One-pot Hydrothermal Synthesis of Mesoporous V-SBA-16 with a Function of the pH of the Initial Gel and its Improved Catalytic Performance for Benzene Hydroxylation

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Received: 19 August 2011/Accepted: 19 January 2012/Published online: 29 March 2012 © Springer Science+Business Media, LLC 2012

Abstract V-SBA-16 catalysts with uniform cubic mesoporous structure were prepared by direct hydrothermal method as a function of the pH of the initial gel and characterized by ICP, XRD, TEM, N₂ adsorption-desorption, DRUV-vis and Raman spectra. The pH of the initial gel in synthesis of V-SBA-16 show important effects on the maintenance of well ordered mesoporous structure, introduced vanadium content and the incorporation of vanadium into the network of SBA-16 type mesoporous material. The initial gel system with a pH value of 2.0 was found to be a suitable for incorporation of vanadium and retaining the mesostructure of SBA-16. The catalytic activities of V-SBA-16 catalysts were evaluated for the hydroxylation of benzene using molecular O₂ as the oxidant. The highest phenol yield of 30.4% with a selectivity of 90% and turnover number of 105 were obtained over the VS-2.0 (1.67) sample prepared at the initial gel system with pH value of 2.0, which is attributed to its high V content and uniform framework V species that highly dispersed on the well ordered SBA-16 type mesoporous materials.

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Keywords V-SBA-16 \cdot One-pot hydrothermal synthesis \cdot pH Adjustment \cdot Benzene \cdot Hydroxylation

1 Introduction

In the family of mesoporous materials, SBA-n materials exhibit large surface area, uniform pore sizes, thicker pore walls and higher hydrothermal stability than M41S materials [1]. In particular, SBA-16 materials with a 3D cagelike structure have attracted great attention in many fields including catalysis, adsorption, separation and nanoscience [2]. However, the absence of active sites in the framework of these pure siliceous materials has limited their applications [3]. Many efforts have been devoted to the synthesis of metal-containing SBA-15 and SBA-16 type mesoporous materials by direct synthesis and impregnation methods [4–11]. Nevertheless, it is very difficult to incorporate metal species into the SBA-n silicious framework by direct synthesis due to the difficulties in the formation of metal-O-Si bonds under strongly acidic conditions [8]. Recently, Gallo et al. attempted to incorporate aluminum into SBA-16 framework using a pH-adjustment method through a two-step route, obtaining a disordered SBA-16-relatedaluminosilicate material [9]. Park et al. synthesized the Fe-SBA-16 by the adjustment of the molar ratio of a series of reactants, such as the molar ratio of co-surfactant n-butanol, TEOS, n_{H2O}/n_{HCl} ratio, Si/Fe ratio, and aging conditions [10]. Shah et al. reported the hydrothermal synthesis of Cu-SBA-16 by internal pH-modification method using hexamethylenetetramine (HMTA) as a complexing agent and internal pH-modifier [11]. The prepared products possessed either an ordered structure with very low metal content under strongly acidic conditions, or a poorly ordered structure with higher amount of metallic species under weak

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acidic condition. These studies showed that the synthesis conditions, especially the pH value of initial gel, were an important factor for the formation of well ordered structure and the introduction of metal ions into SBA-16 framework in the total hydrothermal synthesis process.

Compounds of vanadium, due to their reactivity and remarkable stability, have been utilized as efficient catalysts for a variety of catalytic reactions [12–16], especially for the catalytic selective oxidation of benzene to phenol [17-21]. Recently, various vanadium containing mesoporous molecular sieves such as V-MCM-41 [22, 23], V-MCM-48 [24] and V-SBA-15 [25, 26] have been prepared by hydrothermal methods through different synthesis routes. Park and co-workers [27] have firstly reported the synthesis of well ordered V-SBA-16 with isolated framework V species and examined the effects of reaction conditions including pH, stirring temperature, aging and Si/V ratio. However, only a narrow pH range was selected to investigate the synthesis of V-SBA-16 materials, and most of their attention was paid to the structure characterizations of V-SBA-16 samples with very low initial V/Si ratio (1/200).

