

Prospective application of carbon-silica derived from SiC-Si sludge as a support for Fe catalysts

Mi Sun Lee*, Kyun Young Park*, Hoey Kyung Park*, Tae Won Kang*,
Hee Dong Jang**,†, Sang Sup Han***, and Jong-Ki Jeon*,†

*Department of Chemical Engineering, Kongju National University,
1223-24 Cheonan-Daero, Cheonan, Chungnam 31080, Korea

**Rare Metals Research Center, Korea Institute of Geoscience and Mineral Resources,
124 Gwahang-ro, Yuseong-gu, Daejeon 34132, Korea

***Petroleum and Gas Research Laboratory, Korea Institute of Energy Research,
152 Gajeong-ro, Yuseong-gu, Daejeon 34129, Korea

(Received 16 July 2016 • accepted 19 August 2016)

Abstract—A unique carbon-silica (30 wt%) material was prepared by H₂O activation at 700 °C for 8 h with the carbon derived from SiC-Si sludge and the in-situ hydrolysis of the SiCl₄ trapped in the pores of the carbon into silica. The BET surface area of the carbon-silica was 1,750 m²/g and the pore volume by QSDFT was 1.13 cm³/g, 40% of which stemmed from micropores smaller than 2 nm with 60% from mesopores between 2 nm and 50 nm. The activated carbon-silica was loaded with Fe by means of chemical vapor infiltration (CVI) and incipient wetness impregnation (IWI). A hydrogen temperature-programmed reduction test showed that the activated carbon-silica is a prospective support material for Fe catalysts and that the dispersion of Fe in the carbon-silica is higher with CVI than with IWI.

Keywords: Carbon-silica, SiC-Si Sludge, Surface Area, Fe

INTRODUCTION

A large amount of SiC-Si sludge is generated during the slicing of silicon ingots into the wafers used for integrated circuit (IC) chips and solar cells. Recently, a type of SiC-Si sludge was chlorinated to produce SiCl₄ and a carbon that is similar in terms of the pore structure to the carbide-derived carbons (CDC) from various metal carbides (e.g., SiC, TiC, Mo₂C, ZrC, TaC), but contains silica as an impurity [1]. CDCs are known to have good properties as raw materials for supercapacitors [2], lithium-ion batteries [3], and gas-storage devices [4,5]. In contrast, the carbon from sludge may not be suitable for such electronics applications due to impurities, whereas it may be allowable as an adsorbent for gas storage applications. The application of the carbon from sludge for gas storage has not attracted much attention, as CDCs with even higher specific surface areas exhibit gas-storage capacities lower than those required for industrial applications [4].

In the present study, we explored the possibility of utilizing the carbon obtained by the chlorination of sludge as a support for Fe catalysts. Large specific surface area and metal impregnation capabilities, as well as large numbers of surface functional groups of carbon catalysts enable their use for physical and chemical adsorption in various applications [6–9]. The as-produced carbon is microporous with pore sizes ranging from 1.1 to 2.1 nm [1], likely implying

unacceptable resistance to the mass transfer of certain reactants and products. The carbon was activated with H₂O vapor to create mesopores to facilitate mass transfer and to enhance the surface area. Moreover, the SiCl₄ trapped in the pores of the resulting carbon after chlorination was not removed, instead being hydrolyzed in-situ into silica [10] during the activation step by utilizing the H₂O that was admitted to activate the carbon. The silica-bearing carbon is referred to henceforth in this paper as carbon-silica. The activated carbon-silica was loaded with iron by means of chemical vapor infiltration (CVI) and incipient wetness impregnation (IWI) and was then characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), nitrogen adsorption, and temperature-programmed reduction (TPR) with hydrogen.

EXPERIMENTAL

SiC-Si sludge composed of SiC (79.4 wt%), Si (14.2 wt%), Fe (5.06 wt%) and other minor components was chlorinated in a tubular quartz reactor (2.4 cm in diameter and 32 cm in length) at 900 °C for 4 h under a flow of a mixture of chlorine (10 mol%) and nitrogen at 300 ml/min (STP). The SiCl₄ vapor produced by chlorination was condensed with dry ice, while the excess chlorine was captured in a NaOH flask. More details about the preparation method are described in the literature [1]. Compared to an earlier previous method, one difference is that the SiCl₄ and chlorine trapped in the carbon were not removed in the chlorination step. The as-produced carbon-silica had a particle size of 0.1–30 μm with a volume average diameter of 5.4 μm and with a chlorine content

†To whom correspondence should be addressed.

