A stepwise loading method to magnetically responsive Pt-Fe$_3$O$_4$/MCNT catalysts for selective hydrogenation of 3-methylcrotonaldehyde

Shaofei Song, Jianyan Yu, Qiang Xiao*, Xiangrong Ye*, Yijun Zhong and Weidong Zhu

Abstract
Pt-loaded multi-walled carbon nanotubes (Pt/MCNTs) and magnetically responsive Pt-Fe$_3$O$_4$/MCNT catalysts were prepared by a stepwise loading of preformed Pt and Fe$_3$O$_4$ nanoparticles onto multi-walled carbon nanotubes (MCNTs). The structure, composition, and magnetism of the catalysts were characterized by X-ray diffraction (XRD), TEM, H$_2$-O$_2$ titration, inductively coupling plasma-atomic emission spectroscopy (ICP-AES), and superconducting quantum interference device (SQUID) techniques. Ascribed to the well-controlled particle size in the preformed Pt colloids, Pt particles in the consequent Pt/MCNT and Pt-Fe$_3$O$_4$/MCNT catalysts are of high uniformity and dispersion. The prepared Pt catalysts show an excellent catalytic performance in the liquid phase hydrogenation of 3-methylcrotonaldehyde, one of typical $\alpha,\beta$-unsaturated aldehydes. A very high selectivity to 3-methylcrotonalcohol of 98% at a conversion of about 80% was available on the magnetic Pt-Fe$_3$O$_4$/MCNT catalyst. The magnetic catalyst, with good superparamagnetism, can be easily recovered from the liquid phase system under the external magnetic field. Moreover, both the Pt/MCNT and magnetic Pt-Fe$_3$O$_4$/MCNT catalysts show a good recyclability, confirmed by five cycles of reusage.

Keywords: Magnetic; Platinum; Hydrogenation; Unsaturated aldehyde

Background
Selective hydrogenation of $\alpha,\beta$-unsaturated aldehyde is an important reaction in industry for the synthesis of fine chemicals. As illustrated in Figure 1, the hydrogenation of 3-methylcrotonaldehyde (3-MeCal), one of typical $\alpha,\beta$-unsaturated aldehydes, leads to 3-methylcrotonalcohol (3-MeCal), 3-methylbutyraldehyde (3-MeBal), and 3-methyl-1-butanol (3-MeBol) as the main products. The half-hydrogenated C = O product 3-MeCol as an intermediate finds wide application in the production of perfumes and pesticides. However, the hydrogenation of the C = C bond is more favorable based on both thermodynamic and kinetic considerations [1]. Additionally, due to the very close boiling points (3-MeBol: approximately 131°C and 3-MeCal: approximately 133°C), it is rather difficult to separate the fully hydrogenated product 3-MeBol from the starting material 3-MeCal by distillation. Consequently, the selective hydrogenation of 3-MeCal into 3-MeCol is highly desirable yet of a great challenge [2,3].

Metallic catalysts, e.g., Pt, Pd, Ru, Cu, Co, and Au, have been intensively studied in the selective hydrogenation of $\alpha,\beta$-unsaturated aldehydes [4-10]. Among the most active and selective catalysts, Pt has been retained in the majority of the published work for the selective hydrogenation of $\alpha,\beta$-unsaturated aldehydes [11-14]. Its selectivity depends critically on the particle size, i.e., the larger the particle size, the higher the selectivity to the unsaturated alcohol. As a result, heterogeneity in size distribution would induce the descent of the overall selectivity. It is therefore highly desirable to have a narrow-sized distribution of Pt nanoparticles which exhibits decent selectivity in addition to high conversion. Loading a preprepared Pt colloid on support has been practiced to prepare supported Pt particles with uniform size [19]. However, organic stabilizers are often used in the preparation of colloidal Pt solution. After the Pt particle deposition on supports, the stabilizer...
has to be removed typically by heat treatment, during which, unfortunately, the size of Pt particles varies, depending on the temperature and time applied in heat treatment.

On the other hand, the filtration-based recovery of expensive Pt catalyst from the liquid reaction system is rather time- and energy-consuming. The introduction of magnetically responsive substances to the catalyst could endow the catalyst magnetic properties, which makes it easy to recover the catalyst under a magnetic field and improves the separation efficiency [20-24]. Although magnetically responsive catalyst has been intensively reported [25-31], scarce work has been dedicated to their application in the selective hydrogenation of unsaturated aldehydes [32].

