

Modification of metal cations to the supported metal colloid catalysts

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Abstract

The influence of metal cations on supported metal colloids prepared by the modified coordination capture was investigated in three selective hydrogenation reactions: *o*-chloronitrobenzene to *o*-chloroaniline, cinnamaldehyde to cinnamyl alcohol and citronellal to citronellol. It was found that some metal cations (e.g., Ni²⁺, Co²⁺) increased both the activity and the selectivity at the same time. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Modification; Selective hydrogenation; Platinum colloid; Metal cation

1. Introduction

In the field of catalysis, metal colloids dispersed in solutions displayed many interesting catalytic performances [1–10]. However, the surfactant-stabilized colloids are not stable and intend to agglomerate during the reaction even under very mild conditions [11]. Although polymer-stabilized colloids are very stable relatively, it is not economic and convenient to

recover them from products by conventional methods. So, some researchers investigated how to immobilize them onto supports in view of practical application [12–25]. By improving the coordination capture approach [24,25], we proposed a new method named as ‘modified coordination capture’, by which the as-prepared supported metal colloid catalysts exhibited some novel catalytic properties compared to other methods [26,27]. Here, three reaction systems were investigated on the as-prepared supported metal colloid catalysts. One is the selective hydrogenation of *o*-chloronitrobenzene (**1**) to *o*-chloroaniline (**2**), the second is the selective hydrogenation of cinnamaldehyde (3-phenyl-2-propenal, **3**) to cinnamyl alcohol (3-phenyl-2-propen-1-ol, **4**), and the third is the selective hydrogenation of citronellal (3,7-dimethyl-6-oc-

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tenal, **5**) to citronellol (3,7-dimethyl-6-octene-1-ol, **6**). It has been known that metal cations and

metal complex ions can markedly affect the catalytic properties of polymer-stabilized metal

