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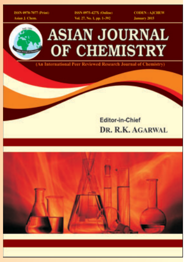

Synthesis of Pt/Al_2O_3 Catalysts by Microemulsion Technique and Hydrogenation of *p*-Chloronitrobenzene

FENG LI[1], RUI MA[1], HUA-LIN SONG[2] and HUA SONG[1,*]

[1]Provincial Key Laboratory of Oil and Gas Chemical Technology, College of Chemistry and Chemical Engineering, Northeast Petroleum University, Daqing 163318, Heilongjiang Province, P.R. China
[2]Key Laboratory of Cancer Prevention and Treatment of Heilongjiang Province, Mudanjiang Medical University, Mudanjiang 157011, Heilongjiang Province, P.R. China

*Corresponding author: Tel./Fax: +86 459 6503167; E-mail: songhua2004@sina.com

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A water-in-oil microemulsion method for preparing Pt nanoparticles supproted on Al_2O_3 catalysts based on cetyltrimethylammonium bromide/*n*-butanol/cyclohexane/H_2PtCl_6 solution were described. The effects of the microemulsion composition and reduction condition on hydrogenation properties over Pt/Al_2O_3 catalysts were investigated using the hydrogenation of *p*-chloronitrobenzene as model reactions. Compared with the impregnation-derived catalyst, the microemulsion-derived catalyst showed smaller (about 3 nm) and highly dispersed Pt nanoparticles with much higher *p*-chloronitrobenzene hydrogenation conversion of 76.8 %, which improved by 46.7 %. The result could be attributed to the small Pt nanoparticles with high dispersion on Al_2O_3 prepared by microemulsion method.

Keywords: Microemulsion, Pt/Al_2O_3, Selective hydrogenation, *p*-Chloronitrobenzene.

INTRODUCTION

Chloranilines (CANs) are important intermediates for synthesis of organic fine chemicals, such as dyes, drugs, herbicides and pesticides[1,2]. Chloranilines are mainly produced from the selective hydrogenation of the corresponding chloronitrobenzenes (CNBs) over heterogeneous metal catalysts. The metals such as Ag[3], Ni[4], Pt[5-8], Rh[9], Ru[10] and Pd[11] have been normally chosen as active compositions for chloronitrobenzenes hydrogenation catalysts. Among them, Pt-based catalysts have received much attention owing to the minimized dehalogenation and the fast nitro-group reduction in chloronitrobenzenes hydrogenation[6-8].

In general, high catalytic activity hinges on maintaining high accessible catalyst surface area. For Pt/Al_2O_3 catalyst, high accessible area can be attained by minimizing the active Pt particle size. The Pt/Al_2O_3 catalysts prepared by the reduction Pt^{4+} with BH_4^- in an aqueous solution showed a better performance in the hydrogenation of *o*-chloronitrobenzene to *o*-chloroaminobenzene[5]. However, the vigorous and exothermic reactions between Pt^{4+} and BH_4^- usually induce particle aggregation and thereby reduce the catalytic activity due to a lower active specific surface. Therefore, much attention has been paid on to explore a new approach to suppress particle aggregation and even control the particle size according to the actual need.

Microemulsion systems have been widely investigated for synthesis of highly dispersed catalysts[12,13]. Water-in-oil (w/o) microemulsion is a transparent and isotropic dispersion system with nanosized water droplets which are dispersed in a continuous oil phase and stabilized by surfactant molecules at the water/oil interface. The microemulsion is heterogeneous at molecular level, but thermodynamically stable[13]. During the synthesis of microemulsion, the reverse micelle forms nanosized droplets with an aqueous phase core, which acts as the microreactor for reactants and inhibits particle agglomeration. The advantage of using w/o microemulsion system is that the uniform shape and size of the particles can be designed effectively by simply changing the w/o microemulison composition.

In this study, Pt/Al_2O_3 catalysts with uniformly nanosized Pt particles were successfully synthesized using a water-in-oil (w/o) microemulsion of cetyltrimethylammonium bromide (CTAB)/*n*-butanol/cyclohexane/chloroplatinic acid (H_2PtCl_6) solution. Attention was paid to the catalyst preparation technique, especially the effects of the microemulsion composition and reduction condition on the catalytic properties for hydrogenation of *p*-chloronitrobenzene (*p*-CNB).

