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Research Article

Mesoporous Silica Supported Au Nanoparticles with Controlled Size as Efficient Heterogeneous Catalyst for Aerobic Oxidation of Alcohols

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A series of Au catalysts with different sizes were synthesized and employed on amine group functionalized ordered mesoporous silica solid supports as catalyst for the aerobic oxidation of various alcohols. The mesoporous silica of MCM-41 supported Au nanoparticles (Au-1) exhibited the smallest particle size at ~1.8 nm with superior catalytic activities owing to the confinement effect of the mesoporous channels. Au-1 catalyst is also very stable and reusable under aerobic condition. Therefore, this presented work would obviously provide us a platform for synthesizing more size-controlled metal catalysts to improve the catalytic performances.

1. Introduction

Since the pioneering work of Hutchings and Haruta [1–7], Au nanoparticles were found to be an active material in catalytic science for a number of oxidation and hydrogenation reactions. Some recent work suggests that Au nanoparticles can be efficient catalysts for the selective oxidation of alcohols, olefins, and alkanes in the presence of molecular oxygen as oxidant [1, 2, 8–15]. The unique catalytic performance of Au nanoparticles is strongly depending upon the solid supports, particle size, shape, and some other factors [1, 2, 5–7, 16–23]. In many cases, Au nanoparticles size and the solid supports have a crucial role in enhancing the catalytic activity [1, 2, 5–23]. Furthermore, the junction between Au nanoparticles and metal oxide support contributes as active site for the catalytic reactions. Normally, Au nanoparticles supported on inert metal oxide supports (e.g., silica) result in relatively poor catalytic performances due to the lack of electronic interaction between the active sites and support [24, 25]. Therefore, the development of highly active Au nanoparticles on inert supports is very important for producing an efficient Au nanocatalyst.

The size dependent catalytic performance of Au nanoparticles has been extensively studied by previous reports, where the Au nanoparticle sizes were controlled by employing expensive ligand molecules with low loading efficiency on the solid supports in order to obtain highly active Au nanoparticles. For example, Wang and coworkers reported the pyrrolidone modified silica supported small-size Au nanoparticle (~4 nm) is highly active for aerobic oxidation of alcohols [26]; Liu and coworkers found that the sub-2 nm Au nanoparticles synthesized using mercapto ligand are more active for the alkane oxidation than the larger ones [27]. More recently, Zhang and coworkers demonstrated that nanoporous ionic organic network could stabilize the small-size Au nanoparticle at ~2 nm, giving high activity in aerobic oxidation of alcohols [28].

After the discovery of M41S family [29–33], ordered mesoporous silica (OMS) has emerged as an active material

Table 1: Structural parameters and supported Au nanoparticles size on mesoporous silica with different amounts of Au loading.

Sample	Support	Pore diameter (nm)	Weight ratio of Au (%)[a]	Au nanoparticles size (nm)	
				From XRD patterns[b]	From TEM images
Au-1	MCM-41	3.0	2.4	1.4	1–3
Au-2	SBA-15	8.5	3.0	2.3	2–4
Au-3	SBA-15	8.5	9.1	4.2	5–9
Au-4	MCM-41	3.0	10.3	5.4	5–15

[a] The ratio of Au calculated from ICP.
[b] The particle grain size calculated from Scherrer's equation.

to support metal nanoparticles for catalytic applications due to their high surface area, tunable and confined mesopores, diverse morphology, and large adsorption capacity. A significant amount of work has already been devoted to Au nanoparticles supported on mesoporous silica using variety of methods, but limited attention was only paid to the catalytic activity of size-controlled Au nanoparticles on OMS for aerobic oxidations [34, 35]. In this work, we demonstrate an easy strategy to synthesize size-controlled Au nanoparticles as catalysts by using amine functionalized OMS solid support for aerobic oxidation of alcohols. MCM-41 and SBA-15 with same mesostructure (*p6mm*) but different pore sizes were considered as solid supports. The channel confinements of mesopores are utilized as template for the size-controlled synthesis of Au nanoparticles.

