Chinese Journal of Catalysis 35 (2014) 1833–1839

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

Article

Hydrogen production from decalin dehydrogenation over Pt-Ni/C bimetallic catalysts

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A R T I C L E I N F O

Article history:
Received 6 April 2014
Accepted 23 May 2014
Published 20 November 2014

Keywords:
Platinum
Nickel
Bimetallic
Decalin
Dehydrogenation
Density functional theory

A B S T R A C T

Pt-Ni bimetallic catalysts and the corresponding monometallic Pt catalysts supported on active carbon were prepared by incipient wetness impregnation and characterized by X-ray diffraction, N_2 adsorption, and NH_3-temperature programmed desorption. Their activities for decalin dehydrogenation were investigated at a superheated liquid film state in a batch reactor. The effects of temperature, impregnation sequence, and Pt/Ni molar ratio on the dehydrogenation activity and the naphthalene yield were investigated. The results show that the Pt-Ni bimetallic catalyst significantly enhanced hydrogen evolution compared with either Ni or Pt monometallic catalyst. The highest dehydrogenation conversion and naphthalene yield were obtained when the Pt/Ni molar ratio was 1:1 and Pt was impregnated first. The experimental results were correlated with density functional theory calculations of hydrogen binding energy (HBE) on different catalytic surfaces. The correlation confirmed that bimetallic surfaces with stronger HBEs had higher dehydrogenation activities.

1. Introduction

Hydrogen as a clean energy carrier has good prospects in hydrogen fuel cells and alternative energy sources. However, the key to using hydrogen on a large scale lies in its storage, transportation, and distribution [1,2]. Some cyclic hydrocarbons such as decalin, tetralin, and cyclohexane are receiving an increasing amount of attention as organic liquid hydrogen storage materials [3–13]. Their hydrogenation and dehydrogenation cycles offer the possibility of using these molecules as hydrogen storage media because of their high hydrogen storage density and convenient transportation.

Among all the liquid organic hydrides, decalin is one of the best candidates because of its excellent hydrogen storage density of 7.2 wt%. Moreover, decalin is an environmentally friendly hydrogen carrier with zero CO_2 emission in the dehydrogenation process [14–21]. It is well known that the decalin dehydrogenation reaction is an endothermic reaction. Higher temperatures would be favorable for dehydrogenation, but the selectivity toward naphthalene would decrease because of side effects such as hydrogenolysis or coking at high temperatures. These side reactions would hinder the reversible cycle of hydrogen storage and release.

Bimetallic catalysts [22–24], which often show distinctly different electronic and chemical properties from those of the parent metals, offer the opportunity to design new catalytic materials with enhanced activity, selectivity, and stability. Kariya et al. [7] reported that Pt-Re, Pt-Pd, and Pt-Rh catalyzed cycloalkane dehydrogenation better than Pt monometallic catalysts. However, high cost prohibits widespread use of noble metal catalysts, so some metal oxide catalysts have been investigated in the dehydrogenation reaction [25].

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This work was supported by the National Natural Science Foundation of China (21006076), the Specialized Research Fund for the Doctoral Program of Higher Education, China (20110201130002), and the Fundamental Research Funds for the Central Universities, China (xjj2011062).

DOI: 10.1016/S1872-2067(14)60178-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 11, November 2014

In our previous work, the Pt-Ni bimetallic catalyst was identified as an active catalyst toward low-temperature hydrogenation and dehydrogenation of cycloalkenes including cyclohexene, 1,3-cyclohexadiene, and 1,4-cyclohexadiene [26–28]. Both experimental and theoretical investigations have revealed that for the Pt-Ni bimetallic catalyst, the formation of a subsurface Pt-Ni-Pt structure with an atomic layer of Ni underneath the surface Pt atoms is responsible for the higher hydrogenation activity than the corresponding monometallic surfaces. In contrast, a surface bimetallic structure, Ni-Pt-Pt, with a layer of Ni residing on top of the Pt substrate, binds adsorbates more strongly than either the Pt or Ni surfaces alone [29,30]. The strong binding on the Ni-Pt-Pt surface structure leads to facile production of hydrogen from the dehydrogenation of cycloalkenes, oxygenates [31], and ammonia [32].