In this paper, we adopt a stepwise loading approach using multi-walled carbon nanotube (MCNT) as a model support to prepare Pt-loaded multi-walled carbon nanotube (Pt/MCNT) and magnetically responsive Pt-Fe$_3$O$_4$/MCNT catalysts. As illustrated in Figure 2, the uniform-sized Pt and Fe$_3$O$_4$ nanoparticles were beforehand prepared by a two-phase liquid-liquid method and a simple organic-phase method, respectively. Then the Fe$_3$O$_4$ and Pt nanoparticles were successively dispersed on MCNT. Ascribed to the high uniformity in the size of Pt and Fe$_3$O$_4$ nanoparticles, a good performance in the selective hydrogenation of 3-MeCal in terms of selectivity, recovery, and reusability is highly anticipated.

## Methods

### Catalyst preparation

#### Pt/MCNT

The Pt nanoparticles were prepared by a two-phase liquid-liquid method (for more details, see Additional file 1). The as-made Pt nanoparticles were dispersed in toluene (15 mL) and then mixed with an appropriate aliquot of MCNT. After ultrasonic treatment for 1 h, the mixture was magnetically stirred overnight. Finally, Pt/MCNT catalyst was recovered by filtration and dried at 80°C overnight. The Pt/MCNT catalysts are referred to as xPt/MCNT, where x is the stoichiometric loading in weight percent.

#### Pt-Fe$_3$O$_4$/MCNT

Fe$_3$O$_4$ nanoparticles were prepared by a simple organic-phase synthesis (for more details, see Additional file 1) [33,34]. The prepared Fe$_3$O$_4$ nanoparticles were redispersed in hexane in the presence of oleic acid and oleylamine and mixed with an appropriate aliquot of MCNT. The mixture was ultrasonicated for 1 h and stirred overnight. Then the magnetic composites were recovered by filtration and dried at 100°C and referred to as yFe$_3$O$_4$/MCNT, where y is the stoichiometric loading in weight percent. The as-made Pt nanoparticles were redispersed in toluene (15 mL) and then the as-made Fe$_3$O$_4$/MCNT magnetic composite was added. After ultrasonic treatment for 1 h and magnetically stirred overnight, the mixture was filtered and dried at 80°C overnight to obtain zPt-yFe$_3$O$_4$/MCNT magnetic catalysts. Here, z is the stoichiometric loading in weight percent based on MCNT.

### Catalyst characterization

X-ray diffraction (XRD) patterns were recorded on a Philips PW3040/60 diffractometer (Philips Analytical, Almelo, Netherlands) using CuK$_\alpha$ radiation ($\lambda$ = 1.54 Å). The scans were recorded in the 2$\theta$ range between 10° and 80° with a step width of 0.03°. Transmission electron microscopy (TEM) observations were carried out on a 2100 JEOL TEM (JEOL Ltd., Akishima, Tokyo, Japan) working at 200 kV. The sample was diluted in ethanol to give a 1:5 volume ratio and sonicated for 10 min. The ethanol slurry was then dripped onto a Cu grid covered with a holey film of carbon. H$_2$-O$_2$ titration measurements...
were performed on a Micromeritics AutoChem II chemisorption analyzer (Micromeritics Instrument Co., Norcross, GA, USA) to determine the Pt dispersion of the Pt/MCNT catalysts. Prior to the measurement, the catalyst was preheated in a helium flow at 373 K for 30 min and completely reduced in an Ar flow with 10 vol.% H₂ at 573 K for 1 h. The concentrations of the effluent gases were monitored by a calibrated thermal conductivity detector (TCD). Pt loading of the Pt/MCNT and Pt-Fe₃O₄/MCNT catalyst was determined by a Jarrell-Ash 1100 inductively coupling plasma-atomic emission spectrometer (ICP-AES, MOA Instrumentation, Inc., Levittown, PA, USA). Each sample was analyzed three times and the results were averaged. The magnetic measurements were carried out on a superconducting quantum interference device (SQUID, MPMS, Quantum Design, San Diego, CA, USA) at 27°C. About 2.5 g of sample was used in each measurement.

