



Transesterification of canola oil on potassium-supported TiO₂ catalysts

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ABSTRACT

The transesterification reaction of canola oil was studied on titania-supported catalysts with varying loadings of potassium. It was found that the most active catalysts fall in the range where the adsorption/desorption of CO₂ was the highest. Total conversion to methyl esters was achieved on a catalyst with 20% K-loading under air conditions and with no in situ pre-treatment before reaction.

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1. Introduction

The transesterification of fresh and used oils for the production of biodiesel is an interesting approach as a potential source of alternative renewable energy. Although the homogeneous pathway occurs at a much higher rate than the heterogeneous route, the amounts of waste water produce in the former are massive. The heterogeneous transesterification of oils is an interesting alternative to reduce the costs associated with the purification and separation of reaction products.

Recently, Noiroj et al. [1] achieved a biodiesel yield of 91% using KOH/Al₂O₃ and KOH/NaY catalysts. They also observed an important amount of K leaching into the reaction media. Similarly, Xie et al. [2] studying a KOH-promoted NaX zeolite, and Vyas et al. [3] using K/Al₂O₃, achieved 86% (in 8 h) and 70% (in 6 h) conversion to methyl esters, respectively. Similarly, 91% conversion was achieved after 10 h of reaction on a KI/Al₂O₃ catalyst [4]. Here we report the catalytic activity of K/TiO₂ catalysts in the production of biodiesel from canola oil.

2. Experimental

Two sets of catalysts were prepared: K/TiO₂ and K/TiNT, where TiO₂ and TiNT denote titanium oxide of different surface area. The amount of potassium loaded onto these supports were 10, 20, 30, 40, and 50 w/w% by using KNO₃ (Merck) as the K precursor. The addi-

tion of K to the supports was done by using the wet impregnation method: the appropriate amount of KNO₃ was diluted in a small amount of water. Then the support was added to the previous solution and heated slowly to evaporate the excess of water. On the first set, commercial TiO₂ (150 m²/g, Aldrich) was used as support. For the second set of catalysts, a higher surface area TiO₂ support (hereafter denoted TiNT) was obtained by a hydrothermal treatment described elsewhere [5,6]. Briefly, 2 g of TiO₂ was heated in a 10 M solution of NaOH at 110 °C for 24 h and thereafter contacted with a 0.1 M solution of HCl overnight at room temperature. Then the resulted solid was washed and dried. The final TiNT support had a BET area of 286 m²/g. Both sets of impregnated catalysts, K/TiO₂ and K/TiNT, were calcined in air at 500 °C for 3 h and stored in contact with air.

The transesterification reaction of commercial edible grade canola oil was carried out in a glass batch reactor under reflux and stirring at 70 °C. No inert atmosphere was used and all reactions occurred in contact with air and at ambient pressure. The solid catalyst corresponded to 6 w/w% of the loaded oil, and a molar ratio of oil to methanol of 1:36 was used. To monitor the evolution of the reaction a small aliquot was analyzed by a chromatograph (Perkin-Elmer, Autosystem) equipped with an Omegawax 250 capillary column (30 m × 0.25 mm × 0.25 μ) (Supelco) and FID detector.

The surface area (BET) and pore size distribution of all samples were obtained on a Micromeritics 2010 adsorption apparatus. X-ray diffraction was carried out on a Siemens D-5000 diffractometer using Cu K_α radiation at a scan rate of 0.02° per minute. Diffuse reflectance infrared (DRIFTS) experiments were done in a Vector 22 (Bruker) equipped with a diffuse reflectance cell (Harrick). Temperature program desorption (TPD) of CO₂ was carried out in an

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Table 1
K-containing catalysts after calcination at 500 °C.

