

NANO EXPRESS

Open Access

Facile preparation of highly-dispersed cobalt-silicon mixed oxide nanosphere and its catalytic application in cyclohexane selective oxidation

Qiaohong Zhang¹, Chen Chen², Min Wang², Jiaying Cai², Jie Xu^{2*} and Chungu Xia^{1*}

Abstract

Highly dispersed cobalt-silicon mixed oxide [Co-SiO₂] nanosphere was successfully prepared with a modified reverse-phase microemulsion method. This material was characterized in detail by X-ray diffraction, transmission electron microscopy, Fourier transform infrared, ultraviolet-visible diffuse reflectance spectra, X-ray absorption spectroscopy near-edge structure, and N₂ adsorption-desorption measurements. High valence state cobalt could be easily obtained without calcination, which is fascinating for the catalytic application for its strong oxidation ability. In the selective oxidation of cyclohexane, Co-SiO₂ acted as an efficient catalyst, and good activity could be obtained under mild conditions.

Introduction

The preparation of a highly dispersed nanosphere with the desired properties has been intensively pursued not only for the fundamental scientific interest of the nanomaterials, but also for their wide technological applications. Up to the present, different methods, such as the Stöber method, a layer-by-layer deposition, a sol-gel process, or a hydrothermal method, etc., have been developed to prepare a highly dispersed nanosphere [1-5]. Various monocomponent nanospheres including SiO₂, Fe₂O₃, CuO, ZnS, or metal materials Au and Pt could be successfully obtained [4-8]. These materials showed good properties during utilization in gas sensors, biomedicine, electrochemistry, catalysis, etc. Furthermore, for the demand of the application, much effort has been devoted to prepare a bi- or multicomponent nanocomposite [9-14]. Among these materials, silica was often utilized as a carrier to disperse the active phase on its surface or in its matrix because silica can not only be easily obtained from several precursors, but also remains stable in most chemical and biological

environments. What's more is that the rapid development of the modern nanotechnology has supplied flexible methods to modulate the morphology and structure of silica, which could be adopted for the preparation of the SiO₂-based nanocomposite [15,16].

Cobalt oxide system or cobalt-silicon mixed oxide is a widely studied system in material domain, which could be used as catalyst for many reactions involving hydrogen transfer, such as methane reforming, oxidation of hydrocarbon, Fischer-Tropsch synthesis, and hydrogenation of aromatics [17-22]. For the bi-component cobalt-silicon mixed oxide, it was acknowledged in the recent studies that the preparation method could show an obvious effect on the type and dispersion of cobalt oxide species, and thus on the catalytic performance of the derived catalysts [23-25]. For the traditional two-step method, silica was firstly prepared as a support, and then, cobalt species were introduced through ion-exchange, impregnation, or grafting techniques. Compared with this method, one-step condensation method owns its predominance in that it allows a better control of the textural properties of the silica matrix and a more effective dispersion of cobalt oxide in the matrix on a nanometric scale.

From a particle-preparation point of view, microemulsion method is such a good method to prepare a uniform-sized nanosphere [26-29]. The water nanodroplets present in the bulk oil phase serve as nanoreactors to

* Correspondence: xujie@dicp.ac.cn; cgxia@licp.cas.cn

¹State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China

²State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, People's Republic of China
Full list of author information is available at the end of the article

control the size and the distribution of the nanoparticles. While for cobalt-silicon mixed oxide, it seems that the uniform particle size distribution remains a delicate task with the normal sol-gel method or microemulsion methods [30-34]. In our previous work, a modified reverse-phase microemulsion method was successfully adopted to prepare a highly dispersed SiO₂-based nanocomposite [35,36]. Herein, a similar method was used to prepare cobalt-silicon mixed oxide materials, and the obtained material presents as a kind of highly dispersed, uniform-sized nanosphere. In the catalytic application, this novel nanosphere showed a good activity for the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone.

Experiment

Material preparation

Tetraethyl orthosilicate [TEOS] (99%), cobaltous acetate [Co(OAc)₂·4H₂O] (99%), ethanol [C₂H₅OH] (99.5%), acetone [C₃H₆O] (99.5%), cyclohexane [C₆H₁₂] (99.5%), *n*-butyl alcohol [C₄H₉OH] (99.5%), and aqueous ammonia [NH₃·H₂O] (28%) were obtained from Tianjin Kermel Chemical Reagent Development Center, Tianjin, China. Poly (oxyethylene) nonylphenol ether [NP-7] (industrial grade) was purchased from Dalian Chemical Ctl., Dalian, China. Cobalt oxide [Co₃O₄] (98%) denoted as C-Co₃O₄ was purchased from Tianjin Institute of Jinke Fine Chemical, Tianjin, China.

