Catalytic reactions over PVP-stabilized Pd and Pd–Pt colloidal clusters were also investigated for comparison. Table 1 shows the catalytic properties of the different catalysts on the hydrogenation of *o*-CNB. It is found from Table 1 that Pd–Fe_3O_4 and Pd–Pt–Fe_3O_4 (Nos. 1 and 5) have good catalytic properties with nearly 100% conversions of *o*-CNB and high selectivities to *o*-CAN. Compared with the colloidal catalysts without the magnetic support, Pd–Fe_3O_4 and Pd–Pt–Fe_3O_4 exhibit much higher selectivities than PVP–Pd and PVP–Pd–Pt (Nos. 9 and 10). The selectivities to *o*-CAN are greatly improved from ∼45% to ∼80%. In addition, it is found that PVP–Pd–Pt catalyst presents higher catalytic activity (indicated as catalytic average rate) than PVP–Pd catalyst with the similar selectivities to *o*-CAN. However, Pd–Pt–Fe_3O_4 gives a 10% higher selectivity to *o*-CAN and similar activity compared to Pd–Fe_3O_4. In one word, the above magnetic catalysts provide a distinct catalytic selectivity, although their catalytic activities are several times slower than the colloidal catalysts. One of the factors for the slower catalytic activity may be the small remanence of the Fe_3O_4 support, which would hinder the dispersion of the magnetic catalyst in the reaction system due to the presence of the magnetic stirrer. It is noticed that the catalytic activity can be adjusted by some modifiers. The addition of transition metal ions can considerably modify both the activity and selectivity. From Table 1, we can see that the addition of Fe^{3+} ions improves both the catalytic activity and the selectivity. Meanwhile, the addition of Ni^{2+} ions inhibits the activity of the catalysts. Upon the addition of Fe^{3+} ions into the PVP–Pd–Pt catalytic system (No. 11), the activity could be improved greatly and the selectivity increases to 50.2%. As is seen from the Table 1, among the catalysts, Pd–Pt–Fe_3O_4–Fe^{3+} (No. 6) shows the best catalytic activity with 100% conversion of *o*-CNB and 83.4% selectivity to *o*-CAN. In summary, the magnetic supported metal nanoclusters display good catalytic properties and their catalysis is different from the colloidal metal nanoclusters. Modification effects of the magnetic supports on the catalytic properties of the Pd and Pd–Pt nanoclusters are pronounced.

After the *o*-CNB hydrogenation was carried out for 90 min (reaction conditions are shown in Table 1), the Pd–Fe_3O_4 or Pd–Pt–Fe_3O_4 catalyst could be separated from the reaction system by the magnetic stirrer. Washed with methanol, the recovered catalyst was reused in the next reaction cycle. Fig. 3 shows the catalytic properties of the Pd–Pt–Fe_3O_4 catalyst used in different cycles. It is found that the conversion of *o*-CNB decreases greatly from 99.9% to 83% from the first time to the third time and then keeps constant in the subsequent reuse. Meanwhile, the recovered catalyst exhibits nearly the same selectivity to *o*-CAN in four cycles and a slight decrease in the fifth time.

As reported by Wang and coworkers [13], the Pt–Fe_2O_3 magnetic catalysts present the catalytic rate of 5.3×10^{-3} $\mathrm{mol}_{o\text{-CNB}}/(\mathrm{mol}_{\mathrm{Pt}}\,\mathrm{s})$ and 99.9% selectivity to *o*-CAN. In our case, the Pd–Fe_3O_4 catalyst gives the higher catalytic rate (2.89×10^{-2} $\mathrm{mol}_{o\text{-CNB}}/\mathrm{mol}_{\mathrm{Pt}}\,\mathrm{s}$) and lower selectivity (73.0%). When some amount of Pt is included to form the bimetallic nanocluster catalyst Pd–Pt–Fe_3O_4, the selectivity increases to 82.0%. It indicates that Pt contributes to the high selectivity. Moreover, for the fact that Pd is much cheaper than Pt, the present Pd–Fe_3O_4 and Pd–Pt–Fe_3O_4 catalysts are promising for their industrial applications.

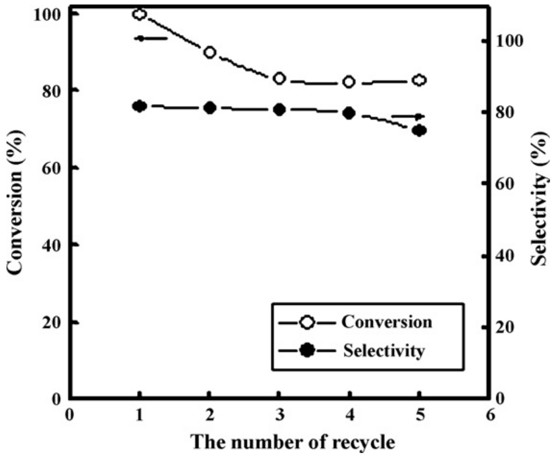

Fig. 3. Hydrogenation of *o*-CNB over Pd–Pt–Fe_3O_4 catalyst as a function of the recycle times.

