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Article

Catalytic conversion of *n*-butane over Au-Zn-modified nano-sized HZSM-5

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ABSTRACT

An Au-Zn-modified HZSM-5 catalyst was prepared using deposition-precipitation and wet impregnation methods. To obtain a better understanding of the relationship between catalyst characteristics and catalytic performance, a thorough study of various catalyst samples (HZSM-5, Au/HZSM-5, Zn/HZSM-5, and Au-Zn/HZSM-5) was performed. The interactions between Au and Zn species in Au-Zn/HZSM-5 were determined using ultraviolet-visible and X-ray photoelectron spectroscopies. Compared with Zn/HZSM-5, the introduction of Au to give Au-Zn/HZSM-5 effectively promotes the dehydrogenation and aromatization of *n*-butane, and also suppresses hydrogenolysis over Zn species. The *n*-butane conversion (70.8%) and selectivity for olefins and aromatics (61.98%) increased significantly. The dry gas selectivity also decreased significantly to 28.4%. Au-Zn-containing HZSM-5 is a useful catalyst for the conversion of light alkanes.

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1. Introduction

Large amounts of *n*-butane are produced as by-products in catalytic cracking units and in extraction in oil fields [1–3]. *n*-Butane is a good feedstock for steam cracking for producing more valuable olefins. However, steam cracking has a high energy consumption. It is therefore important to find effective catalysts for converting *n*-butane to olefins and aromatics under relatively mild condition [4–12].

Acidic MFI zeolites modified with Ga or Zn are the best catalysts for *n*-butane conversion [13]. The metal sites of this type of bifunctional catalyst are generally considered to be responsible for dehydrogenation reactions, whereas acidic sites are responsible for cracking, isomerization, oligomerization, and aromatization reactions [14,15]. According to previous studies

[13,16–22], Zn is a good dehydrogenation agent, but it has the obvious disadvantage of generating substantial amounts of dry gas (methane and ethane) [23,24] because of 1) the relatively strong acidity of Zn/HZSM-5, which results in C–C bond cracking reactions, and 2) the strong interactions between Zn species and hydrogen (produced during dehydrogenation), which result in hydrogenolysis. Au-containing catalysts have been shown to have good performance in many selective reactions, including hydrogenation of 1,3-butadiene [25,26]. Recently, Wannakao et al. [27] studied methane activation over Au-cation-exchanged zeolites using a density functional theory method, and concluded that Au/HZSM-5 was effective in methane activation. We therefore think that the introduction of Au into Zn/HZSM-5 would influence the chemical environment of the Zn active centers in Zn/HZSM-5, and that the combination

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of Au-Zn on HZSM-5 would suppress side reactions in *n*-butane conversion. However, until now, the physicochemical properties and catalytic performance of Au-Zn/HZSM-5 have not been studied.

2. Experimental

2.1. Catalyst preparation

A commercial ZSM-5 zeolite powder (20–50 nm, SiO₂/Al₂O₃ = 26, Dalian Ligong Qiwangda Chemical Technology) was used. HZSM-5 was obtained using a conventional ammonium-ion-exchange method. Au/HZSM-5 with a 0.3 wt% Au loading was prepared using a deposition-precipitation (DP) method [28,29]. Typically, a mechanical mixture of urine (AR, Tujian Chemreagent) and HZSM-5 was evacuated under vacuum (70.36 kPa) for 4 h at 80 °C. Then 100 ml of HAuCl₄·H₂O were added to the mixture and the resulting suspension was stirred for 20 h at 80 °C and then kept static for another 4 h in a special airtight container. The solid material was recovered by filtration and washed with deionized water, dehydrated at 80 °C for 10 h, and then calcined at 540 °C for 4 h. Au-Zn/HZSM-5 (with 0.3 wt% Au and 6.0 wt% Zn loadings) was prepared from Au/HZSM-5 (dehydrated at 80 °C for 10 h without calcination) by incipient wet impregnation of Zn(NO₃)₂ solution at 80 °C. The impregnated sample was dried at 110 °C for 24 h and calcined at 540 °C for 3 h. For the purpose of comparison, Zn/HZSM-5 was also prepared from HZSM-5 by incipient wet impregnation of Zn(NO₃)₂ solution at 80 °C.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) analysis was carried out using a Rigaku D/max-2004 diffractometer with Cu K α radiation (40 kV, 100 mA) at a scanning rate of 0.02°/min (2 θ). Ultraviolet-visible (UV-Vis) spectra were obtained with a JASCO UV-550 spectrometer, using BaSO₄ as a reference. Physical adsorption of N₂ was investigated using an ASAP 2020 analyzer. The chemical composition of Au-Zn/HZSM-5 was determined using a Shimadzu ICPS-8000E inductively coupled plasma