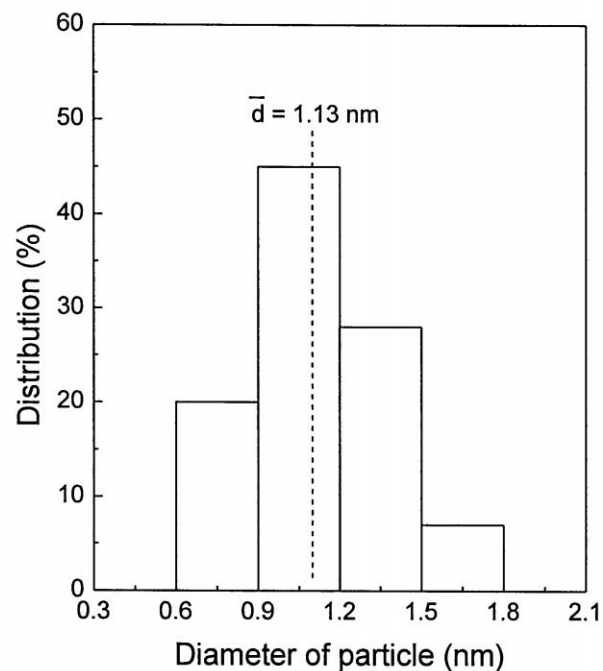
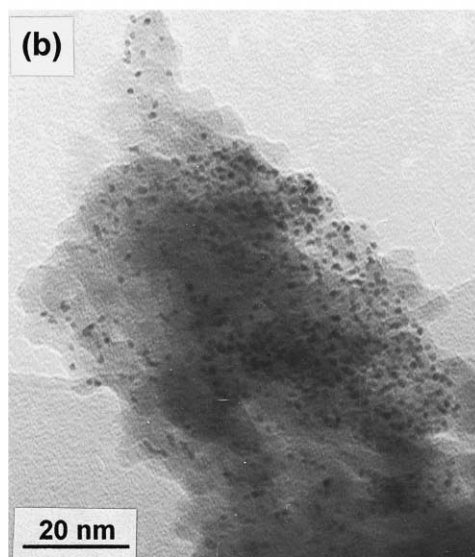
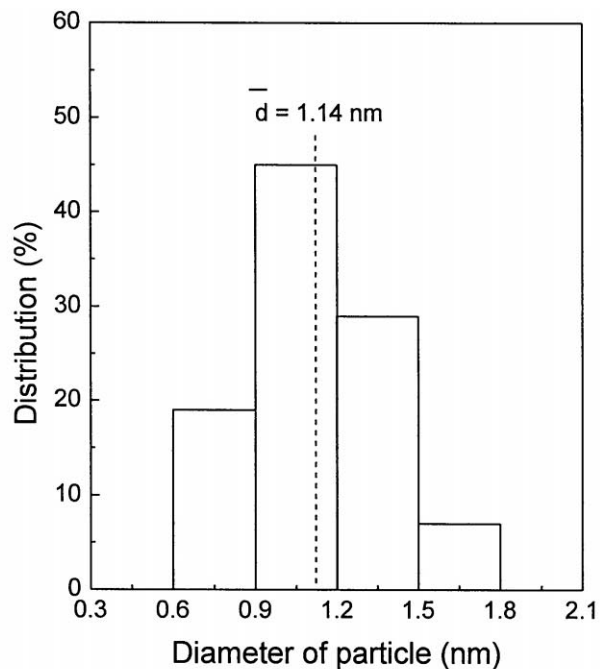
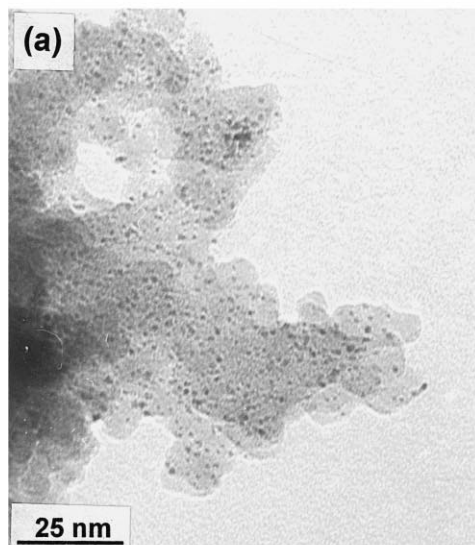


Fig. 1. TEM photographs (left) and the corresponding particle size distribution histograms (right) of (a) Pt/PS, (b) Pt/Al₂O₃, (c) Pt/MgO and (d) Pt/TiO₂.