Based on the experimental data in Table 1, two points will be discussed later. One is the improvement of the selectivity due to the existence of the magnetic support. The other is that the differences in the catalytic properties between Pd–Pt–Fe_3O_4 and Pd–Fe_3O_4. For understanding the above two points, the structure of the bimetallic Pd–Pt nanoclusters and interaction between the metal clusters and the magnetic support are studied.

3.3. Computational simulation on structure of the Pd–Pt nanoclusters

As we know, catalytic property of bimetallic cluster depends not only on its size but also on its structure including its component and atomic ordering [18]. By using the Monte Carlo (MC) simulation method based on the second-moment approximation of the tight-binding (TB-SMA) potentials, the structure of bimetallic cluster can be simulated [19]. Because the Pd–Pt cluster is synthesized in methanol–water-refluxing system, the temperature is set to be 350 K for the simulation. The metal atom ratio of the Pd–Pt clusters is about Pd/Pt = 2/1 and the average diameter of the Pd–Pt is 2.3 nm [14], which indicate that the Pd_{374}–Pt_{187} (the number denotes number of the metal atoms) cluster can be regarded as the model for Monte Carlo simulation. The simulation results indicate that the synthesized Pd–Pt bimetallic cluster is nearly “core–shell” structure with Pd atoms enriched on the surface layer and Pt atoms enriched on the subsurface layer. The structure scheme of the bimetallic cluster is shown in Fig. 4. The surface layer contains 99.0% Pd atoms, the subsurface layer 94.6% Pt atoms and the third layer (from surface to center) 91.9% Pd atoms. In conclusion, although there is one third of Pt in the Pd–Pt cluster, the surface of the bimetallic cluster is almost covered with Pd atoms.

3.4. XPS characterization of the Pd–Pt–Fe_3O_4 nanoclusters

XPS can give an important clue in characterizing the oxidation state of the metal particles. To understand the effect of the magnetic support on the metal clusters, Pd–Pt–Fe_3O_4 and PVP–Pd–Pt clusters were characterized by XPS for comparison. Fig. 5 is the XPS spectra of Pd_{3d} and Pt_{4f} electrons in the Pd–Pt–Fe_3O_4 and PVP–Pd–Pt catalysts. The binding energy (BE) scales are referenced by setting the C 1s BE to 285.0 eV. The Pd_{3d} BEs of the bulk Pd metal are $Pd_{3d_{5/2}} = 335.1$ eV and $Pd_{3d_{3/2}} = 340.3$ eV, meanwhile the Pt_{4f} BEs of the bulk Pt metal are $Pt_{4f_{7/2}} = 71.2$ eV and $Pt_{4f_{5/2}} = 74.5$ eV,

Table 1
Catalytic properties for the hydrogenation of *o*-CNB over the Pd and Pd–Pt catalysts

Number	Catalysts[a]	Conversion (%)	Catalytic average rate[b]	Selectivity to *o*-CAN (%)
1	Pd–Fe_3O_4	100	2.89×10^{-2}	73.0
2	Pd–Fe_3O_4–Fe^{3+}	99.5	3.84×10^{-2}	78.2
3	Pd–Fe_3O_4–Co^{2+}	99.8	3.85×10^{-2}	68.2
4	Pd–Fe_3O_4–Ni^{2+}	60.7	2.34×10^{-2}	84.7
5	Pd–Pt–Fe_3O_4	97.0	2.59×10^{-2}	82.0
6	Pd–Pt–Fe_3O_4–Fe^{3+}	100	3.86×10^{-2}	83.4
7	Pd–Pt–Fe_3O_4–Co^{2+}	83.6	3.22×10^{-2}	82.8
8	Pd–Pt–Fe_3O_4–Ni^{2+}	33.9	1.30×10^{-3}	77.7
9	PVP–Pd	100	1.14×10^{-1}	45.8
10	PVP–Pd–Pt	100	1.72×10^{-1}	47.2
11	PVP–Pd–Pt–Fe^{3+}	100	4.70×10^{-1}	50.2

[a] Reaction conditions: amount of metal Pd or Pd–Pt in the reaction solution is 4.8×10^{-6} mol; amount of the reactant *o*-CNB is 1 mmol; the molar ratio of metal ion to the catalyst metal is 1; reactions are carried out at 303 K and 0.1 MPa for 90 min.