This work extends the previous surface science results to supported Pt-Ni bimetallic catalysts prepared by the incipient wetness impregnation method. Decalin dehydrogenation was selected as a probe reaction to demonstrate the enhanced dehydrogenation activity on the bimetallic catalysts. The dehydrogenation activity of the Pt-Ni/C bimetallic catalyst was compared with those of the corresponding monometallic Pt and Ni catalysts. It was found that supported Pt-Ni bimetallic catalysts exhibited much better performance than either of the monometallic catalysts. On the other hand, for the Pt-Ni bimetallic catalyst, an effect of the impregnation sequence was observed and discussed. In addition, the catalytic activity and hydrogen binding energy (HBE) on different Pt-Ni surfaces from density functional theory (DFT) calculations were shown to be correlated [33,34].

2. Experimental

2.1. Catalyst preparation

A series of Ni or Pt catalysts were prepared by the incipient wetness impregnation method. $Ni(NO_3)_2\cdot6H_2O$ (AR, Tianjin Chemical Reagent Research Institute, China) or chloroplatinic acid (AR) was selected as the source of active metal and impregnated into active carbon (C). The Pt-Ni bimetallic catalysts were prepared by sequential impregnation and co-impregnation. After impregnation, the different precursors were dried at 110 °C for 2 h and then calcined in N_2 atmosphere at 400 °C for 1 h. The different bimetallic catalysts are denoted 1Pt-1Ni/C(CI), 1Pt-1Ni/C, and 1Ni-1Pt/C. Pt-Ni/C(CI) means that the catalyst was prepared by Pt and Ni co-impregnation. Pt-Ni/C means that Ni was impregnated first, while Ni-Pt/C means that Pt was impregnated first. 1Pt-1Ni indicates that the atomic ratio of Pt to Ni was 1:1. Other Pt-Ni bimetallic catalysts with different Pt/Ni ratios were also prepared for comparisons to the 1Pt-1Ni catalysts. They are denoted 0.5Ni-1Pt/C, 2Ni-1Pt/C, 4Ni-1Pt/C, and 8Ni-1Pt/C. Pt loadings of all catalysts were 3 wt%.

2.2. Catalyst characterization

The specific surface area and pore volume measurements of the different catalysts were measured by N_2 adsorption-desorption at liquid nitrogen temperature using a Beckman Coulter Sorption Analysis 3100 Plus instrument. Powder X-ray diffraction (XRD) patterns of various catalysts were recorded with a Rigaku D/Max-2400 X-ray diffractometer using Cu K_α radiation with a scanning angle (2θ) range of 5°–80°, operated at 36 kV and 80 mA. NH_3-temperature programmed desorption (NH_3-TPD) tests were performed to determine the catalyst surface acidity. In a U-shaped tubular quartz reactor heated by an electric furnace, 0.1 g sample was pretreated in flowing He (99.99%, 30 mL/min) at 400 °C for 0.5 h, followed by NH_3 saturated adsorption at 30 °C, and then flushed with flowing He at the same temperature for 1 h. NH_3-TPD experiments were performed using a temperature ramp from 30 to 600 °C at 10 °C/min using a thermal conductivity detector.

2.3. Catalyst evaluation

The catalytic activities of different catalysts for decalin dehydrogenation were evaluated using a batch reactor. The batch reactor consisted of a three-necked flat-bottomed flask of 100 mL capacity, fitted with a condenser in the central opening. A sampling device and a thermocouple were fitted in the other two openings. The reaction temperature was maintained by an electric furnace equipped with a temperature controller.

In a typical run, 0.3 g catalyst was added into the bottom of the flask and reduced with H_2 for 1 h at the reaction temperature, and then the reactor was flushed with flowing N_2 for 0.5 h to remove residual H_2. Thereafter, 1 mL decalin (6.48 mmol) was added to the reactor, and the reaction started and was allowed to proceed for 0.5 h. During the reaction, the continuous vaporization-condensation reflux of decalin ensured the formation of a decalin liquid film on the catalyst surface, which remained covered by the decalin liquid film. The temperature of the catalyst surface was higher than the boiling point of decalin, which was in an overheated state. The evolving H_2 was collected and measured by the water drainage method. After the reaction, the contents remaining in the flask were dissolved with *n*-hexane. The dissolved mixture was collected and separated by centrifugation to remove the catalyst particles completely, and then analyzed by a HP-4890D gas chromatograph equipped with a flame ionization detector. The yield of naphthalene was calculated by dividing the moles of naphthalene actually obtained by the moles of naphthalene theoretically obtained.

