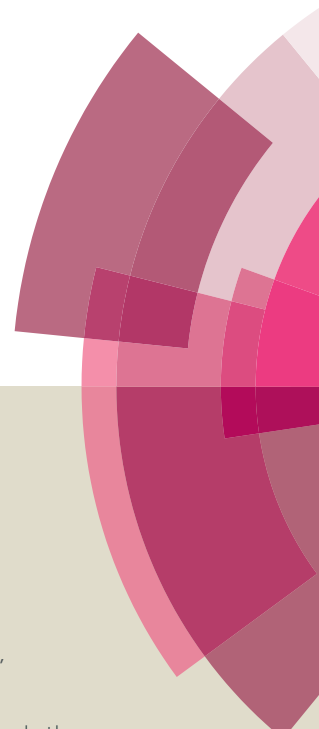


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ARTICLE TYPE

A comparative study of PdZSM-5, Pd β , and PdY in hybrid catalyst for syngas to hydrocarbons

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Catalytic conversion of syngas into hydrocarbons over hybrid catalyst consisting of methanol synthesis catalyst and Pd modified zeolite (PdZSM-5, Pd β , and PdY) was investigated. The results indicate that the intermediate dehydration step of DME in syngas to hydrocarbon process mainly happens on the Brönsted acid sites of the Pd zeolite. The large pores and cavities of Pd β and PdY promote the formation of C₄⁺ hydrocarbons, which are mainly gasoline-type branched hydrocarbons. Moreover, the large pores and cavities provide enough space for the formation of higher aromatics which are the precursor of coke. The blockage of micropores in Pd-zeolite by hydrocarbon-type coke results in the deactivation of hybrid catalysts.

Introduction

It is well-known that petrochemicals are mainly produced from oil refineries. With the depletion of petroleum resources, synthesis of petrochemicals from other resources becomes more attractive. Syngas can be produced from various non-petroleum resources such as natural gas, biomass and other carbonaceous materials including coal, recycled plastics and municipal wastes^{1, 2}. Thus, developing a syngas to hydrocarbon process can effectively reduce the consumption of petroleum resources.

There are two typical routes for producing hydrocarbons from syngas: Fischer-Tropsch synthesis (FTS)³⁻⁵ and syngas-to-hydrocarbons via methanol/dimethyl ether (DME)⁶⁻⁸. The FTS process usually gives a wide carbon number distribution of hydrocarbons due to the limitation of Anderson-Schulz-Flory (ASF) polymerization kinetics⁹. Many efforts have been made to increase the selectivity to fractions within a certain range by designing novel catalysts, such as core-shell structured catalyst¹⁰ and mesoporous zeolite supported catalyst^{11, 12}. However, it was reported that the formed methane (CH₄) from secondary cracking was relatively high. Compared with the FTS process, the syngas-to-hydrocarbons via methanol/DME process could selectively achieve hydrocarbons with different cuts while keeping the methane selectivity low^{8, 13, 14}. The process had been realized in producing liquefied petroleum gas (LPG, C₃ and C₄ alkanes)¹⁴⁻¹⁶, aromatic hydrocarbon mixtures¹⁷ and gasoline fractions^{8, 18}. The hybrid catalyst usually consists of two components: a methanol synthesis catalyst and a zeolite or metal modified zeolite. Syngas was first converted into methanol over a methanol synthesis catalyst, and then to hydrocarbons over a zeolite or metal modified zeolite. For example, syngas could be selectively converted into LPG over a hybrid catalyst composed of Cu-ZnO-Al₂O₃ methanol synthesis catalyst (CZA) and PdY¹⁴ while the major product became gasoline over CZA/PdZSM-5¹⁸. Such

combination could break the thermodynamic equilibrium limitation of methanol synthesis due to the in situ removal of methanol. In addition, the modification of Pd in Pd modified zeolite was found to promote the stability of the hybrid catalyst as well as the formation of saturated hydrocarbons^{8, 18}. Herein, we have carried out a comparative study around syngas conversion over hybrid catalysts containing different types of Pd modified zeolites: PdZSM-5, Pd β and PdY, with similar SiO₂/Al₂O₃ ratios. All these zeolites were modified with Pd by ion-exchange methods and then physically mixed with Cu-ZnO-Al₂O₃ methanol synthesis catalyst to form a hybrid catalyst. Catalyst coke analysis was investigated by TPO-MS and N₂-Physical adsorption techniques.