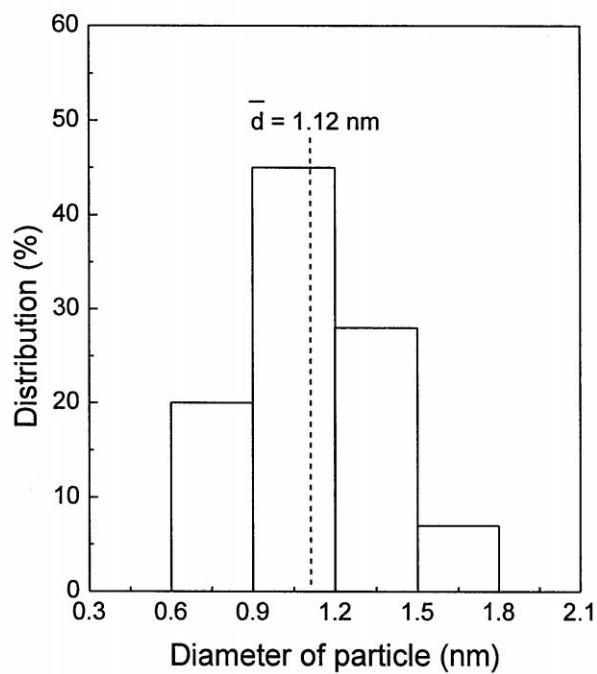
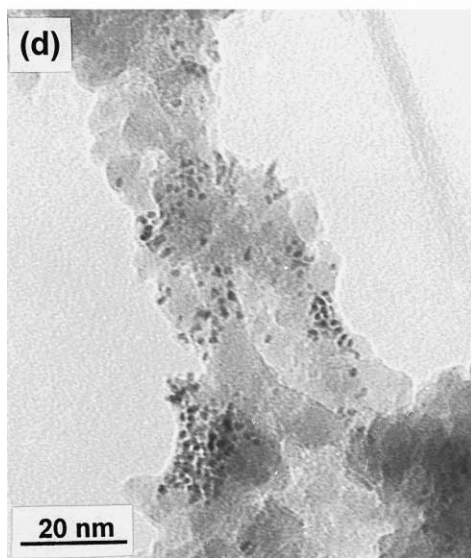
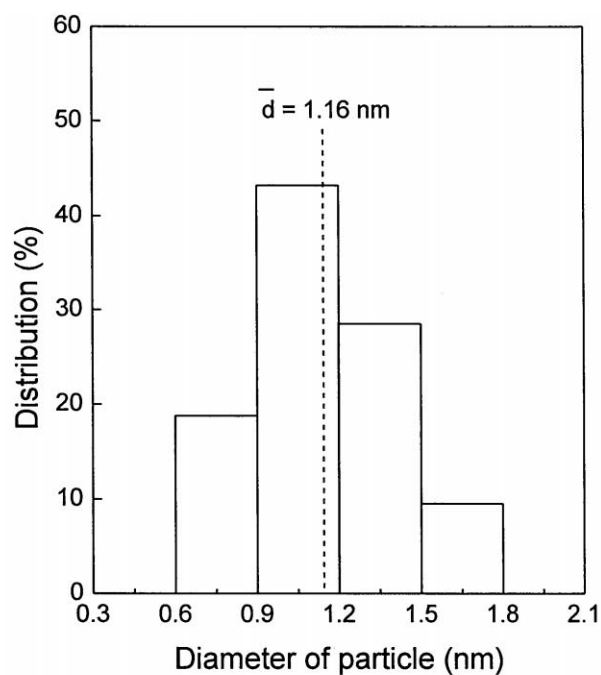
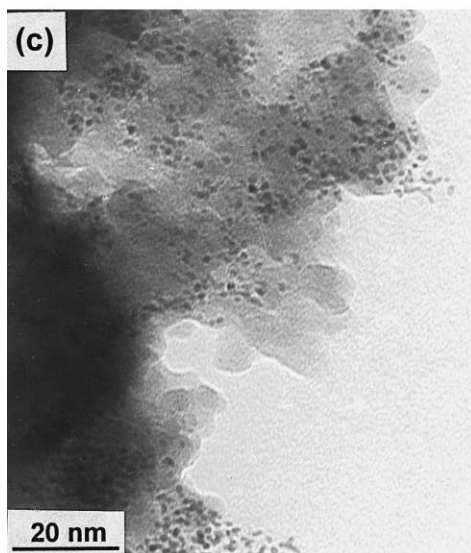


Fig. 1 (continued).

colloids [28–35]. In this paper, we describe the modification of metal cations to supported metal

colloid catalysts prepared by the modified coordination capture.

2. Experimental

2.1. Materials and instruments

All reagents were purchased from Beijing Chemicals and had a level of analytical grade. Compound **1** was recrystallized in 95% ethanol and **3** and **5** were redistilled under reduced pressure before use. Hydrogen (H_2) with a purity of 99.999% was supplied by Beijing Gases Factory.

Poly(styrene-*co*-divinylbenzene) beads (PS) were thoroughly treated according to the literature [36] and had a surface area of $340 \text{ m}^2 \text{ g}^{-1}$. Other supports, Al_2O_3 , MgO and TiO_2 with surface areas of 16.8, 56.9 and $10.6 \text{ m}^2 \text{ g}^{-1}$ respectively, were used as purchased.