Firstly, two kinds of solution (solutions A and B) were obtained, respectively. Solution A was composed of 15.05 g of NP-7, 35.05 g of cyclohexane, and 8.05 g of *n*-butyl alcohol. Solution B was obtained with the addition of 2.00 g of NH₃·H₂O (16%) to the cobalt acetate aqueous solution (0.13 g of Co(OAc)₂·4H₂O and 5.35 g of deionized H₂O). Microemulsion was obtained with the blending of solutions A and B. After stirring for 15 min, to this microemulsion, 5.2 g of TEOS was added slowly under stirring. After stirring was continued for 12 h, 10 ml of acetone was added to destroy the microemulsion. It was then centrifugated, washed with hot ethanol for three times, and dried at 353 K for 12 h. This material was denoted as Co-SiO₂.

Characterization

The microstructure of the material was examined by transmission electron microscopy [TEM] on an FEI Tecnai G2 Spirit electron microscope (FEI Company, Hillsboro, OR, USA) at an accelerating voltage of 100 kV. The surface morphology was observed by scanning electron microscopy [SEM] on an FEI Quanta 200F microscope (FEI Company, Hillsboro, OR, USA). The X-ray powder diffraction [XRD] patterns were obtained using Rigaku D/Max 2500 powder diffraction system (Rigaku Corporation, Tokyo, Japan) with Cu K α radiation with a

scanning rate of 5°/min. Fourier transform infrared [FT-IR] spectra were collected between 4,000 and 400 cm⁻¹ on a Bruker Tensor 27 FT-IR spectrometer (Bruker Corporation, Billerica, MA, USA) in KBr media. Ultraviolet-visible diffuse reflectance spectra [UV-Vis DRS] were collected over a wavelength range from 800 to 190 nm on a Shimadzu UV-2550 spectrophotometer (Shimadzu Corporation, Kyoto, Japan) equipped with a diffuse reflectance attachment. X-ray absorption spectroscopy [XAS] measurement was performed at room temperature on the XAS Station of the U7C beam line of the National Synchrotron Radiation Laboratory (NSRL, Hefei, China).

Catalytic oxidation of cyclohexane

Catalytic reactions were performed in a 100-ml autoclave reactor with a Teflon insert inside in which 0.12 g of catalyst, 15.00 g of cyclohexane, and 0.12 g of tert-butyl hydroperoxide [TBHP] (initiator) were added. When the reaction stopped, the reaction mixture was diluted with 15.00 g of ethanol to dissolve the by-products. The reaction products were identified by Agilent 6890N GC/5973 MS detector and quantitated by Agilent 7890A GC (Agilent Technologies Inc., Santa Clara, CA, USA) equipped with an OV-1701 column (30 m × 0.25 mm × 0.3 μ m) and by titration. The analysis procedure was the same with that in the literature [21,37]. After the decomposition of cyclohexylhydroperoxide [CHHP] to cyclohexanol by adding triphenylphosphine to the reaction mixture, cyclohexanone and cyclohexanol were determined by the internal standard method using methylbenzene as an internal standard. The concentration of CHHP was determined by iodometric titration, and the by-products acid and ester, by acid-base titration. All the mass balances are above 92%.

Results and discussion

TEM and SEM were utilized to study the morphology of the material Co-SiO₂. It can be observed in Figure 1a and 1b that the obtained material Co-SiO₂ presented as a highly dispersed, uniform-sized nanosphere, which was further proved by the characterization of SEM (Figure 1c). The distribution of the particle size was centered at about 110 nm (Figure 1d). By comparison, in our previous work, the highly dispersed nanosphere could not be obtained with the normal operation of blending two microemulsions before adding a silicon source [38]. A similar situation also happened during the preparation of silica-supported cobalt materials [30,31]. As pointed out by Boutonnet et al., there are two main ways of preparing nanoparticles from the microemulsion method: (1) by mixing two microemulsions, one containing the precursor and the other, the precipitating agent; and (2) by adding the precipitating agent directly to the