K (w/w%)	TiO ₂			TiNT		
	BET area (m ² /g)	Pore volume (cm ³ /g)	k* (h ⁻¹)	BET area (m ² /g)	Pore volume (cm ³ /g)	k* (h ⁻¹)
0	86	0.33	0	102	0.71	0
1	77	0.36	0.018	–	–	–
5	55	0.27	0.207	–	–	–
10	31	0.21	0.304	83	0.62	0.417
20	8	0.05	0.217	19	0.16	0.705
30	3	0.02	0.183	6	0.04	0.419
40	<1	0.003	0.200	3	0.02	0.435
50	<1	0.002	0.033	<1	0.003	0.076

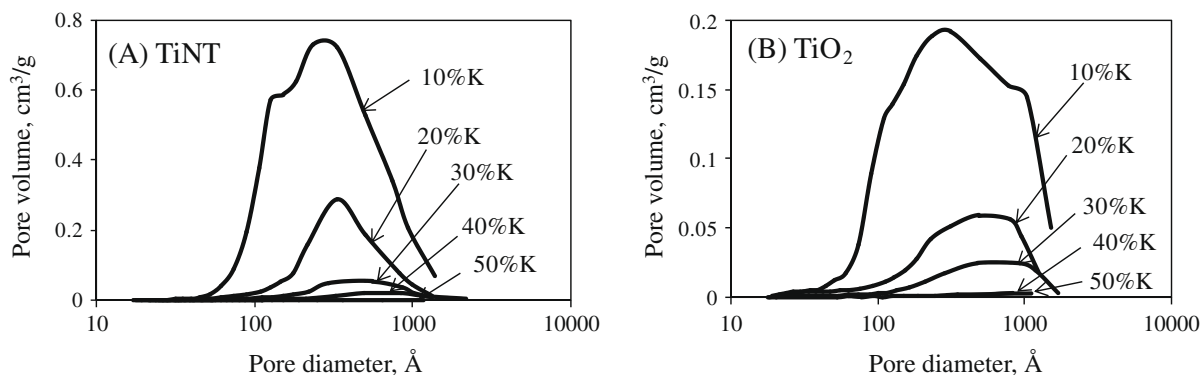


Fig. 1. Pore size distribution of the (A) K/TiNT and (B) K/TiO₂ catalysts.

infrared analyzer (California Analytical Instruments) equipped with CO and CO₂ microflow detectors. The sample was calcined at 500 °C for 1 h. After cooling in He, 10%CO₂/He was flown at room temperature for 1 h. Then He was flown for 1 h, followed by a heating ramp of 10 °C/min in flowing He.

3. Results and discussion

3.1. Structural characterization

3.1.1. BET surface area measurement

Table 1 shows the effect of the K-loading on the surface area of the support. Initially, with no K added, the calcined TiNT support (102 m²/g) has a higher surface area than the calcined TiO₂ support (86 m²/g). A similar behavior is observed after increasing the loading of K, with the K/TiNT catalysts having higher surface area than the K/TiO₂ catalysts. It can also be observed that the BET area along with the pore volumes of all catalysts continuously decrease with the K-loading. In all cases, the K/TiNT catalysts show higher pore volumes than the K/TiO₂ catalysts. The pore distribution of all catalysts (Fig. 1A and B) indicates that small pores are first filled by the deposition of K. Then at higher loadings of potassium, pores of higher size are gradually filled. The latter would explain the continuous decrease of the pore volume as the loading of K increases.

3.1.2. X-ray diffraction and pore distribution

Fig. 2 shows the X-ray diffraction spectra of the 20% and 50% K-loaded catalysts on TiO₂ and TiNT after calcinations at 500 °C. It shows that in all cases the TiO₂ and TiNT support is mostly anatase with small amounts of rutile. Although it is expected that the calcination temperature of 500 °C is able to decompose the K precursor around 400 °C, it is clearly observed that potassium is being trapped inside the support in the form of stable KNO₃, especially at the high 50% K-loading. The latter is consistent with the above described decrease of the pore volume with higher K-loadings (Table 1) and the gradual filling of pores with K (Fig. 1). Potassium in