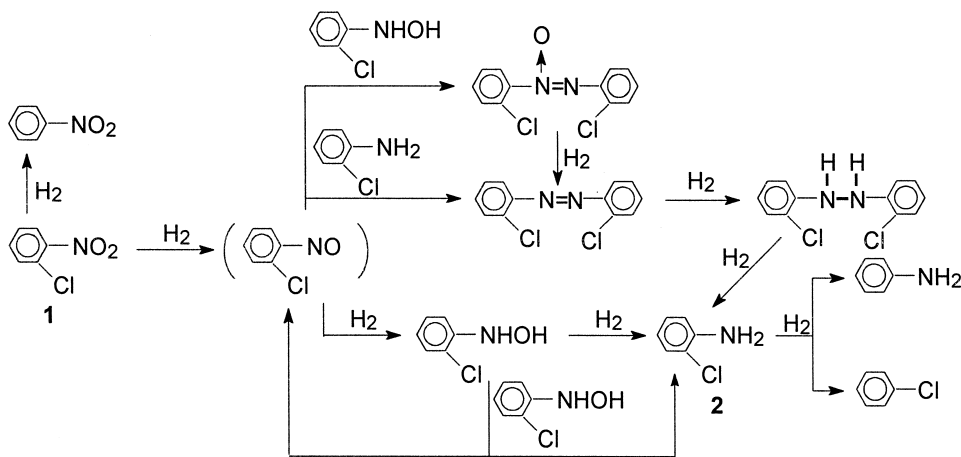
Transmission electron microscopy (TEM) photographs were taken by using a Hitachi-9000NAR instrument. Specimens were prepared by placing a drop of the solid suspension upon a copper grid covered with a perforated carbon film and then evaporating the solvent. The particle diameters were measured from the enlarged photographs. The particle-size distribution histogram was obtained on the basis of the measurements of more than 300 particles. The hy-

drogenation products were analysed by a Shang-Fen Model 103 gas chromatograph (GC).

2.2. Preparation of supported metal colloid by the modified coordination capture

Poly(*N*-vinyl-2-pyrrolidone)-stabilized platinum colloid (PVP-Pt) was prepared by the literature method [37] as a dark brown homogeneous dispersion.

The modified coordination capture method for the preparation of supported metal colloids was described in detail elsewhere [26]. For example, 2.0 g PS was stirred with 0.11 g triphenylphosphine dissolved in EtOH for 3 h, and was dried by rotatory evaporation. Then, platinum colloidal dispersion (containing $Pt \ 7.60 \times 10^{-5} \text{ mol}$) was added and stirred with the support for 24 h. After filtration, the support was first extracted in a Soxhlet extractor with H_2O for 48 h, and toluene/EtOH (4:1) mixed solvents for 48 h, then dried under vacuum for 5 h to give the PS-supported platinum colloid, Pt/PS. Pt/ Al_2O_3 , Pt/MgO and Pt/ TiO_2 were prepared with corresponding support in a similar way. The content of platinum was adjusted to about 0.5% by weight. The supported metal colloid catalysts were recovered by filtration and rinsed.



Scheme 1.

Table 1

Modification of metal cations to the supported metal colloid catalysts in the selective hydrogenation of **1** to **2**^a

Catalytic system	Average rate ^b (mol H ₂ /mol Pt s)	Selectivity (%) ^c			
		2	Nitrobenzene	Aniline	Others
Pt/PS	0.760	81.9	1.3	11.1	5.7
Pt/PS–FeCl ₃	0.581	83.0	0.4	4.6	12.0
Pt/PS–CoCl ₂	0.896	78.0	0	2.5	19.5
Pt/PS–NiCl ₂	0.905	93.5	0	3.8	2.7
Pt/Al ₂ O ₃	0.983	79.9	9.3	7.7	3.1
Pt/Al ₂ O ₃ –NiCl ₂	0.747	95.8	1.0	1.1	2.1
Pt/MgO	1.03	71.0	0	4.0	25.0
Pt/MgO–NiCl ₂	0.680	86.3	0	0	13.7
Pt/TiO ₂	0.191	92.2	5.6	1.3	0.9
Pt/TiO ₂ –NiCl ₂	0.0894	95.5	3.9	0	0.6

^aReaction condition: **1** = 7.00×10^{-4} mol, supported metal colloid catalyst = ~ 0.1 g (containing Pt = 2.60×10^{-6} mol), metal cations (added as their chlorides) = 2.60×10^{-6} mol, solvent = MeOH (whole volume = 15.0 ml), H₂ = 0.1 MPa, temperature = 303 K.

