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ARTICLE

Effects of residual double bonds on the catalytic activity and stability of Pt/SDB hydrophobic catalyst

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Pt/SDB hydrophobic catalysts, platinum supported on cross-linked styrene-divinyl benzene copolymer (SDB), were prepared by an impregnating method. Results indicated that the contents of residual double bonds was positively proportional to the amount of divinyl benzene (DVB) and negatively proportional to the amount of initiator. When the molar ratio of DVB to St was 1:1, the content of residual double bonds reached a highest value of 1.248 mmol/g. The influences of the contents of residual double bonds on the loading amounts of Pt, as well as the catalytic activity and stability of Pt/SDB catalysts were investigated. Performance tests demonstrated that the loading amounts of Pt increased correspondingly, as the contents of residual double bonds increased. Moreover, Pt/SDB with a higher content of residual double bonds generally had a higher column efficiency and a better stability. Interestingly, the column efficiencies of Pt/SDB with a highest content of residual double bond were all above 90% under all experiment conditions.

1. Introduction

Liquid phase catalytic exchange (LPCE), hydrogen isotope exchange between liquid water and gaseous hydrogen, is an efficient approach for separating tritium from tritiated water [1]. Due to its lower energy consumption and higher equilibrium separation factor, LPCE has been widely applied in producing and upgrading heavy water, removing tritium from light water or heavy water, and recovering tritium for fusion reactor [2-4]. In LPCE, an efficient and stable hydrophobic catalyst plays a key role in the catalytic exchange process [1-5].

Platinum is usually the most active metal used in the hydrophobic catalysts of LPCE, such as metallic oxide supported Pt catalysts [6-8], Pt/C/polytetrafluoroethylene (PTFE), Pt/PTFE [9-12], and Pt/SDB [13-15]. However, the metallic oxide supported Pt catalysts usually suffer strong mass-transfer limitations and catalyst poisoning when contacted with liquid water [16]. Generally, Pt/PTFE has a low stability and a short service life due to the weak interactions between Pt and PTFE [17]. Besides, the catalytic activities of Pt/C/PTFE are comparatively low because that the Pt supported on activated carbon are inevitably covered by PTFE and thus the interfacial areas of Pt/C/PTFE are small [18]. It is noted that Pt/SDB hydrophobic catalysts usually have a good stability and a high catalytic activity, which have become the focus of research and application [19-23].

For Pt/SDB, synthesis of a hydrophobic SDB carrier with a large surface area is the most important. SDB carrier is usually synthesized via a copolymerization of St and DVB, of which the mechanisms and kinetics were previously studied [24-26]. Experiments indicated that there were some unreacted vinyls remained in SDB, which were called "residual double bonds" [27]. This was because the activities of the two vinyls in DVB were different in copolymerization, and the activity of the second vinyl decreased significantly after the first vinyl participated in

polymerization. Theoretically, coordination bonds could be formed between Pt and residual double bonds as well benzene rings [28]. The existence of both residual double bonds and benzene rings in SDB could provide a strong interaction between Pt and SDB carrier and thus improve the stability of Pt/SDB catalysts. To the best of our knowledge, the effects of the contents of residual double bonds on the stabilities and catalytic activities of Pt/SDB catalysts have not been investigated. In this work, SDB carriers with different contents of residual double bonds were synthesized. Furthermore, the effects of the residual double bonds on the loading amounts of Pt, as well as the stabilities and catalytic performances of Pt/SDB hydrophobic catalysts were studied.

2. Experimental section

2.1. Chemicals and Apparatus

All reagents used were analytical grade: Styrene (St), Polyvinyl alcohol-2499 (PVA-2499), Sodium dodecyl benzene sulfonate (SDBS), Calcium carbonate (CaCO_3), Anhydrous ethanol, Toluene, N-heptane, Dichloroethane, Benzoyl peroxide (BPO), Dioxane, Sodium bromide, Methanol, Sodium thiosulfate, Potassium iodide, and Acetone. Divinyl benzene (DVB) was purchased from Aladdin Chemical Co. Hexahydrated chloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) was obtained from Suzhou Jinwo Chemical Co., Ltd. of China.