EXPERIMENTAL

Preparation of catalysts: The Pt nanoparticles were prepared by the w/o microemulsion method. A microemulsion containing H_2PtCl_6 was prepared by adding desired amount of the H_2PtCl_6 solution to the mixture of CTAB, *n*-butanol, cyclohexane. The mass ratio of *n*-butanol to CTAB is 7:3 and the mass ratio of (CTAB+*n*-butanol) to cyclohexane is 3:7. The amount of the H_2PtCl_6 solution ($H_2PtCl_6 \cdot 6H_2O$ 0.02 g/mL) is 4 wt. % of the total mass of the microemulsion. After vigorous stirring the microemulsion for 15 min, a complete transparent light yellow solution was obtained. The Pt^{4+} in the solution was reduced by dropwise addition of KBH_4 solution at 303 K and the Pt nanoparticles were formed. The resulting mixture was stirred constantly for 1 h and then added with appropriate amount of Al_2O_3 and tetrahydrofuran (THF). After filtration, the solid was washed with ethanol and dried at 373 K for 4 h. The obtained catalyst with Pt loading of 1 wt. % was denoted as Pt/Al_2O_3-ME.

For comparison, a Pt/Al_2O_3 catalyst with Pt loading of 1 wt. % was also prepared by conventional impregnation and denoted as Pt/Al_2O_3-IMP. Pre-dried Al_2O_3 was impregnated with the H_2PtCl_6 solution. The mixture was dried first at 343 K and then at 383 K overnight to obtain solid without the residual water. The Pt^{4+} was reduced by dropwise addition of KBH_4 solution under vigorous stirring. After filtration, the solid was washed with distilled water and then dried at 373 K for 4 h to obtain the Pt/Al_2O_3 catalyst.

Catalyst characterization: A Tecnai G2 F20 unit was used in transmission electron microscopy (TEM). Each specimen was prepared by placing a drop of the colloid dispersion upon a copper covered with a perforated carbon film and then evaporating the solvent.

Catalytic tests: A typical hydrogenation procedure was conducted as follows: 0.05 g of a catalyst and 5 mL of ethanol were mixed in a 50 mL three-necked flask, which was closed with a silicon rubber cap and connected to a hydrogen gas burette. The catalyst was activated under hydrogen with magnetic stirring at 303 K for 0.5 h. After that, 5 mL of ethanolic solution of *p*-chloronitrobenzene (2×10^{-3} mol *p*-chloronitrobenzene) was injected into the reactor. Catalytic hydrogenation of *p*-chloronitrobenzene was carried out at 303 K and atmospheric pressure for 1 h. The liquid product was analyzed by a gas chromatograph (GC) equipped with a flame ionization detector (FID). The liquid products were identified by an Agilent GC/mass spectrometer (MS) 5890.

RESULTS AND DISCUSSION

The morphology of Pt/Al_2O_3-ME and Pt/Al_2O_3-IMP was studied by TEM and typical photographs are shown in Fig. 1. The needle-like Al_2O_3 was distributed randomly on Pt/Al_2O_3-ME and the Pt particles were well dispersed with a narrow size distribution (Fig. 1a). The Pt particle size was about 3 nm. In comparison with Pt/Al_2O_3-ME, however, the Pt particles on Pt/Al_2O_3-IMP aggregated to irregular shapes and large size (3-11 nm). It is well known that KBH_4 is a very strong reducing agent. During the preparation of Pt/Al_2O_3-IMP, the reduction rate of Pt^{4+} was too high and caused aggregation of Pt particles in the aqueous solution[14,15]. During the preparation of Pt/Al_2O_3-ME, the Pt nanoparticles were formed in the reverse microemulsion. Therefore, the microemulsion composition is a key factor that affects the catalytic performance.