Experimental

1. Catalyst preparation

Parent HZSM-5 (SiO₂:Al₂O₃=23), H β (SiO₂:Al₂O₃=25) and HY (SiO₂:Al₂O₃=30) were purchased from Zeolyst International. CuO-ZnO-Al₂O₃ catalyst (CZA) powder and γ -Al₂O₃ (197.4 m²/g) powder were mixed uniformly at a weight ratio of 9:5 to form DME synthesis catalyst. The DME synthesis catalyst was crushed into 20-40 mesh and denoted as CZAA. The prepared CZAA showed excellent performance for DME synthesis in our previous work⁸.

Pd modified HZSM-5 (SiO₂:Al₂O₃=23), H β (SiO₂:Al₂O₃=25), and HY (SiO₂:Al₂O₃=30) were prepared by ion-exchange methods while the theoretical loading of Pd in Pd modified zeolite was 0.5 wt%. After washing with deionized water, the Pd modified zeolite catalysts were dried at 120°C for 4 hrs and calcined at 550°C for 4 hrs. Finally, the Pd modified zeolite catalysts were crushed into particles of 20-40 mesh and denoted as PdZSM-5, Pd β , and PdY, respectively. Cu-ZnO-Al₂O₃ catalyst (CZA) and Pd modified zeolite were physically mixed together at a weight ratio of 1:1 to form the hybrid catalyst. The

hybrid catalysts were denoted as CZA/PdZSM-5, CZA/Pd β , CZA/PdY and CZA/ γ -Al₂O₃, respectively.

2. Catalyst test

A pressurized flow type reaction apparatus with a fixed bed reactor was used for this study. The fixed bed reaction system consisted of a 12 mm inner diameter tubular reactor and an electronic temperature controller for the furnace. The reaction apparatus was equipped with four gas mass flowmeters for controlling gas flow rate and a back-pressure valve for regulating the pressure of system. Before the reaction, the hybrid catalyst was activated at 250°C for 4 hrs in pure hydrogen flow. Then synthesis gas was introduced into the reaction system. The hybrid catalysts were evaluated under the condition of 260°C, 2 MPa, and 1875 ml.h⁻¹.g⁻¹. CO, CO₂, CH₄ and N₂ were analyzed by a GC equipped with a thermal conductivity detector (TCD), and organic compounds were analyzed by another GC equipped with a flame ionization detector (FID).

3. Catalyst characterization

NH₃-TPD Temperature-programmed desorption of NH₃ (NH₃-TPD) was conducted on an Autochem 2910 instrument (Micromeritics). A 100 mg sample was pre-treated at 500°C for 1 hr and then heated from 100°C to 700°C at a constant rate of 10°C/min after saturation adsorption of NH₃ at 100°C.

Py-IR A pyridine adsorption Fourier-transform Infrared (Py-IR) spectrum was recorded by a Bruker IF113V FTIR spectrometer to study the type of acidity. The IR spectrometer was equipped with an in-situ cell containing CaF₂ windows. In Py-IR experiment, the sample disc was pre-treated under vacuum (1×10⁻³ Pa) at 450°C for 1 hr and then cooled down to room temperature. Subsequently, pyridine was introduced into IR cell at room temperature for 5 minutes to ensure that all acid sites were covered. The sample was heated to 200°C and 350°C respectively at a rate of 10°C/min and the IR spectra was collected at each temperature.

