

UDC 665.5

A. Nulahong¹, Mo Wenlong¹, Ma Fengyun¹, S. Aldabergenova²

¹Xinjiang University, Urumqi, China;
²Ye.A. Buketov Karaganda State University
(E-mail: aldsau@mail.ru)

The preparation and characterization of Au/HZSM-5 catalyst and its application in CH₄ adsorption

Au/HZSM-5 catalysts were prepared by negative deposition-precipitation method in this paper. XRD/Uv-vis/TEM/NH₃-TPD/FT-IR technologies were used to analysis the characterization of prepared catalysts, and the evaluation of the catalysts was carried out by methane adsorption experiment. XRD and TEM showed that 2.0Au/ HZSM-5 catalyst calcined under N₂ atmosphere held metal particle size about 5–10 nm; Uv-vis indicated that the method of calcination changed Au from ion-valent state to zero-valent state, and the zero-valent absorption peak of 2.0Au/HZSM-5 catalyst calcined under N₂ atmosphere was weaker, which indicated that its corresponding particle size was smaller; NH₃-TPD showed that the peak area of relatively strong acid center of Au/HZSM-5 catalyst declined respect to HZSM-5; FT-IR showed that the Au/HZSM-5 catalysts could convert methane to adsorbed species containing olefin double bond at low temperature, showing better C–H bond activation capability for methane.

Key words: Au/HZSM-5; catalyst; methane; adsorption.

Introduction

In 1980s the catalysts based on MgO, Al₂O₃ and SiO₂ carriers were of catalytic activity in hydrogenation reaction of olefins and redox reaction involved hydrogen [1]. Recently, it is reported that the high dispersive Au-based catalysts showed positive performance in many reactions [2, 3].

The calcination conditions had important influence on the performance of catalyst. The active phase couldn't acquire once the calcination temperature was too low; otherwise, the Au particle size increased and affected the catalytic activity. The calcination conditions affected catalytic performance by altering the morphology, dispersity and electronic property of catalysts. In our research, the negative deposition-precipitation method was used to prepare Au/HZSM-5 catalyst, and we aim at studying the effect of calcination atmosphere on the physicochemical property and the adsorption mechanism of methane by Au/HZSM-5.

Experimental

Preparation of Au/HZMS-5 catalysts. Au/ZSM-5 catalyst was prepared by negative deposition-precipitation method using urea as precipitant: ZSM-5 (nSiO₂/nAl₂O₃ = 30) manufactured by Dalian University of technology and certain amount urea manufactured by Shenyang Reagent Factory were sequentially added to HAuCl₄·4H₂O (manufactured by Sinopharm Chemical Reagent Co., Ltd.) solution (100 ml, 24.26 mol/L) and this mixture was stirred at 80 °C for 12h in our specialized airtight container and then cool down for 4h. The Cl⁻ in solution was washed off by deionized water then dehydrated at 100 °C and finally calcinated at 540 °C for 4h by temperature programming. The prepared Au/HZSM-5 catalysts were signed as xAu/HZ x(weight percentage) = 1.0 %, 2.0 % and 3.0 %. Abbr: 1.0Au/HZ, 2.0Au/HZ and 3.0Au/HZ.

Characterization of Au/HZ catalysts. Transmission electron microscopy (TEM) micrographs were obtained by using a JEOL JEM-2100 electron microscope operating at 200 kV with a point resolution of 0.23 nm. The UV-vis spectra were obtained on a JASCO UV-550 spectrometer using BaSO₄ as reference. The Powder X-ray diffraction (XRD) patterns were collected using a Rigaku D/max-2004 diffractometer with Cu K α radiation, 40 kV, 100 mA with a scanning rate of 0.02° min⁻¹ (2 θ). FT-IR spectra for the framework vibrations were recorded on a Nicolet iS10 FTIR instrument with a resolution of 4 cm⁻¹ using the KBr wafer technique.