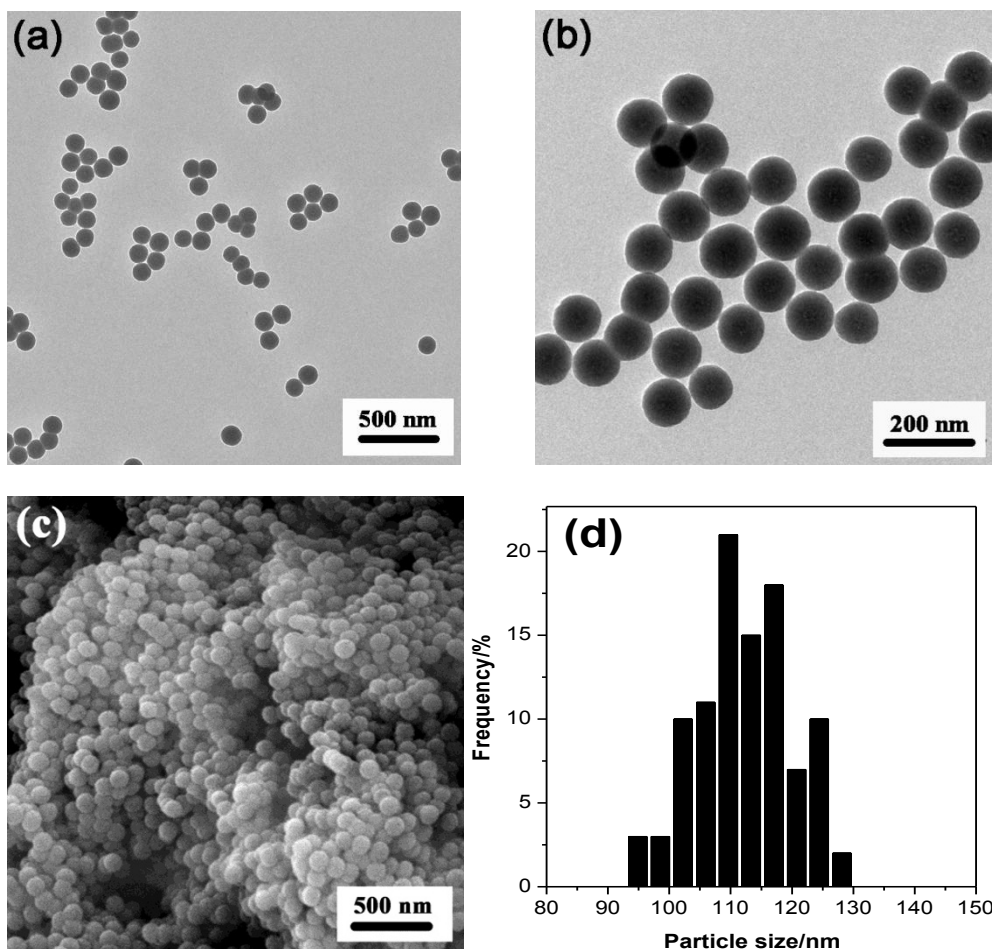


Figure 1 TEM (a, b), SEM (c), and particle size distribution (d) of Co-SiO₂.

microemulsion containing the metal precursor [26]. Different with the above two methods, in the present work, the metal precursor was firstly prepared as an aqueous solution of a cobalt ammonia complex, which acted as the water phase in the microemulsion and could also supply a base environment for the hydrolysis of TEOS. No more bases are necessary to be added during the preparation process. This method can also avoid the blending of two microemulsions that might affect the properties of the water droplet in the microemulsion and then affect the morphology of the prepared materials. With the same method, highly dispersed Cu-SiO₂, Ni-SiO₂, and Zn-SiO₂ nanospheres could also be successfully prepared.

The composition of the material Co-SiO₂ was primarily recognized through the XRD pattern measurement, which was shown in Figure 2. As a comparison, the pattern of the C-Co₃O₄ was also supplied in which eight peaks corresponding with the cubic structure of Co₃O₄ with the *Fd3m* space group can be clearly observed [21].

These peaks do not emerge in the pattern of Co-SiO₂, and it shows only a broad peak at $2\theta = \text{ca. } 22^\circ$, which is assigned to the amorphous silica. These results indicate that Co species in Co-SiO₂ are amorphous and/or the particle size is too small [33].

The FTIR spectrum of the material Co-SiO₂ is illustrated in Figure 3. Strong absorption bands at 1,090, 800, and 473 cm⁻¹ agree well with the SiO₂ bond structure. The band at 1,090 cm⁻¹ was assigned to the asymmetric stretching vibration of the bond Si-O-Si in the SiO₄ tetrahedron. The band at 800 cm⁻¹ was assigned to the vibration of the Si-O-Si symmetric stretching vibration. The band at 473 cm⁻¹ is related to the bending modes of the Si-O-Si bonds [37,39]. Besides these three bands, one weak shoulder band emerged at 960 cm⁻¹ that was usually attributed to the Si-OH stretching vibration. The absorption bands at 3,440 and 1,635 cm⁻¹ were caused by the absorbed water molecules [40]. For the as-prepared sample without solvent extraction, intense characteristic absorption bands associated with