2. Experimental Section

2.1. Synthesis of Au Nanoparticles. MCM-41 and SBA-15 samples were prepared by using previously reported procedure. The samples were washed with the mixture of ethanol and HCl to remove the unreacted surfactants. 1 g of washed mesoporous silica was dried at 120°C under vacuum for 3 hours and then followed by the addition of 50 mL of pretreated toluene containing 1 g of DAPTS. The mixture was refluxed overnight. The experiments above were carried out using anhydrous condition to avoid any reaction between amine ligands and H_2O. Finally, the samples were collected by rotary evaporation and washed with a large quantity of ethanol for several times. 0.5 g of amine functionalized mesoporous samples was separately added into different volume of $HAuCl_4$ solution (as shown in Table 1) and then stirred overnight. The product was collected and dried under vacuum for 1 h at 100°C. Then, $NaBH_4$ was used to reduce the gold(III) into gold nanoparticles as the following: 1 g of mesoporous silica containing gold(III) was added into 40 mL of anhydrous toluene and followed by the addition of $NaBH_4$ under stirring. After 10 minutes of stirring, 10 mL of anhydrous ethanol was added into the mixture and stirred overnight. The products were collected by rotary evaporation and washed with a large quantity of ethanol and water for several times.

2.2. Characterization. X-ray diffraction (XRD) patterns were obtained with a Siemens D5005 diffractometer and Rigaku D/MAX 2550 diffractometer using CuKα radiation. The average grain size of gold nanoparticles was calculated by using half-width of the gold peak at $2\theta = 38.3^\circ$ by applying Scherrer's equation. Transmission electron microscopy (TEM) analysis was performed on a JEM-200CX electron microscope (JEOL, Japan) with an acceleration voltage of 300 kV. The nitrogen adsorption and desorption isotherms at the temperature of using liquid nitrogen were measured by using a Micromeritics ASAP Tristar system. The samples were outgassed for 10 h at 150°C before the measurements. The pore size distribution for mesoporous silica was calculated by using the Barrett-Joyner-Halenda (BJH) model. The contents of Au were determined by using inductively coupled plasma (ICP) with a Perkin-Elmer plasma 40 emission spectrometer. Diffuse reflectance ultraviolet-visible (UV-Vis) spectra were recorded on spectrometer of PE Lambda 20, and $BaSO_4$ was an internal standard sample.

2.3. Catalytic Study. The catalytic study was performed on a 50 mL of glass reactor and the solution was stirred with a magnetic stirrer. The substrate and catalyst were mixed in the reactor and heated up to the given temperature. Then, oxygen was introduced into the reactor and sealed the reaction system. After 24 h reaction, the product was taken out from the system and analyzed by using gas chromatography (GC-17A, Shimadzu, using a flame ionization detector) with a flexible quartz capillary column coated with OV-17. The turnover frequencies (TOFs) were calculated based on the total number of Au atoms in the reaction system according to the following equation:

$$\text{TOF} = \frac{\text{Converted mole of substrate}}{\text{Mole of Au atoms} * \text{Reaction time}}. \qquad (1)$$

3. Results and Discussion

3.1. Characterization of Au Nanoparticles Supported on Mesoporous Silica. XRD patterns of various Au nanoparticles supported on mesoporous silica samples are shown in Figure 1. The samples with higher amount of Au loading exhibited four well-resolved peaks in the range of 20–80° as shown in Figure 1(a), indexed to the Au nanoparticles crystal planes of (111), (200), (220), and (311). However, the samples with lower amount of Au loading display a very broad peak at around 38.5°, suggesting decreased particle size compared

