

Two-dimensional Thermal-stable Catalytic System: Encapsulation of Nanocatalysts in Mesoporous Silica Nanosheets Through Graphene Oxides-mediated Strategy

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Abstract Herein, two-dimensional (2D) sandwich-like structures in which noble metal or metal oxide nanocatalysts were encapsulated in two layers mesoporous silica oxide ($m\text{SiO}_2@M(\text{MO})@m\text{SiO}_2$) nanosheets were synthesized by using graphene oxide as sacrificial template. As a model catalyst, Pt nanocatalysts encaged in mesoporous silica sheets can be stable under the calcination temperature as high as 650 °C. Moreover, the length of mesoporous transfer channel of these catalysts can be reduced to several ten nanometres, and this two-side mesoporous structure provides more channels access to the Pt core. Therefore, it exhibits higher catalytic activity for hydrogenation of 4-NP compared with one-side mesoporous structure catalyst (such as $\text{SiO}_2@Pt@m\text{SiO}_2$ sphere). These results suggest that these 2D $m\text{SiO}_2@M(\text{MO})@m\text{SiO}_2$ nanosheets are robust nanocatalytic systems with high activity, thermal and cycling stability and have great potential applications in catalytic reactions.

Keywords: Nanocatalysts, Mesoporous silica, Graphene, Nanosheets, Thermal-stable.

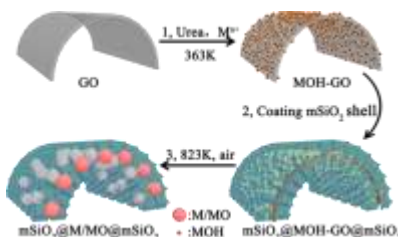
1. Introduction

Recently, nanocatalysts in heterogeneous catalysis have attracted much attention due to the improved catalytic activities.(Bell 2003; Serp and Philippot 2013) However, in practical applications, especially under harsh reaction conditions such as high temperatures and long-term operation, nanocatalysts can easily aggregate or sinter because of their high surface energy and increased mobility on supports, leading to the significant decrease of catalytic activity(Cao, Lu et al. 2010; De Rogatis, Cargnello et al. 2010; Wang, Liu et al. 2013) (Kim, Jeon et al. 2013).

Herein, we report a novel synthetic strategy for a robust and efficient nanocomposite catalysts in which metal or metal oxide nanocatalysts are sandwiched between two thin-layer $m\text{SiO}_2$ nanosheets ($m\text{SiO}_2@M(\text{MO})@m\text{SiO}_2$), utilizing graphene oxide (GO) as 2D sacrificial template. This new type of sandwich-like nanocomposite catalyst is expected to be able to reconcile the above-mentioned apparent contradiction between catalytic activity and recycling of nanocatalysts very well. First, nanocatalysts are isolated by the mesopores in thermal-stable $m\text{SiO}_2$ nanosheets so that the aggregation or sintering of nanocatalysts could be suppressed under harsh reaction conditions such as high temperatures. Secondly, the thickness of one layer of $m\text{SiO}_2$ nanosheet can be easily controlled within ~15 nm which is much shorter than the channel length of big-sized classic mesoporous materials such as MCM-41 and SBA-15, and beneficial to the diffusion of catalytic species for fast reaction rate. Thirdly, one single-layer of nanocatalysts is sandwiched between two layers of $m\text{SiO}_2$ nanosheets so that the pore channels of $m\text{SiO}_2$ can hardly be blocked by the nanocatalysts. Fourthly, in our mesoporous sandwich-like structure, more surface atoms of nanocatalysts can be exposed and enter into catalytic reactions for improved catalytic activities like 0D single-core/mesoporous shell composite catalysts. Lastly, the size of $m\text{SiO}_2@M(\text{MO})@m\text{SiO}_2$ nanosheets is in micrometer and submicrometer scale which is very advantageous for their separation and recovery.

2. Results and Discussion

Our strategy for the preparation of $mSiO_2@M(MO)@mSiO_2$ nanosheet catalysts is illustrated in Scheme 1. First, a precursor (MOH) for metal or metal oxide nanoparticles was deposited on GO nanosheets by a commonly used deposition-precipitation method. (Van Der Lee, Van Dillen et al. 2005; Fang, Chaudhari et al. 2009) Then, a $mSiO_2$ sheath was coated on the surface of MOH-GO composite by the hydrolysis and condensation of TEOS with CTAB as the pore-generating agent. Subsequently, the $mSiO_2@MOH-GO@mSiO_2$ intermediates were heated in air to remove both CTAB and GO, meanwhile MOH nanoparticles were converted to metal or metal oxide nanoparticles, resulting in the formation of $mSiO_2@M(MO)@mSiO_2$ nanosheets.



Scheme 1. Preparation of $mSiO_2@M(MO)@mSiO_2$ nanosheets.

As shown in Figure 1a, $mSiO_2@Pt@mSiO_2$ is a typical sheet-like nanostructure (Fig. 2a) similar to that of GO, with lateral dimensions ranging from several hundred nanometers to a few micrometers, and a thickness of ~ 30 nm. The larger sizes of $mSiO_2@Pt@mSiO_2$ nanosheets are more advantageous for the separation and recovery of catalysts as compared with 0D single-nanoparticle catalysts or 0D single-core/shell nanocatalysts (Joo, Park et al. 2009). More detailed structure information can be found from the TEM image of $mSiO_2@Pt@mSiO_2$ (Figure 1b). It can be clearly seen that Pt nanoparticles with a diameter of ca. 5 nm are well encapsulated between two layers of $mSiO_2$ nanosheets with a pore size of ~ 3 nm without any aggregation. Figure 1c-e show that the size and shape of Pt nanoparticles keep almost unchanged with temperature increasing from 250 to 650 $^{\circ}C$. This is a sharp contrast to Pt nanoparticles loaded on the surface of supports such as SiO_2 and carbonaceous materials which can be easily coalesced at temperatures above 350 $^{\circ}C$ (Sun, Zhang et al. 2011). These results demonstrate that the $mSiO_2$ shell in $mSiO_2@Pt@mSiO_2$ plays very key roles in preventing the aggregation and coalescence of Pt nanoparticles even at very high temperatures, which is vitally important for their practical applications in catalytic reactions.