In previous work, we have reported the mesoporous $VO_x/$ SBA-16 catalysts prepared by the impregnation method [28], which exhibit efficient catalytic properties for the hydroxylation of benzene. Nevertheless, the phenol yield (13.8%) and turnover number (32.4) are still very low. In this paper, uniform cubic mesoporous V-SBA-16 catalysts with highly dispersed framework V species and relative high vanadium content were prepared by a one-pot hydrothermal method as a function of the pH of the initial gel. The influence of the pH of the initial gel upon vanadium introduction, structure reservation and V species dispersion were carefully characterized by ICP, XRD, TEM, nitrogen adsorption, DRUV-vis and Raman spectra. The catalytic performances of V-SBA-16 materials were first evaluated for the hydroxylation of benzene using molecular oxygen as the oxidant. The relationship between vanadium species and catalytic activity was also investigated.

2 Experimental

2.1 Synthesis of V-SBA-16

V-SBA-16 materials were synthesized under acidic conditions, using tetraethyl orthosilicate (TEOS) and ammonium metavanadate as silica and vanadium precursors, respectively. Nonionic triblock copolymer surfactants $EO_{106}PO_{70}EO_{106}$ (F-127, BASF) and $EO_{20}PO_{70}EO_{20}$ (P-123, BASF) were used as the structure-directing agents. Typically, the samples were synthesized by a method based on the direct hydrothermal synthesis procedure [29]. An aqueous solution of copolymers was prepared by dissolving F-127 and P-123 in a solution of hydrochloric acid and distilled water (solution A). TEOS and a certain amount of ammonium metavanadate were mixed with deionized water to get solution B. A set of samples were prepared by changing the molar ratio of HCl to silicon. Briefly, the starting molar composition was 0.0016 P-123:0.0037 F-127:x HCl:1.0 TEOS:117 H₂O:0.06 NH₄VO₃, and the amount of hydrochloric acid is fit for the final pH value (pH = 0.5, 1.0, 1.5, 2.0 and 2.5). Solution B was stirred at room temperature until the solution becomes clear, and then it was added dropwise to solution A with magnetic stirring at 313 K. The final mixture was stirred vigorously for 24 h and then transferred to an autoclave and aged for 4 days at 373 K. The green solid precipitate was isolated by filtration, washed and dried under vacuum at 323 K. Finally, the precursor is calcinated in ambient air with a heating rate of 1 K/min to 823 K and kept at this temperature for 4 h. The prepared V-SBA-16 samples were denoted to VS-n(x) (where n denotes the pH condition and x represents V content determined by ICP).

2.2 Characterization

X-ray diffraction (XRD) measurements were carried out on a Bruker D8 Advance X-ray diffractometer with Cu Ka $(\lambda = 1.5418 \text{ Å})$ radiation (40 kV, 40 mA). Nitrogen adsorption-desorption measurements were performed at -196 °C on a Quantachrome Autosorb-1 automated gas adsorption system. The samples were outgassed at 300 °C for 4 h before the measurement. The pore size distribution was obtained from the analysis of the adsorption branch of the isotherms using the BJH method. Vanadium content of the samples was analyzed with inductively coupled plasma atomic emission spectrometry allied analytical system (Thermo iCAP 6000 ICP-OES) after an aliquot of the sample was dissolved in a mixture of HF and HNO₃. Transmission electron microscopy (TEM) measurements were taken on a JEM-2100 electron microscope operating at 200 kV. Raman spectra were recorded with the laser Raman spectrometer (JY HR800) equipped with an Ar⁺ laser (458 nm). The laser was operated at a power level of 20 mW measured at the sample with a power meter (Coherent). The diffuse reflectance UV-vis (DRUV-vis) spectra were measured with Shimadzu UV-2550, and BaSO₄ was used as an internal standard. All spectra were recorded in the wavelength range of 200–700 nm. The Kubelka–Munk function $(F(R_{\infty}))$ was used to convert diffuse reflectance data into absorption spectra.

2.3 Catalytic activity tests

Hydroxylation of benzene to phenol by O_2 was typically performed in stainless steel reactor using the mixture (acetic acid:water, 2:1) as the reaction medium. 0.88 g benzene (11.3 mmol), 0.10 g catalysis and 1.50 g ascorbic acid (8.5 mmol) were introduced into the reactor. The reactor was charged with O_2 (1.7 MPa) and the reaction was held for 10 h at 80 °C.

