Catalysis Communications 42 (2013) 1–5

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Sulfated tin oxide as an efficient solid acid catalyst for liquid phase selective dehydration of sorbitol to isosorbide

Aasif Asharaf Dabbawala, Dinesh Kumar Mishra, Jin-Soo Hwang *

Biorefinery Research Center, Korea Research Institute of Chemical Technology (KRICT), Daejeon, Republic of Korea

ARTICLE INFO

Article history:
Received 17 June 2013
Received in revised form 10 July 2013
Accepted 10 July 2013
Available online 18 July 2013

Keywords:
Dehydration
Sorbitol
Isosorbide
Solid super acid
Sulfated tin oxide

ABSTRACT

Sulfated tin oxides (STO) with different sulfur content (1–8 wt%) were prepared via straightforward thermal decomposition of stannous sulfate. The catalyst performances of STO were investigated in liquid phase dehydration of sorbitol under solvent free condition. The calcination temperature of STO affected sulfur content and isosorbide selectivity. The STO exhibited high catalytic activity compared to sulfated zirconia affording complete conversion of sorbitol with 65% isosorbide selectivity in 2 h at 180 °C. Effects of reaction temperature, catalyst amount and reaction time on conversion and selectivity were studied and the catalyst was also reused.

1. Introduction

The limited availability and increasing cost of petroleum feedstock have given rise to a growing interest in the conversion of renewable resources, such as cellulosic biomass to conventional fuels and value added chemicals as several perspectives [1–3]. The sorbitol, a sugar alcohol, is derived from cellulose or lignocellulosic biomass via glucose hydrogenation and is considered as an important platform molecule to synthesis varieties of organic chemicals [3–5]. In particular, isosorbide and sorbitan are obtained by sequential dehydration of sorbitol (Scheme 1) and have numerous industrial and commercial applications in the field of in pharmaceuticals, cosmetic and polymers [6–14].

The dehydration of sorbitol is conventionally performed using mineral acids like sulfuric acid, although requirement of base to neutralize acid, significant handling risk, corrosive nature of catalyst and stability issues of products are major concerns of this process [7–14]. Therefore, the use of solid acid catalysts such as Amberlyst-15 resin, metal (IV) phosphates, phosphated Nb_2O_5, sulfated copper oxides, sulfated zirconia/titania, supported heteropoly acid have been illustrated for the production of isosorbide to replace homogeneous acids [8–14]. Among the reported solid acid catalysts, sulfated metal oxides exhibited high catalyst activity than their metal oxide phosphate analogues and their activity/selectivity varied on which metal used to prepare sulfated metal oxide catalyst [11–13]. For example, Xia et al. [11] studied sulfated metal oxides of three different metals such as Ni, Cu, Al and observed high catalyst performance with sulfated copper oxide (67.5% isosorbide selectivity at 200 °C). Khan et al. [12] reported 61% isosorbide selectivity at 210 °C using sulfated zirconia. Nevertheless, requirement of comparative high temperature and longer reaction time are important issues related with such solid acid catalysts [8–14]. It is therefore need to develop efficient solid acid catalysts which exhibit high catalyst activity/selectivity and also can be operated comparatively at lower temperature.

Sulfated tin oxide (STO) is another potential candidate of solid super acid which possesses higher acid strength than sulfated zirconia [15,16]. There are several reports in which STO exhibited high catalyst performance than sulfated zirconia and its acid sites are not easily poisoned by water during the reaction [16,17]. In this context and in continuation of our work to develop effective catalyst for dehydration sorbitol [12,13], the STO catalysts were prepared by calcination of stannous sulfate at different temperature and characterized by XRD, SEM, SEM-EDX, FT-IR and N_2 adsorption. The catalytic performance of these catalysts towards liquid phase dehydration of sorbitol was investigated. The various parameters have been studied in detail and results are compared with that of sulfated zirconia.

2. Experimental

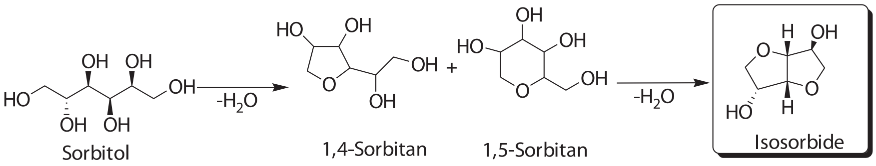
2.1. Catalysis preparation, dehydration reaction and analysis

The STO, solid super acid catalysts with different sulfur contents (1–8 wt%), were prepared by calcining Sn(II)SO_4 (≥95%, Sigma-Aldrich, USA) at different temperatures (350, 400, 450, 500 and 600 °C) for 4 h

---

* Corresponding author. Tel.: +82 42 860 7382; fax: +82 42 860 7676.
E-mail address: jshwang@krict.re.kr (J.-S. Hwang).

