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Non-noble metal catalyst for carbon monoxide selective oxidation in excess hydrogen

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Abstract

The present work investigates the catalytic properties of the Ni, Co and Co-Ni supported activated carbon (AC) catalysts for the selective oxidation of carbon monoxide in an excess hydrogen gas. The results shows that Co/AC and Co-Ni/AC exhibit a higher catalytic activity than Ni/AC, meanwhile, Co-Ni/AC gives a high CO conversion in a wide reaction temperature region of 130–150 °C, the CO conversion can reach up to above 99.5%. The X-ray power diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) characterizations show that Co_3O_4 is the main cobalt oxide phase in Co/AC and Co-Ni/AC catalysts. The XRD and temperature-programmed reduction (TPR) results indicate that Co_3O_4 species of Co-Ni/AC exhibits a higher dispersion than that on Co/AC. Based on the XPS results, the function of nickel oxide in Co-Ni/AC is to enrich Co_3O_4 species, and decrease the electronic cloud density of cobalt. Therefore, we conclude that Co_3O_4 species is an important catalytic active center, the higher activity of Co-Ni/AC in comparison with Co/AC is attributed to the higher dispersion of active Co_3O_4 species and the lower electronic cloud density of cobalt on the surface of Co-Ni/AC.

Keywords: Selective oxidation; Carbon monoxide; Excess hydrogen; Activated carbon; Non-noble metal catalyst

1. Introduction

Hydrogen fueled polymer electrolyte membrane fuel cells (PEMFC) can produce electricity without environmental pollution, and possess the necessary specific power, power density and durability to replace the conventional internal combustion engines from their current applications [1]. PEMFC are becoming increasingly attractive for the environmentally compatible supply of electric energy. In this system, hydrogen is oxidized over Pt or alloy electrodes to generate electric energy, with ideally the only reaction product being H_2O [2]. Hydrogen can be generated by several different methods using alternative energy sources, such as natural gas, methanol and gasoline [3–5], via the direct partial oxidation, steam reforming and/or water gas shift (WGS) reactions. However, the product steam usually contains about 0.5–2 vol.% CO, which can lead to the poisoning of anode due to the strong adsorption of CO. The acceptable CO concentration is <10 ppm for Pt anodes and ≤100 ppm for the CO tolerant alloy anodes, respectively [6–8]. Therefore, in order to ensure a long lifetime of electrodes in the fuel cell, the concentration of CO must be decreased to less than 100 ppm by utilizing different techniques.

In fact, among the various available methods for CO removal from excess hydrogen atmospheres, the selective catalytic oxidation of CO with molecular oxygen has been regarded as the most straightforward, simpler and cost effective ones [9,10]. In the last decades, great efforts have been made on the development of catalysts, which can selectively oxidize CO in the presence of excess hydrogen. This kind of catalyst must possess a high activity for the CO oxidation (>99%) at the low temperature with a wide range, and should also be inactive for the oxidation of hydrogen

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in order to avoid the loss of fuel hydrogen, simultaneously.

So far, most of effective catalysts for this system have been reported to use the supported noble metals, such as Pt [7,11,12], Pd [12], Au [13], Ru [2,14,15] and Rh [16,17]. These catalysts exhibited high activities for CO oxidation, however they have some disadvantages with a high cost, a limited availability and low selectivity at high temperatures. Therefore, the supported transition metals catalysts have attracted more and more attentions due to their low cost and a high activity for CO selective oxidation in excess hydrogen [18–22].

In the latest years, some researchers reported [20–22] that CuO-CeO_2/Al_2O_3 mixed oxides exhibited a similar catalytic property to the noble metal catalysts in CO selective oxidation in presence of excess hydrogen, but their optimal reaction temperature approached about 200 °C. And cobalt oxide was verified to be a good promoter on improving the catalytic activity of CuO-CeO_2/Al_2O_3 based catalyst for CO selective oxidation in excess hydrogen [22]. Recently, cobalt oxide catalyst was found to show a very high activity for the CO oxidation in an excess oxygen atmosphere at a low reaction temperature [23]. However, there have been few reports about the CO selective oxidation on the cobalt oxide-supported catalysts in excess hydrogen.