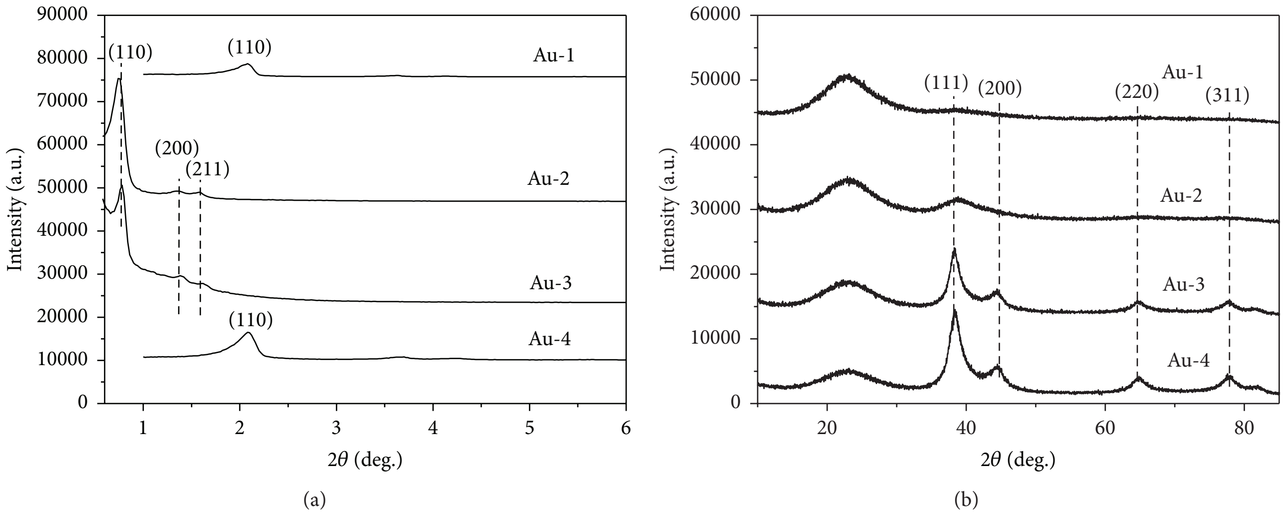


Figure 1: (a) Small- and (b) wide-angle XRD patterns of various Au nanoparticles supported mesoporous silica samples.

to the samples with higher Au loading. Additionally, the mesostructure of mesoporous silica remained stable during the Au loading process which confirmed with the low angle XRD patterns in Figure 1(b).

TEM analysis provides direct evidence for the Au nanoparticles size and the stable structure of the mesoporous silica (Figure 2). According to the TEM results, it is clear that the highly ordered structures along (110) or (100) crystal planes for 2D hexagonal mesoporous silica occurred in all samples. The well-dispersed Au nanoparticles within the mesoporous matrix except the sample of Au-4 are shown in Figure 2(d). The size of Au nanoparticles was measured to be in the range 1–3 nm for the samples with low amount of Au loading as shown in Figures 2(a) and 2(b), which shows good agreement with the XRD patterns in Figure 1. Figure 2(c) shows TEM image for Au/SBA-15 with higher amount of Au loading, and the particle size distribution was centered in the range of 6–8 nm without any obvious aggregation. But an obvious aggregation occurred for Au nanoparticles supported on MCM-41 (Au-4) when higher amount of Au was loaded as shown in Figure 2(d) (Table 1).