TPO-MS Temperature-programmed oxidation (TPO) was carried out using a quadrupole mass spectrometer Omnistar™ GSD 301 (Pfeiffer Vacuum) for signal collection. A 40 mg sample was heated from ambient temperature to 900°C with a heating rate of 10°C/min under a flow of 5%O₂/95%Ar.

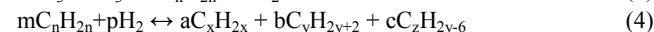
N₂-Physical Absorption N₂ adsorption isotherms were measured by QuadraSorb SI4 instrument at -196°C. Before the N₂ absorption, all the samples were pretreated at 300°C for 5 hrs under vacuum. The total surface area was determined by the BET method while the total pore volume was calculated by the amount of N₂ adsorbed at p/p⁰=0.98. The t-plot method was used for the calculation of micropores volume and surface area.

Result and discussion

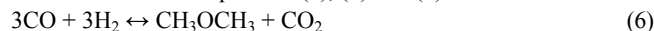
1. Syngas conversion over different hybrid catalysts

Syngas to hydrocarbon process over a hybrid catalyst of CZA/Pd-zeolite mainly involves the following reactions: (1) the hydrogenation of CO to methanol, (2) the dehydration of methanol to DME, (3) the further dehydration of DME to light olefins, (4) light olefins to final hydrocarbon products, and (5) water-gas shift (WGS) reaction. The relevant reaction equations

are as follows.



Overall reaction of Equations (1), (2) and (5):



Overall reaction of Equations (1)-(5):

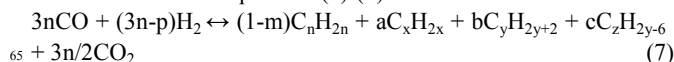


Figure 1 shows the relationship of CO conversion with time on stream (TOS) over different hybrid catalysts. It is observed that the CO conversion over hybrid catalysts is far higher than that over CZA catalyst. This phenomenon is due to the in-situ removal of methanol from methanol/DME dehydration component, which breaks the thermodynamic equilibrium limitation of the methanol synthesis process (Equation 1)^{19, 20}. Compared with the other three hybrid catalysts, the CO conversion over CZA/Pd β was sharply decreased within the primary 60 minutes while the CO conversion over CZA was still stable under the same reaction conditions. The above results indicate that the deactivation of Pd β leads to the quick deactivation of CZA/Pd β .

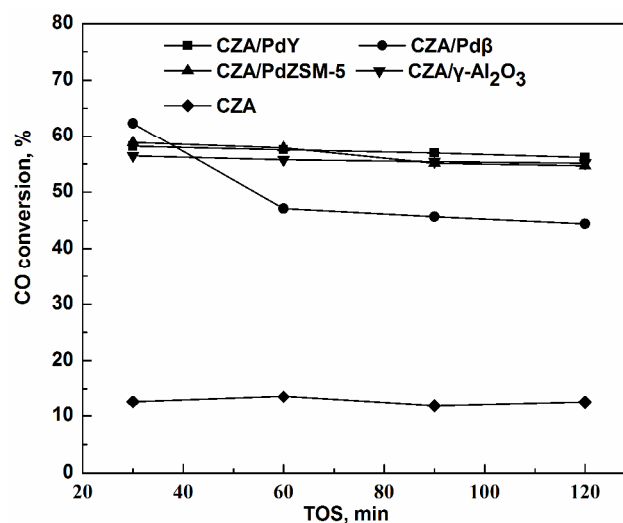


Figure 1. TOS data of CO conversion over different hybrid catalyst. Reaction condition: T=260°C, P=2 MPa, H₂/CO=2, GHSV=1875 ml.g⁻¹.h⁻¹.