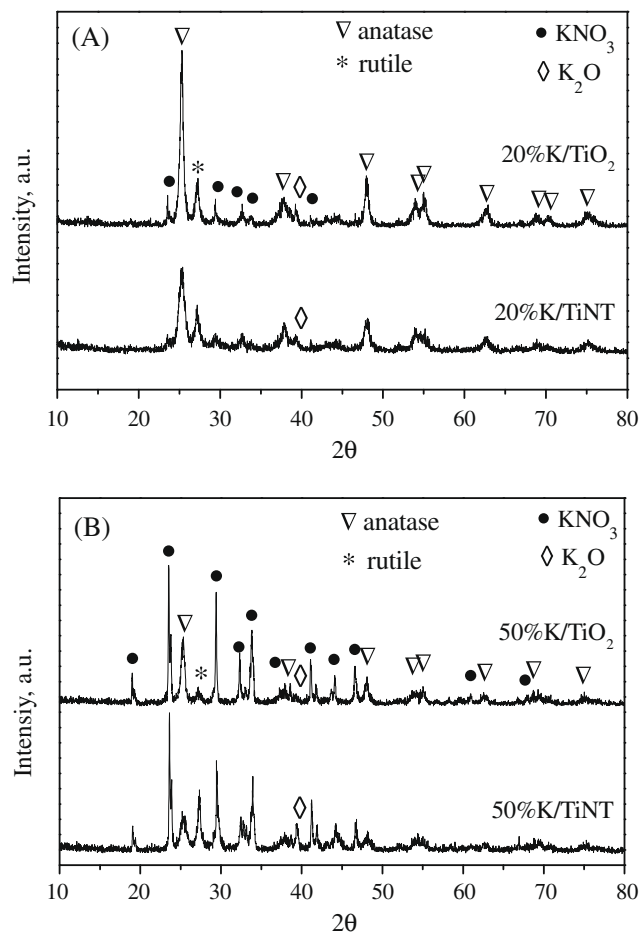


Fig. 2. X-ray diffraction spectra of the (A) 20% K/TiO₂, 20% K/TiNT, (B) 50% K/TiO₂, and 50% K/TiNT catalysts.

the form of K_2O can be barely observed on the 20% K catalysts, whereas its signal is more intense on the 50% K/TiNT catalyst.

3.2. Infrared diffuse reflectance spectroscopy

After heating the samples in He at 200 °C and eliminating adsorbed water for 1 h, infrared diffuse reflectance was recorded from all catalysts in a background of air. Fig. 3 shows that both series of K-supported catalysts have a broad peak with a maximum at 1382 cm^{-1} , which is attributed to the presence of adsorbed carbonate-like species [7]. The presence of the latter species is attributed to the adsorption of CO_2 from exposing the samples to air, which is reasonable given that the presence of the alkali turns the support into a more basic material [8]. The formation of adsorbed species on the K-free supports was negligible.

After degassing in He at 200 °C, the IR reactor was cooled to room temperature and a background was recorded. At the same room temperature 10% CO_2/He was flown during 1 h, then purged with He for 30 min and IR spectra were recorded. Fig. 3C and D compares the integrated area of IR bands without and with the described CO_2 pre-treatment, respectively. With no CO_2 pre-treatment, it is observed that the integrated area shows a slight dependence with the K-loading (Fig. 3C). After the CO_2 treatment, all catalysts were able to adsorb CO_2 showing a maximum around 10% K-loading and then decreasing with higher loadings (Fig. 3D). This result shows that degassing at 200 °C is able to release some of the weakly adsorbed CO_2 , which is re-adsorbed upon the CO_2 treatment.