E-mail: jkjeon@kongju.ac.kr, hdjang@kigam.re.kr

Copyright by The Korean Institute of Chemical Engineers.

of 1.4 at% according to energy dispersive spectroscopy (Tescan, Model Mira LMH). ICP (Perkin Elmer, Model 2100DV) showed 0.1 wt% of iron and a thermo-gravimetric analysis (Shimadzu, Model TGA-50) showed silica ash at 14 wt%, equivalent to 2.2% of the silicon initially present in the sludge either in elemental form or in SiC.

An amount of 0.07 g of the raw carbon-silica was put into a glass boat in the center of a vertical quartz reactor 2.5 cm in diameter and 30 cm tall surrounded by an electric heater. The reactor was purged with nitrogen at a flow rate of 100 ml/min for 1 h and then heated to a predetermined temperature, at which the purge gas was replaced with a mixture of H₂O vapor (activator) and nitrogen at the same flow rate. The mole fraction of H₂O in the gas mixture was controlled by the temperature of the bath, which contained a water bottle through which nitrogen gas was bubbled. After the reaction, the activated carbon-silica was removed and weighed.

The activated carbon-silica was loaded with Fe using the two different methods of CVI and IWI. As a precursor, Fe(CO)₅ (Aldrich, 99.999%) was used with the CVI method and Fe₂(NO₃)₆·nH₂O (Aldrich, 99.999%) was used with the IWI method. For Fe loading with CVI, 0.4 ml of Fe(CO)₅ was thermally decomposed in a nitrogen atmosphere at 60 °C for 1 h in a 0.5 L batch reactor in which 0.1 g of the activated carbon-silica had been placed. After the thermal decomposition step, the reactor was cooled to room temperature. The Fe-loaded carbon-silica was then oxidized in situ with air for 0.5 h. IWI was performed by dropping an iron nitrate solution into the activated carbon-silica and subsequently drying and calcining the carbon-silica at 250 °C for 3 h.

The morphology of the carbon-silica samples was examined by TEM (JEOL, model JEM-3000). The crystalline structure of the Fe-loaded carbon-silica was investigated by XRD with Cu K α radiation (SCINCO, model SMD 3000). The specific surface area was measured by nitrogen adsorption with a Micromeritics ASAP 2010 instrument using a multi-point BET model, and the pore size distribution was calculated via quenched solid density functional theory (QSDFT) (Quadasorb-SI/MP, Quantachrome). The Fe content in the carbon-silica was measured by means of ICP (Perkin Elmer, Model 2100DV). The dispersion of the Fe in the carbon-silica was studied by hydrogen TPR using a BEL-CAT-B instrument in which a stream of hydrogen in argon was passed over the carbon-silica, 0.023 g in mass, at a rate of 50 ml/min, with the temperature increased to a predetermined set point at a rate of 10 °C/min.

RESULTS AND DISCUSSION

The raw carbon-silica produced in the chlorination unit was activated at 700 °C for 8 h at a gas flow rate at 100 ml/min with the mole fraction of H₂O in the gas set to 0.5. The activation temperature was lower than the range of 760–910 °C used by Bleda-Martines et al. [11], who activated different carbon materials for capacitors. In the present activation step, the silica content was increased from 14.2 wt% to 30 wt% due to the 62% burn-off rate of the carbon, and the BET surface area was increased from 940 m²/g to 1,750 m²/g. The pore size distribution of the activated carbon-silica as calculated by QSDFT with a slit/cylinder pore model is shown in Fig. 1. The total pore volume was determined to be 1.13 cm³/g, 40%

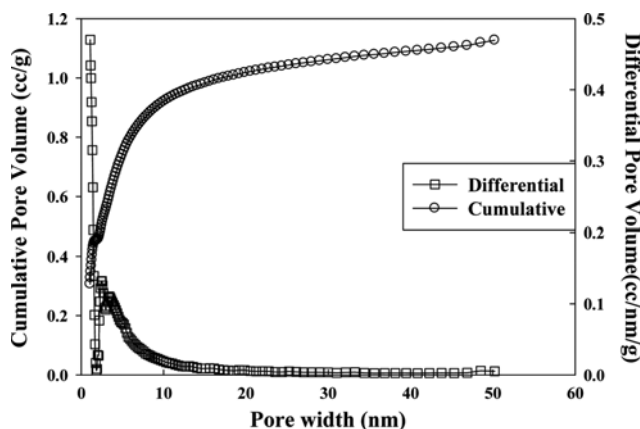


Fig. 1. Pore size distribution of carbon-silica activated with H₂O vapor at 700 °C for 8 h (H₂O mole fraction: 0.5; gas flow rate: 100 ml/min at STP).