3. Results and discussion

Table 1 lists the surface area and average pore diameter of the different catalysts. The addition of metal leads to a small decrease in the catalyst surface area, which indicates that metal species on the support might migrate into internal channels after calcination. The surface area of the Pt-Ni bimetallic catalysts decreases with increasing Ni content, following the order 1Ni-1Pt/C > 1Pt-1Ni/C(CI) > 1Pt-1Ni/C. For the decalin dehydrogenation reaction, smaller pore sizes can prevent diffusion of the intermediate product tetralin and help tetralin further

Table 1
Surface area and average pore diameter of different catalyst samples.

Catalyst	Surface area (m^2/g)	Average pore diameter (nm)
C	407	8.6
Pt/C	360	9.7
1Pt-1Ni/C(CI)	340	10.3
1Pt-1Ni/C	318	11.0
0.5Ni-1Pt/C	379	9.2
1Ni-1Pt/C	373	9.4
2Ni-1Pt/C	366	9.5

convert to naphthalene, which is favorable for dehydrogenation selectivity.

The Pt diffraction peaks are clearly seen in Fig. 1, indicating that the Pt species were in a good crystaline form and well dispersed on the support surface. The impregnation sequence has a slight impact on the particle dispersion of the bimetallic catalysts. The Pt diffraction peaks of the 1Ni-1Pt/C catalyst are slightly broader than those of the other two catalysts, especially at $2\theta = 40°$. With increases in the Ni/Pt ratio, the Pt diffraction peaks decrease in size, while the Ni diffraction peaks can be seen to become sharper (Fig. 1(b)). The metal particle size of the supported metal catalyst is correlated with the width of the corresponding diffraction peak. The Pt particle size decreases as the diffraction peak broadens. This implies that the addition of Ni promotes dispersion of Pt. However, too high Ni loading leads to aggregation of Ni particles.

Figure 2 shows the NH_3-TPD profiles of Pt and Pt-Ni catalysts. Both spectra exhibit a single characteristic peak. Normally, the area of a specific peak corresponds to the amount of NH_3 desorbed from the sample, and it can be taken as a standard to quantify the acidity of the sample. Comparing the Pt/C catalyst with the 1Ni-1Pt/C catalyst, the amounts of desorbed NH_3 are similar. However, the peak position of the 1Ni-1Pt/C catalyst shifts to higher temperatures than that of the Pt/C catalyst. This implies an increase in the strength of acid sites, which is suggested to be associated with the interaction of Ni and Pt. The 1Ni-1Pt/C catalyst shows better dehydrogenation activity, indicating that the slight increase of the number of acid centers has a positive effect on the catalytic dehydrogenation activity.

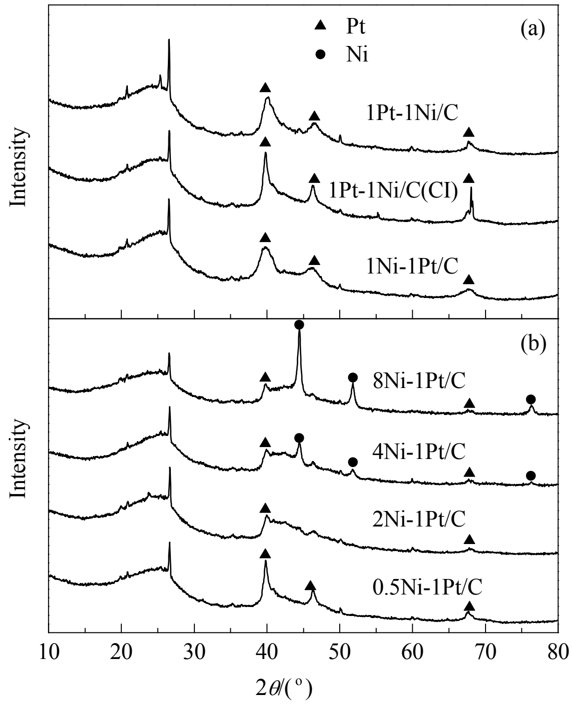

Fig. 1. XRD patterns of carbon supported Pt-Ni bimetallic catalysts prepared by various impregnation sequences (a) and various Pt/Ni molar ratios (b).

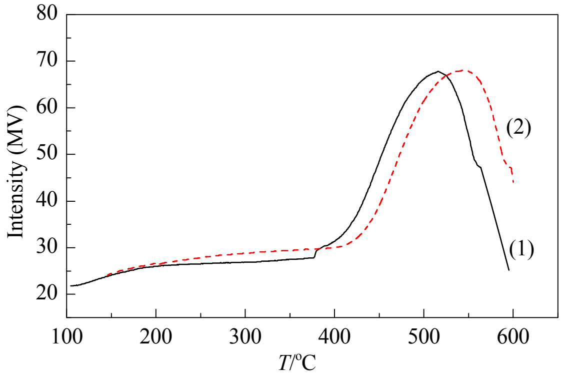

Fig. 2. NH_3-TPD profiles of Pt/C (1) and 1Ni-1Pt/C (2) catalysts.