1566-7367/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.catcom.2013.07.020



Scheme 1. Dehydration of sorbitol to isosorbide.

with a heating rate of 5 °C min^{-1} in flowing air. According to the calcination temperature, STO catalysts were denoted as STO-T (where T = temperature). The dehydration of sorbitol was carried out in liquid phase according to our previously reported procedure [12,13]. The composition of the dehydrated product was analyzed using HPLC (Younglin Instrument, Acme 9000) equipped with RI detector and Asahipak column (NH2P-50 4E, No. N712004). The products detected were isosorbide and sorbitan (mostly 1,4- or 3,6-sorbitan with small amount of 1,5- and 2,5-anyhydrides). The selectivity of isosorbide (IS) and sorbitan (ST) were based on molar composition. The non-indentified soluble and insoluble compounds were considered as "others" (unknown). The reproducibility of the experimental results was confirmed by repeating the same experiment at least two times and was found to be in a range of ±3–5% due to process and analytical variations. After dehydration reaction, the recovered catalyst was thoroughly washed with water and ethanol. The catalyst was then dried and finally calcined at 450 °C for 5 h to get the regenerated catalyst.

3. Results and discussion

3.1. Characterization of the catalyst

Powder XRD of STO catalysts calcined at different temperature indicates the change in the crystalline phase of stannous sulfate before and after calcination at 350, 400, 450, 500 and 600 °C (Fig. 1). The diffraction peaks at 24.95°, 27.02°, 29.08°, 32.48°, 41.69° and 42.99°, corresponding to the characteristic diffraction of $SnSO_4$, with additional peaks at 26.63°, 33.97°, 38.10° and 51.83°, corresponding to the characteristic diffractions of SnO_2 appeared in the sample calcined at 350 °C. This suggests that the decomposition of $SnSO_4$ to SO_4^{2-}/SnO_2 occurred at 350 °C. The characteristic diffraction peaks of $SnSO_4$ disappeared in all the samples calcined above 350 °C, indicating complete conversion of $SnSO_4$ to SnO_2 phase.

The SEM images of STO calcined at 450 °C are shown in Fig. 2 along with SEM-EDX spectrum. From the SEM images, it is clear that the catalyst has crystalline cubic morphology with particles sized in the range of 30–35 nm, whereas SEM-EDX spectrum indicates the presence of tin, oxygen and sulfur.

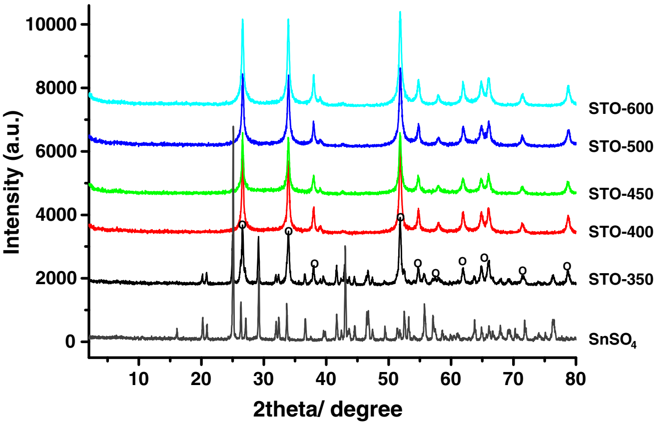


Fig. 1. XRD patterns of STO calcined at different temperatures (**O**–SnO_2).

The BET surface area and S content (determined by element analysis) of catalysts are listed in Table 1. The S content remain unchanged when the calcination temperature was below 350 °C but decreased sharply with an increase of the calcination temperature above 350 °C. BET surface area of samples increased first and then decreased with an increase of the calcination temperature. An abrupt change in surface area and S content above temperature of 350 °C during the calcination confirmed the transformation of $SnSO_4$ to SnO_2 by desulfation, which is necessary to generate medium–strong acid sites on the surfaces. The above results are in accordance with reported literatures indicating that the acidic properties and catalytic activities of STO catalyst depend on BET surface area and the sulfur content which are function of the calcination temperature [15–17].