The products were collected, filtered and analyzed by gas chromatography (GC) fitted with an OV-1 capillary column (30 m \times 0.25 mm \times 0.33 µm) connected to a FID detector. Phenol, catechol and hydroquinone in the liquid product were identified by GC-MS (Agilent 6890/5973 N). The quantitative analysis of the mixture was determined by the calibration curves, using toluene as the internal standard.

3 Results and discussion

3.1 Characteristics of V-SBA-16

The pH value is an important synthesis parameter for effective vanadium incorporation and to obtain an ordered mesoporous material [27, 30]. A serial of V-SBA-16 catalysts at different pH range from 0.5 to 2.5 in the initial gel were prepared and characterized by ICP, XRD, TEM, nitrogen adsorption, DRUV—vis and Raman spectroscopy.

3.1.1 ICP-OES results

The vanadium content of V-SBA-16 samples prepared at the initial gel system with different pH value was measured by ICP–OES analysis (see Table 1). It is clear that the lack of V present in the V-SBA-16 sample under the pH of 0.5 is due to the high acidity condition. The V species in the solution exists as VO_2^+ which could not co-condense with Si(OC₂H₅)₄, thus, it is difficult to introduce vanadium into the structure of SBA-16 [26]. As a result, the VS-0.5(0) is finally prepared as a pure siliceous SBA-16 like sample. With the increase of pH, the V species was successfully

Table 1 Physicochemical parameters of VS-n(x) catalysts

incorporated into V-SBA-16 catalysts. The V content of the samples prepared at pH of 1.0, 1.5, 2.0 and 2.5 are determined to be 0.38, 1.03, 1.67 and 1.60, respectively. This trend is attributed to the change of V species from VO₂⁺ to polymeric $H_2V_{10}O_{28}^{4-}$, and these $H_2V_{10}O_{28}^{4-}$ species that show interaction with the silicon alkoxide. The ICP results imply that the pH at the initial gel in hydrothermal synthesis plays an important role in the introduction of V species. In summary, when the pH was adjusted to 2.0, a relative higher V content of 1.67 was obtained.

3.1.2 XRD

The small-angle XRD (SAXRD) patterns of V-SBA-16 catalysts are shown in Fig. 1a. It is obvious that the patterns of VS-n catalysts (n = 0.5, 1.0, 1.5 and 2.0) exhibit a very strong reflection peak corresponding to (110) reflection peak, characteristics of the cubic (Im3 m) mesoporous structure of SBA-16 [1, 4, 27, 31], indicating that ordered mesoporous materials have been obtained at pH range from 0.5 to 2.0. In addition, two weak peaks attributed to the (200) and (211) reflections in 1–1.5 degrees can also be observed for the VS-1.5(1.03) and VS-2.0(1.67) sample, show that well ordered V-SBA-16 mesoporous materials have been synthesized within this pH range. However, when the pH value is adjusted to 2.5, the pattern of VS-2.5(1.60) displays a very weak peak at around 0.82° with the disappearance of higher order peaks, which implies that the ordered long-range structure of mesoporous SBA-16 is damaged in spite of a high amount of vanadium that was introduced. The damage may be caused by the absence of sufficiently strong electrostatic, hydrogen bonding and van der Waals interactions between chargeassociated EO units and the cationic silica species at low acidity, leading to the formation of disordered porous silica [32, 33]. Moreover, as shown in Table 1, the d_{110} value and unit-cell parameter (a_0) of V containing SBA-16 catalysts

Sample	pН	V content (wt%)	Si/V ^a	d ₁₁₀	a _o ^b (nm)	$\frac{S_{BET}}{(m^2g^{-1})}^c$	$\frac{V_{T}^{d}}{(cm^{3}g^{-1})}$	D _{BJH} ^e (nm)
VS-0.5(0)	0.5	0	∞	10.64	15.04	933.5	0.87	5.46
VS-1.0(0.38)	1.0	0.38	220	12.09	17.09	997.6	0.99	7.83
VS-1.5(1.03)	1.5	1.03	81	12.27	17.35	946.3	1.05	6.64
VS-2.0(1.67)	2.0	1.67	50	11.31	15.99	943.8	1.13	6.58
VS-2.5(1.60)	2.5	1.60	52	-	_	685.9	1.10	4.35/6.57