Figure 3 is the product distribution of decalin dehydrogenation over the Pt/C catalyst at different temperatures when the decalin feedstock was 1 mL. At this point the catalyst surface was at an overheated liquid film state, having a higher temperature and larger contact area. The results show that the yield for naphthalene keeps increasing from 230 to 290 °C, while the amount of the intermediate product tetralin remains at nearly the same level over this range. This indicates that high temperatures favor the further dehydrogenation of tetralin.

Figure 4 shows the dehydrogenation behavior of decalin over Pt-based catalysts at 290 °C in a batch reactor. The dehydrogenation of decalin over the 1 wt% Ni/C catalyst was also examined, and the catalytic activity for this sample was nearly zero. The naphthalene yields over Pt-Ni/C bimetallic catalysts were much higher than that obtained over Ni/C or Pt/C monometallic catalysts. On the other hand, both catalytic activity and naphthalene yield over the Pt-Ni catalysts were influenced

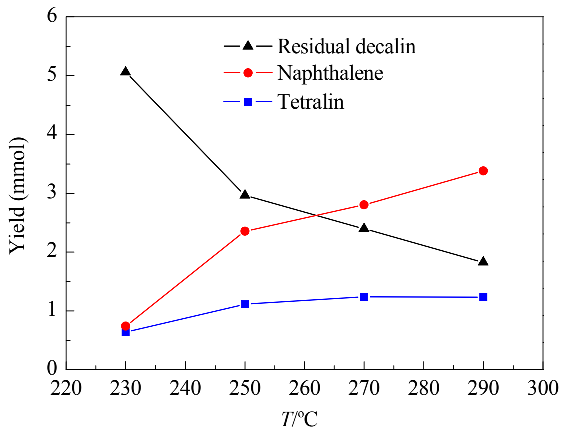

Fig. 3. Effect of temperature on decalin dehydrogenation over the Pt/C catalyst.

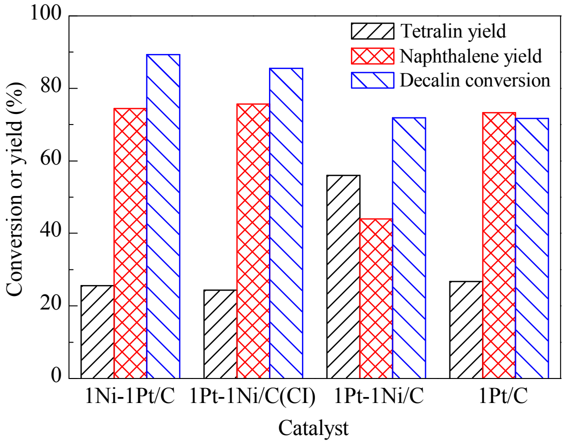

Fig. 4. Decalin dehydrogenation over different Pt-based catalysts in a batch reactor. Reaction conditions: 290 °C, decalin 1 mL, catalyst 0.3 g, 0.5 h.

by the impregnation sequence; they followed the order of 1Ni-1Pt/C > 1Pt-1Ni/C(CI) > 1Pt-1Ni/C. The 1Ni-1Pt/C catalyst, which has Ni residing on top of the Pt substrate, has the best catalytic activity, which is consistent with the DFT results (discussed below). It is most likely that Pt deposited first would remain outside the support and further prevent subsequently deposited Ni from entering the inter cavities of the support, facilitating the formation of the Pt–Ni bond [30,33].

The dehydrogenation activities of decalin over bimetallic catalysts with different Pt/Ni molar ratios were discussed in light of Fig. 5. The yield for naphthalene first increased and then decreased with the addition of Ni, while the byproduct tetralin remained nearly unchanged after the Pt/Ni ratio exceeded 0.5. The 1Ni-1Pt/C catalyst exhibited the best activity and naphthalene yield; its enhanced catalytic activity likely benefits from the formation of the Pt-Ni bimetallic bonds. However, excessive Ni atoms may block the Pt active sites and lead to a decline of the catalytic activity.