NH₃-TPD spectra were measured as follows: the samples pre-treated with He at 500 °C for 1h were performed to desorb water at the Au/HZSM-5 catalysts before NH₃ adsorption. TPD signal was collected in a stream of He flow (40 ml/min) at a heating rate of 15 °C/min until 700 °C. The concentration of NH₃ in the exit gas was continuously monitored by the TCD.

Results and discussion

XRD results of Au/HZ catalysts. Figure 1 shows the XRD results of Au/HZ catalysts. It demonstrated that all the catalysts enjoyed 4 characteristic peaks of Au⁰ (111), (200), (220) and (311) crystal face at $2\theta = 38.08^\circ, 44.32^\circ, 64.48^\circ$ and 77.68° and the strength of these peaks increased with the increasing of Au loading amount.

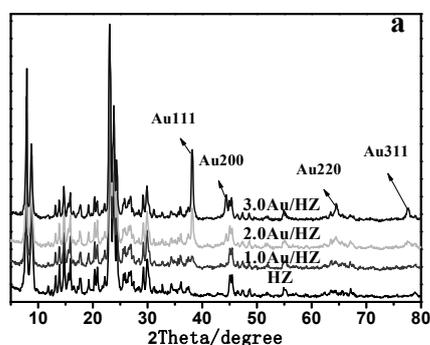


Figure 1. XRD patterns of Au/HZ catalysts with different loadings of nano Au calcination in air

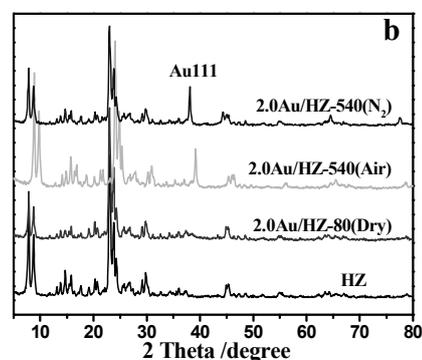


Figure 2. XRD patterns of 2.0Au/HZ catalysts calcined under different atmosphere

Figure 2 (b) shows the XRD results of Au/HZ catalysts calcined under different atmosphere. It indicated that 2.0Au/HZ catalyst before calcination didn't enjoy the characteristic peaks of Au⁰, and the 2.0Au/HZ catalyst after calcination held obvious Au⁰ peaks. In addition, from Scherrer's ($d=0.89\lambda/(B\cos\theta)$) equation, the peaks of 2.0Au/HZ catalyst calcinated in nitrogen shifted to the lower diffraction angle indicating smaller Au⁰ particle size [4].

TEM. Figure 3 shows the TEM images of 2.0Au/HZ catalysts calcined under different atmosphere.

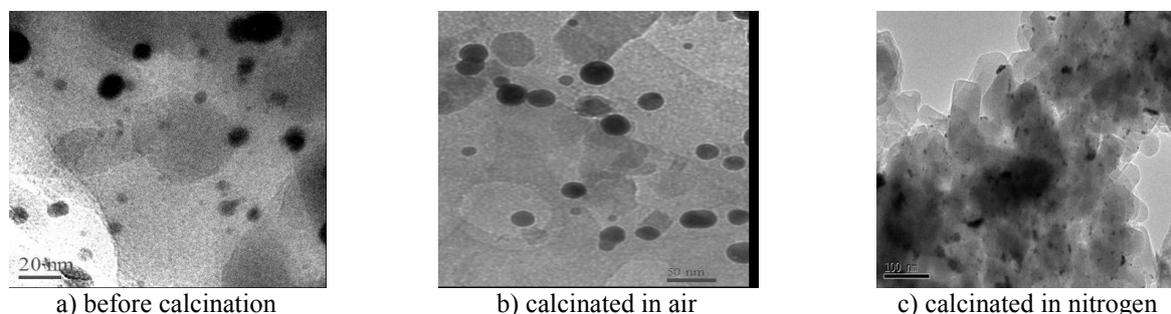


Figure 3. TEM images of 2.0Au/HZ catalysts

From Figure 3(a), the small gold particles less than 10 nm could be observed. From Figure 3(b) and (c), the gold particles in the Au/HZ catalyst calcinated in air (10~20 nm) were larger than that of catalyst calcina-

tion in nitrogen (5~10 nm). That is to say, calcination in nitrogen could promote the size distribution around the catalysts.