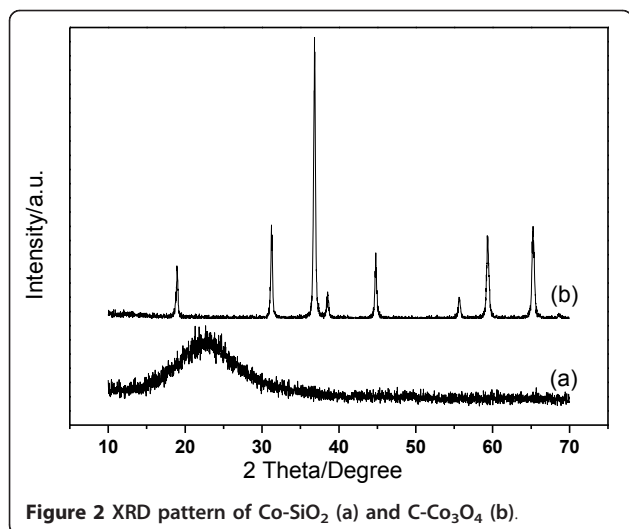


Figure 2 XRD pattern of Co-SiO₂ (a) and C-Co₃O₄ (b).

C-H bond (about 1,500 and 3,000 cm⁻¹) are evident for the presence of the organic surfactant, which almost disappeared for the spectrum of Co-SiO₂. This indicates that the surfactant could be totally removed with the solvent extraction method.

UV-Vis DRS is a powerful characterization method to study the coordination geometry of cobalt incorporated in the materials, and the spectrum of Co-SiO₂ was shown in Figure 4. Between 450 and 750 nm, this spectrum displays three absorption peaks (525, 584, and 650 nm), which can be unambiguously assigned to the ⁴A₂(F) → ⁴T₁(P) transition of Co(II) ions in tetrahedral environments [41,42]. Moreover, a broad band in the UV region centered at 224 nm is also observed. This has been assigned to a low-energy charge transfer between the oxygen ligands and central Co(II) ion in tetrahedral symmetry [43]. Besides the above absorption, another broad absorption was centered

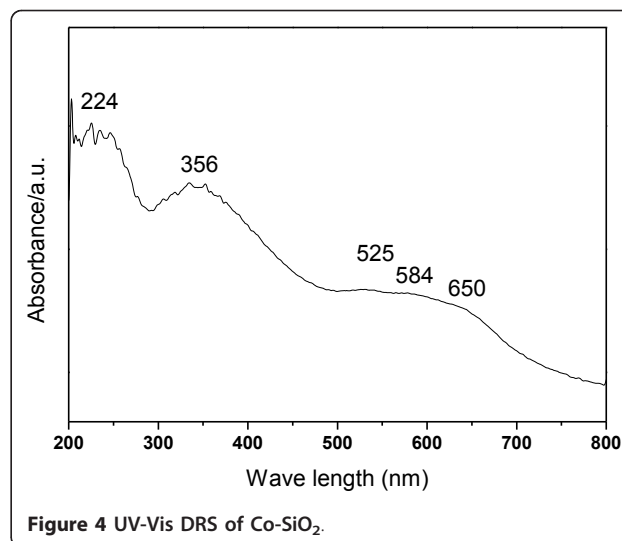


Figure 4 UV-Vis DRS of Co-SiO₂.

at 356 nm, which was assigned to Co(III) species [44]. It could be found in the literature that Co(III) was usually obtained through a heating treatment such as calcination [21,32,33]. In the present work, however, Co(II) salt precursor was firstly converted to cobalt(II) ammonia complex during the preparation process. The formation of a Co(II) ammonia complex would decrease the standard potential of Co(III)/Co(II) from 1.84 to 0.1 v, and then Co(III) ions were formed via the automatic oxidation of the Co(II) ammonia complex by dissolved dioxygen. As identified in a previous study [42], the emergence of this absorption was taken as a strong evidence for the presence of a distinct Co₃O₄ phase. So, it can be deduced from the above results that a Co₃O₄ phase exists in the material Co-SiO₂.

In addition, from the characterization result of X-ray absorption spectroscopy near-edge structure [XANES] measurement (Figure 5), the information about the valence state of cobalt ions could be further acknowledged. It was believed that the main-edge should be shifted to a higher energy with the mixing of Co(III) with Co(II), and the distance between the pre-edge peak and the main edge can be used to measure the oxidation state of cobalt ions. Compared with the reference data, Co-SiO₂ has an edge position that is consistent with cobalt ions aligning with Co₃O₄ that contains both oxidation states, not with CoO or CoAl₂O₄ [45]. The main-edge emerged at a higher energy (7,726.9 eV) for Co-SiO₂, and the distance between the pre-edge peak and the main edge ($E_{\text{main-edge}} - E_{\text{pre-edge}}$) reached 17.2 eV. These situations are quite similar with those of Co₃O₄, manifesting that cobalt ions in Co-SiO₂ own a close coordination environment with the cobalt ions in Co₃O₄ [45]. This is consistent with the result of UV-Vis DRS.