of which consisted of micropores smaller than 2 nm and 60% of mesopores between 2 nm and 50 nm. The highest BET area ever reported for SiC-CDC as a raw material was 2,200 m²/g by Korman and Popovska [12], in whose work an SiC-CDC sample at 1,180 m²/g was activated with CO₂ at 850 °C for 9 h. Their burn-off rate of carbon was 55.6% and the pore volume was 1.16 cm³/g, which are nearly identical to those in the present study, but their mesopore fraction is much lower, at 16.1%. The silica in the present carbon-silica was suspected to be the cause of the higher mesopore volume, in reference to a report which found that pore sizes of gel-type silica ranged from 30 to 53 nm [13]. The carbon was removed by burning to collect the silica. We attempted to analyze the residual silica to determine the pore size distribution, but the silica was too fluffy to be degassed during the preparation process for N₂ adsorption. An SEM-EDX analysis revealed that the residual chlorine in the raw carbon-silica was removed during the activation step with H₂O. A similar dechlorination step with water

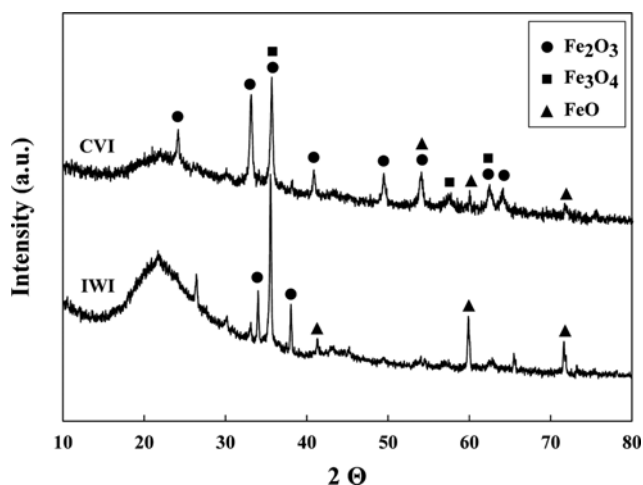


Fig. 2. X-ray diffraction patterns of Fe (2 wt%)-loaded carbon-silica for CVI and IWI loading methods. The carbon-silica used for the loading was obtained by activation of raw carbon-silica with H₂O vapor at 700 °C for 8 h.