atomic emission spectrometer. Ammonia temperature-programmed desorption (NH₃-TPD) measurements were carried out using a Quantachrome Chembet 3000 instrument. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 250Xi system with an Al K α (1486.6 eV) X-ray source. A pass energy of 20 eV was used. The base pressure of the analysis chamber was greater than 1 $\times$ 10⁻⁸ Pa. The spectra were calibrated against the binding energy of C 1s (284.6 eV), and were fitted using an appropriately weighted sum of Lorentzian and Gaussian component curves after Shirley background subtraction. The acidic sites were identified using pyridine adsorption bands measured using a Nicolet 6700 Fourier-transform infrared (FT-IR) spectrometer at a resolution of 4 cm⁻¹ [30].

2.3. Catalytic activity evaluation

The catalytic activity of the Au/HZSM-5 catalyst was evaluated by *n*-butane transformation in a microcatalytic pulsed reactor at atmospheric pressure, with a fixed-bed catalyst (ϕ 6 mm, catalyst 0.15 g, 40–60 mesh, pulse size 0.3 ml) connected to an on-line gas chromatograph (Shimadzu GC-14B) with a flame ionization detector (N₂ carrier gas 50 ml/min; OV-1 capillary column 50 m $\times$ 0.2 mm). The *n*-butane conversion and product selectivity were calculated using the following equations:

$$X(n\text{-C}_4^0) = [(n\text{-C}_4^0 \text{ mass in feed} - n\text{-C}_4^0 \text{ mass in product}) \times 100\%]/(n\text{-C}_4^0 \text{ mass in feed})$$

$$S(\text{product}) = [(\text{product mass}) \times 100\%]/(n\text{-C}_4^0 \text{ mass in feed} - n\text{-C}_4^0 \text{ mass in product}).$$

3. Results and discussion

3.1. Characterization of Au-Zn-modified HZSM-5 catalysts

Figure 1 shows that the modified and unmodified samples both have the five diffraction peaks characteristic of the MFI structure. No characteristic peaks from metal species appeared in the XRD patterns, indicating that the metal species were well dispersed on the supports. Figure 2 shows the subtractions of

Fig. 1. XRD patterns of HZSM-5, Zn/HZSM-5, Au/HZSM-5, and Au-Zn/HZSM-5.

Fig. 2. UV-Visible adsorption spectra of HZSM-5, Zn/HZSM-5, Au/HZSM-5, and Au-Zn/HZSM-5.

Fig. 3. X-ray photoelectron spectra of Au/HZSM-5 and Au-Zn/HZSM-5.

UV-vis spectra for modified samples, with HZSM-5 as the benchmark sample. Au/HZSM-5 and Au-Zn/HZSM-5 have clear peaks at 522 and 533 nm, respectively, associated with metallic Au nanoparticles in the samples. Notably, the Au-Zn/HZSM-5 peak is at a higher wavelength (533 nm) than that of Au/HZSM-5 (522 nm), which indicates that the Au nanoparticles on Au-Zn/HZSM-5 are smaller than those on Au/HZSM-5 [31,32]. This implies that the interactions between Au and Zn species result in a decrease in the Au particle size.