2.2. Preparation of SDB carrier

The amounts of different reagents used for the preparation of SDB are shown in Table 1. PVA-2499, CaCO_3 , and SDBS were added to deionized water in a three-necked flask at 30 °C. After being dissolved completely, a mixture of St, DVB, toluene, n-heptane, dichloroethane, and BPO were added dropwise into the three-necked flask with stirring. The resulting reaction

mixture was heated to 85 °C and kept at this temperature for 4 h. SDB particles obtained by filtration were thoroughly washed with water, ethanol, as well as acetone, and dried in vacuum at ambient temperature.

Table 1 The amounts of reagents used for the preparation of SDB.

Ingredients	Weight (g)	Ingredients	Weight (g)
PVA-2499	1.0	St	10
SDBS	0.12	DVB	6, 8, or 10
CaCO ₃	0.5	Toluene	15.8
Water	200	n-heptane	12.4
BPO	0.5, 1, 2, 3,4, or 5	Dichloroethane	11.6

2.3. Preparation of Pt/SDB carrier

H₂PtCl₆·6H₂O (255 mg) was dissolved in isopropyl alcohol solution (68 mL). In this solution, 5 g of SDB was impregnated for more than 24 h at room temperature. Isopropyl alcohol and water were then evaporated with stirring at 60 °C. The resulting particles were reduced in a reduction furnace under hydrogen at 220 °C for 8 h. When the reduction furnace was cooled to room temperature, hydrogen was purged with nitrogen and a Pt/SDB hydrophobic catalyst was thus obtained.

2.4. Determination of the contents of residual double bonds [30]

To a 250 mL iodine flask was added 0.5 g of SDB, 10 mL of dioxane, and 10 mL of NaBr·Br₂ methanol solution (0.25 mol/L). The resulting mixture was kept in dark overnight. Then 10 mL of potassium iodide aqueous solution (10 wt%) was added into the iodine flask. The iodine released was titrated by standard sodium thiosulfate solution. The contents of residual double bonds were determined as follow:

$$R_{C=C} = \frac{(V_0 - V_1) * 0.1}{2000m}$$

Where R_{C=C} is the contents of residual double bonds (mmol/g), V₀ is the volume of standard sodium thiosulfate solution consumed by 15ml NaBr·Br₂ methanol solution, V₁ is the volume of standard sodium thiosulfate solution consumed by the tested SDB sample, and m is the weight of tested SDB sample.

2.5. Catalytic performance evaluation

The catalytic performances of Pt/SDB were tested in a glass column with an internal diameter of 20 mm and a height of 300 mm [31]. The Pt/SDB hydrophobic catalysts and an insert packing of Dixon gauze rings were mixed well with a volume ratio of 1:3 and then used to fill the glass column. Thereafter, column was packed at both ends with a 80 mm-height of Dixon gauze rings layer to promote liquid and gas distribution. The total height of all the packing was 240 mm.

In LPCE, hydrogen gas was fed from the bottom end of the glass column and deuterated water (deuterium (D)/hydrogen (H) atomic ratio = 1.0 × 10⁻²) was added from the top end with a fixed molar

ratio of hydrogen to deuterated water of 1:1.5. The catalytic activities were tested at 50 °C, 65 °C, and 80 °C under different flow rates of hydrogen gas and deuterated water (Table 2). The catalytic performances were evaluated by the column efficiency η of the glass column.

$$\eta = \frac{y_b - y_t^*}{y_b - y_t} \times 100\%$$

Where y_b is the HD concentration in the hydrogen gas at the inlet, y_t is the HD concentration in the hydrogen gas at the outlet and y_t^{*} is the HD equilibrium concentration in the hydrogen gas at the outlet. The y_t^{*} value was calculated according to the reaction equilibrium and the separation constant.

Table 2 The flow rate of hydrogen gas and deuterated water.