Selective oxidation of cyclohexane to cyclohexanone and cyclohexanol (the so-called K-A oil) is the

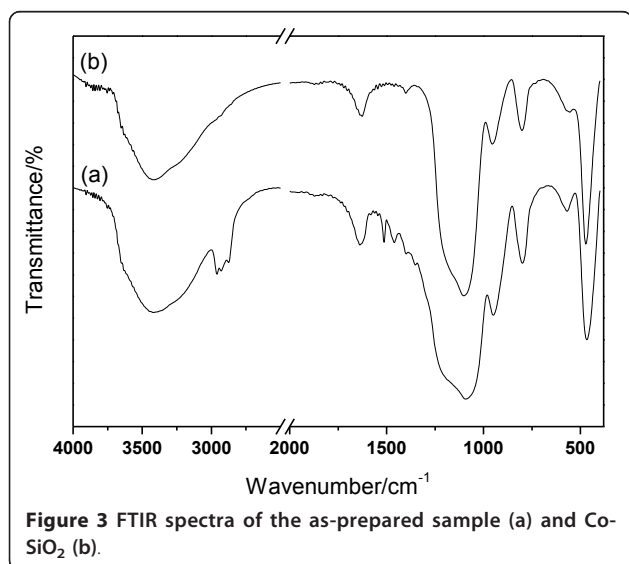
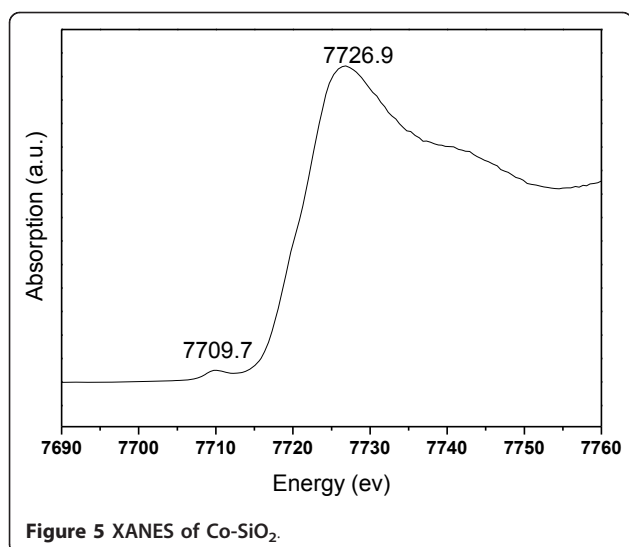


Figure 3 FTIR spectra of the as-prepared sample (a) and Co-SiO₂ (b).



centerpiece of the commercial production of Nylon. Although many attempts have been made to develop various catalytic systems for this reaction, it continues to be a challenge [46-48]. The present industrial process for cyclohexane oxidation is usually carried out above 423 K and 1 to approximately 2 MPa pressure without catalyst or with metal cobalt salt as homogeneous catalyst. For obtaining higher selectivity of K-A oil (about 80%), the conversion of cyclohexane is always controlled by about 4% [48]. It is one of the lowest efficient technologies that have been put into application among the present petrochemical domain. The main reason for the low yield of K-A oil is that it is easily overoxidized to the acids and further transformed to other by-products.

In the present work (Table 1), when Co-SiO₂ was used as catalyst for the selective oxidation of cyclohexane, encouraging results were obtained. Under more mild conditions (388 K, which is 35 K lower than that of the industrial process), the conversion reached 6.0%, while the selectivity of K-A oil reached as high as 85.7% at the

Table 1 Catalytic oxidation of cyclohexane over the catalysts

Catalysts	Conversion (mol%)	K-A oil (mol%)	Products distribution (mol%) ^a				
			A	K	CHHP	Acid	Ester
Co-SiO ₂	6.0	85.7	45.7	40.0	0.3	10.3	3.7
C-Co ₃ O ₄	3.8	78.4	50.4	28.0	9.3	10.8	1.5
Co(OAc) ₂	3.3	78.2	43.2	35.0	4.3	15.0	2.5
Co-HMS ^b	4.8	76.9	39.6	37.3	0.4	15.6	7.1

Reaction was carried out with 0.12 g of catalyst and 0.12 g of TBHP in 15 g of cyclohexane at 388 K for 6 h under 1.0 MPa O₂.^a A, cyclohexanol; K, cyclohexanone; CHHP, cyclohexylhydroperoxide; Acid, mainly adipic acid; Ester, mainly dicyclohexyl adipate; K-A oil, A and K.^b Results from Chen et al. [19] under the same reaction conditions.