UV-vis. Figure 4 shows the UV-vis spectra of Au/HZ catalysts prepared under different calcination treatments. It could be seen from 4(a) that the catalysts before calcination had obvious peaks at the wavelength of 250 nm and shoulder peaks at 300~390 nm and there was no peak at the place of 500~600 nm. It was reported [5–7] that the peak located in 250 nm belonged to Au^+ , and the peak situated in 300~390 nm was taken as Au^{+3} and $(\text{Au})^{\text{no}+}$ clusters, and the peak seated at 500~600 nm was thought as Au^0 . So, the Au^0 species was not existed at the catalysts before calcination.

And from 4(b), the catalysts showed that the peaks at 250 nm weakened after the calcination at 540 °C. And there were strong peaks at about 525 nm, which enhanced with the increasing of Au loadings. The above results indicated that the calcination method could acquire Au^0 species from ionic species, which was in accordance with XRD and TEM results.

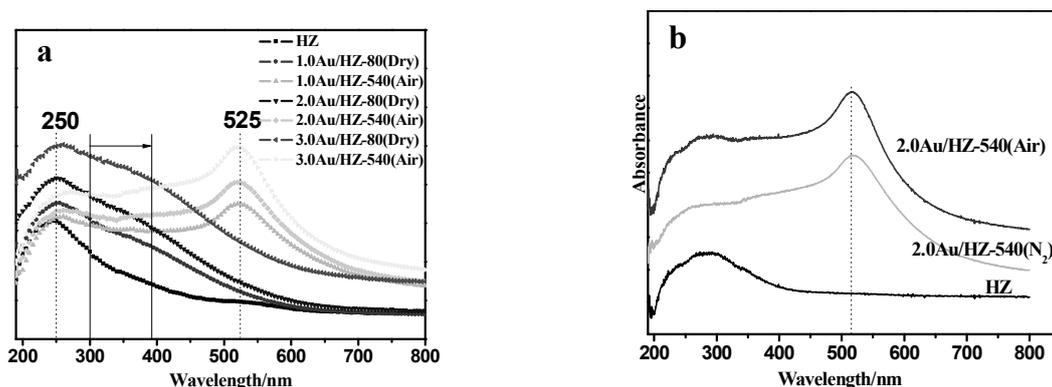


Figure 4. UV-vis spectra of Au/HZ catalysts prepared under different calcination treatments

NH₃-TPD. Figure 5 shows the NH_3 -TPD spectra of Au/HZ catalysts prepared under different calcination treatments. There are two obvious desorption peaks for all catalysts from Figure 5(a). The peaks of lower temperature ascribed to the mild acid center, and the higher one belonged to the strong acid center. And the volume of desorption of both acids decreased with the increasing of Au loadings.

It could be seen from Figure 5(b) that the 2.0Au/HZ catalyst calcinated in nitrogen for 4 h showed high volume of NH_3 desorption area at 200~400 nm, which could be assigned to mediate acid center.