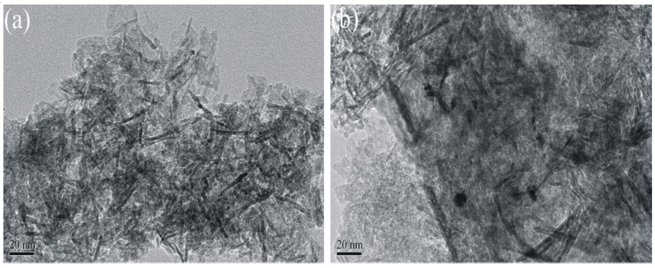

Fig. 1. TEM images of (a) Pt/Al_2O_3-ME and (b)Pt/Al_2O_3-IMP

Fig. 2 shows the effect of mass ratio of *n*-butanol to CTAB on the hydrogenation of *p*-chloronitrobenzene over Pt/Al_2O_3-ME. The selectivity to *p*-CAN is higher than 94.1 % for all the range tested, showing the mass ratio of *n*-butanol to CTAB has little effect on the selectivity to *p*-CAN within this range. However, the conversion of *p*-chloronitrobenzene changed in a way different from the selectivity to *p*-CAN. The conversion of *p*-chloronitrobenzene increased with increasing mass ratio of *n*-butanol to CTAB, reached maximum of 73.5 % at 6:4 and then decreased rapidly. In a w/o microemulsion synthesis, the droplets are dispersed in a continuous oil phase and surrounded by an interfacial film of surfactant (CTAB) and cosurfactant (*n*-butanol). The role of *n*-butanol is to adjust the spontaneous curvature of the film to a negative value (curvature towards the aqueous domain), which cannot be attained by CTAB. Therefore, it is understandable that an increase in *p*-chloronitrobenzene conversion was observed by increasing mass ratio of *n*-butanol to CTAB at first. However, excessive *n*-butanol would dilute CTAB in the interface and therefore increase the lability of the interface. And the greater mobility of the interface favored the formation of larger Pt particles, which would lead to lower catalytic activity.

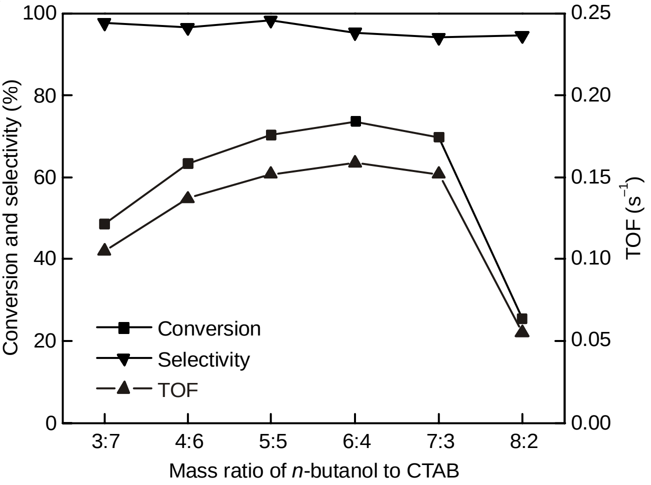

Fig. 2. Effect of mass ratio of *n*-butanol to CTAB on catalytic performance

Fig. 3 shows the effect of mass ratio of (CTAB + *n*-butanol) to cyclohexane on the hydrogenation of *p*-chloronitro-benzene over Pt/Al_2O_3-ME. The variation of the mass ratio did not significantly change the selectivity to *p*-CAN. On the other hand, the catalytic activity was affected by this mass ratio and was maximized at the mass ratio of 4:6.

The relatively low mass ratio of (CTAB + *n*-butanol) to cyclohexane would reduce the interface rigidity, which would

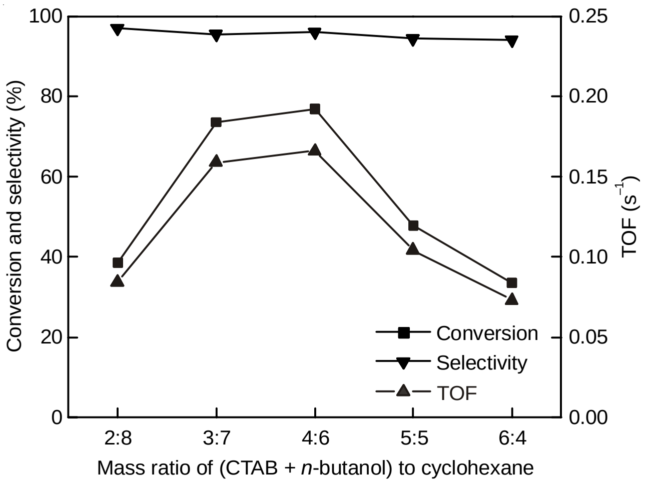

Fig. 3. Effect of mass ratio of (CTAB+*n*-butanol) to cyclohexane on catalytic performance

lead to the formation of larger microemulsion droplets and larger Pt particles. However, excessive high mass ratio of (CTAB + *n*-butanol) to cyclohexane would lead to an increase in the interface rigidity and confine the contact between the reducing agent (KBH_4) and the precursor (H_2PtCl_6), which is unfavorable for the reduction of Pt^{4+}.