same time. As a comparison, the commercial C-Co₃O₄ could give a moderate activity with a conversion of 3.8% and a K-A oil selectivity of 78.4%. In addition, compared with the reported data, the predominance of the present Co-SiO₂ is evident. Under the same conditions, when cobalt acetate was used, which was a homogeneous catalyst being widely used in the industrial process, the conversion was only 3.3% and the selectivity of K-A oil was also below 80% [19]. Moreover, the activity of Co-SiO₂ is higher than that of the cobalt-containing mesoporous silica [Co-HMS] system (Table 1). Through N₂ physical adsorption-desorption measurement, it could be acknowledged that the BET surface area of Co-SiO₂ is 60 m²/g and average pore size is about 17 nm, respectively, which manifest that most of the pores come from the aggregation of the nanospheres. So, the accessible catalytic active sites of Co-SiO₂ should exist all on the outer-surface of the nanospheres, which is contrary with the situation for the porous materials such as mesoporous silica or molecular sieves. For those porous materials, most of the catalytic active sites exist on the interface of the pore. Though the surface area of Co-SiO₂ is much lower than that of Co-HMS (682 m²/g) [37], the absence of a long channel of inner pore may facilitate the fast diffusion of the substrate and the oxygenated products. Thus, the primary oxygenated products such as cyclohexanone and cyclohexanol are easily desorbed from the surface of the catalyst, which would decrease the chance for them to be overoxidized. This might be the main reason for the evident enhancement of the selectivity for K-A oil. The deeper study of the relationship between the structure of the material and the activity is underway.

Conclusions

With a modified reverse-phase microemulsion method, highly dispersed cobalt-silicon mixed oxide nanosphere was successfully prepared for the first time. The utilization of cobalt ammonia complex as metal source is favorable not only for controlling of the morphology, but also for obtaining a high valence state cobalt without calcination. These two factors are fascinating for the catalytic application, and Co-SiO₂ was found to act as an efficient catalyst for the selective oxidation of cyclohexane. Considering that many kinds of metal ions can be converted to metal ammonia complex, we can extend this method to prepare such highly dispersed SiO₂-based nanocomposite, which might show good application properties for its specific morphology and structure.

Acknowledgements

This study was financially supported by the National Natural Science Foundation of China (21103175 and 21103206) and the Doctor Startup Foundation of Liaoning Province.

Author details

¹State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, People's Republic of China ²State Key Laboratory of Catalysis, Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, People's Republic of China

Authors' contributions

JX and CX designed the experiment. QZ and CC carried out the experiment and drafted the manuscript. MW and JC participated in some of the characterizations and performed the data analysis. All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

