Performance of Pd-B/SiO₂ Catalyst in Hydrogenation of Sunflower Oil

A. Alshaibani[*] and Z. Yaakob[*]

Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, Bandar Baru Bangi 43650, Malaysia

*Corresponding authors: Tel: +60 389216420; E-mail: majeedsh70@yahoo.com

An investigation study for conversion and *trans*-isomerization selectivity of sunflower oil hydrogenation on Pd/SiO₂ and Pd-B/SiO₂ catalysts was performed. The Pd/SiO₂ catalyst was prepared by wet impregnation, then a chemical reduction was performed on Pd/SiO₂ to produce Pd-B/SiO₂ catalyst. Both catalysts were characterized by Brunauer-Emmett-Teller surface area analysis, X-ray powder diffraction, scanning electron microscopy, energy-dispersive X-ray spectroscopy and transmission electron microscopy. The chemically reduced palladium catalyst (Pd-B/SiO₂) showed different properties than Pd/SiO₂ catalyst. Hydrogenation of sunflower oil was performed on both Pd/SiO₂ and Pd-B/SiO₂ catalysts at 383 K, hydrogen pressure of 500 kPa and agitation of 1450 rpm for 1 h. The Pd-B/SiO₂ catalyst exhibited distinctive behaviour in terms of conversion and *trans*-isomerization selectivity. It achieved around a 12.8 % higher conversion and a 35 % lower tendency to form *trans*-fatty acids than Pd/SiO₂. Furthermore, Pd-B/SiO₂ exhibited higher overall activity than the Escat 1351 commercial catalyst and some other reported palladium catalysts. The chemical reduction for Pd/SiO₂ catalyst enhances the catalyst activity and *trans*-isomerization selectivity. The chemical reduction of palladium supported catalyst using potassium borohydride has a noticeable effects on the catalyst morphology, conversion and tendency to form *trans*-fatty acids.

Keywords: Conversion, *trans*-Isomerization selectivity, Overall catalyst activity.

INTRODUCTION

The hydrogenation of edible oils is a basic process in a wide range of food and nonfood industries that aims to improve the oxidation stability and thermal properties of the oil[1,2]. It is applied to increase the shelf life and modify the plasticity of shortening, margarine and baking fats[3,4]. This process also has strategic applications in the manufacturing of biodiesel from soft oils, where the iodine value (IV), cetane number (CN) and oxidative stability (OS) need to be improved to meet application requirements. In order to produce biodiesel from sunflower oil, it is necessary to reduce the degree of unsaturation of fatty acid methyl esters through partial hydrogenation[5]. Moreover, the hydrogenation of fatty acid methyl esters produces a good source of sustainable raw material for manufacturing of non-anionic surfactants[6].

The most important factor affecting the properties of hydrogenated oil is the catalyst including the type and concentration[7]. Nickel is a conventional catalyst used in the vegetable oil hydrogenation process, which is usually performed in a stirred reactor at 423-498 K and 200-413 kPa[8]. An attention has been given to palladium catalyst due to its unique hydrogenation performance in terms of good overall activity, low

toxicity, ability to work under moderate processing conditions and the possibility of altering its properties through modifications[9,10]. A monometallic supported palladium catalyst gains different advantages through the introduction of small additives of other metals in order to change its attributes[11]. Many researchers have reported the hydrogenation of sunflower oil using mono and bimetallic catalysts supported on silica[11-13]. Belkacemi *et al.*[11] stated that a bimetallic palladium catalyst (Pd-Co and Pd-Sr) supported on SBA-15 enhanced the overall activity by 61 % compared to mono Pd/SBA-15 catalyst under similar sunflower hydrogenation conditions, whereas a Pd-Ru bimetallic catalyst demonstrated enhanced overall activity of only 43 %.

The application of a palladium-boron catalyst supported on silica for hydrogenation of hydrocarbon has rarely been reported. It was used first time in nitrobenzene hydrogenation reported by Yu *et al.*[14]. Boron element has a capability to improve the palladium activity and selectivity for the hydrocarbon hydrogenation through its effect on palladium electronic structure[14,15].