Fig. 4 shows the effect of H_2PtCl_6 content on the hydrogenation of *p*-chloronitrobenzene over Pt/Al_2O_3-ME. The conversion of *p*-chloronitrobenzene increased first and then decreased with the increasing H_2PtCl_6 solution content. The conversion of *p*-chloronitrobenzene reached maximum when the H_2PtCl_6 solution content was 4 wt. %. With increasing the H_2PtCl_6 solution content, the water content in microemulsion increased, this would cause the permeation channel for KBH_4 widened which was favorable for the reduction of Pt^{4+}. However, higher water content would reduce the rigidity of the surfactant protective layer and promote particles aggregation upon collision. Moreover, the size of the reverse micelles would be correspondingly increased[16].

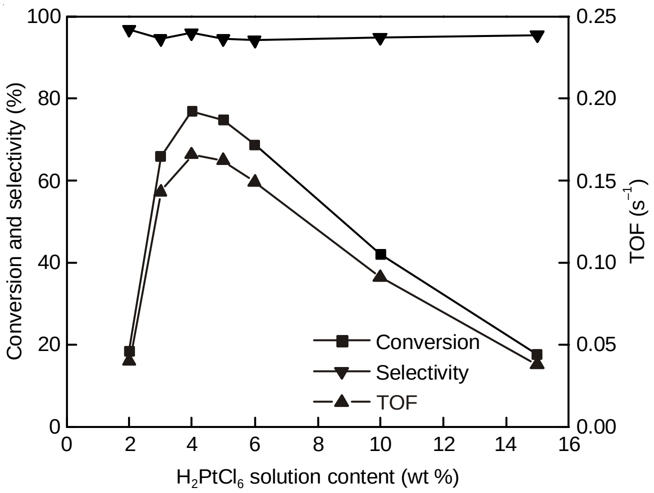

Fig. 4. Effect of H_2PtCl_6 solution content on catalytic performance

Besides the microemulsion composition, the reduction conditions such as molar ratio of KBH_4 to H_2PtCl_6 and temperature are also important in synthesis Pt particles by microemulsion since they influence the formation and growth of Pt particles.

Fig. 5 shows the effect of molar ratio of KBH_4 to H_2PtCl_6 on the hydrogenation of *p*-chloronitrobenzene over Pt/Al_2O_3-ME. Clearly, the optimal molar ratio of KBH_4 to H_2PtCl_6 was 50:1. At a lower KBH_4 to H_2PtCl_6 molar ratio of 10:1, the reduction rate of Pt^{4+} was slow and only a small amount of nuclei were formed at the early period. The Pt atoms formed at the latter period were mainly used to collide with the nuclei already formed, rather than in the formation of new nuclei and therefore led to the formation of larger particles. With increasing the molar ratio of KBH_4 to H_2PtCl_6, the enhanced reduction rate would promote the generation of more nuclei and smaller Pt particles. However, with excessive large KBH_4 to H_2PtCl_6 molar ratio, the reduction rate of Pt^{4+} was much higher than the nucleation rate and almost all Pt^{4+} was reduced to atoms before nuclei could be formed. On this occasion, the nucleation rate was not further raised with the increase of KBH_4 to H_2PtCl_6 molar ratio. Therefore, the grain growth rate was accelerated and eventually led to the formation of large particles.

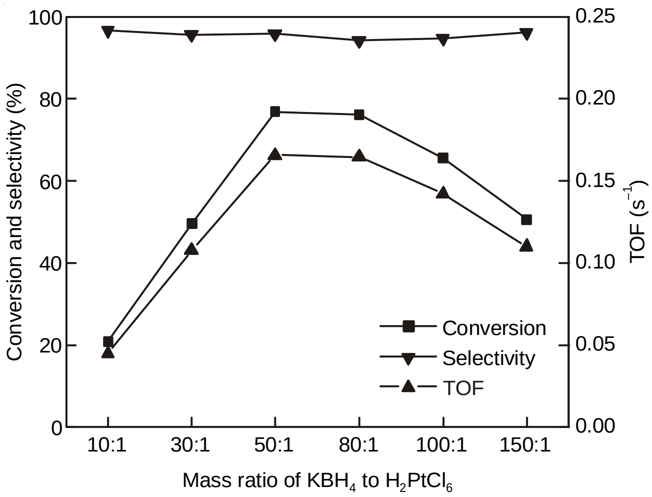

Fig. 5. Effect of molar ratio of KBH_4 to H_2PtCl_6 on catalytic performance

The reduction temperature varied from 283 to 313 K while other parameters were kept constant. Fig. 6 shows that the conversion of *p*-chloronitrobenzene was increased with increasing temperature and maximized to 76.8 % at 303 K. With further increase in temperature, the catalytic activity decreased. Lower temperature favored nucleus growth and the formation of larger Pt particles, while higher temperature generally facilitated the formation of nuclei and finer Pt particles. However, higher temperature might disturb the microemulsion system, preventing the formation of Pt particles. In addition, excessive higher temperature could accelerate Brownian motion, which would result in collision between particles and reunion of particles.