The present work purposed to search the new non-noble metal (such as Co, Ni) catalysts with a high activity for the CO selective catalytic oxidation in excess hydrogen. Therefore, Ni, Co and Co/Ni supported activated carbon (AC) catalysts were prepared and characterized by X-ray power diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and temperature-programmed reduction (TPR), their catalytic properties were also investigated by the CO selective catalytic oxidation in the presence of excess hydrogen.

2. Experimental

2.1. Catalysts preparation

Ni/AC, Co/AC and Co-Ni/AC (1:1 in atom ratio) catalysts were prepared by the excess impregnation method. $Ni(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ were used as metal oxides precursors, and the commercial activated carbon (granules size 40–48 mesh) as support. A desired amount of corresponding metal nitrate was dissolved in the deionized water to come into being a saturated solution, in which the activated carbon particles were appended, and then the mixtures were evaporated at a fixed temperature, dried at 110 °C for 10 h and calcined in nitrogen at 250 °C for 2.5 h. All obtained catalysts contained 35 wt.% of the total metal oxides.

2.2. Catalysts characterization

The X-ray powder diffraction of catalysts was performed on a Philips X'Pert MPD X-ray diffractometer with Cu Kα radiation at 50 kV and 35 mA with a scan rate of 6°/min. The chemical states of Ni and Co in the Co/AC, Co-Ni/AC catalysts were certified by the X-ray photoelectron spectroscopy measurements. The signals were collected by a KRATOS X-ray sources (model XSAM800) with an aluminium crystal, operating at 12 kV anode voltage and 12 mA emission current, was used to generate the required Al Kα radiation (resolution: ∼0.9 eV). All binding energy values (BE (eV)) were determined with respect to the scale calibrated versus the Au_{4f} line at 84.0 eV and Ag_{3d} line at 386.3 eV. The temperature programmed reduction was carried out as following procedure: 50 mg of catalyst sample was placed in a U-type quartz tube (6-mm-i.d.), 3.2 vol.% H_2/N_2 gas mixture was passed at a flow 30 ml/min, the reduction temperature was raised from the room temperature to 600 °C at a rate of 10 °C/min. The consumption of hydrogen was measured by a thermal conductivity detector (TCD).

2.3. Catalytic activity measurement

The selective catalytic oxidation of CO in excess hydrogen gas was carried out in a quartz tube (12 mm-i.d.) fixed-bed reactor at atmospheric pressure. The quartz tube reactor containing 0.4 ml catalyst was placed inside a tubular furnace. The reaction temperature was monitored by a temperature programmable controller (ÜGU, model 708P, China). The feed gas contains 1 vol.% CO, 0.5 vol.% O_2 and 98.5 vol.% H_2. The reacted mixture gas was analyzed by an on-line gas chromatograph (GC-1026, China) equipped with a methanizer and FID detector using hydrogen as carrier gas. Teng et al. [18] reported that methane could not be formed over the Ni- or/and Co-contained catalysts, even when the reaction temperature was higher than 200 °C. Therefore, the detection of CO using the above-mentioned method would not be affected when the reaction temperature was less than 200 °C. The detection limit of CO was 5 ppm.

3. Results and discussions

3.1. XRD characterization

The crystalline structure of Co-Ni/AC calcined in nitrogen at 250 °C for 2.5 h was examined by the X-ray diffraction patterns, and compared with that of Co/AC. As shown in Fig. 1, series of typical peaks at $2\theta = 31.5°$, 37.0°, 45.0°, 55.9°, 59.4° and 65.4°, respectively, which are attributed to the characteristics of Co_3O_4 [24], can be easily observed in both Co/AC and Co-Ni/AC samples. For Co-Ni/AC, accept that the nickel oxide (NiO) are also observed at $2\theta = 36.9°$, 43.5° and 62.5°, the other cobalt oxides (such as CoO and Co_2O_3 so on) are absent. It indicates that Co_3O_4 is the major cobalt oxide phase in both Co/AC and Co-Ni/AC. However, the unclear peaks of Co_3O_4 and the presence of NiO crystal structure in Co-Ni/AC are detected, showing that Co_3O_4 in the Co-Ni/AC catalyst has a more amorphous structure than