^bCalculated at 100% conversion of **1**.

^cObtained at 100% conversion of **1**. Others = *o*-chlorophenylhydroxylamine, *o*-chloronitrosobenzene, chlorobenzene, azo- and azoxy-dichlorobenzenes.

2.3. Hydrogenation reaction

Selective hydrogenation of **1** to **2** was carried out at 303 K and atmospheric pressure. In a two-necked flask equipped with a magnetic stirrer and a thermostatic water bath, there were placed about 0.1 g supported Pt colloid catalysts (containing Pt 2.60×10^{-6} mol), 0.10 ml *n*-C₁₄H₃₀ (as internal standard for GC) and 13.9 ml MeOH. H₂ was charged several times to replace air and the catalyst was activated at 303 K for 60 min. After 1.00 ml **1**/MeOH solution (containing **1** 7.00×10^{-4} mol) was injected into the flask, the reaction started. The hydrogen

consumption was monitored with a graduated gas burette. When the volume of the theoretical uptake of H₂ was reached, the reaction was stopped.

Selective hydrogenation of **3** to **4** was carried out in a 100-ml stainless-steel autoclave. The reaction solution contained 25 ml EtOH, 5 ml H₂O, 0.1 mg NaOH, 0.200 g **3** (1.51×10^{-3} mol), 0.200 g tetradecanol (as an internal standard for GC) and about 0.1 g catalyst (containing 2.60×10^{-6} mol Pt). H₂ was charged several times to replace air and the final pressure of H₂ was 4.0 MPa. The hydrogenation reaction was performed at 333 K for 2 h.

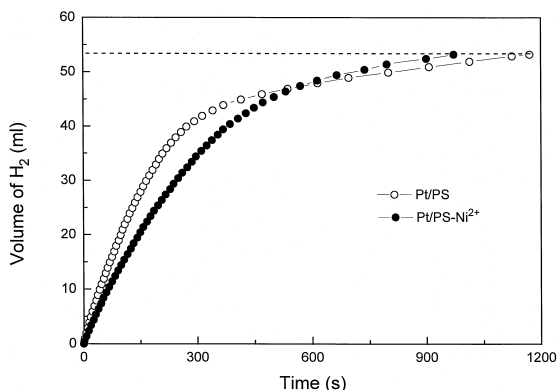


Fig. 2. Time courses of hydrogenation of **1** over Pt/PS and Pt/PS–Ni²⁺.

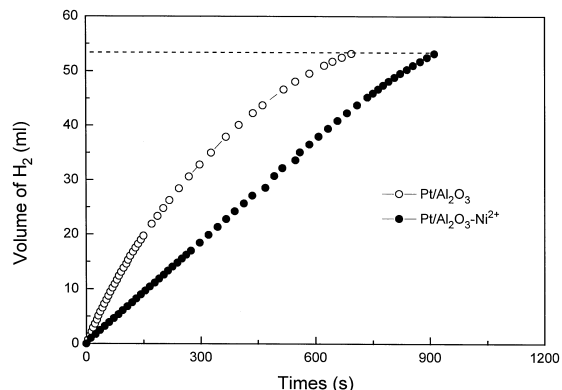
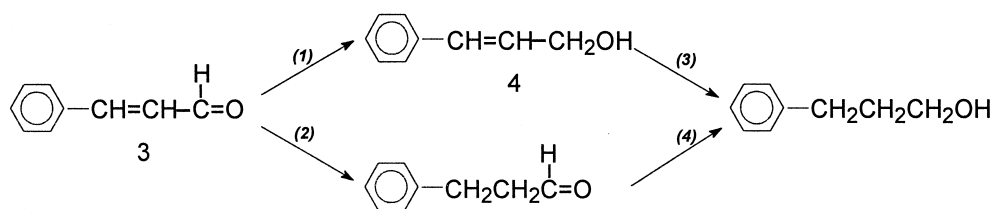