^a The mol ratio of Si/V is calculated from the ICP results

^b The lattice constant was calculated by $a_0 = 1.414 \times d_{(110)}$

^c BET specific surface area

^d Total pore volume

^e Pore diameter calculated by the adsorption branch of isotherm using the BJH method



Fig. 1 SAXRD patterns (a) and WAXRD patterns (b) of various VS-n(x) catalysts



Fig. 2 N_2 adsorption-desorption isotherms (a) and pore size distributions (b) of VS-n(x) catalysts

(VS-1.0(0.38), VS-1.5(1.03), VS-2.0(1.67)) are larger than that of the pure siliceous SBA-16 like sample (VS-0.5(0)), which is attributed to the presence of vanadium in the SBA-16 silicate framework [27, 29, 34]. This is consistent with what would be expected since the radius of the V^{5+} cation is larger than that of the Si⁴⁺ cation and the V–O bond length is longer than the Si–O bond length [27].

The wide-angle XRD (WAXRD) patterns of V-SBA-16 catalysts are shown in Fig. 1b. All catalysts prepared in the pH range of 0.5–2.5 show similar profiles as amorphous SiO_2 of the SBA-16 silica. No characteristic reflections of the V_2O_5 phase were observed, which further confirms the

incorporation of V species into SBA-16 framework. These highly dispersed V species can not be identified by XRD methods [28].

3.1.3 N₂ adsorption-desorption

The nitrogen adsorption–desorption isotherms of V-SBA-16 catalysts are shown in Fig. 2. The VS-n samples (n = 0.5, 1.0, 1.5 and 2.0) show type IV isotherms and H2 hysteresis loops, which are typical of the mesoporous SBA-16 materials with 3D cage-like structures [1, 35, 36]. However, the VS-2.5(1.60) displays type IV isotherms with a typical H3 hysteresis loop, which indicates that the ordered mesoporous structure of SBA-16 is destroyed. These results are in good agreement with small-angle XRD analysis. The physical structure parameters of V-SBA-16 samples are displayed in Table 1. The VS-n samples (n = 0.5, 1.0, 1.5 and 2.0) exhibit large specific surface area $(>930 \text{ m}^2/\text{g})$ with uniform pore size distribution (5.46-7.83 nm) and pore volume (>0.87 m³/g), while the VS-2.5(1.60) sample shows relatively poor structure parameters due to its disordered mesoporous structure. Furthermore, the pore diameter, BET surface area and total pore volume of well ordered V containing SBA-16 catalysts (VS-1.0(0.38), VS-1.5(1.03) and VS-2.0(1.67)) are obviously larger than that of siliceous SBA-16 like materials VS-0.5(0), which confirm the incorporation of V species into the SBA-16 framework due to the expansion of the mesoporous structure [37]. It is in accordance with the XRD results that the unit-cell parameter (a_0) of VS-n(x) catalysts is larger than that of the pure siliceous SBA-16 like sample.

3.1.4 TEM

The TEM images of V-SBA-16 catalysts are shown in Fig. 3. It can be clearly observed that the VS-0.5(0) sample (Fig. 3a) has well ordered mesoporous cubic arrays along the (111) and (100) directions and also exhibits a typical 3D cubic (*Im3 m*) pore structure of SBA-16 [1, 38, 39]. With the increase of the pH of the initial gel, the TEM images of VS-1.5(1.03) (Fig. 3b) and VS-2.0(1.67) (Fig. 3c) catalysts still show the ordered mesoporous structure though the quality of pore ordering decreases slightly. The VS-2.5(1.60) sample shows a disordered mesoporous structure (see Fig. 3d), which is consistent with the XRD and N₂ adsorption–desorption results. Moreover, the vanadium oxide (VO_x) can also be clearly observed on the surface of VS-2.5(1.60) catalyst.

From the XRD, TEM, ICP and N_2 adsorption–desorption isotherms discussed above, it is clear that a function of the pH of the initial gel plays an important role in the synthesis of V-SBA-16 catalysts. The V species could not



Fig. 3 TEM images of V-SBA-16 catalysts: a VS-0.5(0), b VS-1.5(1.03), c VS-2.0(1.67) and d VS-2.5(1.60)

be introduced into SBA-16 material in the pH range lower than 0.5, while the ordered mesoporous structure of SBA-16 would be damaged in the pH range higher than 2.5. Therefore, it is necessary to control the proper pH range of 1.0–2.0 at the initial gel system in order to obtain uniform mesoporous V-SBA-16 catalysts with high V content.