Hydrogenation reaction
Hydrogenation of 3-MeCal was carried out in a 50-mL Teflon-lined stainless steel autoclave equipped with a hydrogen inlet, a pressure gauge, and a thermocouple. Prior to the first reaction, the catalyst was activated in a N₂ flow at 300°C for 1 h. The catalyst (0.1 g), 3-MeCal (2.0 mL), deionized water (2.0 mL), and ethanol (16.0 mL) were mixed and sealed into the autoclave under vigorous magnetic stirring at a speed of 960 rpm. For the sake of safety, N₂ was firstly charged to replace the air, and subsequently, H₂ was charged several times. Afterwards, the autoclave was heated up to 80°C. The reaction was started by raising H₂ pressure up to 1.4 MPa. The reaction solution was periodically sampled and analyzed by a gas chromatography Shimadzu GC-2014 (Shimadzu, Kyoto, Japan) equipped with an FID detector and a DB-5 capillary column. As for the recovery of Pt-Fe₃O₄/MCNT, a magnet with a magnetic field strength of 10.5 to 11.0 kOe was put near the Teflon container, driving the magnetic catalyst to be attached to the side with the magnet. Then, the liquid phase was poured out. The catalyst was washed with ethanol twice and used for a next reaction without activation.

Results and discussion
Pt/MCNT
A two-phase (water-toluene) reduction method was adopted to prepare uniform-sized Pt colloids with TOAB and oleylamine as stabilizers. Figure 3A shows the TEM image of the as-obtained Pt colloids, suggesting the monodispersion and good uniformity of the Pt nanoparticles. The corresponding histogram obtained from the TEM image indicates a narrow Pt particle size distribution ranging from 1.5 to 3.5 nm. The weighted average particle size is determined to be 2.6 nm (see Additional file 1: Equation 1). Pt/MCNT catalysts with different Pt loadings were prepared by direct loading the Pt particle colloids on MCNTs followed by an identical activation procedure. TEM images show that Pt nanoparticles are well dispersed on the outer surface of MCNTs without altering the particle size (Figure 3B,C,D).

The XRD patterns of the Pt/MCNT catalysts are presented in Figure 4 alongside the pristine MCNT used as a comparison. As shown in Figure 4(a), the pattern for MCNT exhibits typical diffraction peaks at 25.9°, 43.2°, and 53.9°, which can be assigned to diffraction
from the (002), (100), and (004) planes, in agreement with those for MCNTs [35,36]. Besides the peaks assigned to MCNT phase, a diffraction peak of Pt (111) plane is observed for the Pt/MCNT catalysts. With the increase of Pt loadings, the intensity of the Pt (111) peak increases accordingly.

The as-prepared Pt/MCNT catalysts exhibit good performance in the hydrogenation (see Additional file 1: Figure S1). On the three catalysts, the molar fraction of 3-MeCol in the reaction system linearly increases with the reaction going on, and more than 95% selectivity to 3-MeCol can be achieved at the initial reaction period. The initial reaction rate increases with increasing of the Pt loadings. Selectivities higher than 92% are always available even at the conversions more than 95%.

Initial turn-over frequencies (TOFs) and dispersions of the Pt/MCNT catalysts are reported in Table 1. The as-prepared Pt/MCNT catalysts show almost the same Pt particle sizes determined by either the TEM technique or the H$_2$-O$_2$ titration. The calculated initial TOFs show approximately the same values for the three catalysts, accounting for the similar activity of the Pt particles on Pt/MCNT catalysts whatever the Pt loadings. The similar TOF values indicate that the Pt particles maintain their original uniform sizes during the preparation process.

The catalyst was recovered through filtration after reaction, washed with ethanol twice, and then used for the next reaction without other treatments. The 3Pt/MCNT catalyst, as an example, maintained its original activity and selectivity during the five cycles (Additional file 1: Table S1). The Pt loading was monitored by inductively coupling plasma (ICP), showing that no leaching of Pt occurs.

### Magnetic Pt-Fe$_3$O$_4$/MCNT catalysts

The magnetic phase of Fe$_3$O$_4$ was introduced to the catalyst by the stepwise loading method to prepare the magnetic responsive catalyst. Easy catalyst recovery from

---

**Table 1 Pt particle data of the Pt/MCNT catalysts and TOF values in the hydrogenation of 3-methylcrotonaldehyde (3-MeCal)**

| Samples       | Pt loading/ wt.% | Pt particle size (nm) | Dispersion (%) | initial TOF (s$^{-1}$) |
|---------------|------------------|-----------------------|----------------|------------------------|
| 0.5Pt/MCNT    | 0.5              | 2.6                   | 2.7            | 41.6                   | 1.8                     |
| 3Pt/MCNT      | 2.9              | 2.6                   | 2.8            | 40.5                   | 1.5                     |
| 5Pt/MCNT      | 4.8              | 2.6                   | 2.9            | 39.4                   | 1.3                     |

$^a$The average value determined by TEM observations; $^b$determined by the H$_2$-O$_2$ titration; $^c$calculated from the data in Additional file 1: Figure S1.
the reaction system is anticipated under the magnetic field.