In previous work, the hydrogenation activity of Pt-Ni bimetallic catalysts has been correlated to weaker HBEs on bimetallic surfaces [28,30]. Herein, DFT calculations were performed to explore whether such correlation can be extended to dehydrogenation. Table 2 shows the DFT results of HBE on the closed-packed Pt(111) surface, the Ni-Pt-Pt(111) surface with a monolayer of Ni residing on top of Pt(111), and the subsurface Pt-Ni-Pt(111) configuration with one monolayer of Ni between the first and second layers of Pt. The DFT calculations were performed using the Vienna ab-initio simulations package (VASP) with spin polarization. The Generalized Gradient Approximation with Perdew Burke Ernzerhof (GGA-PBE) exchange-correlation functional was used. A 3×3 slab with four metal layers was used to model the adsorption of atomic hydrogen (one adsorbate per unit cell). The top two layers were allowed to relax to the lowest energy configuration while the bottom two layers were fixed at a bulk Pt–Pt bond length as previously described in detail [28,29]. A 3×3×1 Monkhorst-Pack K-point grid mesh was used to determine the electronic energies.

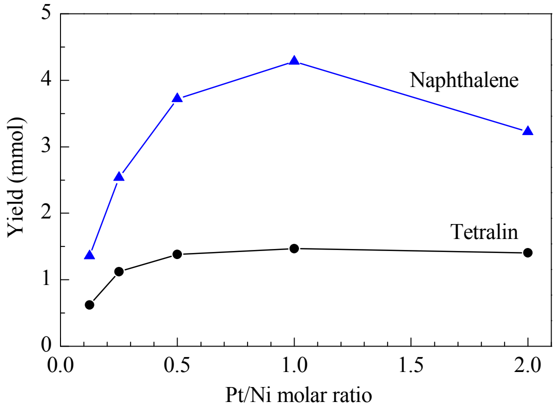

Fig. 5. Effect of the Pt/Ni ratio on product yield of decalin dehydrogenation over Ni-Pt/C catalysts. Reaction conditions: 290 °C, decalin 1 mL, catalyst 0.3 g, Pt first impregnated, 0.5 h.

Table 2
Hydrogen binding energies (HBE) on Pt(111), Ni(111), and Ni/Pt(111) surface as predicted by DFT.

Surface	HBE (kJ/mol)
Pt(111)	–267.3
Ni-Pt-Pt(111)	–285.6
Pt-Ni-Pt(111)	–238.3

That the HBE is higher on the Ni-Pt-Pt(111) surface than on either the Pt(111) or Pt-Ni-Pt(111) surfaces suggests that the Ni-Pt-Pt surface structure should be more thermodynamically favored than the other two surfaces for the dehydrogenation reaction. Although more detailed experimental studies are needed in regards to controllable syntheses of bimetallic catalysts, it is clear that the presence of the Ni-Pt-Pt structure is responsible for the higher dehydrogenation activity on the 1Ni-1Pt/C bimetallic catalyst when compared with the monometallic catalysts and the other two bimetallic catalysts.

4. Conclusions

The catalytic dehydrogenation of decalin was investigated using a combination of experimental methods and DFT calculations. Supported Pt-Ni bimetallic and Ni and Pt monometallic catalysts on active carbon were prepared by incipient wetness impregnation and evaluated using a batch reactor for decalin dehydrogenation. The results showed that Pt-Ni bimetallic catalysts had higher dehydrogenation activities than the corresponding monometallic catalysts. The 1Ni-1Pt/C bimetallic catalyst exhibited the highest activity among all the prepared catalysts toward decalin hydrogenation, which was mostly attributed to the Pt-Ni bimetallic formation. The observed highest activity over 1Ni-1Pt/C agrees well with DFT results, which predict that the Ni-Pt-Pt(111) surface structures bind hydrogen more strongly than Pt(111) and Pt-Ni-Pt(111).

Acknowledgments

We would like to acknowledge the technical assistance on computing platform from Professor Xiangdong Ding's Group at Xi'an Jiaotong University.

Graphical Abstract

Chin. J. Catal., 2014, 35: 1833–1839 doi: 10.1016/S1872-2067(14)60178-9

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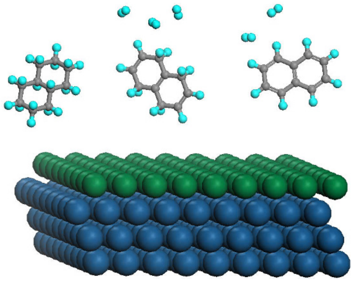

The correlation of experimental results with density functional theory calculations confirmed that bimetallic surfaces with stronger hydrogen binding energies exhibited higher dehydrogenation activity for decalin.