3.1.5 Raman spectra

Raman spectroscopy is used to elucidate the nature of vanadium species on the V-SBA-16 catalysts (see Fig. 4). Figure 4a depicts the laser Raman spectra of various V-SBA-16 samples. The spectra of VS-0.5(0) show no typical Raman bands of V species, which is in consistent with the ICP analysis that no vanadium is present in this sample. With the increase of pH (1.0-2.0) in the initial gel system, the spectra of V-SBA-16 samples exhibit an intense band at around 1,040 cm⁻¹ with a shoulder at 1,072 cm⁻¹, which are assigned to terminal V = O stretch vibration of monomeric tetrahedral VO₄ species (Td-V⁵⁺) [40, 41]. Furthermore, the intensity of these bands increases with the increasing V content (see Table 1). However, the VS-2.5(1.60) that was prepared at a pH 2.5 showed an additional band at 998 cm⁻¹ which is assigned to microcrystalline V₂O₅ species [41, 42]. These results reveal that an aggregation of V species occurred on the surface of the VS-2.5(1.60) catalyst at the pH of 2.5, which may lead to the formation of extra-framework V_2O_5 species. These microcrystalline V_2O_5 species can be easily observed by Raman spectroscopy but can not be detected by XRD measurement [28, 41, 43].

3.1.6 DRUV—vis spectra

DRUV-vis spectra were also recorded in order to identify the nature of observed coordination of vanadium species in the V-SBA-16 catalysts. As shown in Fig. 5, there is no obvious absorption band assignable to V species in the range of 200-700 nm for the VS-0.5(0) sample which agrees well with the ICP, XRD and Raman results. However, the spectra of VS-1.0(0.38), VS-1.5(1.03) and VS-2.0(1.67) samples display an intense band centered at about 262 nm with a shoulder at 303 nm, which can be assigned to the charge-transfer transitions of the ligand O^{2-} to metal center V^{5+} for the isolated tetrahedral VO_4 species $(O_{3/2}V = O)$ [40]. As far as the VS-2.5(1.60) is concerned, the band assigned to VO₄ species shifts to higher wavelength, and one additional band is observed at about 481 nm which could be associated with the presence of octahedral V^{5+} species, as above-mentioned V₂O₅ crystallites that have been determined by Raman spectra [44, 45].

The results of pore structure characterization and V species analysis imply that the V species could not be introduced into the SBA-16 structure for the VS-0.5(0)



Fig. 4 Laser Raman spectrums of VS-n(x) catalysts



Fig. 5 DRUV—vis spectra of VS-n(x) catalysts

sample due to the high acidity though it possesses a well ordered mesoporous structure. When the pH at the initial gel system is adjusted to 2.5, a relative high V content of 1.60 wt% was obtained for the VS-2.5(1.60) sample. However, a low V dispersion is observed which is attributed to the change of partial V species from isolated VO₄ to agglomerated V₂O₅ crystallites along with the formation of disordered mesoporous structure at the weakly acidic condition. Thus, ordered mesoporous V-SBA-16 materials containing monomeric tetrahedral framework V species should be synthesized in the pH range of 1.0–2.0.

3.2 Catalytic evaluations

Figure 6 depicts the catalytic activities of benzene hydroxylation over V-SBA-16 using O₂ as the oxidant. It is clear that the pure siliceous SBA-16 like of VS-0.5(0) catalyst is inactive for oxidation of benzene to phenol. With the substantial incorporation of V species, the V-SBA-16 samples show the obvious catalytic activity of benzene hydroxylation. Phenol is main product, benzoquinone, catechol and hydroquinone are the primary byproducts and no benzene is oxidized to CO and CO₂ for the present research. The yield of phenol over V-SBA-16 catalysts increases quickly with increasing V content and the corresponding increase of synthesis pH from 1.0 to 2.0 at the initial gel system. The highest phenol yield of 30.4% with selectivity of 90% and turnover number of 105 were obtained over VS-2.0(1.67) sample, which may be attributed to its high V content and the highly dispersed VO_4 species on the well ordered SBA-16 type mesoporous materials. However, an obvious decreases of yield and selectivity for phenol was observed for VS-2.5(1.60)