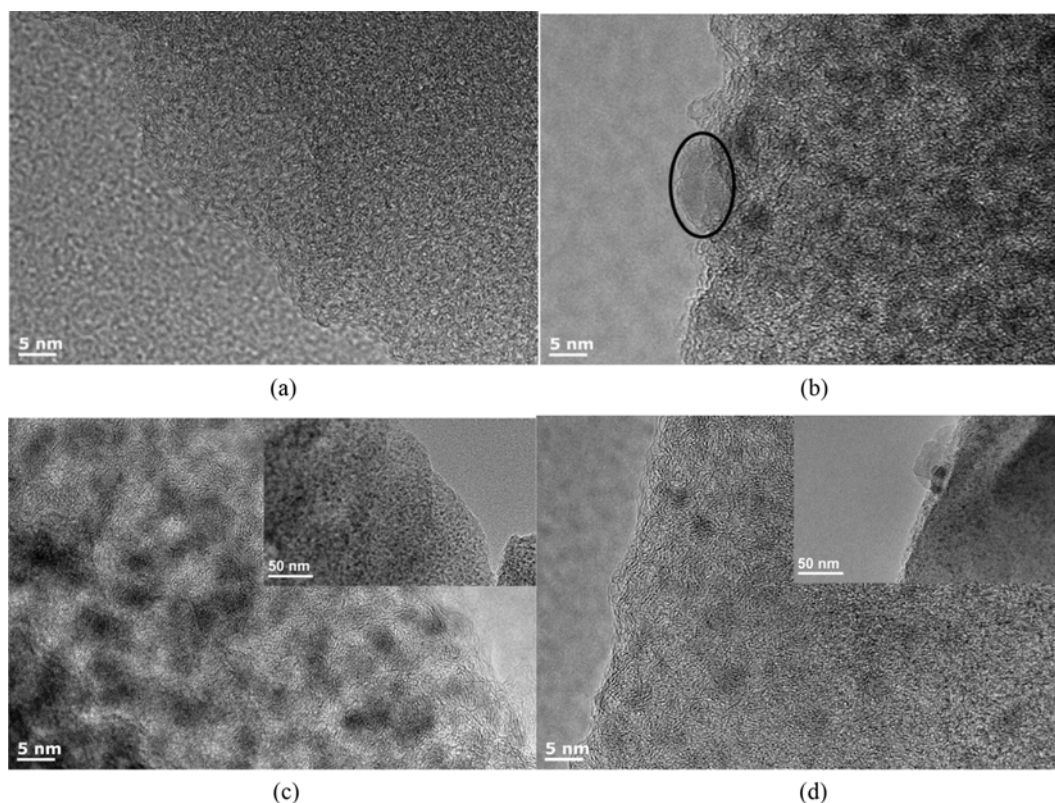


Fig. 3. Comparison of transmission electron microscopic images between (a) raw carbon-silica, (b) raw carbon-silica loaded with Fe (2 wt%) using CVI, (c) activated carbon-silica loaded with Fe (2 wt%) using CVI, and (d) activated carbon-silica loaded with Fe (2 wt%) using IWI. The activated carbon-silica was obtained by activation of raw carbon-silica with H_2O vapor at 700°C for 8 h. The circle in (b) indicates a Fe particle formed on the external surface. The insets in (c) and (d) show the images at a lower magnification.

vapor was patented earlier for mineral active carbon [14].

The carbon-silica samples activated at 700°C for 8 h were loaded with Fe at 2 wt% using the CVI and IWI methods. Fig. 2 shows the XRD patterns of the Fe-loaded carbon-silica samples. Fe_2O_3 and FeO peaks are present in both cases, whereas Fe_3O_4 peaks can only be observed in the carbon-silica processed by means of CVI. Fig. 3 shows TEM images of the raw carbon-silica, the raw carbon-silica loaded with Fe (2 wt%) via CVI, the activated carbon-silica loaded with Fe (2 wt%) by means of CVI, and the activated carbon-silica loaded with Fe (2 wt%) using the IWI method. The raw carbon-silica is nanoporous, as shown in Fig. 3(a). The dark spots in Figs. 3(b), (c) and (d) represent the Fe oxide particles. The dispersion of Fe is more uniform with CVI than it is with IWI, most likely because the precursor is a gas in CVI and a liquid in IWI. The gas molecules infiltrate the small pores more easily than do the liquid molecules.

The hydrogen-TPR profiles of carbons with different loading methods are shown in Fig. 4. The activated carbon-silica processed by CVI exhibits two sharp peaks at 480°C and 605°C . In the activated carbon-silica with IWI, two peaks are observed at temperatures nearly identical to those in the CVI method, but the peaks are broader and shorter. Reduction of iron oxides by hydrogen is known to occur in three steps. In the first step, Fe_2O_3 is reduced to Fe_3O_4 ($\text{Fe}_2\text{O}_3 + 1/3\text{H}_2 = 2/3\text{Fe}_3\text{O}_4 + 1/3\text{H}_2\text{O}$). In the second step, Fe_3O_4 is reduced to FeO ($\text{Fe}_3\text{O}_4 + \text{H}_2 = 3\text{FeO} + \text{H}_2\text{O}$). In the third step, FeO

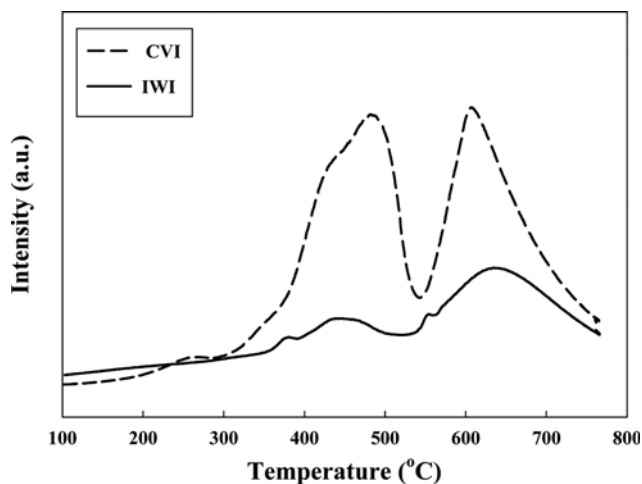


Fig. 4. Comparison of hydrogen-TPR profile of Fe (2 wt%)-loaded carbon-silica between CVI and IWI loading methods. The carbon-silica used for the loading was obtained by activation of raw carbon-silica with H_2O vapor at 700°C for 8 h.