Iodine value is an important criterion that acts as an indicator for the unsaturation degree and oxidation stability of edible oils. It is a factor that can be used in testing of catalyst

activity and measurement of hydrogenation conversion[16,17]. The iodine value declines due to the reduction in saturation of C=C double bonds during the hydrogenation process[18]. The rate of its decline has been used as an indicator in kinetic studies and in measurement of overall activity[11,19].

This study aims to discover the effect of chemical reduction for palladium/SiO₂ catalyst on sunflower oil hydrogenation conversion and *trans*-isomerization selectivity as well as overall activity in the field of sunflower oil hydrogenation.

EXPERIMENTAL

Tetraethylorthosilicate (TEOS-99 %, Alfa Aesar,USA) was used to prepare the SiO₂ support and Pd(acac)₂ (Johnson Matthey, USA) was used as a palladium precursor. The chemical reduction agent was potassium borohydride (KBH₄; Acros Organics, USA) and the alkaline agent was potassium hydroxide (Merck Schuchardt OHG, Germany). Ethanol (Fisher Scientific, USA) was used for SiO₂ support preparation and for catalyst washing. Hydrochloric acid (Fisher Scientific, USA) was used for silica preparation.

Sunflower oil provided by Yemen Company for Ghee and Soap Industry (YCGSI), was used to test the catalysts. The composition (%) of the sunflower oil was C18:0 = 3.23, C18:1 = 30.74, C18:2 = 56.78 and C18:3 = 0.1, where the first number shows the total carbon number of the fatty acid and the second number indicates the total number of C=C double bonds. It has an initial iodine value of 125 g iodine per 100 g oil and 0.6465 mole unsaturation per 145 ml oil.

Hydrogen (99.999 %, chromatographic grade), which is available in the local market was used for the hydrogenation tests. De-ionized water for all stages of catalyst preparation and washing was provided by the laboratories of the National University of Malaysia (UKM).

A 5 % commercial Pd/SiO₂ catalyst (Escat 1351; BASF, Netherlands) was used for the purpose of comparison.

Catalyst preparation: The silica support was prepared following a similar method to that used by Panpranot *et al*.[20]. A blend of 40, 10.5, 12.5 and 1 mL of TEOS, ethanol, de-ionized water and hydrochloric acid, respectively, was stirred vigorously for 1 h. Then the gel was calcined at 773 K for 6 h in order to burn off the organic substances. The SiO₂ powder was then crushed and sieved to a size of 0.42 mm to 0.84 mm[21].

A Pd/SiO₂ catalyst was prepared by the wet impregnation method of Pd(acac)₂ on SiO₂ support. Before impregnation, SiO₂ powder was dried at 423 K for 2 h. The Pd(acac)₂ quantity was calculated to provide 0.9 wt. % of palladium metal on SiO₂ support. The support was impregnated with a toluene solution of Pd(Acac)₂ at 298 K for 24 h. Next, the catalyst was dried at 423 K for 2 h and then annealed at 773 K for 2 h.

The Pd-B/SiO₂ catalyst sample was prepared by the chemical reduction of Pd/SiO₂ using an aqueous solution containing 0.2 M KBH₄ and 1 M KOH. The KBH₄/Pd⁺² molar ratio was equal to 3 for the full reduction of palladium oxide[22]. The KBH₄ solution was added slowly to the catalyst precursor at a low temperature and vigorous agitation. Pd-B/SiO₂ was thoroughly washed using de-ionized water and then using ethanol[22]. Then the Pd-B/SiO₂ was kept in ambient temperature for 2 h for the drying.

Unlike conventional hydrogenation catalysts, Pd-B/SiO₂ catalyst exhibits high stability against oxidation and does not need to be kept under inert conditions.

Catalyst characterization: The structure of the prepared catalyst was characterized by X-ray powder diffraction (XRD) using a D8-advance with CuK$_\alpha$ radiation (Bruker, Germany). The surface morphology was observed by scanning electron microscopy (SEM) using 1450 VP (LEO, UK). The energy-dispersive X-ray spectroscopy (EDX) application was performed to detect metals on the catalyst surface using an INCAx-sight-7353 (Oxford Instruments, UK). Transmission electron microscopy (TEM) was performed using a CM12 transmission electron microscope (Philips, Netherlands). Inductively coupled plasma mass spectrometry (ICP-MS) tests were performed using a spectrometer-ELAN 9000 (Perkin Elmer SCIEX, USA) for analysis the catalyst content of the palladium and B elements.