Diffraction peaks at 18.3°, 30.1°, 35.4°, 53.6°, 56.9°, and 62.5°, which can be attributed to (111), (220), (311), (422), (511), and (440) planes of \( \text{Fe}_3\text{O}_4 \) phase, respectively, can be observed for the \( \text{Fe}_3\text{O}_4/\text{MCNT} \) composite, indicating that the \( \text{Fe}_3\text{O}_4 \) phase has been successfully supported on MCNTs (Figure 5). Additionally, diffraction peak assigned to Pt (111) also appears besides the peaks attributed to \( \text{Fe}_3\text{O}_4 \) and MCNT (Figure 5).

The TEM image of the magnetic composite (5\( \text{Fe}_3\text{O}_4/\text{MCNT} \)) reveals that \( \text{Fe}_3\text{O}_4 \) nanoparticles with diameter of about 2 to 4 nm are well dispersed on the outer surface of MCNTs (Figure 6A). While on the 3Pt-5\( \text{Fe}_3\text{O}_4/\text{MCNT} \) catalyst, some dark spots attributed to the Pt nanoparticles appear besides the grey spots of \( \text{Fe}_3\text{O}_4 \) nanoparticles (Figure 6B). From the magnified image (Figure 6C), one can see the highly dispersed Pt and \( \text{Fe}_3\text{O}_4 \) nanoparticles separately located on the surface. The high resolution TEM image shows that the nanoparticles are single crystalline, confirmed by atomic lattice fringes (Figure 6C, inset). For a grey spot, the distance between two planes is about 0.26 nm, in agreement with \( \text{Fe}_3\text{O}_4 \) (311) plane. While, for a dark spot, lattice spacing is about 0.23 nm, which can be attributed to the Pt (111) plane. Additionally, from the energy-dispersive X-ray spectroscopy (EDS), characteristic X-rays assigned to Fe and Pt elements can be observed, further confirming that Pt and \( \text{Fe}_3\text{O}_4 \) nanoparticles have been successfully supported on MCNT (Figure 6D).

The magnetic properties of \( \text{Fe}_3\text{O}_4/\text{MCNT} \) magnetic composite and Pt-\( \text{Fe}_3\text{O}_4/\text{MCNT} \) magnetic catalysts were investigated by a magnetic property measurement system (MPMS) at room temperature. As shown in Figure 7, all the hysteresis loops go through the origin. Almost no remanence exists when the external magnetic field is removed (Figure 7, inset), revealing the superparamagnetism of the samples. The superparamagnetism implies that the magnetic responsive catalysts can be well redispersed in the absence of a magnetic field. The saturated magnetization value of 5\( \text{Fe}_3\text{O}_4/\text{MCNT} \) is about 3.6 emu·g\(^{-1}\). While, for 3Pt-5\( \text{Fe}_3\text{O}_4/\text{MCNT} \), the value drops to 3.3 emu·g\(^{-1}\). Such a drop may be attributed to the decrease of the relative amount of \( \text{Fe}_3\text{O}_4 \) after loading with Pt. The saturated magnetization values of 3Pt-1\( \text{Fe}_3\text{O}_4/\text{MCNT} \), 3Pt-5\( \text{Fe}_3\text{O}_4/\text{MCNT} \), and 3Pt-10\( \text{Fe}_3\text{O}_4/\text{MCNT} \) are 0.8, 3.3, and 4.7 emu·g\(^{-1}\), respectively. The magnetization of these magnetic samples enhances with the increase of the \( \text{Fe}_3\text{O}_4 \) loading. The saturated magnetizations of \( \text{Fe}_3\text{O}_4 \) nanoparticles calculated from either \( \text{Fe}_3\text{O}_4/\text{MCNT} \) or Pt-\( \text{Fe}_3\text{O}_4/\text{MCNT} \) are 77 to 81 emu·g\(^{-1}\), in accordance with the values reported by Sun et al. [33]. Moreover, the magnetization curves coincide very well for the fresh- and five-cycles-used 3Pt-5\( \text{Fe}_3\text{O}_4/\text{MCNT} \), indicating the good stability in magnetism.