The FT-IR spectra of the STO catalysts are shown in Fig. 3. From FT-IR spectra, it can be seen that the bands at 1165, 1038 and 975 cm^{-1} confirmed the presences of sulfate group and coordination of sulfate to tin ions through a bidentate chelating mode [18]. Due to the existence of sulfate groups on the surface, a strong acidity can be realized in the STO catalysts.

3.2. Catalytic dehydration of sorbitol

The catalytic activities of STO calcined at different temperature were tested in dehydration of sorbitol. To understand the role and effect of sulfate group in catalysts, the dehydration experiments were also performed with SnO_2 and $SnSO_4$ for comparison. All STO catalysts and $SnSO_4$ showed high catalytic activities towards the dehydration of sorbitol compare to unsulfated analogue, SnO_2 (Table 2, entry 1). The catalytic behavior of the STO changed with their calcination temperature due to the variation in sulfur content at different calcination temperature (Table 2, entries 3–7). These results indicated the role of the sulfate group to enhance conversion and selectivity.

The dehydration activity of the catalysts was in the order of $SnSO_4$ > STO 350 > STO 450 > STO 400 > STO 500 > STO 600. The $SnSO_4$ exhibited highest activity due to its homogeneous nature. In the case of STO catalysts, the catalyst activity was decreased with decrease in sulfur content as acidity of catalyst varied with sulfur content [11–13]. The STO calcined at 350 °C having sulfur content 8.02% displayed the complete conversion and high isosorbide selectivity (51%) in 1 h at 180 °C, although it was not fully converted to its oxide form. Therefore, the STO calcined at 450 °C having sulfur content 3.71% showed 46% isosorbide selectivity was selected for further optimization.

The effect of reaction temperature on conversion and selectivity of sorbitol dehydration was studied in the temperature range from 170 to 220 °C for reaction time 1 h using 0.15 g of STO-450 catalyst. The complete conversion was achieved in all cases when temperature was greater than 170 °C, while isosorbide selectivity considerably influence by variation in temperature (Fig. 4).

The low isosorbide selectivity was observed at 170 °C, which increased by factor of 2 at 180 °C. The isosorbide selectivity increased gradually with increasing temperature from 180 to 210 °C then decreased at 220 °C. At 170 °C, isosorbide selectivity was 23% which increased to 46% at 180 °C and enhance up 55% at 210 °C. With an increase in temperature, formation of dark brown colored side products were observed to increase which is difficult to characterize. These side products might be originated from self-polymerization