3.3. CO_2 temperature programmed desorption

In order to analyze the strength of basic sites, all catalysts were subjected to CO_2 temperature programmed desorption (TPD) experiments [9]. The results in Fig. 4 shows that the catalysts with a low

loading of K have a well defined desorption peak around 75 °C, and broad peaks around 200 and 290 °C. The 10% K/TiNT catalyst shows the most intense desorption profile with one peak at 75 °C and a broad convoluted peak around 190 °C. Infrared experiments (not shown) resulted in CO_2 adsorption on the bare TiNT support, whereas the TiO_2 support did not show any CO_2 adsorption. Therefore the broader shape of the TPD for the 10% K/TiNT catalyst might correspond not only to CO_2 desorption from the alkaline oxide but also from the TiNT support. It is possible that the higher population of hydroxyls on the TiNT support contributes to the adsorption of CO_2 as carbonate-like species [10–12]. Nevertheless, hydroxyl infrared signals were similar for K-loadings higher than 10% and, therefore, CO_2 desorption from the support is neglected for higher K-loadings. The K/TiNT catalysts with K-loadings higher than 10% shows only two peaks, the first one located around 75 °C and the second one around 290–300 °C. The intensity of all these peaks (ascribed to weak basic sites) decreases with the K-loading, showing almost no CO_2 desorption with the 50% K/TiNT catalyst. Similar spectra but of lower intensity are observed with the K/ TiO_2 catalysts. In fact the 40% K/ TiO_2 and 50% K/ TiO_2 catalysts do not show CO_2 desorption in the temperature range studied. Clearly the samples with a K-loading below 20% show weak basic sites able to desorb CO_2 at low temperature. At K-loadings of 30% and above, weak basic sites are barely observed. The latter could be due to the decrease in the surface area with the loading of K. Nevertheless, the infrared results (Fig. 3D) show that weak basic sites exist in the whole range of K-loading. The infrared results also show a decrease in intensity of weak basic sites, which can also be related to the lower surface area.

3.4. Activity results

Reported K/ Al_2O_3 catalysts in literature had demonstrated to be active in the transesterification reaction, with conversions in the