The flow rate of hydrogen gas (L·min ⁻¹)	The flow rate of deuterated water (g·min ⁻¹)
1	1.5
2	3.0
3	4.5
4	6.0
5	7.5

2.6. Sample Characterization

SDB and SDB after being titrated with NaBr·Br₂ were characterized by Fourier transform infrared spectra (FT-IR) in the range of 400~4000 cm⁻¹. The crystal structures of SDB and Pt/SDB were characterized by powder X-ray diffraction (XRD) using Cu K α radiation ($\lambda=0.154056$ nm) in the range of 2 θ =10~90°. Scherrer equation was then applied to calculate the diameter of Pt. The loading amounts of Pt were determined by inductively coupled plasma emission spectrum-mass spectrometer (ICP-MS). The sample used for ICP-MS was first burned in a muffle furnace at 800 °C for 2 h with a heating rate of 10 °C/min and then dissolved in aqua regia, and the resulting mixture was diluted to a constant volume. The mass losses of Pt/SDB catalysts were tested by thermal gravimetric analyzer (TG) in N₂ with a constant heating rate of 10 °C/min from room temperature to 800 °C. The binding energy of Pt/SDB was measured by X-ray photoelectron spectrometer (XPS) using Cu K α radiation.

3. Results and discussion

3.1. FT - IR analysis of SDB and SDB after being titrated with NaBr·Br₂

FT-IR spectroscopy was used to detect residual double bonds in SDB. As shown in FT-IR spectra (Fig. 1, curves 1~5), two absorption peaks at 1640 cm⁻¹ and 989 cm⁻¹ were attributed to the stretching vibration of C=C bond and the deformation vibration of =C-H bond, respectively [32]. While the two characteristic peaks of double bond in SDB were not observed in the FT-IR spectrum of polystyrene (PS) (curve 6), and disappeared after being chemically titrated (curves 7~11). These results indicated that there are certainly some residual double bonds existed in the prepared SDB.

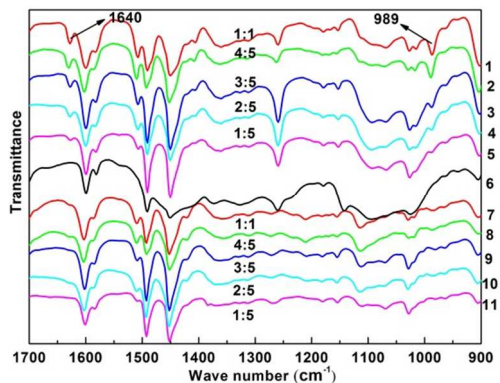


Fig. 1. FT-IR spectra of SDB (curves 1~5) and SDB after being titrated with NaBr-Br₂ with different molar ratios of DVB to St (curves 7~11), and PS (curve 6).

3.2. Determination of the contents of residual double bonds in SDB

When DVB was used as a crosslinking agent, the activity of the second vinyl decreased significantly when the first vinyl participated in polymerization [27]. When gelation took place in the polymerization system, some unreacted double bonds were bounded in the initial formed network, which could not further be reacted [33]. Therefore, some residual double bonds would remain unreacted in the SDB copolymer.

Data show that the contents of residual double bonds increased gradually with the amount of DVB, and reached 1.248 mmol/g when the molar ratio of DVB to St was 1:1 (Table 3). On the other hand, the contents of residual double bonds decreased with the increase of the amount of BPO (Fig. 2), which was probably due to the increase of free radical concentration and crosslinking degree.

Table 3 The contents of residual double bonds in SDB with different molar ratio of DVB to St.

Molar ratio of DVB to St	1:1	4:5	3:5	2:5	1:5
Content of residual double bond (mmol/g)	1.248	1.027	0.906	0.725	0.453

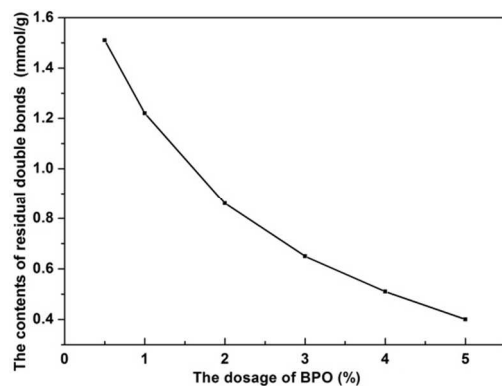


Fig. 2. The contents of residual double bonds in SDB with different dosage of BPO.