Received: 1 September 2011 Accepted: 8 November 2011

Published: 8 November 2011

References

- Liu J, Qiao SZ, Liu H, Chen J, Orpe A, Zhao D, Lu GQ: Extension of the Stöber method to the preparation of monodisperse resorcinol-formaldehyde resin polymer and carbon spheres. *Angew Chem Int Ed* 2011, **50**:5947.
- Caruso F, Susha AS, Giersig M, Mohwald H: Magnetic core-shell particles: preparation of magnetite multilayers on polymer latex microspheres. *Adv Mater* 1999, **11**:950.
- Kobayashi Y, Horie M, Konno M, Rodriguez-González B, Liz-Marzán LM: Preparation and properties of silica-coated cobalt nanoparticles. *J Phys Chem B* 2003, **107**:7420.
- Bigall NC, Härtling T, Klose M, Simon P, Eng LM, Eychmüller A: Monodisperse platinum nanospheres with adjustable diameters from 10 to 100 nm: synthesis and distinct optical properties. *Nano Lett* 2008, **8**:4588.
- Jiang X, Jiang Y, Brinker CJ: Hydrothermal synthesis of monodisperse single-crystalline alpha-quartz nanospheres. *Chem Commun* 2011, **47**:7524.
- Hu X, Yu JC: Continuous aspect-ratio tuning and fine shape control of monodisperse α -Fe₂O₃ nanocrystals by a programmed microwave-hydrothermal method. *Adv Funct Mater* 2008, **18**:880.
- Zhang J, Liu J, Peng Q, Wang X, Li Y: Nearly monodisperse Cu₂O and CuO nanospheres: preparation and applications for sensitive gas sensors. *Chem Mater* 2006, **18**:867.
- Li G, Zhai J, Li D, Fang X, Jiang H, Dong Q, Wang E: One-pot synthesis of monodispersed ZnS nanospheres with high antibacterial activity. *J Mater Chem* 2010, **20**:9215.
- Derrien G, Charnay C, Zajac J, Jones DJ, Rozière J: Copper-containing monodisperse mesoporous silica nanospheres by a smart one-step approach. *Chem Commun* 2008, 3118.
- Xuan S, Wang F, Wang YJ, Yu JC, Leung KC: Facile synthesis of size-controllable monodispersed ferrite nanospheres. *J Mater Chem* 2010, **20**:5086.
- Wang C, Yan J, Cui X, Wang H: Synthesis of raspberry-like monodisperse magnetic hollow hybrid nanospheres by coating polystyrene template with Fe₃O₄@SiO₂ particles. *J Colloid Interf Sci* 2011, **354**:94.
- Kim CY, Jung C, Jung J, Jeong SH, Yi S, Kim WJ: Studies of the factors effecting the preparation of heterogeneous platinum-based catalyst on silica supports. *Mater Res Bull* 2010, **45**:1419.
- Girgis E, Wahsh MMS, Othman AGM, Bandhu L, Rao KV: Synthesis, magnetic and optical properties of core/shell Co_{1-x}Zn_xFe₂O₄/SiO₂ nanoparticles. *Nanoscale Res Lett* 2011, **6**:460.
- Li X, Xu C, Han X, Qiao L, Wang T, Li F: Synthesis and magnetic properties of nearly monodisperse CoFe₂O₄ nanoparticles through a simple hydrothermal condition. *Nanoscale Res Lett* 2010, **5**:1039.
- Lu F, Wu SH, Hung Y, Mou CY: Size effect on cell uptake in well-suspended, uniform mesoporous silica nanoparticles. *Small* 2009, **5**:1408.
- Polshettiwar V, Cha D, Zhang X, Basset JM: High-surface-area silica nanospheres (KCC-1) with a fibrous morphology. *Angew Chem Int Ed* 2010, **49**:1.
- Ruckenstein E, Wang HY: Carbon dioxide reforming of methane to synthesis gas over supported cobalt catalysts. *Appl Catal A* 2000, **204**:257.
- Ho SW, Cruz JM, Houalla M, Hercules DM: The structure and activity of titania supported cobalt catalysts. *J Catal* 1992, **135**:173.
- Chen C, Zhou L, Zhang Q, Ma H, Miao H, Xu J: Design of bifunctionalized hexagonal mesoporous silicas for selective oxidation of cyclohexane. *Nanotechnology* 2007, **18**:215603.
- Wang J, Li D, Hou B, Jia L, Chen J, Sun Y: Textural structure of co-based catalysts and their performance for Fischer-Tropsch synthesis. *Catal Lett* 2010, **140**:127.
- Zhou L, Xu J, Miao H, Wang F, Li X: Catalytic oxidation of cyclohexane to cyclohexanol and cyclohexanone over Co₃O₄ nanocrystals with molecular oxygen. *Appl Catal A: Gen* 2005, **292**:223.
- Liu J, Xia H, Lu L, Xue D: Anisotropic Co₃O₄ porous nanocapsules toward high-capacity Li-ion batteries. *J Mater Chem* 2010, **20**:1506.
- Dunna BC, Cole P, Covington D, Webster MC, Pugmire RJ, Ernst RD, Eyring EM, Shah N, Huffman GP: Silica aerogel supported catalysts for Fischer-Tropsch synthesis. *Appl Catal A: Gen* 2005, **278**:233.
- Zhang Y, Hanayama K, Tsubaki N: The surface modification effects of silica support by organic solvents for Fischer-Tropsch synthesis catalysts. *Catal Commun* 2006, **7**:251.
- Ghattas MS: Cobalt-modified mesoporous FSM-16 silica: characterization and catalytic study. *Microporous Mesoporous Mater* 2006, **97**:107.
- Eriksson S, Nylén U, Rojas S, Boutonnet M: Preparation of catalysts from microemulsions and their applications in heterogeneous catalysis. *Appl Catal A: Gen* 2004, **265**:207.
- Tartaj P, Serna CJ: Synthesis of monodisperse superparamagnetic Fe/silica nanospherical composites. *J Am Chem Soc* 2003, **125**:15754.
- Miyao T, Minoshima K, Naito S: Remarkable hydrogen occlusion ability of hollow Ir-SiO₂ nanoparticles prepared by reversed micelle techniques. *J Mater Chem* 2005, **15**:2268.
- Tago T, Shibata Y, Hatsuta T, Miyajima K, Kishida M, Tashiro S, Wakabayashi K: Synthesis of silica-coated rhodium nanoparticles in reversed micellar solution. *J Mater Chem* 2002, **37**:977.
- Takenaka S, Orita Y, Matsune H, Tanabe E, Kishida M: Structures of silica-supported Co catalysts prepared using microemulsion and their catalytic performance for the formation of carbon nanotubes through the decomposition of methane and ethylene. *J Phys Chem C* 2007, **111**:7748.
- Kouachi K, Lafaye G, Especel C, Cherifi O, Marécot P: Preparation of silica-supported cobalt catalysts from water-in-oil microemulsion for selective hydrogenation of citral. *J Mol Catal A: Chem* 2009, **308**:142.
- Esposito S, Turco M, Ramis G, Bagnasco G, Pernice P, Pagliuca C, Bevilacqua M, Aronne A: Cobalt-silicon mixed oxide nanocomposites by modified sol-gel method. *J Solid State Chem* 2007, **180**:3341.
- Fouad OA, Makhlof SA, Ali GAM, El-Sayed AY: Cobalt/silica nanocomposite via thermal calcination-reduction of gel precursors. *Mater Chem Phys* 2011, **128**:70.
- Umegaki T, Yan JM, Zhang XB, Shioyama H, Kuriyama N, Xu Q: Co-SiO₂ nanosphere-catalyzed hydrolytic dehydrogenation of ammonia borane for chemical hydrogen storage. *J Power Sources* 2010, **195**:8209.
- Wang M, Chen C, Ma J, Xu J: Preparation of superhydrophobic cauliflower-like silica nanospheres with tunable water adhesion. *J Mater Chem* 2011, **21**:6962.
- Chen C, Xu J, Zhang Q, Ma Y, Zhou L, Wang M: Superhydrophobic materials as efficient catalysts for hydrocarbon selective oxidation. *Chem Commun* 2011, **47**:1336.
- Chen C, Xu J, Zhang Q, Ma H, Miao H, Zhou L: Direct synthesis of bifunctionalized hexagonal mesoporous silicas and its catalytic performance for aerobic oxidation of cyclohexane. *J Phys Chem C* 2009, **113**:2855.
- Ning J, Xu J, Liu J, Lu F: Selective hydrogenation of benzene to cyclohexene over colloidal ruthenium catalyst stabilized by silica. *Catal Lett* 2006, **109**:175.
- Alba MD, Luan ZH, Klinowski J: Titanosilicate mesoporous molecular sieve MCM-41: synthesis and characterization. *J Phys Chem* 1996, **100**:2178.
- Esposito S, Turco M, Ramis G, Bagnasco G, Pernice P, Pagliuca C, Bevilacqua M, Aronne A: Cobalt-silicon mixed oxide nanocomposites by modified sol-gel method. *J Solid State Chem* 2007, **180**:3341.
- Hamdy MS, Ramanathan A, Maschmeyer T, Hanefeld U, Jansen JC: Co-TUD-1: a ketone-selective catalyst for cyclohexane oxidation. *Chem Eur J* 2006, **12**:1782.