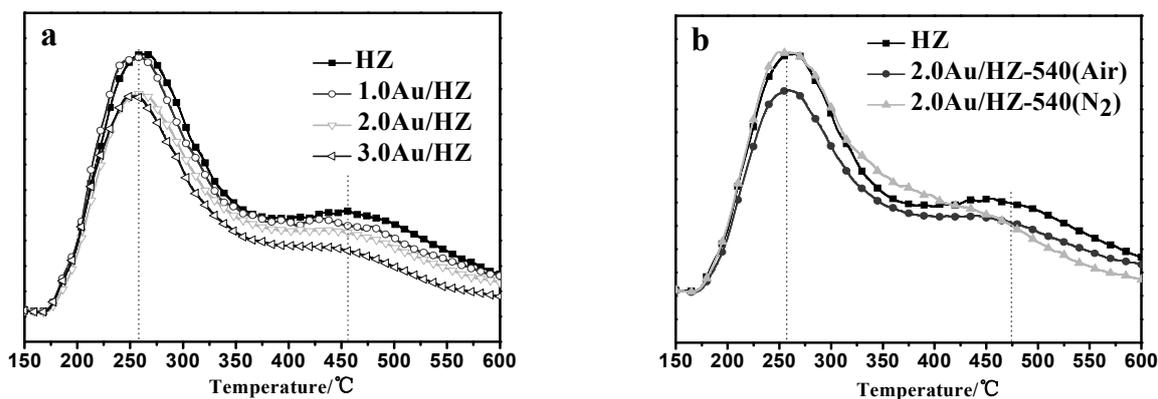


Figure 5. NH_3 -TPD profiles of Au/HZ catalysts calcinated in air (a) and N_2 (b)

FT-IR. Figure 6 shows the FT-IR results with methane as probe molecule.

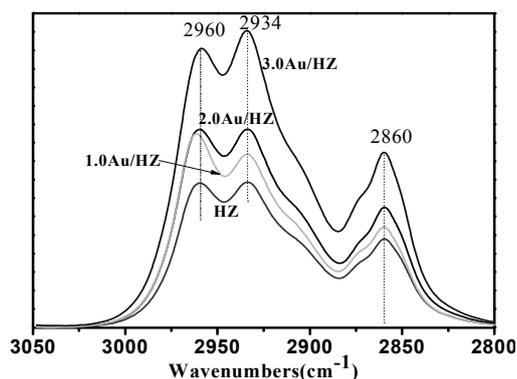


Figure 6. FT-IR spectra of Au/HZ catalysts with methane as probe molecule (150 °C)

The absorption peaks of Au/HZ catalysts could be observed in the range of 2800 cm^{-1} to 3050 cm^{-1} . The peaks at 2960 cm^{-1} assigned to the C-H antisymmetric stretching vibration of $-\text{CH}_3$; the peaks at 2916~2935 cm^{-1} ascribed to the C-H antisymmetric stretching vibration of $-\text{CH}_2$; the peaks at 2860~2870 cm^{-1} belonged to the C-H antisymmetric stretching vibration of $-\text{CH}$ [8–10]. The HZ carrier held weaker C-H vibration absorption peaks than Au/HZ catalysts at 2960~2962 cm^{-1} , 2916~2934 cm^{-1} and 2860~2870 cm^{-1} . And the absorption strength for Au/HZ catalysts increased with the increasing of Au loadings. For the study of $-\text{OH}$ on the catalysts after the absorption of methane, the OH-IR spectra had been achieved in the later work.

OH-IR. Figure 7 shows the OH-IR spectra of Au/HZ catalysts before and after the absorption of CH_4 . There were strong absorption peaks for all the catalysts at 3740 cm^{-1} (silicon hydroxyl), 3661 cm^{-1} (alumina hydroxy) and 3610 cm^{-1} (the silicon aluminum bridge hydroxyl [10, 11]).