XPS was used to study the states of the Au and Zn species in Au/HZSM-5 and Au-Zn/HZSM-5 samples. The spectra are shown in Fig. 3. According to the literature [33], the XPS peaks of Au⁰, Au⁺, and Zn²⁺ appear at 84.20 eV (Au⁰ 4f_{7/2}) and 87.85 eV (Au⁰ 4f_{5/2}), 84.65 eV (Au⁺ 4f_{7/2}) and 88.55 eV (Au⁺ 4f_{5/2}), and 92.93 eV (Zn 3p_{1/2}) and 89.88 eV (Zn 3p_{3/2}), respectively. All these peaks were found for Au-Zn/HZSM-5 and Au/HZSM-5. Compared with pure Au/HZSM-5, a small shift of the Au (Au⁰) peak in Au-Zn/HZSM-5 from 84.20 eV (Au⁰ 4f_{7/2}) to 83.65 eV was observed, which further confirmed interactions between Au and Zn species in the Au-Zn/HZSM-5 catalyst.

The acidities of different samples were measured using NH₃-TPD (Fig. 4) and pyridine-FTIR spectra (Fig. 5). Two NH₃ desorption peaks appeared for all the samples at about 250 and 450 °C, corresponding to weak and strong acidic sites, respectively. Compared with Zn/HZSM-5, Au-Zn/HZSM-5 has a larger number of medium-strength acidic sites (250–450 °C), and almost the same amount of strong acidic sites. Figure 5 shows that the amount of Brønsted acidic sites (1546 cm⁻¹) of HZSM-5 decreased significantly after metal modification, and the

Fig. 4. NH₃-TPD profiles of HZSM-5, Zn/HZSM-5, Au/HZSM-5, and Au-Zn/HZSM-5.

Fig. 5. Pyridine-FTIR spectra of HZSM-5, Zn/HZSM-5, Au/HZSM-5, and Au-Zn/HZSM-5 at 150 °C.

amount of Lewis acidic sites (1440 and 1454 cm⁻¹) significantly increased. It is easy to see that the amount of Lewis acidic sites on Au-Zn/HZSM-5 increased as a result of Au modification of Zn/HZSM-5. The combined UV-Vis, XPS, and NH₃-TPD results clearly show that the interactions between Zn and Au species in Au-Zn/HZSM-5 induce the formation of Lewis acidic sites of medium strength.

3.2. *n*-Butane conversion over Au-Zn-modified HZSM-5 catalysts

The results of *n*-butane conversion over different catalysts are listed in Table 1. The activity of Au/HZSM-5 is similar to

Table 1

Product distribution of *n*-butane (99.9 wt%) conversion over all catalyst samples.

Catalyst	<i>X</i> (%)	Product selectivity (%)									Distribution of aromatics (%)				
		C ₁	C ₂ ⁰	C ₂ ⁼	C ₃ ⁰	C ₃ ⁼	<i>i</i> -C ₄ ⁰	ΣC ₄ ⁼	C ₅	Aro	Benz	Tol	C ₈ A	C ₉ A	C ₁₀ A
HZSM-5	33.9	15.5	21.3	16.4	13.9	14.8	1.6	4.1	0.4	11.9	43.1	44.6	12.1	0.13	0
Au/HZSM-5	31.7	13.3	20.6	16.0	11.6	16.7	10.9	5.7	1.02	4.07	37.7	51.8	10.5	0	0
Zn/HZSM-5	49.1	21.6	9.1	15.3	9.1	5.7	1.9	7.6	0.2	29.0	38.3	48.3	11.6	1.6	0.03
Au-Zn/HZSM-5	70.8	18.2	10.2	9.71	7.71	10.4	1.39	4.85	0.22	37.02	43.8	43.9	12.1	0.24	0.02

Reaction conditions: *T* = 550 °C, *p* = 0 MPa.