Fig. 3. Time courses of hydrogenation of **1** over Pt/Al₂O₃ and Pt/Al₂O₃–Ni²⁺.



Selective hydrogenation of **5** to **6** was similar to that of **3** to **4**. In a 100-ml stainless-steel autoclave, 25 ml EtOH, 5 ml H₂O, 0.10 mg NaOH, 0.500 g **5** (3.24×10^{-3} mol), 1.00 g ethylene glycol (as an internal standard for GC) and about 0.1 g catalysts (containing 2.60×10^{-6} mol Pt) were added. The hydrogenation reaction was performed at 333 K for 2 h at the pressure of H₂ of 6.0 MPa.

All the reaction products were analyzed by GC.

3. Results and discussion

3.1. Characterization of the supported metal colloid catalyst

The supported Pt colloid catalysts were characterized by TEM. The TEM photographs and the corresponding particle-size distribution histograms of the catalysts are shown in Fig. 1. From Fig. 1, it can be seen that the average diameters of the supported colloidal particles were 1.14, 1.13, 1.16 and 1.12 nm with standard deviation (σ) of 0.31, 0.31, 0.33 and 0.30 nm, respectively. This indicated that all of them have the same size and size distribution as their precursor—PVP-Pt dispersed in solution (average diameter 1.12 nm and $\sigma = 0.30$ nm) [37].

3.2. Modification of metal cations to the supported metal colloid

According to the study on the modification of metal cations to polymer-stabilized platinum colloids in the selective hydrogenation of **1**, **3**, **5**

and crotonaldehyde, Fe³⁺, Co²⁺, Ni²⁺ were the most effective modifiers [26–35]. Thus, we chose them to modify the supported catalysts.

3.2.1. Selective hydrogenation of **1** to **2**

Compound **2** is an important intermediate in the chemical and pharmaceutical industries. The selective hydrogenation of **1** to **2** is a well documented area [38–41], and Coq et al. have carefully studied this process over a series of Pt catalysts [42–44]. It can be seen from Scheme 1 that it is very complicated and many by-products will be formed in the hydrogenation. Hence, how to obtain **2** with high selectivity is a key problem (this reaction was usually carried out under ambient conditions and it is easy to get 100% conversion of **1**).

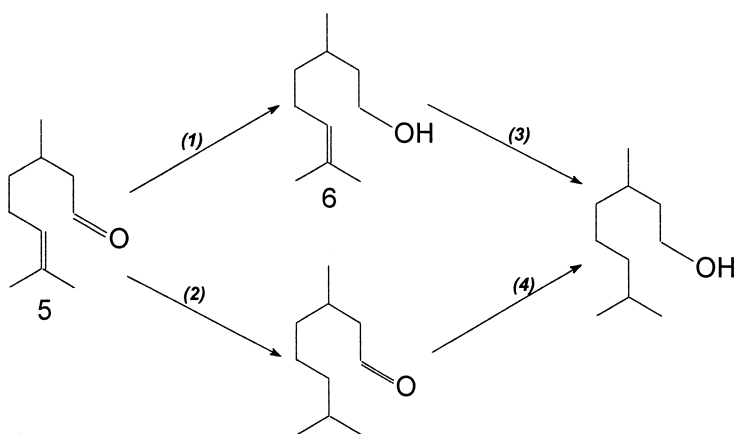
It was reported that the PVP-Pt gave 60.2% selectivity to **2** with activity of 0.690 mol H₂/mol Pt s [26]. By supported Pt colloids, it displayed much higher selectivity and activity than PVP-Pt except for Pt/TiO₂ in activity (Table 1). The differences of various supported