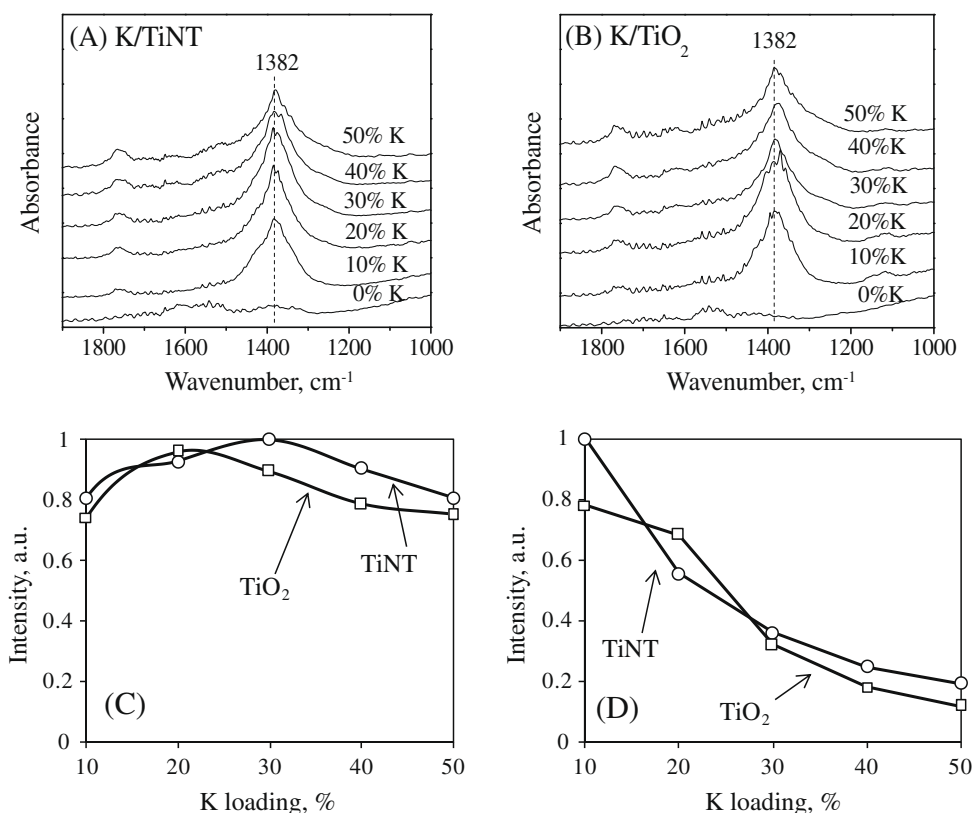


Fig. 3. Diffuse reflectance infrared spectra of (A) K/TiNT and (B) K/ TiO_2 with varying amounts of K-loading in flowing He at 200 °C. Integrated infrared absorbance between 1600 and 1200 cm^{-1} for TiO_2 (\square) and TiNT (\circ), (C) in flowing He at 200 °C, and (D) in He after CO_2 adsorption at room temperature for 1 h.

range of 70–90% [1–4]. This section reports the activity on biodiesel conversion by the use of potassium-based catalysts supported on titanium oxide. The experimental results on the transesterification of canola oil to methyl esters were fit by a first-order rate law (Fig. 5A and B). The rate constants calculated from the slopes of Fig. 5A and B are listed in Table 1. Clearly the higher rate constants represent the more active catalysts, with a maximum of 0.705 h^{-1} for the 20% K/TiNT and 0.304 h^{-1} for the 10% K/TiO₂. As the loading of K increased, the activity on both K/TiNT and K/TiO₂ series gradually decreased, which is reflected in lower slopes in the activity

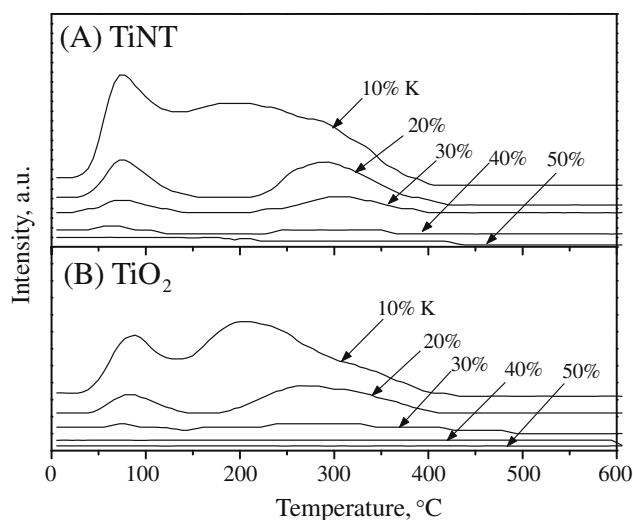


Fig. 4. CO₂ TPD of K/TiNT and K/TiO₂ catalysts with K-loadings of 10%, 20%, 30%, 40%, and 50%. Prior TPD experiments, all catalysts were calcined at 500 °C for 1 h, cooled to room temperature, treated in 10% CO₂/He for 1 h, and purged with He.