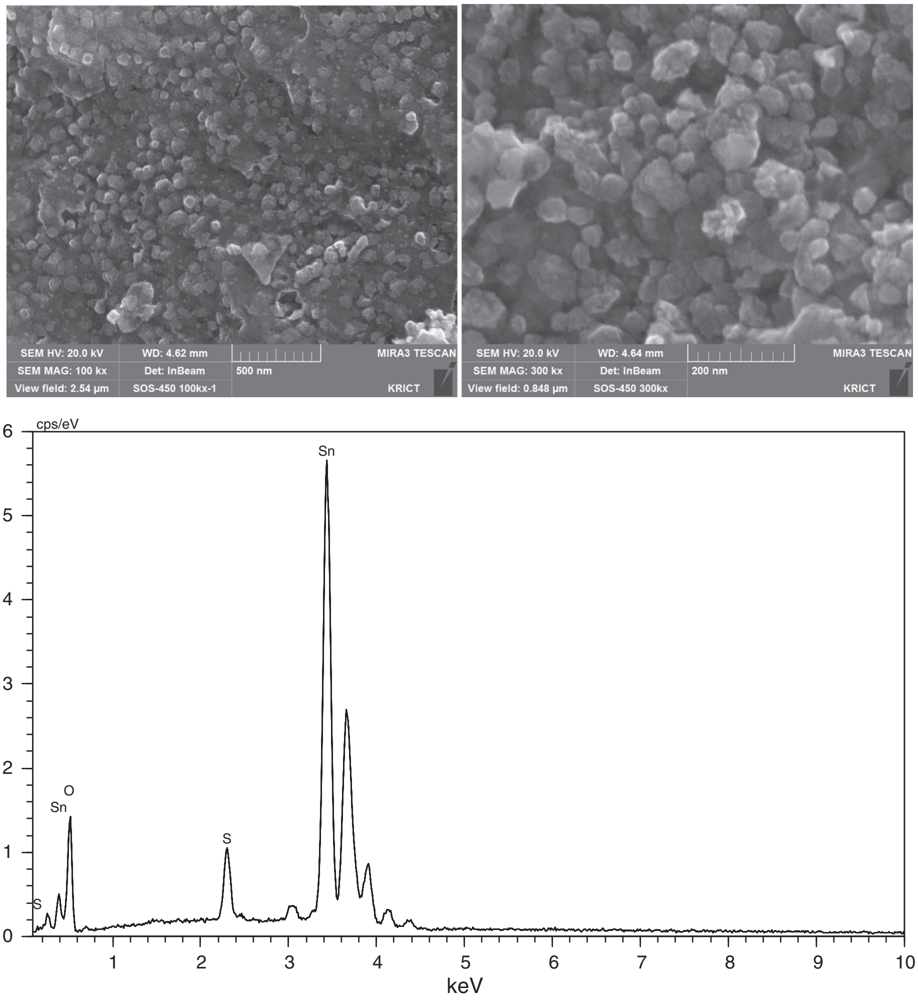


Fig. 2. SEM images and SEM-EDX spectrum of STO-450.

(or oligomerization) of isosorbide or cross-polymerization between isosorbide and sorbitan resulted into decrease in isosorbide selectivity at higher temperature.

Effect of catalyst amount on sorbitol conversion and isosorbide selectivity was investigated at 180 °C (Table 3). The conversion and isosorbide selectivity were found 96% and 39%, respectively, in 1 h using 0.1 g of STO-450 catalyst. With an increase in catalyst amount, the isosorbide selectivity increased (52%) gradually up to 0.2 g catalyst amount. The addition of more amount of catalyst than 0.2 g had no significant effect on isosorbide selectivity.

The dehydration reaction was also carried out at different reaction times using 0.2 g STO-450 catalyst. As shown in Table 3, the conversion and isosorbide selectivity increased with an increasing reaction time, the 100% conversion of sorbitol and high isosorbide selectivity (65%) were obtained in 60 min and 2 h respectively at 180 °C. It is worth to note that the liquid phase dehydration of sorbitol has been carried out first time with STO and exhibited high selectivity to isosorbide at comparative low temperature than sulfated zirconia [12] as well as other reported heterogeneous catalysts [9–14], which makes this catalyst proficient for this process. The reusability of the STO–450 for the dehydration of sorbitol has also been carried out for several runs. Sorbitol conversion was found almost 100% up to the fourth run with

Table 1
BET surface and sulfur content of STO calcined at different temperature.

Catalyst	BET Surface area (m^2/g)	S content[a] (%)
STO-350	10.95 ± 0.09	8.02 ± 0.08
STO-400	37.58 ± 0.06	2.85 ± 0.06
STO-450	40.51 ± 0.14	3.71 ± 0.07
STO-500	43.12 ± 0.16	1.41 ± 0.02
STO-600	34.74 ± 0.14	1.09 ± 0.02

[a] Determined by elemental analysis.

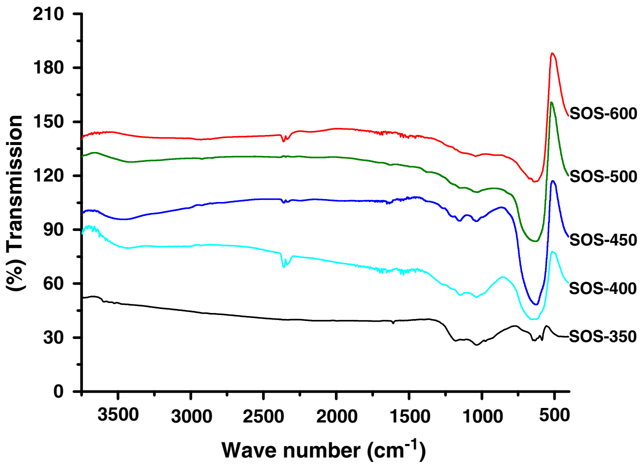


Fig. 3. FT-IR spectra of STO calcined at different temperatures.