Table 2
Modification of metal cations to Pt/PS in the selective hydrogenation of **3** to **4**^a

Catalytic system	Conversion of 3 (%)	Selectivity (%) ^b	
		4	7
Pt/PS	79.7	94.7	5.3
Pt/PS–FeSO ₄	93.2	98.3	1.7
Pt/PS–CoCl ₂	95.5	99.0	1.0
Pt/PS–NiCl ₂	85.8	92.1	7.9

^aReaction condition: **3** = 0.200 g, Pt/PS = 0.100 g (containing Pt 2.60×10^{-6} mol), metal cations (added as their chlorides) = 2.60×10^{-6} mol, NaOH = 0.1 mg, H₂O = 5.0 ml, EtOH = 25.0 ml, H₂ = 40 atm, temperature = 333 K, time = 2 h.

^bThere was trace of 3-phenylpropanol detected by GC.



Scheme 3.

Pt colloids in catalytic performances should be ascribed to the different peculiarity of the supports [26,27].

It can be seen from Table 1 that there are some changes in the catalytic performance of supported metal catalysts after introducing metal cations. To Pt/PS, its activity was decreased by Fe^{3+} and increased by Co^{2+} but the selectivity remained nearly the same. Ni^{2+} enhanced both of them. To Pt/ Al_2O_3 , Pt/MgO and Pt/ TiO_2 , the addition of Ni^{2+} decreased the activity and increased the selectivity.

Figs. 2 and 3 recorded the time courses of selective hydrogenation of **1** to **2** over Pt/PS and Pt/ Al_2O_3 . They showed two different reaction processes when adding Ni^{2+} .

3.2.2. Selective hydrogenation of **3** to **4**

To be highly selective to the production of α,β -unsaturated alcohols from α,β -unsaturated aldehydes is an important work in the preparation of fine chemicals (Scheme 2) [45]. Boudart [46] has proposed it as one of the two important researches in catalysis over nanoclusters or colloids.

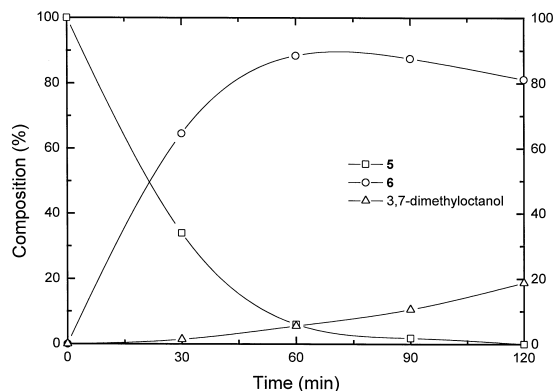
The supported Pt colloids displayed good performance in this reaction. From Table 2, it can be seen that the incorporation of Fe^{3+} , Co^{2+} and Ni^{2+} promoted the reaction and increased the selectivity for **4** to a higher level.

Co^{2+} is the best one, and this is parallel to the results for PVP-Pt [35].

3.2.3. Selective hydrogenation of **5** to **6**

Compounds **5** and **6** are nonconjugated unsaturated aldehyde and unsaturated alcohol, respectively. The selective hydrogenation of **5** is another type of work compared to that of **3** to **4**. It also undergoes two parallel and continuous reactions (Scheme 3).

We chose Pt/PS as a catalyst to study this reaction. Figs. 4 and 5 show the hydrogenation reactions without and with the modification of Co^{2+} . Using Pt/PS as a catalyst, 88.5% yield of **6** was obtained (conversion 94.0% and selectivity 94.1%) in 60 min. But it was decreased to 81.2% (conversion 100% and selectivity 81.2%)

Fig. 4. Selective hydrogenation of **5** over Pt/PS.

for another 60 min, because **6** was further hydrogenated to 3,7-dimethyloctanol (yield 18.8%). When introducing Co^{2+} into Pt/PS catalytic system, the yield of **6** comes close to 95.8% (conversion 98.2% and selectivity 97.6%) in 60 min and 97.3% (conversion 100% and selectivity 97.3%) in 120 min, respectively. Only 2.7% of 3,7-dimethyloctanol was obtained. This indicated that Co^{2+} enhances not only the activity but also the selectivity of supported metal colloid catalysts.