3.3. XRD analysis of Pt/SDB hydrophobic catalysts

As shown in Fig. 3, the characteristic diffraction peaks at $2\theta = 39.7^\circ$, 46.2° and 67.5° were ascribed to the (111), (200), and (220) planes of Pt, respectively. This was consistent with the face-centered cubic (fcc) structure of platinum [34]. However, the three characteristic diffraction peaks were not observed for SDB. This indicated that Pt were successfully supported on SDB carriers. As the contents of residual double bonds increased, the diffraction peak intensities of Pt increased correspondingly, indicating that the loading amounts of Pt were positively proportional to the contents of residual double bonds. The particle size of Pt was calculated using the diffraction peaks of Pt in SDB by Scherrer equation. When the molar ratios of DVB to St were 1:1, 4:5, and 3:5, the diameters of Pt were 6.8 nm, 4.5 nm, and 2.3 nm, respectively.

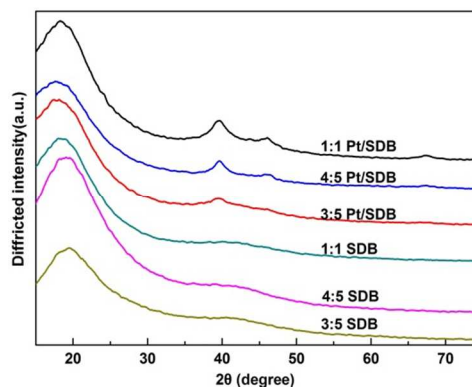


Fig. 3. XRD spectra of Pt/SDB and SDB with different molar ratios of DVB to St.

3.4. ICP-MS analysis of Pt/SDB hydrophobic catalysts

The loading amounts of Pt supported on SDB were measured by ICP-MS. As shown in Table 4, the Pt contents of Pt/SDB catalysts were positively proportional to the contents of residual double bonds, which was consistent with the result obtained from XRD analysis. When the highest contents of residual double bonds was 1.248 mmol/g, the highest Pt contents of 1.467% was obtained. Theoretically, both benzene rings and residual double bonds could form coordination bonds with Pt [28]. In the Pt/SDB catalysts, the existence of both benzene rings and residual double bonds could probably strengthen the interaction force between Pt particles and SDB carrier. Thus, the loading amounts of Pt increased accordingly with the increase of the contents of residual double bonds.

Table 4 The loading amounts of Pt in Pt/SDB hydrophobic catalyst with different molar ratios of DVB to St.

molar ratio of DVB to St	1:1	4:5	3:5
Content of residual double bond (mmol/g)	1.248	1.027	0.906
Loading amounts of Pt (%)	1.467	1.069	0.878

3.5. Column efficiency analysis of Pt/SDB hydrophobic catalysts

The catalytic performance of Pt/SDB was evaluated by column efficiency, which was measured at different temperatures with different hydrogen gas flow rates. As shown in Fig. 4, Pt/SDB with a higher content of residual double bonds generally had a higher column efficiency. When the highest contents of residual double bonds was 1.248 mmol/g, the column efficiencies of Pt/SDB were excellent and all above 90% under all the experimental conditions. However, the column efficiencies of Pt/SDB with less contents of residual double bonds declined obviously as the hydrogen gas flow rates grow. Interestingly, improving the contents of residual double bonds could provide Pt/SDB a better column efficiency in a larger range of hydrogen flow rates. It was probably because that a higher content of residual double bonds provides a stronger interaction between Pt and SDB, which in turn improve the loading amount of Pt.

