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Article

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

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ABSTRACT

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.

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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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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. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (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 $\text{Cu } K\alpha$ 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(Cl)	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 crystalline 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 $2\theta = 40^\circ$. 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 NH₃-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 NH₃ desorbed from the sample, and it can be taken as a standard to

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. NH₃-TPD profiles of Pt/C (1) and 1Ni-1Pt/C (2) catalysts.

quantify the acidity of the sample. Comparing the Pt/C catalyst with the 1Ni-1Pt/C catalyst, the amounts of desorbed NH₃ 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.

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 dehy-

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

drogenation. 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.

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).

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Graphical Abstract

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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* (朱刚利, 杨伯伦. 化学进展), 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* (催化学报), 2012, 33: 697
- [25] Gao X F, Chen C L, Ren S Y, Zhang J, Su D S. *Chin J Catal* (高旭峰, 谌春林, 任士远, 张建, 苏党生. 催化学报), 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* (齐随涛, 俞伟婷, Lonergan W W, 杨伯伦, 陈经广. 催化学报), 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* (陈经广, 齐随涛, Humbert M P, Menning C A, 朱月香. 物理化学学报), 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

活性炭负载Pt-Ni双金属催化剂上十氢化萘脱氢

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摘要: 采用等体积浸渍法制备了活性炭负载的具有脱氢活性的Pt-Ni双金属催化剂及相应的Pt单金属催化剂, 并用X射线衍射、N₂吸附-脱附和NH₃-程序升温脱附对其进行了表征。在290 °C下, 研究了间歇反应条件下催化剂以过热液膜状态催化十氢化萘脱氢活性, 考察了温度、浸渍顺序和Pt/Ni摩尔比对十氢化萘脱氢活性和萘产率的影响。结果表明, 与单金属催化剂相比, Pt-Ni双金属催化剂上产氢效率显著提高。当Pt/Ni摩尔比为1:1, Pt首先浸渍时, 得到的催化剂上脱氢转化率和萘产率最高。将实验结果与密度泛函理论计算的氢原子在不同催化表面的结合能关联证实, 具有更强原子氢结合能的双金属表面具有更高的脱氢活性。

关键词: 铂; 镍; 双金属; 十氢化萘; 脱氢; 密度泛函理论

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1. 前言

氢气是一种清洁能源, 在氢燃料电池和替代能源上有着广阔的应用前景. 但是氢气的储存、运输和配送是其大规模使用的关键^[1,2]. 环烷烃(如十氢化萘、四氢化萘和环己烷等)可逆加氢脱氢反应的特点使其成为可能的有机储氢材料^[3–13], 且其储氢密度高, 便于运输, 因此越来越受关注.

在液态有机氢化物中, 十氢化萘具有较高的质量储氢密度(7.2 wt%), 因而是最好的储氢材料之一, 且脱氢反应中无CO₂排放, 是一种环境友好型储氢材料^[14–21]. 由于十氢化萘脱氢是吸热反应, 高温有利于脱氢的进行, 但高温下也易发生氢解或结焦等副反应, 从而使萘的选择性下降, 进而阻碍储氢和放氢可逆循环.

双金属催化剂^[22–24]因其具有与相应单金属不同的独特的电子和化学特性, 在催化剂设计中会表现出更好的催化活性、选择性和稳定性. Kariya等^[7]研究发现, 在环己烷脱氢反应中, Pt-Re, Pt-Pd和Pt-Rh双金属催化剂比Pt单金属催化剂更好. 然而, 昂贵的催化剂成本妨碍了贵金属催化剂的广泛应用, 因此也有研究将金属氧化物用于催化脱氢反应^[25].

我们前期工作发现铂-镍双金属催化剂是环烯烃(包括环己烯、1,3-环己二烯和1,4-环己二烯)低温加氢和脱氢反应的有效催化剂^[26–28]. 研究表明, 与相应的单金属表面相比, 具有Pt-Ni-Pt次表面结构的铂-镍双金属催化剂, 即Ni原子层位于表层Pt原子下的结构, 具有更高的加氢活性. 而Ni-Pt-Pt结构的铂-镍双金属催化剂, 即Ni原子层位于Pt基体最上方, 表面与吸附质的结合比Pt或Ni单金属表面更强^[29,30], 因此Ni-Pt-Pt表面上强的结合力有利于环烯烃、含氧化合物^[31]和氨^[32]的脱氢.

本文以十氢化萘脱氢作为探针反应来说明双金属催化剂更好的脱氢活性. 与单金属Pt和Ni催化剂相比, 负载型Pt-Ni双金属催化剂的催化性能更优. 同时, 进一步讨论了浸渍顺序对Pt-Ni双金属催化剂催化性能的影响, 并将催化活性与密度泛函理论计算结果进行了关联^[33,34].