Catalyst testing: A 400 mL batch reactor was used for the catalyst tests. The reactor was equipped with a control system for the operating factors (temperature pressure and agitation). The batch consisted of 145 mL of refined sunflower oil. The reactor was injected with nitrogen gas inorder to remove air and oxygen before operatiion[23]. Hydrogenation was performed on a Pd/SiO₂, Pd-B/SiO₂ and Escat 1351 catalysts at a temperature of 383 K, hydrogen pressure of 500 kPa and agitation of 1450 rpm for 1h. The catalyst concentration in the sunflower oil was 0.032 kg m⁻³ for the Pd/SiO₂ and Pd-B/SiO₂ prepared catalysts and 0.046 kg m⁻³ for the Escat 1351 commercial catalyst.

The Pd/SiO₂ catalyst was pre-reduced inside the reactor at 423 K for 6 h before using for sunflower oil hydrogenation.

Analytical and calculation procedures: The *trans*-fatty acid content (TFAs) and iodine value were obtained using the relevant American Oil Chemists' Society (AOCS) test methods[24]. Tests were performed in the food technology and nutrition unit of the Malaysian palm oil board (MPOB). The change in the *trans*-fatty acids composition of sunflower oil was confirmed by fourier transform infrared spectroscopy using a NICOLET 6700 (Thermo Scientific, USA).

The (C=C) conversion was calculated according to the methods previously reported by Tonetto *et al*.[16].

$$\text{Conversion} = \frac{\text{IV}_o - \text{IV}_f}{\text{IV}_o} \qquad (1)$$

Catalyst overall activity and hydrogenation rate constant were calculated using the method previously followed by Deliy *et al*.[7] as shown in eqn. 2.

$$m, k_r = \frac{\ln\left(\dfrac{\text{IV}_o}{\text{IV}_f}\right)}{t} \qquad (2)$$

where IV$_o$ and IV$_f$ are the iodine value at time (t = 0) and (t = t), respectively, m is the catalyst dose in the oil (Kg m⁻³), k$_r$ is the hydrogenation rate constant and t is the reaction time.

trans-Isomerization selectivity as a measure of the catalyst's tendency to form the *trans*-fatty acid was calculated by eqn. 3 which was suggested by Lausche *et al*.[25].

$$\textit{trans-}\text{Isomerization selectivity} = \frac{\Delta(\% \text{ TFAs})}{\Delta(\% \text{ conversion})} \qquad (3)$$

where Δ (% *trans*-fatty acids) is the difference in the oil *trans*-fatty acid content before and after hydrogenation and Δ (% conversion) is the hydrogenation conversion estimated using eqn. 1.

RESULTS AND DISCUSSION

Catalyst characterization: The structure of the prepared catalysts was characterized by X-ray powder diffraction XRD. Fig. 1 shows the patterns of the Pd/SiO$_2$ and Pd-B/SiO$_2$. The broad peaks at 2 = 23° of both catalyst patterns are assigned to the amorphous silica[26], whereas the peaks at 2 = 34.1, 54.9 and 72° reperesent PdO[21,27]. It can seen that the peaks in the Pd/SiO$_2$ pattern are sharp and have stronger intensity than that in the Pd-B/SiO$_2$ pattern. This indicates that the palladium structure in the Pd/SiO$_2$ catalyst is crystalline due to annealing at 773 K, whereas its structure in the Pd-B/SiO$_2$ catalyst is amorphous as a result of the chemical reduction and non thermal treatment performed for this catalyst. This result is consistent with that reported by Xue *et al.*[28] for the Pd-CuO/SiO$_2$ catalyst.
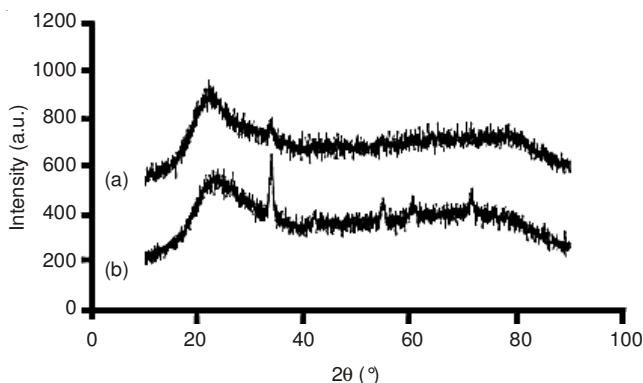