Fig. 6 Catalytic activity of benzene hydroxylation over different V-SBA-16 catalysts (reaction condition:acetic acid and water (2:1) as solvent, 11.3 mmol benzene, 8.5 mmol ascorbic acid, O_2 pressure of 1.7 Mpa, 80 °C for 10 h, 0.10 g of catalyst)

sample, which may be not only attributed to the decrease of the V content, but also related to its low V dispersion with the presence of crystalline V₂O₅ species and its disordered mesoporous structure caused by low acidity during preparation, in accordance with the characterizations of pore structure and V species discussed above. From VS-1.0(0.38) to VS-2.5(1.60) with the increasing the synthesis pH value at the initial gel system, the TON of phenol over V-SBA-16 shows great decline, which may be ascribed to the increase of V content and incidental decrease of V dispersion. Especially, the VS-2.5(1.60) sample with the lowest V dispersion and disordered mesoporous structure displays a relatively low TON of 95. These results indicate that the isolated V species highly dispersed on uniform mesoporous network play an important role in the hydroxylation of benzene over V-SBA-16 catalysts.

The effect of the reaction time on catalytic benzene hydroxylation has also been studied over VS-2.0(1.67) sample shown in Table 2. At a the reaction time of 6 h, the conversion of benzene and the yield of phenol are only 10.2 and 9.8%, respectively. At longer times, both the conversion of benzene and the yield of phenol increase quickly; and the yield of phenol around 30.4% could be acceptable at the proper contact time for 10 h. However, the selectivity to phenol decreases but the selectivity to catechol and hydroquinone increases. This is due to the phenol is the more active than benzene; when the reaction time further increase, the rate of over oxidation occur rapidly.

4 Conclusion

In summary, the influences of the pH of the initial gel system in the synthesis process of V-SBA-16 have been

Table 2 Effect of reaction time on catalytic activity over the VS-2.0(1.67) sample

Time (h)	C ^a (%)	S ^b (%)	S ^c (%)	S ^d (%)	Y ^e (%)	TON
6	10.2	96.5	2.3	1.2	9.8	33.8
8	19.3	92.1	5.8	2.1	17.8	61.4
10	33.7	90.0	6.7	3.3	30.4	105
12	36.3	77.6	6.3	16.1	28.2	97.2

Reaction conditions: acetic acid:water = 2:1 (V:V), benzene (11.3 mmol), catalyst (0.10 g), ascorbic acid (8.5 mmol), 1.7 MPa O_2 , reaction temperature 80 °C

^a The conversion of benzene

- ^b The selectivity of phenol
- ^c The selectivity of catechol
- ^d The selectivity of hydroquinone
- ^e The yield of phenol
- ^f The moles of phenol formed per mol V amount of the VS-2.0(1.67)

examined and shown a dependence on various factors, such as vanadium introduction, reservation of mesoporous structure and dispersion of V species which were carefully studied by ICP, XRD, TEM, nitrogen adsorption-desorption, DRUV-vis and Raman spectroscopy. The results imply the pH of the initial gel system plays an important role in the synthesis of V-SBA-16, and show that well ordered V containing SBA-16 type mesoporous materials with highly dispersed isolated VO₄ species can be synthesized in the pH range of 1.0 to 2.0. The VS-2.0(1.67) catalyst shows fascinating phenol yield of 30.4% with phenol selectivity of 90.0% and high TON of 105 due to its high V content and high dispersion of isolated vanadium species in the framework of mesoporous SBA-16 type materials. These isolated framework tetrahedral VO₄ species is a key factor to acquire the high TON in the benzene hydroxylation reaction. The decrease of V dispersion and appearance of the V₂O₅ crystallites are disadvantageous for selective oxidation of benzene.

Acknowledgments This work is supported by the Natural Science Foundation of China (20876034), Program for New Century Excellent Talents in Heilongjiang Provincial University (1155-NCET-014), Major Foundation of Educational Commission of Heilongjiang Province of China (11531Z11) and Heilongjiang University Natural Science Funds for Distinguished Young Scholar (JCL200802). The authors also thank Dr. Alexander D. Gordon (Department of Chemistry, University of California, Riverside, USA) for his help in the use of the English language.

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