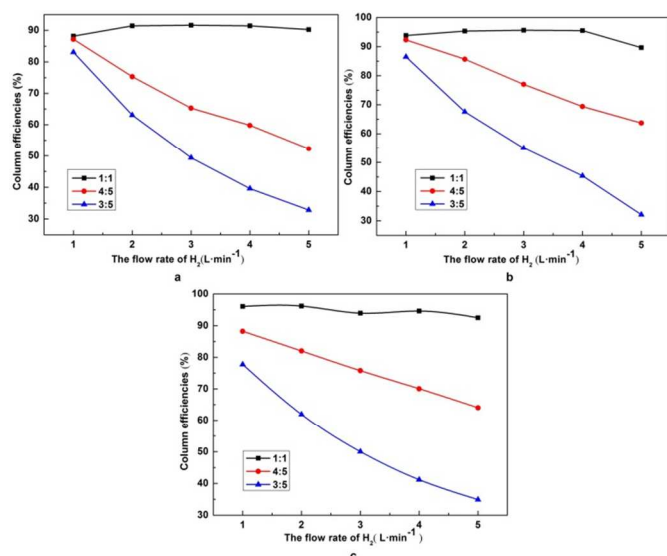


Fig. 4. The column efficiencies of Pt/SDB at different temperatures: (a) 50 °C (b) 65 °C (c) 80 °C.

3.6. Stability of Pt/SDB hydrophobic catalysts

The Pt/SDB hydrophobic catalysts were processed under the same reaction conditions as LPCE for 0 d, 14 d, and 30 d. The mass losses of Pt/SDB catalysts after being treated for different times were measured by TG analysis (Fig. 5). Actually, the residual masses were mainly arrived from the remained Pt loaded on SDB, which could be used to evaluate the stabilities of the Pt/SDB hydrophobic catalysts. As shown in Fig. 5, the Pt losses of Pt/SDB catalysts with less content of residual double bonds were more serious after being treated for 14 d and 30 d. In other words, a higher content of residual double bonds could give Pt/SDB a better stability. It was probably due to the strong interaction formed between Pt and benzene rings as well as residual double bonds [35-37]. Therefore, the contents of residual double bonds were an important factor for the stabilities of Pt/SDB.

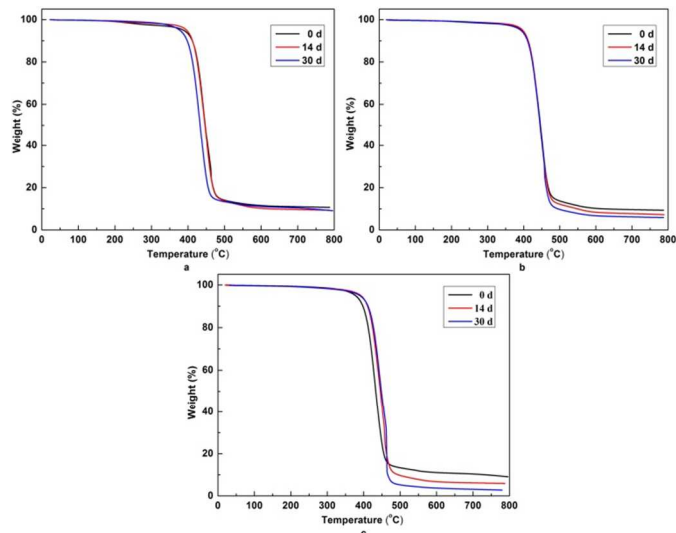


Fig. 5. Stabilities of Pt/SDB with different molar ratios of DVB to St: (a) 1:1 (b) 4:5 (c) 3:5.

3.7. XPS analysis of Pt/SDB hydrophobic catalysts

The Pt4f high resolution spectra of Pt/SDB with different molar ratios of DVB to St are shown in Fig. 6. For element Pt, the electron binding energy of 4f_{7/2} is 71.20±0.1 eV [38]. With the contents of residual double bonds increasing, the binding energy of the Pt4f_{7/2} orbit gradually increased from 71.40 eV to 72.26 eV. It was probably due to the electronic delocalization effect formed between the d orbital of Pt and π conjugated ligand of benzene ring and residual double bond as the electrons transferred from Pt to the SDB [39]. In addition, the activity of Pt/SDB in LPCE was mainly determined by the hydrogen dissociative adsorption rate on platinum and the transition state is expressed as H-Pt/SDB. Due to the electron delocalization effect, the energy of Pt-H bond and the activation energy for desorption of H atoms decreased [40]. Therefore, the catalytic activities of catalysts were improved.