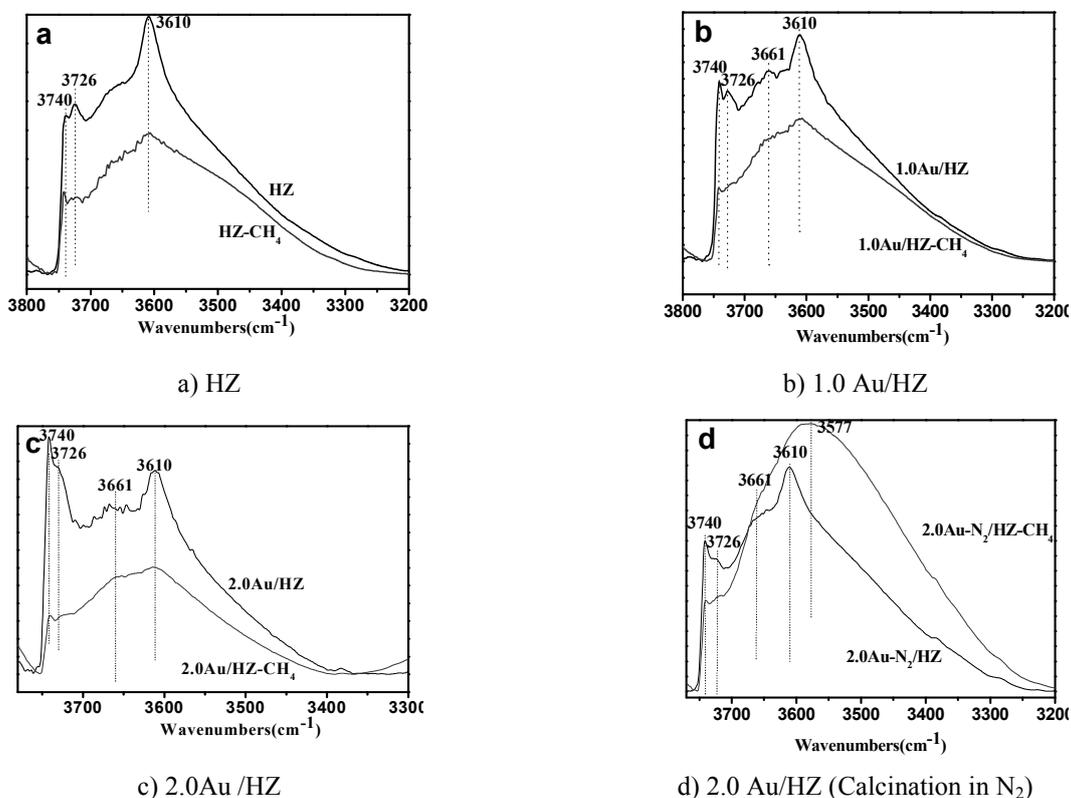


Figure 7. OH-IR spectra of Au/HZ catalysts before and after the absorption of CH_4

For the Au/HZ catalysts calcinated in air, the biggest change of OH-IR spectra was the absorption peaks at 3661 cm^{-1} (alumina hydroxy) and 3610 cm^{-1} (the silicon aluminum bridge hydroxyl), both of which receded after the absorption of CH_4 . That is to say, the methane was firstly combined with alumina hydroxyl and silicon aluminum bridge hydroxyl of the using catalysts. It could be seen from Figure 7(d) that the 2.0Au/HZ catalyst calcinated in nitrogen showed the strongest absorption peak, which would be ascribed to the high degree of dispersity and the small particle size of the catalysts [5–7].

Conclusions

XRD and TEM showed that 2.0Au/HZ catalyst calcined under N_2 atmosphere hold small Au particle size about 5–10 nm. XPS showed that the higher the Au loading was, the higher the proportion of zero-valent Au. NH_3 -TPD showed that the peak area of relatively strong acid center declined respect to HZSM-5 when the Au loading was smaller, and the strong and weak acid centers decreased when the Au loading was larger. FT-IR showed that the Au/HZ catalysts could convert methane to adsorbed species at low temperature, showing better C-H bond activation ability for methane.

Acknowledgements

This work was sponsored by Key Laboratory of Oil & Gas Fine Chemicals, Ministry of Education & Xinjiang Uyghur Autonomous Region, Xinjiang University (XJDX0908–2013–5) and the Natural Science foundation of Xinjiang Uyghur Autonomous Region (2014211A014).