is reduced to Fe ($\text{FeO} + \text{H}_2 = \text{Fe} + \text{H}_2\text{O}$). In the present work, the three reductions were overlapped in two peaks rather than separated to show three distinctive peaks. The number of peaks and the relative peak sizes are known to depend upon various factors,

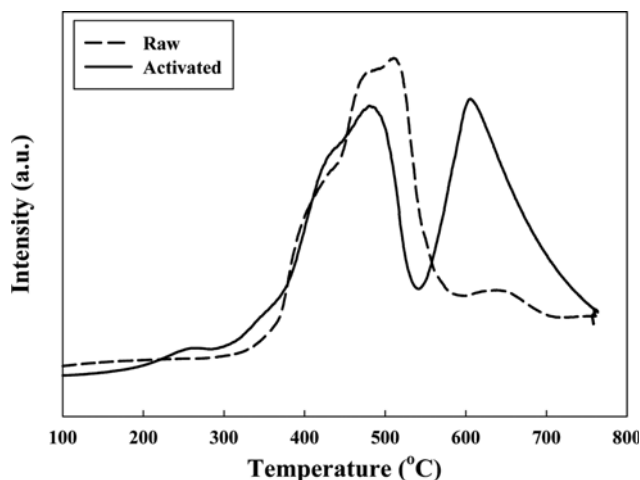


Fig. 5. Comparison of hydrogen-TPR profile of Fe (2 wt%)-loaded carbon-silica by CVI between raw carbon-silica and carbon-silica activated with H₂O vapor at 700 °C for 8 h.

including the heating rate, the particle size of the Fe oxides, and the structure of the carbon [15]. The area under the bimodal curve in Fig. 4 represents the amount of hydrogen consumed for the reduction. The hydrogen consumption rate is higher with CVI, which indicates that the dispersion of Fe with CVI is higher than that with IWI. Agglomerated iron-oxide particles were formed on a surface of the carbon-silica with IWI, as shown in the inset of Fig. 3(d).

TPR profiles with CVI were compared between the raw carbon-silica and the activated carbon-silica while holding the iron content at 2 wt%. As shown in Fig. 5, the temperatures at which the peaks appeared are similar, but the relative sizes of the peaks are different. The two peaks are nearly identical in size with the activated carbon-silica, while they are considerably different with the raw carbon-silica. The first peak with the raw carbon-silica is larger than that with the activated carbon-silica, which means that the reduction at the lower temperature was more active with the raw carbon-silica. This likely occurred because the pores in the raw carbon-silica are smaller and the iron oxide particles captured inside the pores are thus smaller, resulting in higher reactivity toward the hydrogen reduction process. This hypothesis is supported by a report which found that the deposition of iron oxide inside carbon-nanotube pores resulted in easier reduction of the oxide at a lower temperature [16]. The activation reduced the micropores and increased the mesopores. The iron oxide particles in the mesopores, larger than those in the micropores, can be attributed to the increase in the second-peak area, as was observed with the activated carbon-silica. With the raw carbon-silica, iron particles much larger than those trapped in the pores were formed on the external surface, as indicated by the circle in Fig. 3(b), likely due to the limited capacity of the micropores to accommodate all of the Fe molecules produced by the decomposition of Fe(CO)₅. The total area under the two peaks was measured and found to be greater by 55% with the activated carbon-silica, indicating that the activated carbon-silica would outperform the raw carbon-silica as a support for Fe catalysts.

The TPR test result of the Fe-loaded carbon-silica indicates that

carbon-silica is a promising material as a support for Fe catalysts. This catalyst finds potential applications in the Fischer-Tropsch synthesis of chemicals and fuels from biomass, coal, and natural gas [16]; in the hydroxylation of benzene to phenol [17]; and in the conversion of toxic nitrogen dioxide to less harmful species [18]. The pore volumes of the present carbon-silica are nearly twice as great as those used for the conversion of nitrogen oxide, both in terms of micro- and mesopores, and the surface area is larger by more than 50% than a micro-mesoporous type of carbon-silica that was prepared in a complex manner from graphite oxide and tetraethoxysilane [19]. Further studies may be necessary to determine the optimal conditions for both H₂O activation and Fe loading and to test the catalytic activity during chemical reactions.