[b] Unit of catalytic average rate is $mol_{o\text{-CNB}}/(mol_{Pt}\ s)$.

respectively [20]. The XPS spectra show that the BEs of Pd_{3d} and Pt_{4f} have positive shifts when the Pd–Pt clusters are immobilized on the magnetic support Fe_3O_4. The BE of $Pd_{3d_{5/2}}$ shifts from 335.4 eV to 336.8 eV and the BE of $Pt_{4f_{7/2}}$ from 71.4 eV to 72.2 eV. This indicates that the presence of the Fe_3O_4 support causes Pd and Pt in the Pd–Pt–Fe_3O_4 clusters displaying positive-charged states [21]. In other words, the modification of the Fe_3O_4 support on the catalyst Pd–Pt is ascribed to the electron transfer from Pd or Pt to the support. As is known from the above Monte Carlo simulation results, the surface of the Pd–Pt bimetallic cluster is enriched with Pd atoms, which is reasonable for the larger positive shift of BE for Pd than that for Pt. Consequently, the modification effect of Fe_3O_4 can change the adsorbing ability of the reactants on the Pd–Pt clusters and therefore change the reaction activity and selectivity.

As reported in the literature [7], transition metal iron ions can modify the catalyses of Pd and Pt colloidal nanoclusters. The beneficial effect to improve the catalytic selectivity is due to the interaction between the reactant and the electronic transfer from the metal ions to the metal clusters. In the present work, Fe_3O_4 was used as the supports for the Pd and Pd–Pt clusters and the enhancement of the catalytic properties is observed. Here, modification effects of the Fe_3O_4 supports on the catalyses of the Pd and Pd–Pt clusters can be explained. First, the introduced Fe_3O_4 support can improve the selectivity to *o*-CAN. The promotive effect is similar to the effect of iron ions [7]. Based on the XPS results, BEs of Pd_{3d} in the Pd–Fe_3O_4 and Pd–Pt–Fe_3O_4 catalysts have positive shifts, which indicates obviously the electronic transfer from the metal Pd to the support Fe_3O_4. Thus, the NO_2 group in the reactant *o*-CNB can be activated by the positive-charged Pd. The ability of the nearby-dissociated H atoms to attack the O and N atoms of NO_2 groups to form NH_2 is enhanced, which benefits to the high selectivity to *o*-CAN. Similar to Ref. [22], the modification mechanism is shown in Fig. 6. Second, with the addition of Fe^{3+} ions into the Pd–Fe_3O_4 and Pd–Pt–Fe_3O_4 catalytic systems (Nos. 2 and 6 in Table 1), the selectivities to *o*-CAN increase slightly and the

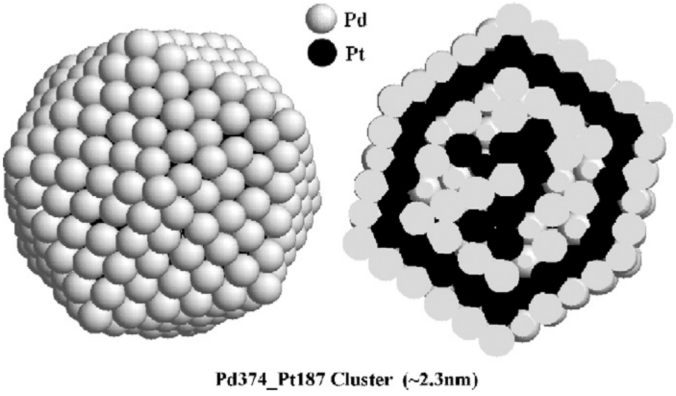

Fig. 4. The structure scheme of the Pd_{374}–Pt_{187} cluster (2.3 nm) from Monte Carlo simulation. (The gray one is Pd atom and the black one is Pt atom.)