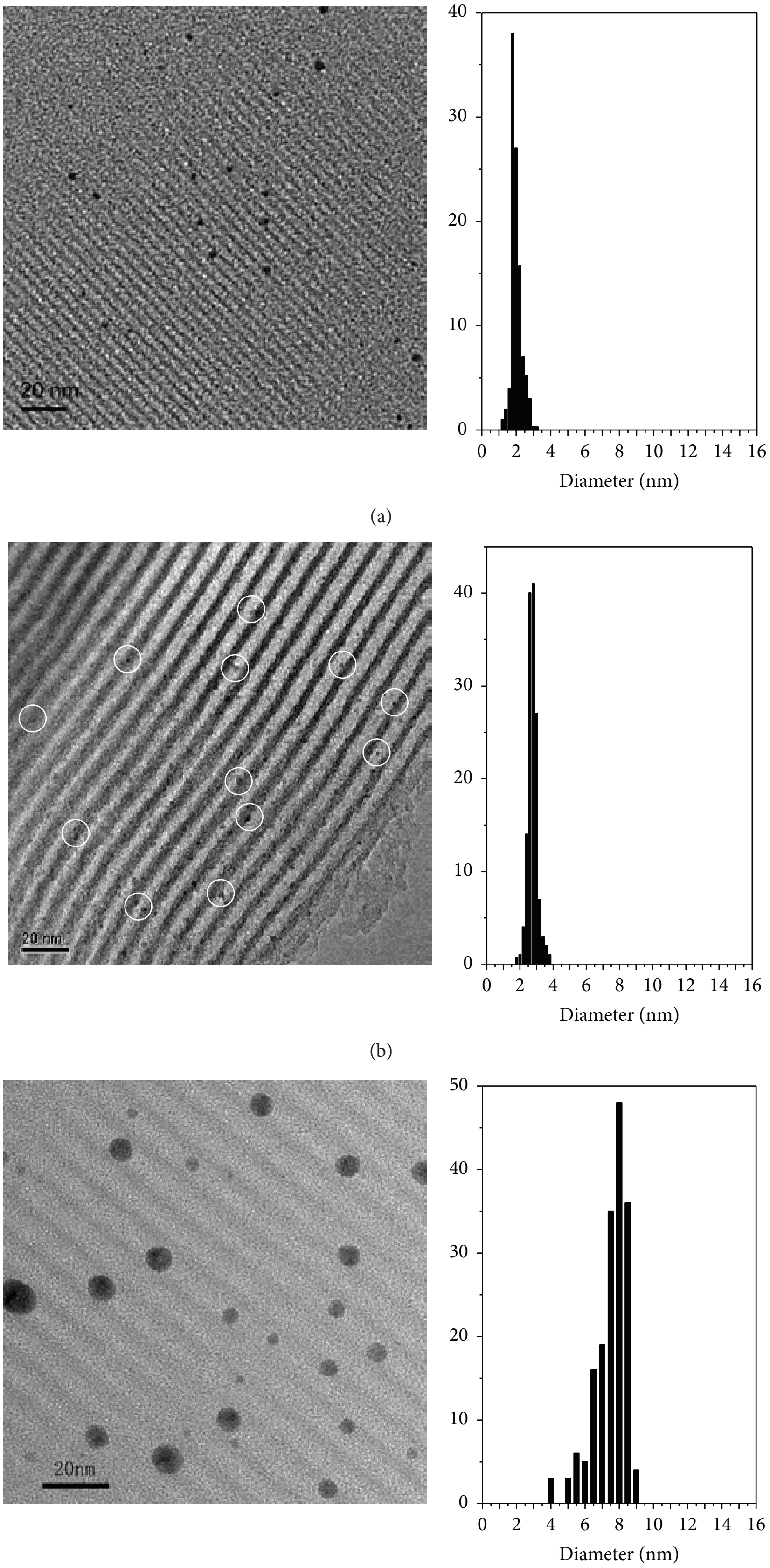
Based on the results above, it can be confirmed that the Au nanoparticles (2-3 nm) were well dispersed in the mesoporous channels for both MCM-41 and SBA-15 when low amount of Au was loaded. In the case of higher amount of Au loading agglomeration occurred for MCM-41 as the pore diameter was relatively smaller at around 3 nm, while SBA-15 has enough space to accommodate larger sized Au nanoparticles isolation with larger pore diameters of around 8.5 nm.

3.2. Catalytic Properties of Au Nanoparticles for Aerobic Oxidation of Alcohols. 1-Phenylethanol and its paraderivates were chosen as model to investigate the catalytic properties of various Au catalysts. The obtained results were summarized in Table 2. Au-1 has showed highest catalytic conversion efficiency for all compounds and the turnover frequency (TOF) was more than 300 h^{-1} which would be 3 times higher than that for efficient soluble catalysts of palladium complex [36]. The catalytic conversion efficiency of Au-2 was also higher than Au-3 and Au-4 with higher amount of Au loading. The excellent catalytic performances of Au-1 and Au-2 should be attributed to the smaller Au nanoparticles size in the matrix of mesoporous silica. On the contrary, Au-4 showed very poor catalytic performance which might be due to the Au nanoparticles agglomeration. Even though there was no obvious aggregation for Au particles on SBA-15(H), the larger sized Au nanoparticles decreased the catalytic conversion.

3.3. Catalyst Stability. To investigate the stability of various Au catalysts, we recycled the samples for 5 times and calculated the catalytic conversion efficiency. Other than highest catalytic conversion efficiency, Au-1 catalyst is also highly stable and reusable as similar catalytic activity was observed while recycling the same sample for 5 times (Table 2). As shown in Figure 3, TEM images of Au-1, no changes were observed in the Au nanoparticles size after recycling the same sample for 5 times, which is totally different from the general phenomenon that the smaller particles would grow and become larger during the catalytic reactions. This is probably due to the limitation of mesopores of MCM-41, which can hinder the Au nanoparticles agglomeration during the catalytic reaction.