Pd/SiO$_2$

Pd-B/SiO$_2$

Fig. 2. SEM images of Pd/SiO$_2$ and Pd-B/SiO$_2$

Fig. 1. XRD patterns of (a) Pd-B/SiO$_2$ and (b) Pd/SiO$_2$

Fig. 2 shows the surface morphology of the prepared catalyst samples. It can be seen that the chemical reduction has altered the surface structure of Pd/SiO$_2$. The micrograph of Pd/SiO$_2$ showed an irregular aggregation of the particles, whereas a cohesive structure with finer particles appeared on Pd-B/SiO$_2$ as a result of the chemical reduction and non thermal treatment performed for catalyst.

Fig. 3 depicts the EDX spectra for Pd/SiO$_2$ and Pd-B/SiO$_2$. These spectra confirm the metallic composition of each catalyst sample. It can be seen that the intensity of the oxygen spectrum of the Pd-B/SiO$_2$ catalyst was lower than the oxygen spectrum of Pd/SiO$_2$ catalyst. This can be attributed to the removal of atomic oxygen in PdO as a result of the chemical reduction by KBH$_4$. Moreover, both spectrums depict the appearance of trace carbon, which may be the remnants of the precursors.

The TEM image for the Pd-B/SiO$_2$ (Fig. 4) showed Pd-B particles with an average size of 17.6 nm. Particles with larger size were also observed. The particle size was correlated with the aggregation and sintering of palladium particles during calcination of Pd/SiO$_2$ at 773 K. This result is consistent with the observations of Panpranot *et al.*[20] for the palladium catalyst supported on silica prepared by sol-gel method.
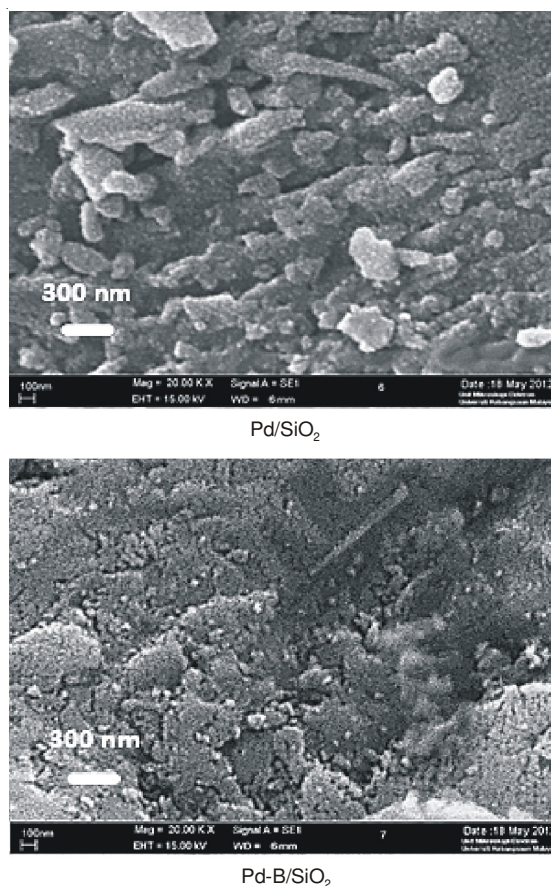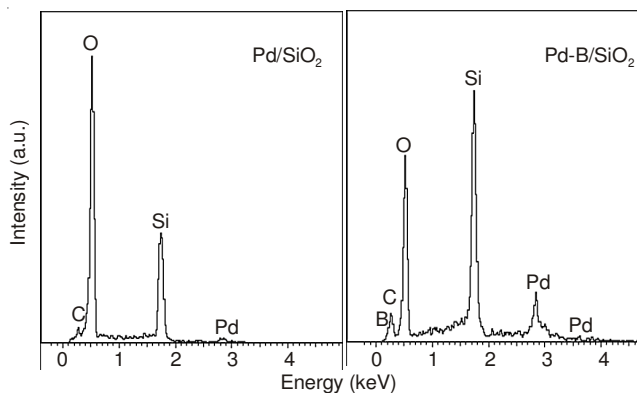