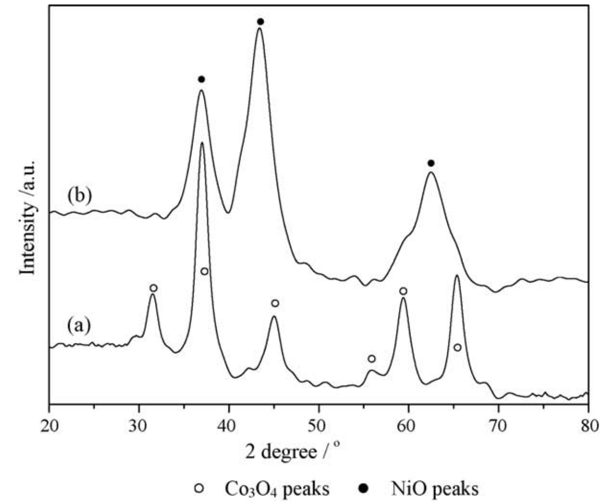

Fig. 1. X-ray diffraction patterns of (a) Co/AC and (b) Co-Ni/AC.

that in Co/AC. Therefore, the dispersion of Co_3O_4 in Co-Ni/AC can be conferred to be higher than that in Co/AC. Due to the fact that new compounds are not detected, it can be inferred that cobalt cannot react with nickel in the low calcined temperature. Comparing curve b with curve a, the crystalline structure of Co_3O_4 is half-baked in the Co-Ni/AC catalyst, and however intact in the Co/AC catalyst, which indicates that the increase Co_3O_4 dispersion in the Co-Ni/AC catalyst is related to the presence of nickel oxide.

3.2. *XPS analysis*

The XPS data of Co/AC and Co-Ni/AC samples calcined in nitrogen at 250 °C for 2.5 h are listed in Table 1. The surface atomic ratios are calculated on the basis of peak area corrected by metal sensitivity. From Table 1, it can be easily seen that the Co $2p_{3/2}$ peak position for both Co/AC and the pure Co_3O_4 locates at the electron binding energy of about 779.9 eV, which is completely coincident with that for Co_3O_4 sample with a single-phase, also in agreement with the previous results as reported [25,26]. However, due to the addition of nickel in the catalyst, the electron binding energy of Co $2p_{3/2}$ is decreased 0.41 eV, however, there is no change for that of Ni $2p_{3/2}$. The results indicate that nickel oxide changes the electron cloud density of cobalt in the Co-Ni/AC catalyst. The decrease of the electron binding energy for Co $2p_{3/2}$ shows that the Co_3O_4 in Co-Ni/AC is easier to provide electron than that in Co/AC.

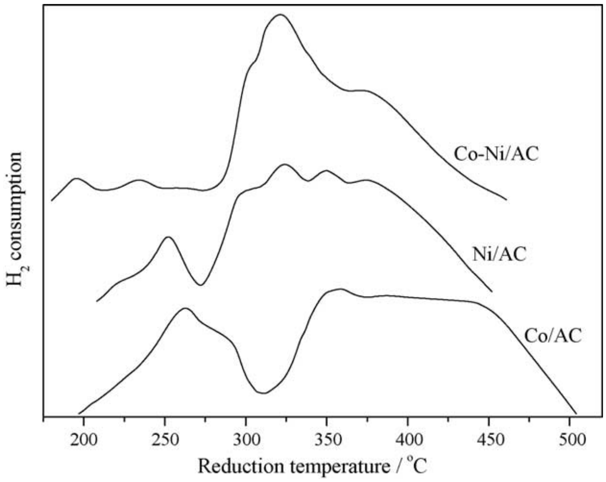

Fig. 2. The TPR profiles of Co/AC, Ni/AC and Co-Ni/AC catalysts.

The peaks area of the electron binding energy of nickel and cobalt (as shown in Table 1) can be obtained by XPS analysis in the Co-Ni/AC catalyst, and the sensitivity of Ni, Co are 1.666 and 1.848, respectively. On the basis of the corrected peaks area according to metal sensitivity, the atomic ratio of Co to Ni can be calculated to be 16 on the surface of the Co-Ni/AC catalyst, which is higher than the atomic ratio of their bulk phase being 1. Therefore, it indicates that nickel can improve the enrichment of cobalt on the surface of Co-Ni/AC catalyst.