that of HZSM-5, but it has higher olefin selectivity (ethylene, propylene, and butene), and lower selectivities for dry gas (methane and ethane) and aromatics. This means that modification with Au benefits dehydrogenation activation, and suppresses cracking and aromatization. In contrast, after the introduction of both Au and Zn into HZSM-5, the *n*-butane conversion (70.8%) and the selectivity for olefins and aromatics (61.98%) all increase significantly, and the selectivity for dry gas decreases significantly. These results indicate that the introduction of Au into Zn/HZSM-5 could effectively promote the dehydrogenation and aromatization of *n*-butane and inhibit the formation of dry gas. Obviously, the catalytic performance of Au-Zn/HZSM-5 is closely related to the above-mentioned physicochemical properties of the catalyst.

4. Conclusions

In Au-Zn-modified HZSM-5, prepared using DP and wet impregnation methods, the introduction of Au effectively promotes the dehydrogenation and aromatization of *n*-butane, and suppresses hydrogenolysis over Zn species. Specifically, the *n*-butane conversion (70.8%) and selectivity for olefins and aromatics (61.98%) increase significantly and the selectivity for dry gas decreases significantly to 28.4%. A detailed study of the catalyst characteristics suggests that the excellent catalytic performance of Au-Zn/HZSM-5 is closely related to the physicochemical properties of the catalyst, e.g., Au dispersion, the oxidation state of the metal atoms, and appropriate acidity. The bimetallic Au-Zn-containing HZSM-5 is a promising catalyst for *n*-butane conversion.

References

- [1] Cheung T K, D'Itri J L, Gates B C. *J Catal*, 1995, 153: 344
- [2] Bedell M W, Ruzsica P A, Steffens T R. Presentation at the 2003 Tulane Engineering Forum, September, 2003
- [3] Park Y K, Lee C W, Kang N Y, Choi C W, Choi S, Oh S H, Park D S. *Catal Surv Asia*, 2010, 14: 75
- [4] Zhang J, Liu X, Blume R, Zhang A H, Schlögl R, Su D S. *Science*, 2008, 322(5898): 73
- [5] Huff M, Schmidt L D. *J Catal*, 1994, 149: 127
- [6] Ge S H, Liu C H, Zhang S C, Li Z H. *Chem Eng J*, 2003, 94: 121
- [7] Lu J Y, Zhao Z, Xu C M, Zhang P, Duan A J. *Catal Commun*, 2006, 7: 199
- [8] Lu J Y, Zhao Z, Xu C M, Duan A J, Zhang P. *Catal Lett*, 2006, 109: 65
- [9] Jiang G Y, Zhang L, Zhao Z, Zhou X Y, Duan A J, Xu C M, Gao J S. *Appl Catal A*, 2008, 340: 176
- [10] Rahimi N, Karimzadeh R. *Appl Catal A*, 2011, 398: 1
- [11] Ono Y, Kanae K. *J Chem Soc, Faraday Trans*, 1991, 87: 663
- [12] Ono Y. *Catal Rev-Sci Eng*, 1992, 34: 179
- [13] Caeiro G, Carvalho R H, Wang X, Lemos M A N D A, Lemos F, Guisnet M, Ribeiro F R. *J Mol Catal A*, 2006, 255: 131
- [14] Xu Y B, Ma H T, Yamamoto Y, Suzuki Y, Zhang Z G. *J Nat Gas Chem*, 2012, 21: 729
- [15] Ai Sha N L H, Liu J X, Zhao W P, Wang G R, Guo H C. *J Mol Catal (China)*, 2012, 26: 257
- [16] Guisnet M, Gnep N S, Aittaleb D, Doyemet Y J. *Appl Catal A*, 1992, 87: 255
- [17] Guisnet M, Gnep N S. *Appl Catal A*, 1996, 146: 33
- [18] Biscardi J A, Iglesia E. *Catal Today*, 1996, 31: 207
- [19] Smiešková A, Rojasová E, Hudec P, Šabo L. *Appl Catal A*, 2004, 268: 235
- [20] Ei-Malki E M, Van Santen R A, Sachtler W M H. *J Phys Chem B*, 1999, 103: 4611
- [21] Biscardi J A, Meitzner G D, Iglesia E. *J Catal*, 1998, 179: 192
- [22] Ivanova I I, Kolyagin Y G, Ordonsky V V, Asachenko E V, Pasyunkova E M, Pirogov Y A. *J Mol Catal A*, 2009, 305: 47
- [23] Kolyagin Y G, Ordonsky V V, Khimyak Y Z, Rebrov A I, Fajula F, Ivanova I I. *J Catal*, 2006, 238: 122
- [24] Liu J X, Ai Sha N L H, He N, Liu G D, Liang C C, Zhang X F, Guo H C. *J Chem Eng*, 2013, 218: 1
- [25] Okumura M, Akita T, Haruta M. *Catal Today*, 2002, 74: 265
- [26] Corma A, Serna P. *Science*, 2006, 313: 332
- [27] Wannakao S, Warakulwit C, Kongpatpanich K, Probst M, Limtrakul J. *ACS Catal*, 2012, 2: 986
- [28] Sun C, Yang Y S, Du J M, Qin F, Liu Z P, Shen W, Xu H L, Tang Y. *Chem Commun*, 2012, 48: 5787
- [29] Hutchings G J. *Catal Today*, 2005, 100: 55
- [30] Xin Q, Gao X. *Progress in Natural Science*, 1995, 5: 279
- [31] Sacaliuc E, Beale A M, Weckhuysen B M, Nijhuis T A. *J Catal*, 2007, 248: 235
- [32] Lee B, Ma Z, Zhang Z T, Park C, Dai S. *Microporous Mesoporous Mater*, 2009, 122: 160
- [33] Wang L, Wang H, Zhang W, Zhang J, Lewis J P, Meng X J, Xiao F S. *J Catal*, 2013, 298: 186