Table 2
Catalytic performance of various tin-based catalysts in the dehydration of sorbitol.[a]

Entry	Catalyst	Conversion (%)	S_{IS} (%)[b]	S_{ST} (%)[c]	S_{others} (%)[d]
1	SnO_2	15	0	95	05
2	$SnSO_4$	100	61	30	09
3	STO-350	100	51	37	12
4	STO-400	100	40	44	16
5	STO-450	100	46	39	15
6	STO-500	100	26	59	15
7	STO-600	96	23	63	14

[a] Reaction condition: sorbitol = 10 g, tin-based catalyst = 0.150 g, temperature = 180 °C, reaction time = 1 h.
[b] Selectivity to isosorbide (IS).
[c] Selectivity to sorbitan (ST).
[d] Selectivity to others.

the regenerated catalyst (Fig. 5). The selectivity to isosorbide decreased slightly up to fourth run indicating reusability of the catalyst. The decrease of the isosorbide selectivity at each run which may be due to the partial destruction of the weakly bonded sulfate groups during regeneration and treatment [12,13]. However, it can be reused up to four times without noticeable loss in conversion and selectivity by regenerating catalyst. The further detail investigation using sulfated metal oxide based catalyst and their application in sugar/sugar alcohols dehydration are currently under way in our laboratory.

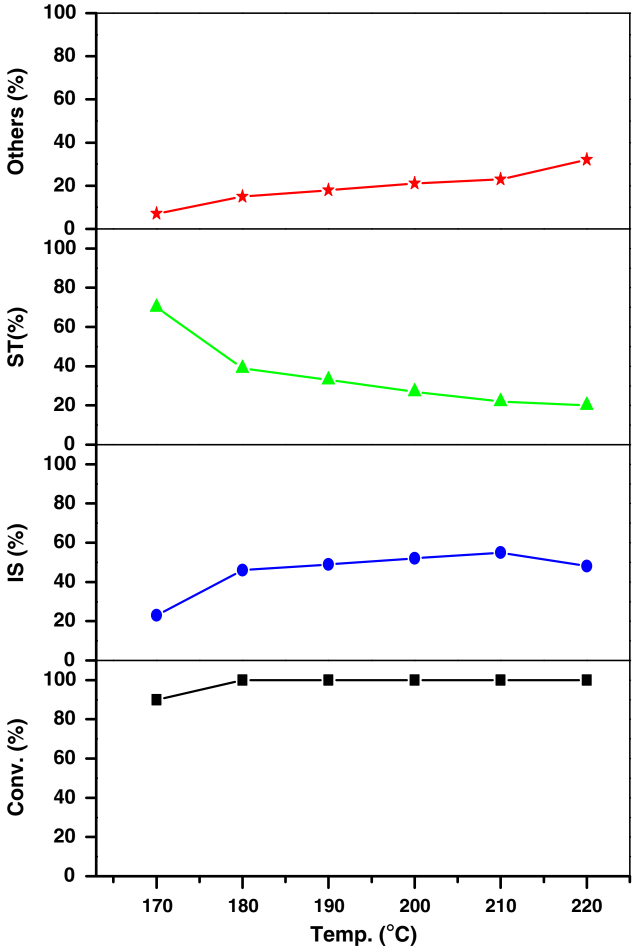


Fig. 4. Effect of temperature on STO-450 catalyzed dehydration of sorbitol. Reaction condition: sorbitol = 10 g, catalyst (STO-450) = 0.15 g, reaction time = 1 h. IS, isosorbide; ST, sorbitan.

Table 3
Dehydration of sorbitol catalyzed by STO-450.[a]

Entry	Catalyst amount (g)	Time (h)	Conversion (%)	S_{IS} (%)[b]
1	0.1	1	96	39
2	0.15	1	100	46
3	0.2	0.5	90	35
4	0.2	1	100	52
5	0.2	1.5	100	60
6	**0.2**	**2**	**100**	**65**
7[c]	**0.2**	**2**	**100**	**61**

[a] Reaction condition: sorbitol = 10 g, temperature = 180 °C.
[b] Selectivity to isosorbide.
[c] Temperature = 210 °C, sulfated zirconia, Ref. [12].