From the above analysis, the addition of nickel in the Co-Ni/AC not only can improve the dispersion of Co_3O_4 but also can change the electron cloud density of cobalt and improve cobalt atoms to enrich on the surface of the Co-Ni/AC catalyst. Nickel acted as an important promoter in the Co-Ni/AC catalyst though it did not play catalysis, directly.

3.3. *TPR studies*

Fig. 2 presents the results of the hydrogen temperature programmed reduction of the Ni/AC, Co/AC and Co-Ni/AC samples calcined at 250 °C for 2.5 h. As observed from Fig. 2, the profiles of both Ni/AC and Co/AC show a H_2-consumption peak at less than 300 °C, and the Co-Ni/AC sample gives double TPR peaks at less than 250 °C. These peaks are attributed to the reduction of the remnants nitrates by hydrogen [27]. A broad temperature peak appears at above 300 °C for Ni/AC, Co/AC and Co-Ni/AC samples, and their temperature region of reduction are in the range of 280–430, 320–460 and 290–390 °C, respectively, which

Table 1
The electron binding energy and peak area of Co_3O_4 and NiO

Binding energy (eV)						Peak area	
Normal species		Ni/AC	Co/AC	Co-Ni/AC		Co-Ni/AC	
Ni $2p_{3/2}$	Co $2p_{3/2}$	Ni $2p_{3/2}$	Co $2p_{3/2}$	Ni $2p_{3/2}$	Co $2p_{3/2}$	Ni	Co
853.50	779.90	853.52	779.96	853.46	779.55	1522.19	27872.29

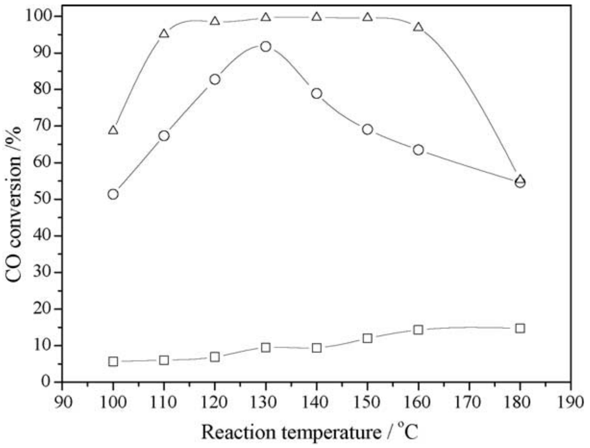

Fig. 3. The effect of reaction temperature on the CO oxidation catalyzed by Co-Ni/AC, Co/AC and Ni/AC catalysts.

are caused from the presence of several reducible species [28].

From Fig. 2, it can be clearly seen that the highest reduction temperature of Co-Ni/AC is lower about 40 and 70 °C than that of Ni/AC and Co/AC, respectively. And at the same time, the temperature of reduction range for Co-Ni/AC can be observed to be sharper at 50 and 40 °C than that for Ni/AC and Co/AC, respectively. It indicates that the metals oxides in Co-Ni/AC are easily reduced compared with those of the other two. According to the previous reports [29,30], a high dispersion of metal oxides will lead to a low reduction temperature. From the above TPR results, it can also be inferred that the metal oxides (NiO, Co_3O_4) supported on the surface of Co-Ni/AC have a higher dispersion than those of Co/AC and Ni/AC, which is consistent with the above XRD results.

3.4. *Catalytic test*

The CO selective catalytic oxidation on Ni/AC, Co/AC and Co-Ni/AC, which were calcined in nitrogen at 250 °C for 2.5 h, were investigated in the presence of excess hydrogen in the reaction temperature range of 100–180 °C and with a space velocity of 5000 h^{-1}. The relationships of their catalytic activity with the reaction temperature are plotted in Fig. 3. From it, it can be observed for Ni/AC to have a poor CO conversion of below 15% at 180 °C, which is very similar to the results over nickel oxide catalysts reported in the previous literature [18]. For the Co/AC as catalyst, CO conversion first increases with the increasing reaction temperature and reaches up to a maximum about 90% at 130 °C, and then decreases with the increase of reaction temperature rapidly. However, Co-Ni/AC catalyst exhibits better catalytic activity than Co/AC catalyst, and moreover the conversion always keeps at above 97% in a wide reaction temperature of 120–160 °C. It is note that Co-Ni/AC catalyst can give above 99.5% of CO conversion at 130–150 °C, it means the concentration of carbon monoxide can be decreased to less than 50 ppm in this temperature range. From Fig. 3, it can also be clearly observed that the CO conversion dramatically decreases with the increasing temperature for Co/AC and Co-Ni/AC catalysts when the reaction temperature is beyond 130 and 160 °C, respectively. It is perhaps due to the oxygen consumption, which is from the reaction with H_2 at corresponding high reaction temperature for both catalysts. The similar results were also found over Pt/alumina catalysts in the previous report [31]. Therefore, Co-Ni/AC is a potential catalyst with a low cost for removing the trace amount of carbon monoxide existed in the resource of PEMFC.