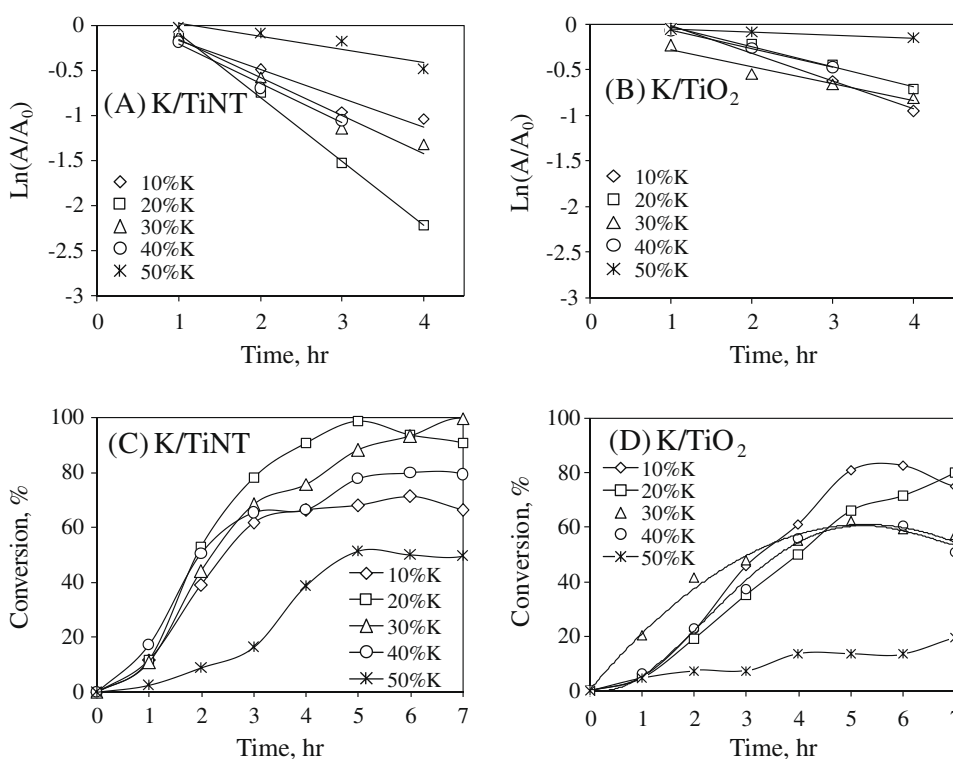


Fig. 5. Transesterification of canola oil fitted to a first order kinetics on (A) K/TiNT and (B) TiO₂ catalysts with varying amounts of K-loading. Conversion of canola oil to methyl esters with time on the (C) K/TiNT and (D) K/TiO₂ catalysts.

curves. Accordingly, the Fig. 5C and D shows the conversion of canola oil to methyl ester with time. It is readily observed that the K/TiNT catalysts with low loadings of K, Fig. 5C, achieve total conversion to methyl esters between 5 and 7 h. On the other hand, none of the K/TiO₂ catalysts is able to reach 100% conversion within 7 h (Fig. 5D). As with the K/TiNT catalysts, the oil conversion gradually decreases at higher K-loadings for the K/TiO₂ catalysts. Loadings of K between 0 and 10% on TiNT and TiO₂ (not shown) led to lower activities than the maxima described above. For example, 1% K/TiO₂ and 5% K/TiO₂ catalysts had rate constant values of 0.018 and 0.207 h^{-1} , respectively. The activity of the bare supports, TiNT and TiO₂, was negligible under the same reaction conditions.

Since leaching of the alkali phase has been reported to occur during the reaction leading to the homogeneous transesterification [1,13], an experiment was designed to quantify this effect. A highly K-loaded catalyst was selected (50% K/TiO₂) and subjected to reflux with methanol for 4 h at 70 °C. Then the resulting solution was centrifuged for removing the suspended catalyst. This solution was used in a regular homogeneous transesterification reaction with no addition of extra solid catalyst. The obtained conversion after 1 h of reaction was below 7% and did not increase with time. These results assure that the observed activities (Fig. 5) occur under heterogeneous conditions.

The behavior of the K/TiNT and K/TiO₂ catalysts on the conversion of canola oil correlates well with the previously shown trend on the presence of weak basic sites, especially at low K-loadings (Figs. 3 and 4). The more active catalysts fall within the range of low K-loadings where CO₂ adsorption on weak basic sites is more important. In fact, a TPD run at higher temperatures (not shown) releases strongly adsorbed carbonate-like species only above 700 °C. The latter is consistent with other studies showing that strong basicity is occluded by air carbonation [8,14]. Therefore, the deposition of CO₂ on the basic surface of the catalyst hinders active sites and a high-temperature treatment is a necessary