4. Conclusion

In conclusion, a series of Au catalysts with controlled sizes were synthesized on mesoporous silica solid supports. The MCM-41 supported Au nanocatalyst with lower amount of Au loading (Au-1) displayed higher catalytic activities than other catalysts for the aerobic oxidation of 1-phenylethanol and benzyl alcohol. The Au-1 catalyst also showed highly stable and reusable capability while recycling the same sample

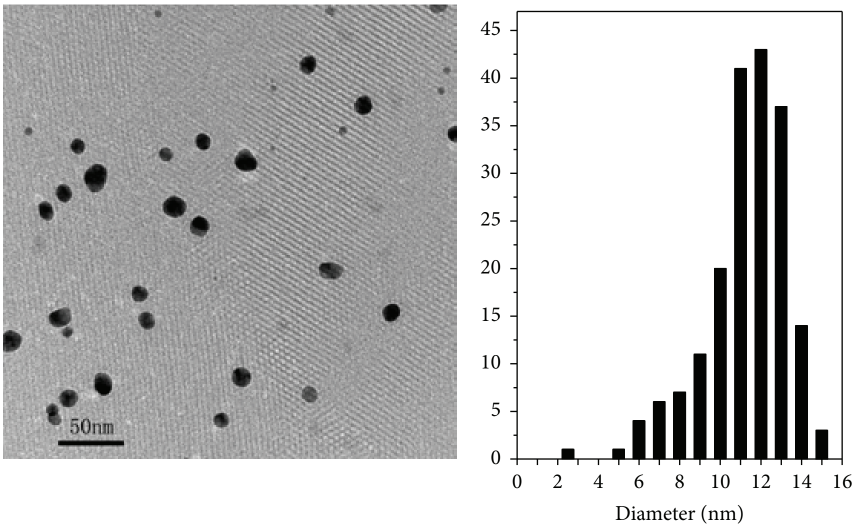


(a)

(b)

(c)

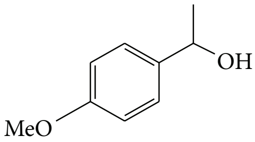
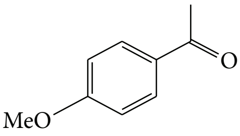
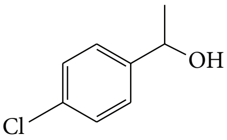
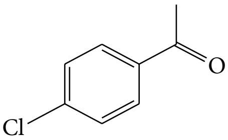
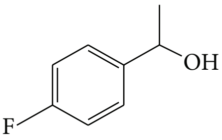
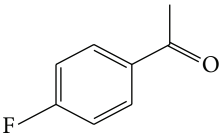
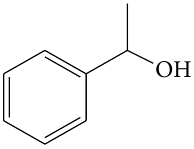
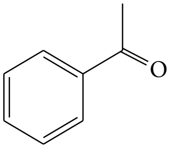
Figure 2: Continued.



(d)

Figure 2: TEM images and size distributions for (a) Au-1, (b) Au-2, (c) Au-3, and (d) Au-4 catalysts.

Table 2: Catalytic activities of various Au/OMS samples for aerobic oxidations of 1-phenylethanol and its paraderivatives[a].

Substrate	Products	Catalysts	Conversion efficiency (%)	TOF (h^{-1})	Selectivity (%)
		Au-1	>99.5[a]	342	>99.5
		Au-1	>99.5[b]	342	>99.5
		Au-1	97.8[c]	334	>99.5
		Au-2	88.0	241	>99.5
		Au-3	80.5	151	>99.5
		Au-4	32.1	29	>99.5
		Au-1	95.0	325	>99.5
		Au-2	83.0	227	>99.5
		Au-3	73.0	199	>99.5
		Au-4	61.5	56	>99.5
		Au-1	96.7	331	>99.5
		Au-2	88.9	243	>99.5
		Au-3	79.0	147	>99.5
		Au-4	46.4	42	>99.5
		Au-1	89.3	305	>99.5
		Au-2	81.7	224	>99.5
		Au-3	70.0	56	>99.5
		Au-4	54.2	49	>99.5

[a] Reactions conditions: 60 mg of catalyst, 0.6 mmol of substrates, 0.3 mmol of Na_2CO_3, 100°C, 24 h, and 6 mL of toluene as solvent.

[b] Recycled results.