A high catalytic activity for Co/AC and Co-Ni/AC and a poor catalytic activity for Ni/AC manifest that Co_3O_4 species, which is measured by XRD and XPS, is an important catalytic active species in the CO selective catalytic oxidation. At the same time, Co-Ni/AC gives rise to a higher activity than Co/AC, indicating the dispersion of Co_3O_4 on the surface of catalyst is another important factor of effecting the catalytic activity of the Co-supported AC. Combining with the results of XRD and TPR characterization, it can be found that the higher the dispersion of Co_3O_4 on the surface of catalyst is, the higher the catalytic activity is. Additionally, the decrease on the binding energy of Co $2p_{3/2}$ in the Co-Ni/AC catalyst will probably results in the easy activation of O_2 in reactant gas due to the presence of nickel oxide.

As well known, two competitive oxidations probably exists in this reaction system of the present work, one is the oxidation of carbon monoxide, and the other is the oxidation of hydrogen. Moreover, both oxidations are irreversible and exothermic, the former reaction heat is about 283 kJ/mol and higher than the latter being 242 kJ/mol [13,32]. From the thermodynamics, it seems to be easier for the oxidation of carbon monoxide than the hydrogen oxidation. Therefore, it is completely possible that only the oxidation of carbon monoxide is carried out in the presence of excess hydrogen, if the proper catalysts are used. In the present work, the amount of O_2 in the feed gas just corresponds with the stoichiometric ratio for the oxidation of carbon monoxide with O_2 (O_2:CO = 0.5:1). From Fig. 3, the conversion of carbon monoxide reaches above 99.5% in the reaction temperature range of 130–150 °C for Co-Ni/AC as catalyst, indicating that above 99.5% of oxygen are devoted in the oxidation of carbon monoxide. That means that the selectivity is at least 99.5% for the oxidation of carbon monoxide and less than 0.5% for the oxidation of hydrogen in this reaction temperature range. Specially, for CO-Ni/AC as catalyst, the selectivity for the oxidation of carbon monoxide can be deduced to reach about 99.5%, when the reaction temperature is in the range of 130–150 °C.

4. Conclusions

(1) Co_3O_4 is detected to be the main phase in the Co, Co-Ni supported AC, which is characterized by XRD and XPS, respectively. The action of nickel oxide in Co-Ni/AC is to enrich Co_3O_4 species, and change the electronic

cloud density of cobalt, and also enhance the dispersion of Co_3O_4 on the surface of catalyst.

(2) Ni/AC has a poor catalytic activity in the CO selective oxidation in the presence of excess hydrogen, Co/AC and Co-Ni/AC give rise to a higher catalytic activity than Ni/AC, showing the Co_3O_4 species is an important catalytic active center.

(3) However, Co-Ni/AC exhibits a high catalytic activity in a wide reaction temperature region of 130–150 °C, the conversion of carbon monoxide can reach above 99.5%. And the selectivity of Co-Ni/AC in CO selective oxidation in presence of excess hydrogen can be deduced to be at least 99.5% at the reaction temperature of 130–150 °C.

(4) The higher activity of Co-Ni/AC than Co/AC is attributed to the higher dispersion of active Co_3O_4 species and lower electronic cloud density of cobalt on the surface of catalysts.