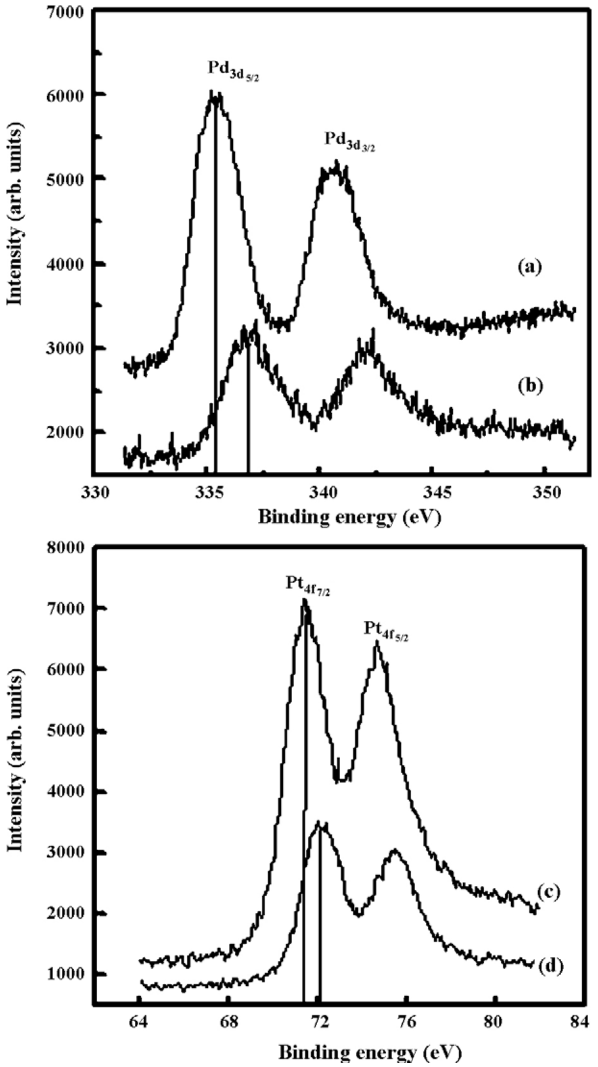

Fig. 5. XPS spectra of Pd_{3d} and Pt_{4f} electrons in the Pd–Pt–Fe_3O_4 clusters (curves (a) and (c)) and PVP–Pd–Pt clusters (curves (b) and (d)).

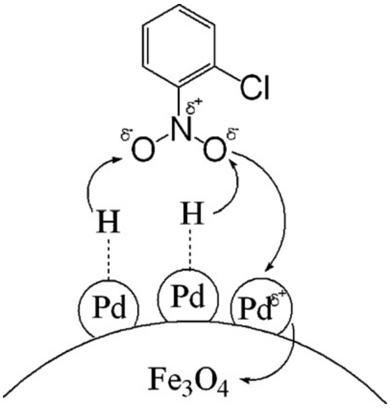

Fig. 6. Modification scheme of the Fe_3O_4 support on the catalysis of the Pd nanoclusters.

reactive rates are enhanced obviously. The beneficial modification effects are similar to the case of the colloidal metal clusters shown in No. 11 Table 1. Therefore, the magnetic support Fe_3O_4 for the colloidal metal nanoclusters improves the catalytic selectivity in the hydrogenation of *o*-CNB and preserves similar characteristics of the colloidal catalyst, where the reaction rate and the selectivity can be improved through the modification of transition metal ions.

From the computational simulation results, the surface layer of Pd–Pt bimetallic nanoclusters in Pd–Pt–Fe_3O_4 catalyst contains 99.0% Pd atoms, which is nearly the same as the Pd nanoclusters with the whole Pd atoms on the surface layer. However, it is found that the Pd–Fe_3O_4 and Pd–Pt–Fe_3O_4 catalysts (Nos. 1 and 5 in Table 1) show different catalytic properties, although they possess similar surface atom distribution. The Pt atoms are distributed in the inner layer (most in the subsurface layer) of the Pd–Pt nanocluster. Despite a trace amount of Pt atom on the Pd–Pt surface layer, the involved Pt atoms in the Pd–Pt catalyst can improve the selectivity obviously. Compared with Pt in the bulk state ($Pt_{4f_{7/2}} = 71.2$ eV), $Pt_{4f_{7/2}}$ electrons in Pd–Pt–Fe_3O_4 clusters show the higher BE with 72.2 eV. This shows that there exists electronic transfer and somewhat interaction between Pt and Pd or Fe_3O_4. Therefore, the involved Pt atoms are capable of altering the electronic structure of active Pd atoms on the surface, which causes the higher selectivity of Pd–Pt–Fe_3O_4 catalysts than Pd–Fe_3O_4 catalysts.

4. Conclusions

Pd and Pd–Pt colloidal nanoclusters have been immobilized on the magnetic support Fe_3O_4. The obtained Pd–Fe_3O_4 and Pd–Pt–Fe_3O_4 catalysts show good catalytic properties in the selective hydrogenation of *o*-CNB, which are different from the colloidal Pd and Pd–Pt catalysts. Modification effects of magnetic supports and bimetallic structures on the catalytic properties have been found. The Fe_3O_4 supports improve the catalytic selectivities of *o*-CNB to *o*-CAN over the Pd and Pd–Pt catalysts. With the addition of iron ions, the catalytic rate can be speeded up. From MC simulation, the Pd–Pt bimetallic clusters show a core–shell structure with Pd enriched on the surface layer and Pt on the subsurface layer. The Pd–Pt–Fe_3O_4 catalyst gives better catalytic selectivity than Pd–Fe_3O_4 because of the modulation of the Pt atoms on the electronic structure of the surface Pd atoms. Compared with the colloidal metal nanoclusters, the Pd–Fe_3O_4 and Pd–Pt–Fe_3O_4 catalysts have advantages of good catalytic properties with better catalytic selectivities and magnetic-induced recycles.

Acknowledgments

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