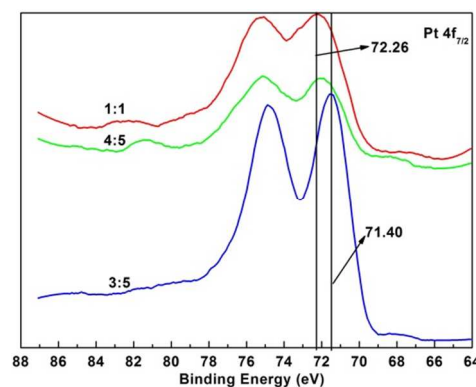


Fig. 6. XPS micrographs of Pt/SDB with different molar ratios of DVB to St.

4. Conclusions

The existence of both benzene rings and residual double bonds in SDB carriers could provide a strong interaction force between Pt particles and SDB carriers. Generally, Pt/SDB with a higher content of residual double bonds had a higher Pt content, a better stability, and a higher catalytic activity. When the highest content of residual double bonds is 1.248 mmol/g, the column efficiencies of Pt/SDB were excellent and all above 90% under all the experimental conditions. Therefore, the contents of residual double bonds were an important factor for the stabilities and catalytic activities of Pt/SDB. XPS analysis showed that the electron delocalization formed between the d orbital of Pt and π conjugated ligand of benzene ring as well as residual double bonds was enhanced with the increase of the contents of residual double bonds. Besides, the energy of Pt-H bond and the activation energy for desorption of H atoms was decreased simultaneously, which was responsible for the catalytic activity improvement of Pt/SDB.