The catalysts were dispersed in ethanol (solvent of hydrogenation) and formed black suspensions. After the catalysts were put in the external magnetic field for 5 min, they were attracted close to the side near the reaction system.
the magnet and thus separated from the solvent. For 3Pt-1Fe3O4/MCNT, the separation is inefficient and part of the catalyst sinks to the bottom. By contrast, the magnetism of the 3Pt-5Fe3O4/MCNT catalyst is strong enough to be separated completely from the solution with the help of an external magnetic field (Figure 8 and Additional file 2).

The selective hydrogenation of 3-MeCal was performed over the prepared magnetic catalysts, and the results are collected in Table 2. The hydrogenation over the bare 5Fe3O4/MCNT magnetic composite was investigated as reference and no conversion was observed, implying the inertness of sole Fe3O4 in the hydrogenation. By contrast, the 3Pt/MCNT catalyst performs good properties in the hydrogenation. The introduction of magnetic responsive phase reduces the conversion of 3-MeCal. With the increase of the Fe3O4 loading amount, the conversion on the prepared Pt-Fe3O4/MCNT decreases correspondingly, due to the decrease of the relative Pt loading. The catalytic activity was normalized by the Pt loading and expressed as specific reaction rate (SRR). The SRR values are very close for all the Pt catalysts (Table 2). On the other hand, a slight increase of selectivity to the desired product of 3-MeCol can be observed at a higher Fe3O4 loading amount. A selectivity as high as 99.3% is available on the 3Pt-10Fe3O4/MCNT at a conversion of approximately 60%

Conclusions
Pt/MCNT catalysts were prepared by loading the fore-handed Pt nanoparticles onto MCNT. Monodispersed Pt particles with high uniformity in size are available during the preparation of Pt colloids. Thus, the Pt particles on the consequent Pt/MCNT catalysts are of good uniformity with size around 2.6 nm and of high dispersion (up to 40%), resulting in an excellent catalytic performance in the liquid phase hydrogenation of 3-methylcrotonaldehyde. Subsequently, Pt-Fe3O4/MCNT magnetic catalysts were prepared by adopting the developed stepwise loading method. The prepared magnetic responsive catalysts exhibit good superparamagnetic behaviors and can be facilely separated from the liquid solvent. The hydrogenation of 3-MeCal results reveal that the magnetic catalysts show excellent hydrogenation properties, achieving a high selectivity to 3-MeCol of 98% at a conversion of more than 80%. Additionally, the magnetic responsive catalysts show a good recyclability. No decay of magnetic and catalytic properties was observed after five-cycle usage.

Additional files
Additional file 1: Experimental details, hydrogenation results, and recycling tests on the catalysts.
Additional file 2: Movie of a magnetically driven separation process of the 3Pt-5Fe3O4/MCNT catalyst from the suspension.

Competing interests
The authors declare that they have no competing interests.

Table 2 Results of the hydrogenation of 3-MeCal over Pt-Fe3O4/MCNT catalysts

| Catalysts        | Pt loading (wt.%) | Fe3O4 loading (wt.%) | Conversion (%) | Specific reaction rate (10^{-2} mol·g^{-1}·min^{-1}) | Selectivity (%)  |
|------------------|-------------------|----------------------|----------------|-----------------------------------------------------|-----------------|
| 3Pt-1Fe3O4-MCNT  | 2.9               | 1                    | 85.9           | 1.72                                                 | 97.6            |
| 3Pt/5Fe3O4-MCNT  | 2.7               | 4.3                  | 79.7           | 1.71                                                 | 98.8            |
| 3Pt/10Fe3O4-MCNT | 2.3               | 6.1                  | 59.4           | 1.50                                                 | 99.3            |

Reaction conditions: T = 80°C, t = 3 h; catalyst amount: 0.1 g; 3-MeCal dose: 2 ml; ethanol dose: 16 ml; deionized water: 2 ml; initial H2 pressure: 1.4 MPa. No H2 was fed during the reaction.
Authors’ contributions
S-FS carried out the synthesis, characterization, and catalytic evaluation of the magnetically responsive catalysts. J-YY participated in the catalytic hydrogenation on catalysts. QX conceived the study, made its design, and wrote the manuscript. X-RY conceived the idea and helped to polish the manuscript. YU and W-DZ participated in the design of the study and data analysis. All authors read and approved the final manuscript.