requirement for desorbing these species prior reaction. In this sense, a TPD experiment with the 10% K/TiNT catalysts with no prior CO₂ adsorption resulted in a very similar CO₂ desorption spectrum than the one shown in Fig. 4. This clearly shows that the K-containing catalysts are able to adsorb CO₂ when exposed to air. The same catalyst was in situ treated in He at 300 °C for 1 h before reaction, and the transesterification reaction was carried out under an inert environment. The calcination temperature of 300 °C was chosen based on the TPD results, which show that most of the weakly adsorbed carbonates are released below 300 °C (Fig. 4). It turns out that 100% conversion to methyl esters was achieved in 3 h compared to 65% on the untreated catalyst at the same time of reaction. In the case of the activity results presented in Fig. 5, although no in situ calcination pre-treatment was used and the reactions were carried out in the presence of air, the catalysts are stirred in methanol and heated to the reaction temperature for 30 min before reaction, which might contribute to the desorption of carbonate-like species and to the exposure of active sites. Xie et al. [15], using K/Al₂O₃ catalysts, found a wide basic site distribution on the catalyst surface, being of higher concentration those with low and mid-strength. The strongly basic sites had the lowest surface concentration on that work. Studies are currently underway to quantify the strength of basic sites on our titania-supported K catalysts, but the results obtained so far indicates that weak basic sites are involved in the transesterification reaction on the K/TiO₂ and K/TiNT catalysts.

4. Conclusions

Potassium supported on titania was studied as a catalyst for the production of biodiesel from canola oil. It was found that the 20%

K/TiNT catalyst achieved a total conversion to methyl esters after 5 h of reaction. Low loadings of potassium lead to the formation of weak basic sites, which in contact with air gave place to the formation of adsorbed carbonate-like species on the support.

The catalysts studied here present interesting activities and have a robust character since no need for in situ pre-treatment or inert reaction environment were needed.

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References

- [1] K. Noiroj, P. Intarapong, A. Luengnaruemitchai, S. Jai-In, *Renew. Energy* 34 (2009) 1145–1150.
- [2] W. Xie, X. Huang, H. Li, *Bioresour. Technol.* 98 (2007) 936–939.
- [3] A.P. Vyas, N. Subrahmanyam, P.A. Patel, *Fuel* 88 (2009) 625–628.
- [4] W. Xie, H. Li, *J. Mol. Catal.* 255 (2006) 1–9.
- [5] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir* 14 (1998) 3160–3163.
- [6] S. Guerrero, M. Di Serio, R.F. Li, E.E. Wolf, *Catal. Lett.* 130 (2009) 19–27.
- [7] D.G. Rethwisch, J.A. Dumesic, *Langmuir* 2 (1986) 73–79.
- [8] H. Hattori, *Chem. Rev.* 95 (1995) 537–558.
- [9] J.C. Lavalley, *Catal. Today* 27 (1996) 377–401.
- [10] S.U. Rege, R.T. Yang, *Chem. Eng. Sci.* 56 (2001) 3781–3796.
- [11] J. Baltrusaitis, J.H. Jensen, V.H. Grassian, *J. Phys. Chem. B* 110 (2006) 12005–12016.
- [12] C. Morterra, G. Magnacca, *Catal. Today* 27 (1996) 497–532.
- [13] D.M. Alonso, R. Mariscal, R. Moreno-Tost, M.D. Zafra-Poves, M. López-Granados, *Catal. Commun.* 8 (2007) 2074–2080.
- [14] M.C.G. Albuquerque, J. Santamaría-González, J.M. Mérida-Robles, R. Moreno-Tost, E. Rodríguez-Castellón, A. Jiménez-López, D.C.S. Azevedo, C.L. Cavalcante Jr., P. Maireles-Torres, *Appl. Catal. A* 347 (2008) 162–168.
- [15] W. Xie, H. Peng, L. Chen, *Appl. Catal. A* 300 (2006) 67–74.