References

- 1 Bond G.C., Sermon P.A. *Gold Bull.*, 1973, 6(4), p. 102–105.
- 2 Bond G.C., Thompson D.T. *Catalysis Reviews*, 1999, 41(3–4), p. 319–388.
- 3 Hashmi A.S.K., Hutchings G.J. *Angewandte Chemie International Edition*, 2006, 45(47), p. 7896–7936.
- 4 Fu Q., Saltsburg H., Flytzani Stephanopoulos M. *Science*, 2003, 301(5635), p. 935–938.
- 5 Liu Jiaxu, Aisha Nulahong, He Ning et al. *Journal of Chemical Engineering*, 2013, 218, p. 1–8.
- 6 Sun Chao, Yang Yisu, Du Junming et al. *Chemical Communication*, 2012, 48(46), p. 5787–5789.
- 7 Jin F., Li Y.D. *Catalysis Today*, 2008, 145(1), p. 101–107.
- 8 Gluhoi A.C., Tang X., Marginean P. et al. *Topics in Catalysis*, 2006, 39(1/2), p. 101–110.
- 9 Margitfalvi J.L., Fasi A., Hegedus M. et al. *Catalysis Today*, 2002, 72(1/2), p. 157–169.
- 10 Pestryakov A., Tuzovskaya I., Smolentseva E. et al. *International Journal of Modern Physics B*, 2005, 19(15/17), p. 2321–2326.
- 11 Ma Shuqi. *Dalian University of Technology*, 2008.

А. Нулахонг, Мо Вэнлонг, Ма Фэн-Юнь, С. Алдабергенова

Au/HZSM-5 катализатордың сипаттамасы мен дайындалуы және оны CH_4 адсорбциясында қолдану

Мақалада Au/HZSM-5 катализаторы кері жиналу-түнбалау әдісі арқылы дайындалғандығы туралы айтылды. Катализаторды зерттеу және оның метанды адсорбциялау тәжірибесіндегі орнын анықтау мақсатында XRD/UV-vis/TEM/ NH_3 -TPD/FT-IR әдісі қолданылды. XRD және TEM әдістері азот атмосферасында кальциялану арқылы дайындалған 2.0Au/HZSM-5 катализаторының құрамында металл бөлшектерінің өлшемдері 5-10 нм құрайтындығын; UV-Vis кальциялау әдісі алтынның күйі иондық валенттіліктен ноль-валенттілікке ауысатындығын көрсетті. Ноль-валентті алтынның адсорбция шыңы 2.0Au/HZSM-5 құрайды, азот атмосферасындағы кальциялау әдісі арқылы дайындалған катализатор қатысында адсорбция шыңы әлсірейді, ол бөлшектер өлшемінің кішірейгенін көрсетті. NH_3 -TPD көрсеткендей, Au/HZSM-5 салыстырмалы күшті қышқылды орталықтың шыңы HZSM-5 салыстырғанда едәуір төмендегенін байқатты; FT-IR 2.0Au/HZSM-5 катализаторы метанды төмен температурада құрамында олефинді қос байланысы бар өнімдерге дейін конвертрлейді, яғни метандағы C-H байланыстың белсенділік қабілетін байқатады.

А. Нулахонг, Мо Вэнлонг, Ма Фэн-Юнь, С. Алдабергена

Приготовление и характеристика катализатора Au/HZSM-5 и его применение для адсорбции CH_4

В статье описан катализатор Au/HZSM-5, который был приготовлен методом отрицательного накопления-осаждения. Для исследования катализатора и оценки его в эксперименте по адсорбции метана были использованы XRD/UV-vis/TEM/ NH_3 -TPD/FT-IR методы. Методами XRD и TEM показано, что 2.0Au/HZSM-5 катализатор, приготовленный кальцинацией в атмосфере азота, содержит частицы металла размером 5-10 нм. UV-vis метод показал, что способ кальцинации изменяет валентное состояние золота с ионного на нуль-валентное. Пик абсорбции нуль-валентного золота 2.0Au/HZSM-5 катализатора, приготовленный кальцинацией в атмосфере азота, стал слабее, что указывает на соответствующее уменьшение размера частиц. NH_3 -TPD метод показывает, что площадь пика сравнительно сильного кислотного центра Au/HZSM-5 уменьшилась по сравнению с HZSM-5. FT-IR показывает, что катализатор 2.0Au/HZSM-5 способен конвертировать метан в продукты, содержащие олефиновую двойную связь, при низкой температуре демонстрирует лучшую способность к активации связи C-H в метане.