CONCLUSION

The BET surface area of carbon-silica derived from Si-SiC sludge was 1,750 m²/g and the pore volume according to QSDFT was 1.13 cm³/g, 40% of which stemmed from micropores smaller than 2 nm with the balance coming from mesopores between 2 nm and 50 nm in size. A hydrogen-TPR test of the carbon-silica activated with H₂O at 700 °C for 8 h and subsequently loaded with Fe at 2 wt% showed that the dispersion of Fe in the carbon-silica is higher with CVI and with IWI. The activated carbon-silica consumed more hydrogen than its raw counterpart by 55% in the TPR test, indicating that at an identical Fe loading rate, the activated carbon-silica is expected to provide higher catalytic activity than raw carbon-silica. Further studies may be necessary to determine the optimal conditions both for H₂O activation and Fe loading and to test the catalytic activity which occurs during chemical reactions.

ACKNOWLEDGEMENT

This study was supported by the R&D Center for Valuable Recycling (Global-Top Environmental Technology Development Program), funded by the Ministry of Environment (Project No. 11-A08-IR).

REFERENCES

1. K. Y. Park, H. K. Park, B. W. Ko, T. W. Kang and H. D. Jang, *Ind. Eng. Chem. Res.*, **52**, 3943 (2013).
2. C. Portet, M. A. Lillo-Rodenas, A. Linares-Solano and Y. Gogotsi, *Phys. Chem. Chem. Phys.*, **11**, 4943 (2009).
3. S.-H. Yeon, K.-N. Jung, S. Yoon, K.-H. Shin and C.-S. Jin, *J. Phys. Chem. Solids*, **75**, 1045 (2013).
4. M. Sevilla and R. Mokaya, *J. Mater. Chem.*, **21**, 4727 (2011).
5. S. H. Yeon, S. Osswald, Y. Gogotsi, J. P. Singer, J. M. Simmons, J. E. Fischer, M. A. Lillo-Rodenas and A. Linares-Solano, *J. Power Sources*, **191**, 560 (2009).
6. J. H. Ko, R. S. Park, J. K. Jeon, D. H. Kim, S. C. Jung, S. C. Kim and Y. K. Park, *J. Ind. Eng. Chem.*, **32**, 109 (2015).
7. Y. Lee, J. T. Jang, J. W. Bae, K. J. Yoon and G. Y. Han, *Korean J. Chem. Eng.* (2016), DOI:10.1007/s11814-016-0144-0.
8. S. Han, G. S. Chae and J. S. Lee, *Korean J. Chem. Eng.*, **33**, 1799 (2016).

9. J. K. Jeon, H. Kim, Y. K. Park, C. H. F. Peden and D. H. Kim, *Chem. Eng. J.*, **174**, 242 (2011).
10. H. K. Park and K. Y. Park, *Mater. Res. Bull.*, **43**, 2833 (2008).
11. M. J. Bleda-Martinez, J. A. Macia-Agullo, D. Lozano-Castello, E. Morallon, D. Cazorla-Amoros and A. Linares-Solano, *Carbon*, **43**, 2677 (2005).
12. M. Kormann and N. Popovska, *Micropor. Mesopor. Mater.*, **130**, 167 (2010).
13. R. K. Iler, *The Chemistry of silica*, John Wiley & Sons, New York, 481 (1979).
14. W. A. Mohun, US Patent, 3,066,099 (1959).
15. W. K. Jozwiak, E. Kaczmarek, T. P. Maniecki, W. Ignaczak and W. Maniukiewicz, *Appl. Catal. A: Gen.*, **326**, 17 (2007).
16. R. M. M. Abbaslou, A. Tavassoli, J. Soltan and A. K. Dalai, *Appl. Catal. A: Gen.*, **367**, 47 (2009).
17. S. Song, H. Yang, R. Rao, H. Liu and A. Zhang, *Appl. Catal. A: Gen.*, **375**, 265 (2010).
18. M. Busch, W. Schmidt, V. Migunov, A. Beckel, C. Notthoff, A. Kompch, U. Bergmann, M. Winterer and B. Atakan, *Appl. Catal. B: Environ.*, **160**, 641 (2014).
19. Z.-M. Wang, K. Hoshinoo, K. Shishibori, H. Kanoh and K. Ooi, *Chem. Mater.*, **15**, 2926 (2003).