3.2.4. Mechanism of the modification of metal cations

Maxted [47,48], Adams et al. [49–52] have extensively studied the effects of various substrates, including Fe^{2+} , Co^{2+} and Zn^{2+} ions. Richard et al. [53] and Goupil et al. [54] investigated the promotion effect of $\text{Fe}(\text{NO}_3)_3$ and FeCl_2 (which had been converted into $\text{Fe}(0)$ before reaction by pretreatment) in the selective hydrogenation of **3** to **4** over the active charcoal-supported platinum catalysts, respectively. Ponec [55] and Gallezot and Richard [56] have reviewed in detail about the role of the promoter, especially the metal ions. Many types of promotion mechanism were summarized, but most of them cannot give a reasonable interpretation to our experiment facts: (1) The cations in the reaction system remained in the ionic state [35]; and (2) the possibility of change in the size and the morphology of the colloidal catalyst particles is scarce. However, there may still be

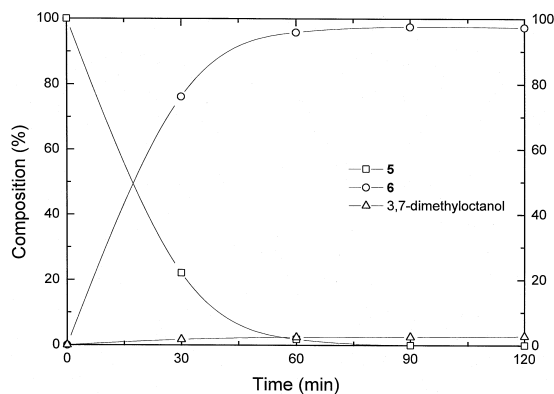


Fig. 5. Selective hydrogenation of **5** over Pt/PS- Ni^{2+} .

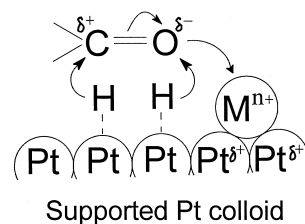


Fig. 6. Modification mechanism of metal cation to the supported Pt colloid.

some changes which could not be observed accurately by conventional means.

Previous results [35] on the research of the modification metal cations to PVP-Pt colloid pointed out that there was a chemical interaction between the reactant and the metal cation: the adsorbed metal cations activated the polar $\text{N}=\text{O}$ and $\text{C}=\text{O}$ groups, then the nearby dissociated H atoms attacked the O and N or C atom of $\text{N}=\text{O}$ or $\text{C}=\text{O}$ groups to give $-\text{NH}_2$ or $-\text{OH}$ groups, respectively (Fig. 6). Although the support effect caused by the characteristics of different supports could not be excluded, it is still reasonable that such an interaction played a primary role in the catalytic process.

Traditionally, the influence of metal ions (especially in the metallic state) to catalysts has been ascribed to the electron transfer from the ions to platinum [57]. But, we suspected that the electron transferred from platinum to the adsorbed metal cation, which enhanced the adsorbing ability of $\text{N}=\text{O}$ or $\text{C}=\text{O}$ double bonds onto the platinum surface and therefore increased the reactivity and the selectivity. This seems more reasonable for metal cations with positive charges.

4. Conclusions

Some metal cations played a beneficial role in the selective hydrogenation of $\text{N}=\text{O}$ and $\text{C}=\text{O}$ double bonds over supported metal colloid catalysts. The mechanism was thought to be a chemical interaction between them and the reactants, which enhanced the activity and the selectivity of the catalysts.

Acknowledgements

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