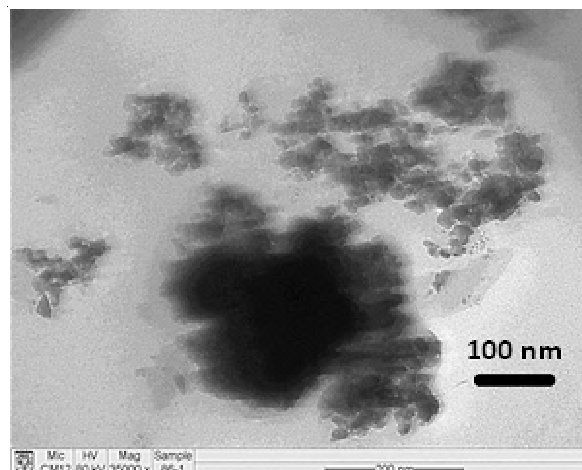Fig. 3. Typical EDX spectrum of the Pd/SiO$_2$ and Pd-B/SiO$_2$ catalysts

Fig. 4. TEM image of Pd-B/SiO$_2$ catalyst

Table-1 shows the results of the metal contents for both Pd/SiO₂ and Pd-B/SiO₂ catalysts performed using ICP-Ms. The palladium content in Pd-B/SiO₂ was noticeably lower than that for Pd/SiO₂ as a result of chemical reduction and washing by water and ethanol.

TABLE-1
CONVERSION AND TRANS-ISOMERIZATION SELECTIVITY OF SUNFLOWER OIL HYDROGENATION (TEMPERATURE 383 K, HYDROGEN PRESSURE 500 kPa, AGITATION 1450 rpm, CATALYST DOSE 32 kg m⁻³ AND TIME 1 h)

Catalyst	Metal content (%)		Conversion (%)	*trans* Selectivity (%)
	Pd	B		
Pd/SiO₂	0.78	0	38.2	0.94
Pd-B/SiO₂	0.70	0.079	43.0	0.61

Catalyst testing

Table-1 also shows the results of sunflower oil hydrogenation using Pd/SiO₂ prepared catalyst before and after chemical reduction. The Pd-B/SiO₂ catalyst exhibited distinctive behaviour in terms of conversion and *trans*-isomerization selectivity. It achieved around a 12.8 % higher conversion and a 35 % lower tendency to form *trans*-fatty acids than Pd/SiO₂. These results can be attributed to the effect of boron on the electronic structure of the palladium metal. On the other hand, the amorphous structure of the Pd-B/SiO₂ catalyst previously confirmed by XRD may contribute on the distinctive activity and *trans*-isomerization selectivity.

The lower content of *trans*-fatty acids in the sample that was hydrogenated using Pd-B/SiO₂ was confirmed by means of FTIR spectroscopy applied to the samples hydrogenated using Pd/SiO₂ and Pd-B/SiO₂ prepared catalysts and also fresh sunflower oil. The peak at 966 cm⁻¹ represents the *trans* isomer and its intensity indicates the *trans*-fatty acids content in the oil[29]. The intensity for the sample hydrogenated using Pd/SiO₂ is higher than that using Pd-B/SiO₂ and the fresh sunflower oil as shown in Fig. 5.
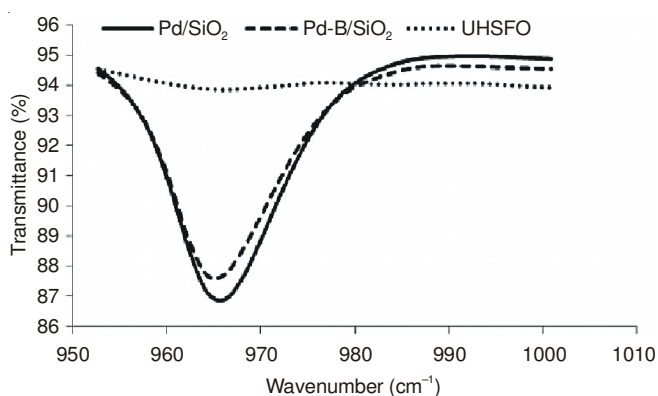