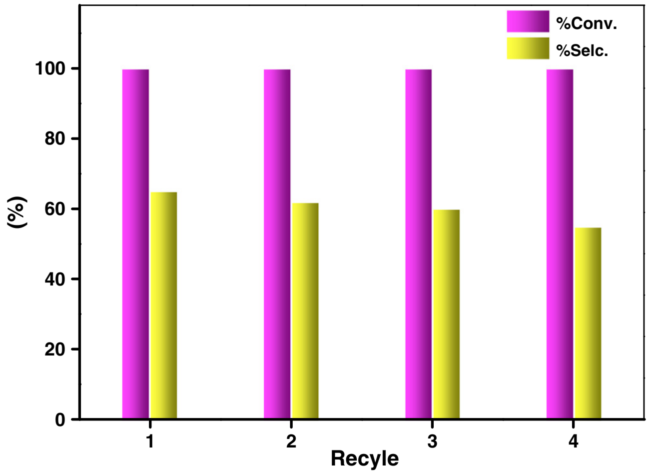


Fig. 5. Catalyst recycles experiments. Reaction conditions: Sorbitol = 10 g, STO-450 = 0.2 g, temperature = 180 °C, reaction time = 2 h.

4. Conclusions

The STO catalysts have been prepared straightforwardly by the thermal decomposition of $SnSO_4$ avoiding multistep complicated procedure and shown to be efficient catalyst for the dehydration of sorbitol to isosorbide. The results demonstrated that the combination of sulfate with tin played an important role in the enhancement of isosorbide selectivity at comparatively lower temperature than reported catalyst system for sorbitol dehydration. The sulfur content and associate catalyst activity/selectivity can be effectively tune by adjusting the calcination temperatures, 100% conversion sorbitol with 65% isosorbide selectivity was achieved in 2 h at the reaction temperature of 180 °C.

Acknowledgements

This work was supported by the Institutional Research Program of KRICT (grant no. SI-1201) and by the cooperative R&D Program funded by the Korea Research Council Industrial Science and Technology, Republic of Korea (grant no. B551179-10-03-00).

References

[1] A. Fukuoka, P.L. Dhepe, Angewandte Chemie International Edition 45 (2006) 5161–5163.
[2] J.N. Chheda, G.W. Huber, J.A. Dumesic, Angewandte Chemie International Edition 46 (2007) 7164–7183.
[3] A. Corma, S. Iborra, A. Velty, Chemical Reviews 107 (2007) 2411–2502.
[4] D.K. Mishra, A.A. Dabbawala, J.-S. Hwang, Journal of Molecular Catalysis A: Chemical 376 (2013) 63–70.
[5] Y. Yang, C.-W. Hu, M.M. Abu-Omar, Green Chemistry 14 (2012) 509–513.
[6] M. Rose, R. Palkovits, ChemSusChem 5 (2012) 167–176.
[7] A. Yamaguchi, N. Hiyoshi, O. Sato, M. Shirai, Green Chemistry 13 (2011) 873–881.

[8] N.A. Khan, D.K. Mishra, J.-S. Hwang, Y.W. Kwak, S.H. Jhung, Research on Chemical Intermediates 37 (2011) 1231–1238.
[9] M. Gu, D. Yu, H. Zhang, P. Sun, H. Huang, Catalysis Letters 133 (2009) 214–220.
[10] Z.-C. Tang, D.-H. Yu, P. Sun, H. Li, H. Huang, Bulletin of the Korean Chemical Society 31 (2010) 3679–3683.
[11] J. Xia, D. Yu, Y. Hu, B. Zou, P. Sun, H. Li, H. Huang, Catalysis Communications 12 (2011) 544–547.
[12] N.A. Khan, D.K. Mishra, I. Ahmed, J.W. Yoon, J.-S. Hwang, S.H. Jhung, Applied Catalysis A: General 452 (2013) 34–38.
[13] I. Ahmed, N.A. Khan, D.K. Mishra, J.S. Lee, J.-S. Hwang, S.H. Jhung, Chemical Engineering Science 93 (2013) 91–95.
[14] P. Sun, D.H. Yu, Y. Hu, Z.C. Tang, J.J. Xia, H. Li, H. Huang, Korean Journal of Chemical Engineering 28 (2011) 99–105.
[15] H. Matsuhashi, M. Hino, K. Arata, Applied Catalysis 59 (1990) 205–212.
[16] S. Furuta, H. Matsuhashi, K. Arata, Applied Catalysis A: General 269 (2004) 187–191.
[17] H. Matsuhashi, Hi. Miyazaki, Y. Kawamura, H. Nakamura, K. Arata, Chemistry of Materials 13 (2001) 3038–3042.
[18] X. Cui, H. Ma, B. Wang, H. Chen, Journal of Hazardous Materials 147 (2007) 800–805.