Graphical Abstract

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Catalytic conversion of *n*-butane over Au-Zn-modified nano-sized HZSM-5

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Au-Zn/HZSM-5 was found to be an excellent catalyst for the light alkanes reaction. Its use significantly increased *n*-butane conversion, olefin and aromatic selectivity, and decreased dry gas selectivity.

正丁烷在Au, Zn组合改性纳米HZSM-5上的催化转化

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摘要: 采用沉积沉淀和浸渍法制备了Au-Zn组合改性HZSM-5催化剂. 并且对比研究了HZSM-5, Au/HZSM-5, Zn/HZSM-5和Au-Zn/HZSM-5催化剂的性质和催化性能. 采用UV-Vis和XPS表征揭示出Au-Zn/HZSM-5催化剂中Au物种与Zn物种的相互作用. 正丁烷探针反应结果表明, 在Zn/HZSM-5催化剂中引入Au有效地提高了正丁烷的脱氢芳构化性能, 同时抑制了正丁烷在Zn活性中心上的氢解副反应. 在相同条件下, 与Zn/HZSM-5催化剂相比, 正丁烷转化率由49.1%增加到70.8%, 烯烃和芳烃产物总选择性由57%增加到61.98%, 干气的选择性由31%降低至28.4%. 上述结果表明, Au-Zn/HZSM-5催化剂在轻烃芳构化反应中具有良好的催化性能.

关键词: 金; 锌; HZSM-5分子筛; 正丁烷转化; 脱氢; 芳构化; 纳米金颗粒; 沉积沉淀法

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更正说明

因编辑工作失误, 本刊2013年第34卷第5期第828~837页发表的文章“Research, development, and application of amorphous nickel alloy catalysts prepared by melt-quenching (急冷非晶态镍合金催化剂的研究开发和工业应用)”(作者: 宗保宁, 慕旭宏, 张晓昕, 孟祥堃, 乔明华)中第829页图1有误, 正确的图及图题如下. 特此更正并致歉.

Fig. 1. DSC traces for amorphous Ni-P and Ni-RE-P alloy catalysts. Cited from Ref. [3].

(《催化学报》编辑部)