Fig. 5. FTIR spectra of unhydrogenated sunflower oil (UHSFO) and hydrogenated samples on (Pd/SiO₂ and Pd-B/SiO₂)

Further confirmation for the Pd-B/SiO₂ catalyst activity was demonstrated by comparing its activity with that of Escat 1351 under similar conditions. Iodine value of the hydrogenated sunflower oil samples using Pd-B/SiO₂ and Escat 1351 catalysts were 71.2 and 79.25 g iodine per 100 g sunflower oil respectively. The difference in the catalyst dose and decrease

in iodine value show that there is a noticeable difference in the overall hydrogenation activity of the Pd-B/SiO₂ prepared catalyst. Furthermore and based on the simplified hypothesis that the hydrogenation of edible oil follows first order kinetics with respect to the iodine value[7,11,19], eqn. 2 was used to estimate the overall catalyst activity (m·k$_r$) and reaction rate constant (k$_r$) for Pd-B/SiO₂ and Escat 1351 catalysts. The initial iodine value at time (t = 0) was considered, the results of the m.kr estimation for Pd-B/SiO₂ and Escat 1351 catalysts were 0.0094 and 0.0076 min⁻¹, respectively, as shown in Fig. 6. These results were compared with those reported by Belkacemi *et al.*[11] for Pd/SBA-15, Pd-Mo/SBA-15 and Pd-Ni/SBA-15 catalysts using a 0.046 kg m⁻³ concentration of palladium and conditions that are similar of those followed in this study. Despite lower palladium concentration, the Pd-B/SiO₂ prepared catalyst showed higher m.kr value compared to the Escat 1351 commercial catalyst and the results reported by Belkacemi *et al.*[11] as shown in Fig. 6. Thus, the k$_r$ for Pd-B/SiO₂ was also higher than that of Escat 1351 commercial catalyst and the reported catalysts.
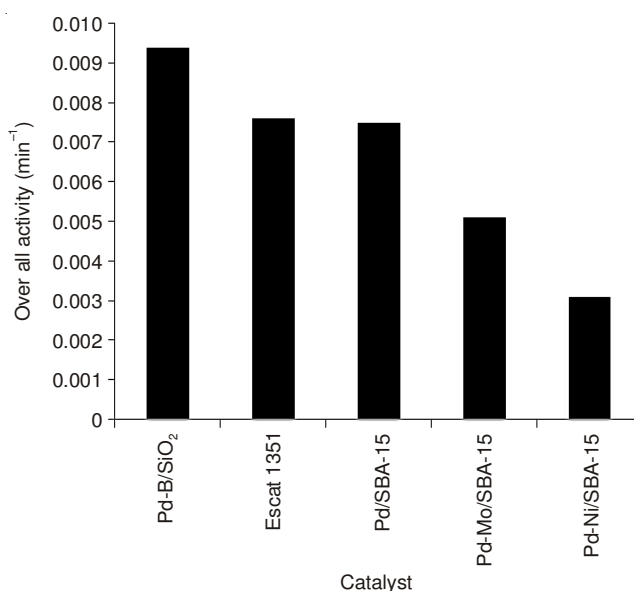

Fig. 6. Overall activity of Pd-B/SiO₂, Escat 2351 and reported catalysts (temperature 383 K, hydrogen pressure 500 kPa, agitation 1450 rpm and time 1 h)

Conclusion

A Pd/SiO₂ catalyst was prepared by wet impregnation and then it was chemically reduced using a water solution of KBH₄. The Pd-B/SiO₂ catalyst exhibited higher conversion and lower *trans*-isomerization selectivity for sunflower oil hydrogenation than the Pd/SiO₂ prepared catalyst. Moreover, it had a higher overall activity compared to that of a commercial catalyst and reported catalysts.