Table 1 shows the product distribution of syngas conversion over different hybrid catalysts. It is shown that the major product in CZA catalyst was MeOH. Byproducts like hydrocarbons were also formed under the reaction condition. Methanol synthesis process was usually operated at an elevated pressure of 5-10 MPa and temperature of 200-300°C²¹. High reaction temperature and low pressure would lead to a low CO conversion as well as promoting the formation of byproducts. The major product of syngas conversion over CZA/ γ -Al₂O₃ became DME and few hydrocarbons were detected in the product. Additionally, plenty of CO₂ was produced. Cu-ZnO based catalyst had great performance for the water gas shift (WGS) reaction (Equation 5)²². Methanol formed from CZA catalyst could be dehydrated to

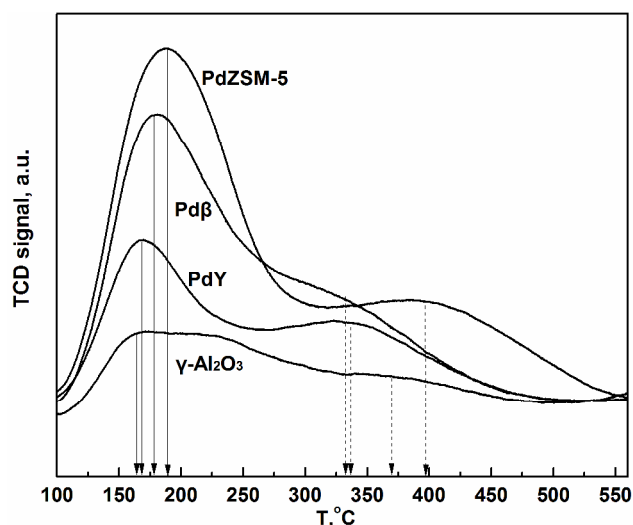


Figure 2. NH_3 -TPD spectrum of different catalyst PdZSM-5, Pd β , PdY and $\gamma\text{-Al}_2\text{O}_3$

Figure 3 shows the carbon number distribution of C_5 - C_{12} hydrocarbons over the three different hybrid catalysts. Few C_{11} - C_{12} hydrocarbons were detected over CZA/PdZSM-5 and CZA/PdY. Meanwhile, about 26% C_{11} - C_{12} hydrocarbons were detected over the CZA/Pd β catalyst. It is noteworthy that almost all the C_{11} - C_{12} hydrocarbons were hexamethylbenzene. This phenomenon has close correlation with the topology of different Pd zeolites.

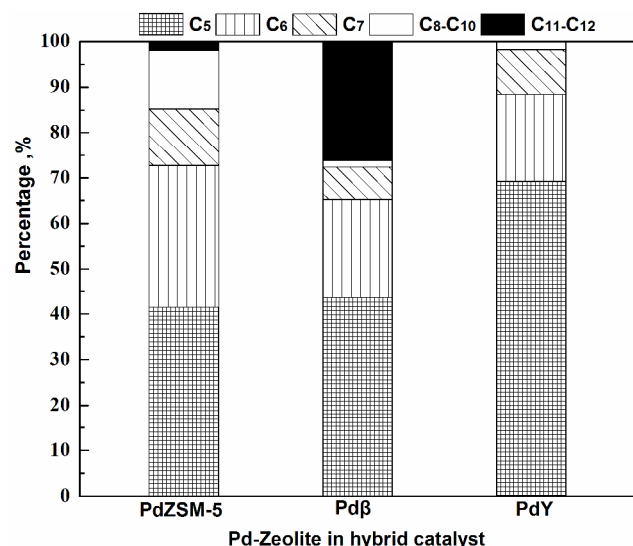


Figure 3. Percentage of different fractions in C_5 - C_{12} hydrocarbon. Reaction conditions: 260°C, 2 MPa, $\text{H}_2/\text{CO}=2$, GHSV=1875 $\text{ml.h}^{-1}\text{.g}^{-1}$. Note: about 100% C_{11} - C_{12} hydrocarbons over CZA/Pd β catalyst is hexamethylbenzene.