References

[1] Eberle U, Felderhoff M, Schüth F. *Angew Chem Int Ed*, 2009, 48: 6608

[2] David E. *J Mater Process Technol*, 2005, 162-163: 169

[3] Biniwale R B, Rayalu S, Devott S, Ichikawa M. *Int J Hydrogen Energy*, 2008, 33: 360

[4] Zhu G L, Yang B L. *Progr Chem*, 2009, 21: 2760

[5] Ninomiya W, Tanabe Y, Sotowa K I, Yasukawa T, Sugiyama S. *Res Chem Intermed*, 2008, 34: 663

[6] Pande J V, Shukla A, Biniwale R B. *Int J Hydrogen Energy*, 2012, 37: 6756

[7] Kariya N, Fukuoka A, Ichikawa M. *Appl Catal A*, 2002, 233: 91

[8] Saito Y, Aramaki K, Hodoshima S, Saito M, Shono A, Kuwano J, Otake K. *Chem Eng Sci*, 2008, 63: 4935

[9] Wang Y G, Shah N, Huffman G P. *Energy Fuels*, 2004, 18: 1429

[10] Tien P D, Satoh T, Miura M, Nomura M. *Fuel Process Technol*, 2008, 89: 415

[11] Du J P, Zhao R H, Jiao G R. *Int J Hydrogen Energy*, 2013, 38: 5789

[12] Chen A B, Zhang W P, Li X Y, Tan D L, Han X W, Bao X H. *Catal Lett*, 2007, 119: 159

[13] Shukla A A, Gosavi P V, Pande J V, Kumar V P, Chary K V R, Biniwale R B. *Int J Hydrogen Energy*, 2010, 35: 4020

[14] Shinohara C, Kawakami S, Moriga T, Hayashi H, Hodoshima S, Saito Y, Sugiyama S. *Appl Catal A*, 2004, 266: 251

[15] Tien P D, Satoh T, Miura M, Nomura M. *Energy Fuels*, 2005, 19: 731

[16] Tien P D, Satoh T, Miura M, Nomura M. *Energy Fuels*, 2005, 19: 2110

[17] Wang Y G, Shah N, Huggins F E, Huffman G P. *Energy Fuels*, 2006, 20: 2612

[18] Jiang N Z, Rao K S R, Jin M J, Park S E. *Appl Catal A*, 2012, 425-426: 62

[19] Suttisawat Y, Horikoshi S, Sakai H, Abe M. *Int J Hydrogen Energy*, 2010, 35: 6179

[20] Yolcular S, Olgun Ö. *Catal Today*, 2008, 138: 198

[21] Nagaraja B M, Shin C H, Jung K D. *Appl Catal A*, 2013, 467: 211

[22] Patil S P, Pande J V, Biniwale R B. *Int J Hydrogen Energy*, 2013, 38: 15233

[23] Alhumaidan F, Tsakiris D, Cresswell D, Garforth A. *Int J Hydrogen Energy*, 2013, 38: 14010

[24] Aboul-Fotouh S M K, Aboul-Gheit N A K. *Chin J Catal*, 2012, 33: 697

[25] Gao X F, Chen C L, Ren S Y, Zhang J, Su D S. *Chin J Catal*, 2012, 33: 1069

[26] Biniwale R B, Kariya N, Ichikawa M. *Catal Lett*, 2005, 105: 83

[27] Qi S T, Yu W T, Lonergan W W, Yang B L, Chen J G. *Chin J Catal*, 2010, 31: 955

[28] Qi S T, Yu W T, Lonergan W W, Yang B L, Chen J G. *ChemCatChem*, 2010, 2: 625

[29] Chen J G, Qi S T, Humbert M P, Menning C A, Zhu Y X. *Acta Phys-Chim Sin*, 2010, 26: 869

[30] Chen J G, Menning C A, Zellner M B. *Surf Sci Rep*, 2008, 63: 201

[31] Skoplyak O, Barteau M A, Chen J G. *ChemSusChem*, 2008, 1: 524

[32] Hansgen D A, Vlachos D G, Chen J G. *Nat Chem*, 2010, 2: 484

[33] Shu Y Y, Murillo L E, Bosco J P, Huang W, Frenkel A I, Chen J G. *Appl Catal A*, 2008, 339: 169

[34] Lima F H B, Zhang J, Shao M H, Sasaki K, Vukmirovic M B, Ticianelli E A, Adzic R R. *J Phys Chem C*, 2007, 111: 404

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