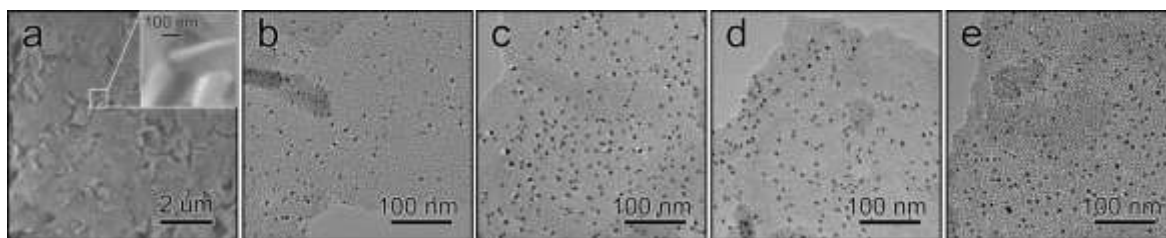


Figure 1 (a) SEM images (inset is at high magnification), (b) TEM image of $mSiO_2@Pt@mSiO_2$, and TEM images of $mSiO_2@Pt@mSiO_2$ obtained by calcination at different temperatures in air: (c) 250 $^{\circ}C$, (d) 450 $^{\circ}C$, (e) 650 $^{\circ}C$.

Due to the two-side mesoporous structure of our $mSiO_2@Pt@mSiO_2$ sheet-like nanostructure, the catalytic performance would be better than one-side mesoporous structure such as $SiO_2@Pt@mSiO_2$ spheres. Here we investigated the catalytic performance of our Pt based catalyst by employing the hydrogenation of 4-Nitrophenol as the model reaction (Figure 2a). As shown in Figure 2b, the 100% conversion time of $mSiO_2@Pt@mSiO_2$ nanosheets and $SiO_2@Pt@mSiO_2$ spheres are 80 min and 120 min, respectively. $mSiO_2@Pt@mSiO_2$ nanosheets showed a better performance than the

SiO₂@Pt@mSiO₂ nanospheres, which could be ascribed to the channels on both sides of mSiO₂ shells since more surface active sites were exposed and contributed to the reaction. Additionally, cycle stability is another essential factor for a useful catalyst in application, especially for expensive noble metal catalysts. Commercial platinum black (C-Pt, Etek) gave the best catalytic activity at the first and second catalytic run because of the smaller sizes of Pt nanoparticles (2-3 nm), but a rapid deactivation of C-Pt was observed since the third run, while the conversion rate dropped to as low as 20% after five catalysis cycles (Figure 2c). Such a dramatic decrease, which corresponds to previous reports, was probably due to the aggregation of Pt nanoparticles as confirmed by TEM (Meier, Galeano et al. 2012). In contrast, the catalytic conversion rate of mSiO₂@Pt@mSiO₂ nanosheet retained 94% after five cycles, only a very slight decrease was found due probably to the irreversible adsorption.

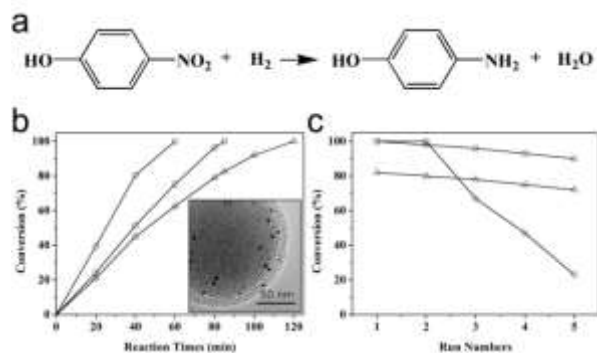


Figure 2 (a) Hydrogenation reaction of nitrophenol; (b) hydrogenation catalytic conversion rate versus time (inset is the TEM image of SiO₂@Pt@mSiO₂ sphere); (c) Catalyst cycle test. The reaction time was 80 min, circle: C-Pt(Etek), square: mSiO₂@Pt@mSiO₂ nanosheet, triangle: SiO₂@Pt@mSiO₂ sphere.

3. Conclusion

In summary, we demonstrate a facile strategy for the preparation of noble metal or metal oxide nanoparticles encapsulated in mesoporous SiO₂ nanosheets. The as-prepared mSiO₂@Pt@mSiO₂ shows not only a good thermal stability, but also enhanced catalytic activity for 4-NP hydrogenation caused by its two-side mesoporous structures. Moreover, the large size of nanosheets makes it easily separated and redispersed. Furthermore, the method can be extended to other nanoparticles such as Pd and PdO. This work could open a new window for the construction of 2D composite catalysts with high activity, thermal and cycling stability.

Acknowledgements

Support from the Ministry of Science and Technology of China (2013CB834505, 2014CB239402), the National Natural Science Foundation of China (51322213, 91127005, 51172245, 20901081), Knowledge Innovation Project of the Chinese Academy of Sciences (KGCX2-EW-311-3), and the 100 Talents Program of the Chinese Academy of Sciences is gratefully acknowledged.

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