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References

[1] H. Tanaka, S. Ito, S. Kameoka, K. Tomishige, K. Kunimori, Appl. Catal. A 250 (2003) 255–263.
[2] R.J.H. Grisel, B.E. Nieuwenhuys, J. Catal. 199 (2001) 48–59.
[3] S. Freni, G. Calogero, S. Cavallaro, J. Power Sources 87 (2000) 28–38.
[4] J.M. Ogden, M.M. Steinbugler, T.G. Kreutz, J. Power Sources 79 (1999) 143–168.
[5] L.J. Pettersson, R. Westerholm, Int. J. Hydrogen Energy 26 (2001) 243–264.
[6] H. Igarashi, T. Fujino, M. Watanabe, J. Electroanal. Chem. 391 (1995) 119–123.
[7] M. Watanabe, H. Uchida, K. Ohkubo, H. Igarashi, Appl. Catal. B 46 (2003) 595–600.
[8] M. Shou, K. Tanaka, K. Yoshioka, Y. Moro-oka, S. Nagano, Catal. Today 90 (2004) 255–261.
[9] R.A. Lemons, J. Power Sources 29 (1990) 251–264.
[10] S.H. Oh, R.M. Sinkevitch, J. Catal. 142 (1993) 254–262.
[11] Ş. Özkara, A.E. Aksoylu, Appl. Catal. A 251 (2003) 75–83.
[12] P.V. Snytnikov, V.A. Sobyanin, V.D. Belyaev, P.G. Tsyrulnikov, N.B. Shitova, D.A. Shlyapin, Appl. Catal. A 239 (2003) 149–156.
[13] R.J.H. Grisel, C.J. Weststrate, A. Goossens, M.W.J. Crajé, A.M. Kraan, B.E. Nieuwenhuys, Catal. Today 72 (2002) 123–132.
[14] A. Wörner, C. Friedrich, R. Tamme, Appl. Catal. A 245 (2003) 1–14.
[15] R.M.T. Sanchez, A. Ueda, K. Tanaka, M. Haruta, J. Catal. 168 (1997) 125–127.
[16] G.W. Chen, Q. Yuan, H.Q. Li, Shulian Li, Chem. Eng. J. 101 (2004) 101–106.
[17] H. Tanaka, S.I. Ito, S. Kameoka, K. Tomishige, K. Kunimori, Catal. Commun. 4 (2003) 1–4.
[18] Y. Teng, H. Sakurai, A. Ueda, T. Kobayashi, Int. J. Hydrogen Energy 24 (1999) 355–358.
[19] O. Korotkikh, R. Farrauto, Catal. Today 62 (2000) 249–254.
[20] J.W. Park, J.H. Jeong, W.L. Yoon, H. Jung, H.T. Lee, D.K. Lee, Y.K. Park, Y.W. Rhee, Appl. Catal. A 274 (2004) 25–32.
[21] J.W. Park, J.H. Jeong, W.L. Yoon, C.S. Kim, D.K. Lee, Y.K. Park, Y.W. Rhee, Int. J. Hydrogen Energy 30 (2005) 209–220.
[22] J.W. Park, J.H. Jeong, W.L. Yoon, Y.W. Rhee, J. Power Sources 132 (2004) 18–28.
[23] P. Thormählen, M. Skoglundh, E. Fridell, B. Andersson, J. Catal. 188 (1999) 300–310.
[24] J. Jansson, A.E.C. Palmqvist, E. Fridell, M. Skoglundh, L. Österlund, P. Thormählen, V. Langer, J. Catal. 211 (2002) 387–397.
[25] M. Oku, Y. Sato, Appl. Surf. Sci. 55 (1992) 37–41.
[26] J. Jansson, J. Catal. 194 (2000) 55–60.
[27] P. Arnoldy, J.A. Moulijn, J. Catal. 93 (1985) 38–54.
[28] E. Steen, G.S. Sewell, R.A. Makhothe, C. Micklethwaite, H. Manstein, M. Lange, C.T. O'Connor, J. Catal. 162 (1996) 220–229.
[29] W.P. Dow, Y.P. Wang, T.J. Huang, J. Catal. 160 (1996) 155–170.
[30] W.P. Dow, T.J. Huang, J. Catal. 160 (1996) 171–182.
[31] A. Manasilp, E. Gulari, Appl. Catal. B 37 (2002) 17–25.
[32] Y. Choi, H.G. Stenger, J. Power Sources 129 (2004) 246–254.