Acknowledgements
The financial supports by the Natural Science Foundation of China (21101139, 21371152, and 21471131) are gratefully acknowledged.

Received: 3 October 2014 Accepted: 3 December 2014

References
1. Yuan Y, Yao S, Wang M, Lou S, Yan H: Recent progress in chemoselective hydrogenation of alpha, beta-unsaturated aldehydes to unsaturated alcohol over nanomaterials. Curr Org Chem 2013, 17:900.
2. Birchem T, Pradier CM, Berthier Y, Cordier G: Reactivity of 3-methyl-crotonaldehyde on Pt(111). J Catal 1994, 146:503.
3. Semagina N, Kisi-Minsker L: Palladium nanohexagons and nanospheres in selective alkyne hydrogenation. Catal Lett 2009, 127:334.
4. Gutierrez V, Nador F, Radivoj G, Volpe MA: Highly selective copper nanoparticles for the hydrogenation of aldehydes in liquid phase. Appl Catal A Gen 2013, 464:465-470.
5. Zhao J, Xu X, Li X, Wang J: Highly selective aldehyde hydrogenation in the liquid phase. J Mol Catal A 2011, 349:202-209.
6. Bhogeswararao S, Srinivas D: Selective hydrogenation of cinnamaldehyde over Ru/C catalysts. Catal Commun 2013, 30:22.
7. Ekou T, Ekou L, Vicente A, Lafaye G, Pronier S, Especel C, Marecot P: Selective hydrogenation over Rh and Pt catalysts supported on TiO2. J Catal 2011, 276:150-157.
8. Ekou T, Ekou L, Vicente A, Lafaye G, Pronier S, Especel C, Marecot P: Selective hydrogenation over Rh and Pt catalysts supported on TiO2. J Catal 2010, 268:94-99.
9. Taniya K, Jinno H, Kishida M, Ichihashi Y, Nishiyama S: Selective hydrogenation of cinnamaldehyde over (111) preferentially oriented Pt particles supported on expanded graphite. Catal Lett 2013, 153:244-250.
10. Tian L, Zhou GB, Li ZH, Pei Y, Qiao MH, Fan KN: Gold supported on aminosilane-functionalized SBA-15 for chemoselective hydrogenation of crotonaldehyde. Acta Phys-Chim Sin 2011, 27:946.
11. Taniya K, Jinno H, Kishida M, Ichihashi Y, Nishiyama S: Preparation of Sn-modified silica-coated Pt catalysts: a new Pt-Sn bimetallic model catalyst for selective hydrogenation of crotonaldehyde. J Catal 2012, 288:94.
12. Ananthan SA, Narayanan V: Liquid-phase hydrogenation of citral over Pt/TiO2 and Pt/Fe/TiO2 catalysts. Asian J Chem 2011, 23:183.
13. Guo Z, Chen YT, Li LS, Wang XM, Haller G, Yang YH: Carbon nanotube-supported Pt-based bimetallic catalysts prepared by a microwave-assisted polyol reduction method and their catalytic applications in the selective hydrogenation. J Catal 2010, 276:314.
14. Tamura M, Tokonami K, Nakagawa Y, Tomishige K: Rapid synthesis of unsaturated alcohols under mild conditions by highly selective hydrogenation. Chem Commun 2013, 49:7034.
15. Bhattacharjee S, Dotzauer DM, Bruening ML: Selectivity as a function of nanoparticle size in the catalytic hydrogenation of unsaturated alcohols. J Am Chem Soc 2009, 131:3601.
16. Piomp AJ, Vuol H, Krause AC, de Jong KP, Bitter JH: Particle size effects for carbon nanofiber supported platinum and ruthenium catalysts for the selective hydrogenation of crotonaldehyde. Appl Catal A Gen 2008, 351:9.
17. Ramos-Fernandez EV, Ramos-Fernandez JM, Martinez-Escandell M, Sepulveda-Escribano A, Rodriguez-Reinoso F: Selective hydrogenation of crotonaldehyde over (111) preferentially oriented Pt particles supported on expanded graphite. Catal Lett 2009, 133:267.
18. English M, Jentsy A, Lerche JA: Structure sensitivity of the hydrogenation of crotonaldehyde over Pt/SiO2 and Pt/TiO2. J Catal 1997, 166:25.
19. Dalmia A, Linekken CL, Savinell RF: Synthesis of ion conducting polymer protected nanometer size platinum colloids. J Colloid Interface Sci 1998, 205:53.