2. 实验部分

2.1. 催化剂制备

采用等体积浸渍法, 将Ni(NO₃)₂·6H₂O (AR, 天津化学试剂研究所)或氯铂酸(AR, 天津化学试剂研究所)浸渍到活性炭上, 然后在110 °C下干燥2 h, 400 °C N₂下焙烧1 h, 制得Pt或Ni单金属催化剂. 分别采用连续浸渍和共浸渍法制备Pt-Ni双金属催化剂. 将所制备的不同双金属催化剂分别记为1Pt-1Ni/C(CI), 1Pt-1Ni/C和1Ni-1Pt/C. 其中, Pt-Ni/C(CI)表示该催化剂用共浸渍法制备; Pt-Ni/C表示先浸渍Ni金属; Ni-Pt/C表示先浸渍Pt金属; 1Ni-1Pt表示该催化剂中Ni和Pt原子摩尔比为1:1. 此外, 还制备出一系列不同Pt/Ni原子比的Pt-Ni双金属催化剂以与1Pt-1Ni催化剂进行比较, 分别表示为0.5Ni-1Pt/C, 2Ni-1Pt/C, 4Ni-1Pt/C和8Ni-1Pt/C. 所有催化剂中Pt含量均为3 wt%.

2.2. 催化剂表征

使用美国Beckman Coulter公司的3100 Plus型吸附分析仪测量催化剂在液氮温度下的N₂吸附-脱附曲线, 得到催化剂的比表面积和孔径. 催化剂的X射线粉末衍射(XRD)谱用Rigaku D/Max-2400型XRD仪测得, Cu K_α射线, 扫描范围5°–80° (2θ), 工作电压36 kV, 工作电流80 mA. 通过NH₃-程序升温脱附测定催化剂表面酸度, 将0.1 g样品加入由电炉加热的U形石英管状反应器, 在400 °C He (99.99%, 30 mL/min)下预处理0.5 h, 30 °C下进行NH₃饱和吸附, 通He吹扫1 h; 再以10 °C/min从30 °C升至600 °C, 热导检测器(TCD)测试脱附信号.

2.3. 催化剂评价

不同催化剂上十氢化萘脱氢反应活性采用100 mL三口平底烧瓶间歇反应装置进行评价. 烧瓶中瓶口装配冷凝器, 另外两个瓶口分别装取样器和热电偶. 通过连接有温控仪的电炉来控制反应过程中的温度.

在烧瓶中加入0.3 g催化剂, 通入H₂并加热至反应温度来还原催化剂1 h. 还原结束后, 通入N₂吹扫30 min以排除反应装置中的H₂. 随后, 加入1 mL十氢化萘(6.48 mmol)反应0.5 h. 在反应过程中, 十氢化萘持续的蒸发-

冷凝回流使催化剂表面形成并覆盖十氢化萘液膜, 因此催化剂表面温度高于十氢化萘的沸点, 十氢化萘处于过热状态. 用排水法收集和测量反应生成的 H_2 . 反应结束后, 向瓶中加入一定量正己烷来溶解反应产物. 最后, 收集溶解所得的液相产物, 离心分离后通过接有FID检测器的Fuli 9790 II型气相色谱仪对产物进行分析. 萘的产率通过实际生成量与理论生成量的比值而算得.

3. 结果与讨论

表1列出了不同催化剂的比表面积和孔径. 可见, 负载金属组分后催化剂的比表面积减小, 表明焙烧后金属组分进入载体内部孔道而导致催化剂比表面积下降. Pt-Ni双金属催化剂的比表面积按以下顺序递减: $1Ni-1Pt/C > 1Pt-1Ni/C(Cl) > 1Pt-1Ni/C$. 并且随着Ni含量的增加, Pt-Ni双金属催化剂的比表面积依次下降. 同时, 对十氢化萘脱氢反应, 较小的孔径阻碍了中间产物四氢化萘的扩散, 有助于其进一步转化为萘, 从而提高了脱氢反应的选择性.

由图1的XRD谱可见, 各样品均出现较强的Pt衍射特征峰, 表明Pt具有良好的晶型且较好地分散于载体表面. $1Ni-1Pt/C$ 催化剂在 $2\theta = 40^\circ$ 处Pt的衍射特征峰比另外两种催化剂稍宽, 说明浸渍顺序对双金属催化剂的颗粒分散有一定影响. 随着Ni/Pt摩尔比增加, Pt的衍射峰越来越小, Ni的衍射峰开始出现且峰形越来越尖锐(图1(b)), 表明Ni的加入有利于Pt的分散, 使得Pt粒径下降, 而Ni含量过高则导致Ni粒子的团聚.