[c] Recycled for 5 times. The sample was dried at 140°C before the 5th recycle.

for 5 times. Therefore, this work would definitely provide a platform for the future about synthesizing more active metal nanoparticles on inert solid supports for the efficient catalytic conversion.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

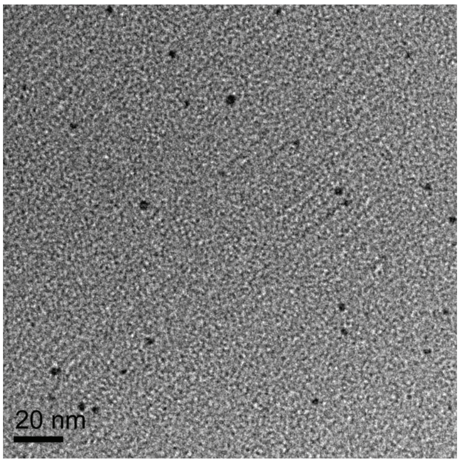


Figure 3: TEM images of Au-1 catalyst after recycling for 5 times.

Acknowledgments

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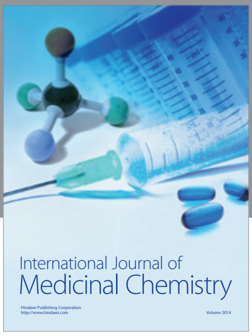
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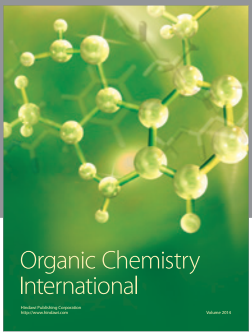
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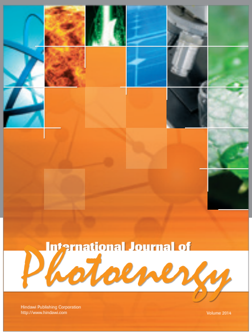
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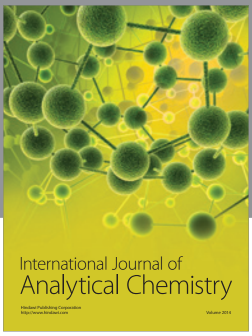
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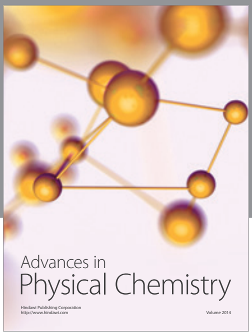
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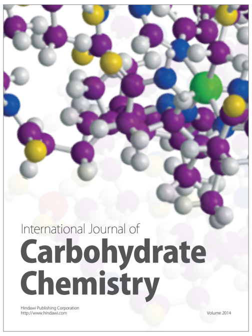
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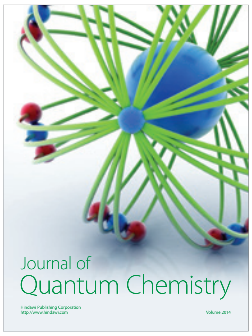
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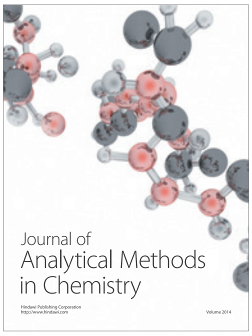
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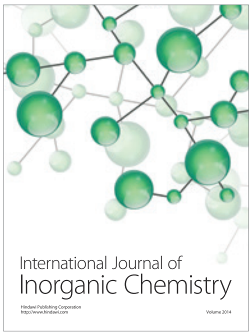
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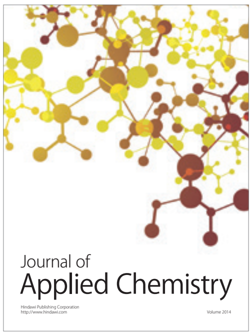
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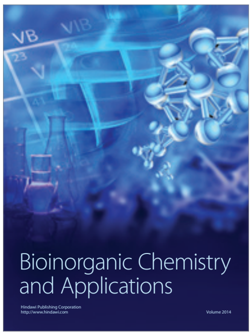
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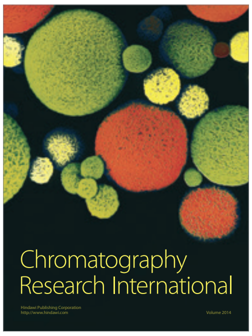
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