For comparison, hydrogenation of p-chloronitrobenzene over Pt/Al_2O_3-IMP was also performed under the same conditions as that for Pt/Al_2O_3-ME. The results are also listed in Table-1. The Pt/Al_2O_3-ME shows a higher catalytic activity (TOF 0.166 s^{-1}) than the Pt/Al_2O_3-IMP (TOF 0.065 s^{-1}). The conversion of *p*-chloronitrobenzene with Pt/Al_2O_3-ME was

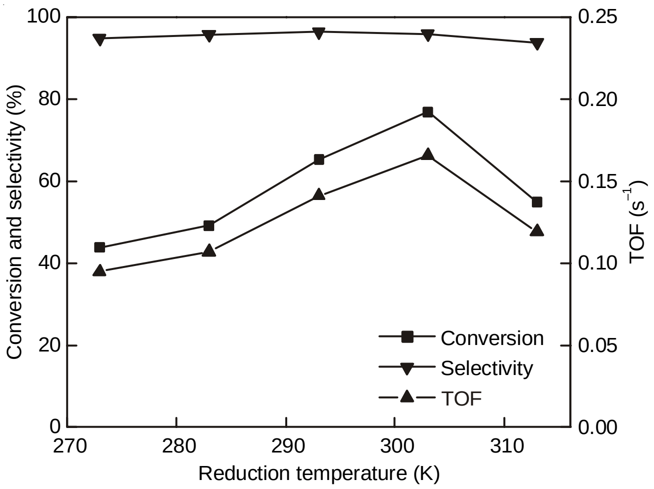

Fig. 6. Effect of reduction temperature on catalytic performance

TABLE-1
HYDROGENATION OF *p*-CHLORONITROBENZENE OVER Pt/Al_2O_3-ME AND Pt/Al_2O_3-IMP

Catalyst	TOF[a]	Con (%)	Sel	
			p-CNB	Others
Pt/Al_2O_3-ME	0.166	76.8	95.9	4.1
Pt/Al_2O_3-IMP	0.065	30.1	92.8	7.2

[a] *p*-CNB (*p*-chloronitrobenzene) mole consumption per mole Pt and per second, $mol_{p\text{-CNB}}/(mol_{Pt}\ s)$

76.8 %, which increased by 46.7 % compared with Pt/Al_2O_3-IMP (*p*-chloronitrobenzene conversion of 30.1 %). It is well known that the morphology of nanoparticles directly influences the catalytic properties of nanocatalysts[17]. A narrow particle size distribution with high dispersion was achieved by the w/o microemulsion method. Moreover, the average diameters of the Pt nanoparticles in the Pt/Al_2O_3-ME are smaller than that of Pt/Al_2O_3-IMP. The highly dispersed and small Pt nanoparticles on Al_2O_3 prepared by microemulsion method could be responsible for its higher *p*-chloronitrobenzene hydrogenation activity.

Conclusion

The synthesis of Pt/Al_2O_3 catalysts with nanosized Pt particles by reduction of H_2PtCl_6 with KBH_4 in the w/o microemulsion of CTAB/*n*-butanol/cyclohexane/H_2PtCl_6 solution was studied. The preparation parameters of the catalyst, including the microemulsion composition and reduction condition, were discussed. The optimum preparation conditions of Pt/Al_2O_3 catalyst were as follows: *n*-butanol to CTAB mass ratio of 6:4, (CTAB + *n*-butanol) to cyclohexane mass ratio of 4:6, H_2PtCl_6 aqueous solution content of 4 wt. %, KBH_4 to H_2PtCl_6 molar ratio of 50:1, reduction temperature of 303 K. Compared with the impregnation-derived Pt/Al_2O_3-IMP catalyst (*p*-chloronitrobenzene conversion of 30.1 %), the microemulsion-derived Pt/Al_2O_3-ME catalyst showed much higher catalytic activity for *p*-chloronitrobenzene hydrogenation (*p*-chloronitrobenzene conversion of 76.8 %), which improved by 46.7 %. Higher activity of the microemulsion-derived Pt/Al_2O_3 catalyst could be attributed to the narrow particle size distribution with high dispersion and smaller particle size.

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