REFERENCES

1. R. Abdullina, I. Voropaev, A. Romanenko, A. Chumachenko, A. Noskov and A. Mashnin, *Russ. J. Appl. Chem.*, **85**, 1204 (2012).
2. T. Schaaf and H. Greven, *Lipid Technol.*, **22**, 31 (2010).
3. D. Singh, M. Rezac and P. Pfromm, *J. Am. Oil Chem. Soc.*, **86**, 93 (2009).
4. U.S. Census Bureau, Fats and Oils Production, Consumption and Stocks-2007, Current Industrial Reports M311K (07)-13, USA (2008).
5. A. Bouriazos, K. Mouratidis, N. Psaroudakis and G. Papadogianakis, *Catal. Lett.*, **121**, 158 (2008).
6. V. Pozdeev, S. Safronov, S. Levanova and E. Krasnykh, *Russ. J. Appl. Chem.*, **85**, 261 (2012).
7. I. Deliy, I. Simakova, N. Ravasio and R. Psaro, *J. Appl. Catal. A*, **357**, 170 (2009).
8. M.B. Fernández, J.F. Sánchez M, G.M. Tonetto and D.E. Damiani, *Chem. Eng. J.*, **155**, 941 (2009).
9. V. Polshettiwar, C. Len and A. Fihri, *Coord. Chem. Rev.*, **253**, 2599 (2009).
10. L. Belykh, Y. Titova, V. Umanets and F. Shmidt, *Russ. J. Appl. Chem.*, **79**, 1271 (2006).
11. K. Belkacemi, N. Kemache, S. Hamoudi and J. Arul, *Int. J. Chem. React. Eng.*, **5**, 1 (2007).
12. K. Belkacemi, A. Boulmerka, J. Arul and S. Hamoudi, *Top. Catal.*, **37**, 113 (2006).
13. N. Kemache, S. Hamoudi, J. Arul and K. Belkacemi, *Ind. Eng. Chem. Res.*, **49**, 971 (2010).
14. X. Yu, M. Wang and H. Li, *Appl. Catal. A*, **202**, 17 (2000).
15. Z. Ma, R. Wu, Z. Gu and Y. Wang, In: Proceedings of the International Conference on Mechanic Automation and Control Engineering (MACE), Wuhan, China, pp: 3675-3678 (2010).
16. G.M. Tonetto, J.F. Sánchez M, M.L. Ferreira and D.D. Damiani, *J. Mol. Catal. Chem.*, **299**, 88 (2009).
17. S. McArdle, S. Girish, J. Leahy and T. Curtin, *J. Mol. Catal. Chem.*, **351**, 179 (2011).
18. M. Fernandez, C. Piqueras, G. Tonetto, G. Crapiste and D. Damiani, *J. Mol. Catal. Chem.*, **233**, 133 (2005).
19. M. Cizmeci, A. Musavi, A. Tekin and M. Kayahan, *Eur. J. Lipid Sci. Technol.*, **111**, 607 (2009).
20. J. Panpranot, K. Phandinthong, T. Sirikajorn, M. Arai and P. Praserthdam, *J. Mol. Catal. Chem.*, **261**, 29 (2007).
21. L. Zhao, Z. Wei, M. Zhu and B. Dai, *Ind. Eng. Chem. Res.*, **18**, 45 (2012).
22. Z. Xiong, Z. Mi and X. Zhang, *Catal. Commun.*, **8**, 571 (2007).
23. S. Pakdehi, M. Sohrabi and A. Moghaddam, *Braz. J. Chem. Eng.*, **27**, 145 (2010).
24. E. Sallee, T. Hopper, W. Link, R. Walker, D. Firestone and V. Mehlenbacher, AOCS, Official Methods and Recommended Practices of the AOCS, Champaign, IL, USA, edn 6 (2011).
25. A. Lausche, K. Okada and L. Thompson, *Electrochem. Commun.*, **15**, 46 (2012).
26. Q. Du, W. Zhang, H. Ma, J. Zheng, B. Zhou and Y. Li, *Tetrahedron*, **68**, 3577 (2012).
27. J. Tarabay, W. Al-Maksoud, F. Jaber, C. Pinel, S. Prakash and L. Djakovitch, *J. Appl. Catal. A Gen.*, **388**, 124 (2010).
28. W. Xue, Y. Wang and X. Zhao, *Catal. Today*, **105**, 724 (2005).
29. N. Numwonga, A. Luengnaruemitchaia, N. Chollacoop and Y. Yoshimura, *J. Appl. Catal. A*, **441-442**, 72 (2012).