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Notes and references

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- 1 L.S. Ye, D.L. Luo, W. Yang, W.S. Guo, Q.Y. Xu, L.Z. Luo. *Int. J. Hydrogen Ener.* 39 (2014) 13793-13799.
- 2 F. Huang, C. Meng. *Int. J. Hydrogen Ener.* 35 (2010) 6108-6112.
- 3 S. Hu, J. Hou, L. Xiong. *Sep. Purif. Technol.* 77 (2011) 214-219.
- 4 L.S. Ye, D.L. Luo, W. Yang, W.S. Guo, Q.Y. Xu, L.Z. Luo. *Int. J. Hydrogen Ener.* 38 (2013) 13596-13603.
- 5 W.H. Stevens. *Process and catalyst for enriching a fluid with hydrogen isotopes. Canadian Patent* (1972). No. 907292.
- 6 N.H. An, X.L. Yuan, B. Pan, Q.L. Li, S.Y. Li, W.X. Zhang. *RSC Adv.* 4 (2014) 38250-38257.
- 7 Y.C. Wei, Z. Zhao, J. Liu, S.T. Liu, C.M. Xu. *J. Catal.* 323 (2015) 1-9.
- 8 D. Murdoch, S. Beloglazov, P. Boucquey, H. Chung, M. Glugla, T. Hayashi. *Fusion Sci. Technol.* 54 (2008) 3-8.
- 9 I. Cristescu, I.R. Cristescu, M. Glugla, G. Hellriegel, R. Michling. *Fusion Eng. Des.* 82 (2007) 2126-2132.
- 10 L.S. Ye, D.L. Luo, W. Yang, W.S. Guo, Q.Y. Xu, L.Z. Luo. *J. Inorg. Mater.* 29 (2014) 387-392.
- 11 I. Popescu, G.H. Ionita, I. Stefanescu, A. Kitamoto. *Fusion Sci. Technol.* 48 (2005) 108-111.
- 12 F. Vasut, A. Preda, M. Zamfirache, A.M. Bornea, I. Stefanescu, C. Pearsica. *Fusion Sci. Technol.* 54 (2008) 437-439.
- 13 S. Paek, D.H. Ahn, H.J. Choi, K.R. Kim, M. Lee. *Fusion Eng. Des.* 82 (2007) 2252-2258.
- 14 H. Ruan, S.L. Hu, Z.Z. Hu. *Atomic Ener. Sci. Technol.* 29 (2005) 218-222.
- 15 K.M. Song, S.H. Sohn, D.W. Kang, S.W. Paek, D.H. Ahn. *Fusion Eng. Des.* 82 (2007) 2264-2268.
- 16 I. Popescu, G.H. Ionita, I. Stefanescu, C. Varlam, D. Dobrinescu, I. Faurescu. *Fusion Eng. Des.* 83 (2008) 1392-1394.
- 17 J.H. Rolston, J. Hartog, J.P. Butler. *J. Phys. Chem.* 80 (1976) 1064-1067.
- 18 S. Hu, C.J. Xiao, Z.L. Zhu, S.Z. Luo, H.Y. Wang, Y.M. Luo, C.B. Wang. *At. Ener. Sci. Technol.* 5 (2007) 527-532.
- 19 J.H. Xie, Q.L. Zhang, K.L. Chuang. *Catal. Lett.* 3 (2004) 181-184.
- 20 T.L. Huang, K.R. Cliffe, J.M. Macinnes. *Environ. Sci. Technol.* 34 (2000) 4804-4809.
- 21 J.H. Xie, Q.L. Zhang, K.L. Chuang. *Appl. Catal. A: Gen.* 220 (2001) 215-220.
- 22 S. Paek, D.H. Ahn, H.J. Choi, K.R. Kim, M. Lee, S.P. Yim, H. Chung. *Fusion Eng. Des.* 82 (2007) 2252-2258.
- 23 S. Hu, J.W. Hou, L.P. Xiong, K.P. Weng, X.B. Ren, Y.M. Luo. *J. Hazard Mater.* 209 (2012) 478-483.
- 24 B. Wang, W. Ran. *Chem. Eng. Commun.* 199 (2012) 1236-1250.
- 25 J.W. Vanderhoff, M.S. El-Aasser, F.J. Micale. *J. Disper. Sci. Technol.* 5 (1984) 231-246.
- 26 H. Kast, W. Funke. *Makromol chem.* 182 (1984) 1567-1578.
- 27 B. Boutevin, E. Fueury, J.P. Parisi, Y. Pietrasana. *Makromol. Chem.* 190 (1989) 2363-2375.
- 28 B. Liu, Q. Yao, J. Yan. *Ion Exch. Adsorpt.* 18 (2002) 89-96.
- 29 G. Ionita, I. Stefanescu. *Fusion Technol.* 28 (1995) 641-646.
- 30 S. Hu, J. Hou, L. Xiong. *J. Hazard Mater.* 209 (2012) 478-483.
- 31 S. Hu, L.P. Xiong. *Int. J. Hydrogen Ener.* 34 (2009) 8723-8732.
- 32 M. Cao, B. Tong, J. Shen. *J. Appl. Polym. Sci.* 109 (2008) 1189-1196.
- 33 L. Jiang, S.T. Wang, B.L. He. *React Polym.* 12 (1990) 269-278.
- 34 J.H. Jung, H.J. Park, J. Kim. *J. Power Sources.* 248 (2014) 1156-1162.
- 35 B.C. Gates. *Chem. Rev.* 95 (1995) 511-522.
- 36 Q. Cui, D.G. Musaev, K. Morrokuma. *J. Chem. Phys.* 108 (1998) 8418-8428.
- 37 L.W. Lin, Y. Kou, M. Zou. *Phys. Chem. Chem. Phys.* 3 (2001) 1789-1794.
- 38 S. Chen, Z. Wei, X.Q. Qi. *J. Am. Chem. Soc.* 134 (2012) 13252-13255.
- 39 Y. Liang, H. Zhang, H. Zhong, X. Zhu. *J. Catal.* 238 (2006) 468-76.
- 40 Z.K. Zhong, L. Zhang, Y. Sun, Y.L. Chen, Z.H. Zhu. *J. At. Mol. Phys.* 4 (2004) 632-675.