图2为Pt/C和Pt-Ni/C催化剂的 NH_3 -TPD图. 由图可见, 两种催化剂均只有一个单峰, 且峰面积相当. 通常, 脱附峰的峰面积对应于样品吸附的氨气量. 由此可知两种催化剂所吸附的 NH_3 量即酸量差别不大, 但 $1Ni-1Pt/C$ 催化剂的脱附峰中心温度更高, 表明Ni的加入使催化剂酸性增强, 可能增强了Ni和Pt间相互作用. $1Ni-1Pt/C$ 催化剂表现出更好的脱氢活性, 表明酸中心的微弱增强对催化脱氢有利.

图3是进料量为1.0 mL, 不同温度时Pt/C催化剂上十氢化萘脱氢反应的产物分布. 结果表明, 在230–290 $^\circ C$, 萘的产率随温度升高而增大, 而中间产物四氢化萘的量几乎保持不变, 说明高温有利于四氢化萘脱氢.

图4是290 $^\circ C$ 时Pt基催化剂上十氢化萘脱氢反应结果. 由图可见, Pt-Ni/C双金属催化剂上十氢化萘转化率高于相应1 wt% Ni/C (几乎为零)和Pt/C单金属催化剂.

各双金属催化剂性能顺序为 $1Ni-1Pt/C > 1Pt-1Ni/C(Cl) > 1Pt-1Ni/C$, 可见Pt-Ni催化剂活性和萘的产率受浸渍顺序的影响, 即Ni位于最外面的 $1Ni-1Pt/C$ 催化剂具有更好的催化活性. 这可能是由于先负载的Pt可能处于载体外表面, 可阻止随后负载的Ni进入载体内腔, 有助于Pt-Ni键的形成^[30,33].

图5是不同Pt/Ni摩尔比的Pt-Ni/C催化剂上十氢化萘脱氢反应结果. 可见, 随着Ni含量增加, 萘的产率先提高后下降, 其中 $1Ni-1Pt/C$ 催化剂活性最好, 萘产率最高. 而当Pt/Ni原子摩尔比超过0.5时, 副产物四氢化萘的量几乎保持不变, 说明Ni的增加有助于Pt-Ni双金属键的形成, 提高了催化活性. 但是, 过量的Ni原子也会阻塞Pt活性位, 导致催化活性下降.

我们曾将Pt-Ni双金属催化剂的加氢活性与双金属表面上的氢结合能相关联^[20,22]. 本文拟进一步确定这种关联是否可推及脱氢反应. 表2列出Pt(111), Ni-Pt-Pt(111)表面和Pt-Ni-Pt(111)次表面三种晶面上氢结合能的DFT结果. DFT的相关计算采用VASP软件, 电子交换相关部分在广义梯度近似(GGA)下用标准PBE (Perdew-Burke-Ernzerhof)交换关联泛函进行描述. 四层的 3×3 平板模型来模拟氢原子的吸附(1个单元表面吸附1个分子), 并考虑了自旋极化. 表面两层进行弛豫来获得能量最低的结构, 而底部两层固定^[20,21]. 计算中采用 $3\times 3\times 1$ 的Monkhorst-Pack K点网格来计算电子的能量.

由表2可见, Ni-Pt-Pt(111)表面上氢结合能的绝对值比Pt(111)和Pt-Ni-Pt(111)都高, 表明Ni-Pt-Pt表面结构比其他两种表面在热力学上更有利于脱氢进行. 虽然双金属催化剂的可控合成还需要更深入的实验研究, 但显而易见的是, 与相应的单金属催化剂和另外两种双金属催化剂相比, 存在Ni-Pt-Pt结构的 $1Ni-1Pt/C$ 双金属催化剂具有更高的脱氢催化活性.

4. 结论

采用等体积浸渍法制备了活性炭负载的Pt-Ni双金属和Ni, Pt单金属催化剂, 用间歇反应装置评价了它们催化十氢化萘脱氢反应性能. 结果表明, 与相应的单金属催化剂相比, Pt-Ni双金属催化剂具有更好的脱氢活性, 其中 $1Ni-1Pt/C$ 双金属催化剂活性最高. 这可能是由于Pt-Ni双金属键的形成. DFT结果表明, Ni-Pt-Pt(111)表面结构上氢的结合能比Pt(111)和Pt-Ni-Pt(111)表面更强, 因而前者具有更好的脱氢活性. 这与实验结果一致.