42. Katsoulidis AP, Petrakis DE, Armatas GS, Trikalitis PN, Pomonis PJ: **Ordered mesoporous CoO_x/MCM-41 materials exhibiting long-range self-organized nanostructured morphology.** *Microporous Mesoporous Mater* 2006, **92**:71.
43. Masuda H, Matsui Y, Yotsuya M, Matsumoto F, Nishio K: **Fabrication of highly ordered anodic porous alumina using self-organized polystyrene particle array.** *Chem Lett* 2004, **33**:584.
44. Carvalho WA, Varaldo PB, Wallau M, Schuchardt U: **Mesoporous redox molecular sieves analogous to MCM-41.** *Zeolite* 1997, **18**:408.
45. Wang C, Lim S, Du G, Loebicki CZ, Li N, Derrouiche S, Haller GL: **Synthesis, characterization, and catalytic performance of highly dispersed Co-SBA-15.** *J Phys Chem C* 2009, **113**:14863.
46. Schuchardt U, Cardoso D, Sercheli R, Pereira R, da Cruz RS, Guerreiro MC, Mandelli D, Spinace EV, Pires EL: **Cyclohexane oxidation continues to be a challenge.** *Appl Catal A* 2001, **211**:1.
47. Raja R, Sankar G, Thomas JM: **Powerful redox molecular sieve catalysts for the selective oxidation of cyclohexane in air.** *J Am Chem Soc* 1999, **121**:11926.
48. Raja R, Thomas JM: **Catalyst design strategies for controlling reactions in microporous and mesoporous molecular-sieves.** *J Mol Catal A* 2002, **181**:3.

doi:10.1186/1556-276X-6-586

Cite this article as: Zhang et al.: Facile preparation of highly-dispersed cobalt-silicon mixed oxide nanosphere and its catalytic application in cyclohexane selective oxidation. *Nanoscale Research Letters* 2011 **6**:586.

Submit your manuscript to a SpringerOpen[®] journal and benefit from:

- ▶ Convenient online submission
- ▶ Rigorous peer review
- ▶ Immediate publication on acceptance
- ▶ Open access: articles freely available online
- ▶ High visibility within the field
- ▶ Retaining the copyright to your article

Submit your next manuscript at ▶ springeropen.com