Table 4 gives detailed information about the topology of zeolite HZSM-5, H β and HY. Both H β and HY possess a cavity with different sizes compared with HZSM-5. The pore size order of the three zeolites is as follows: HZSM-5<H β <HY. Compared with PdZSM-5, it was much easier for produced methanol and DME to enter the channel of PdY and Pd β due to their larger channel openings. The large pore and cavity of Pd β and PdY

could provide more space for chain growth reactions like oligomerization. DME was dehydrated to lower olefins and converted into higher hydrocarbons such as C_5 + olefins, aliphatic hydrocarbons, naphthenes and aromatics by oligomerization, cyclization and aromatization on PdY and Pd β . However, the detected C_5 - C_{12} hydrocarbons over the CZA/PdY catalyst were the least among the three hybrid catalysts. A similar phenomenon was also found by Fujimoto et al⁶. The large pore in HY was considered to enhance the mass transfer of both reactants and products, which would shorten the residence time of lower olefins in the channels of HY and weaken the oligomerization reactions. Note that hydrocarbons in C_5 - C_{12} over the above three hybrid catalysts are mainly gasoline-type branched paraffins (see Figure 4).

Table 4. The structure parameters of zeolite HZSM-5, H β and HY.

Zeolite type	Framework type	Ring size (T-atoms)	Pore size/nm	Channel system	Cavity size/nm
HZSM-5	MFI	10, 6, 5, 4	0.53×0.56	3 D	none
H β	BEA	12, 6, 5, 4	0.67×0.66	3D	~1nm
HY	FAU	12, 6, 4	0.74×0.74	3D	~1.3nm

Note: Data are from IZA.

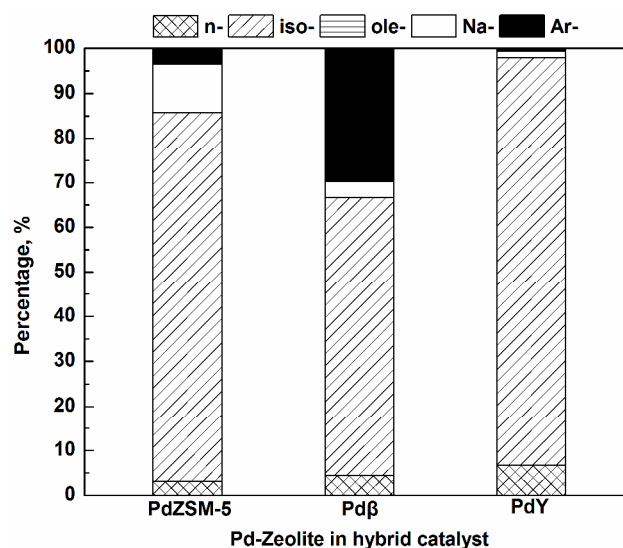


Figure 4. Compositions in C_5 - C_{12} fractions. Note: n-: n-paraffin; iso-: iso-paraffin; ole-: olefins; Na- naphthene; Ar- aromatics. Reaction conditions: 260°C, 2 MPa, $\text{H}_2/\text{CO}=2$, GHSV=1875 $\text{ml.h}^{-1}\text{.g}^{-1}$.

2. Catalyst deactivation analysis

Catalyst deactivation by coke is one of the main problems in the field of catalytic reactions²⁶. M. Guisnet et al thought that the formation of coke had close correlation with the topology of the zeolite²⁷⁻²⁹: (i) pore size (ii) existence or non-existence of cavities and (iii) the diffusion of the reactants and/or the products in zeolite. Additionally, the density of Brönsted acid and Lewis acid also influences coke formation over zeolite catalyst. From the discussion of 3.1, we know that the deactivation of Pd β leads to the quick deactivation of the hybrid catalyst of CZA/Pd β . To understand the reason for the deactivation of the hybrid catalysts

for syngas conversion, TPO-MS and N₂ physical adsorption techniques had been carried out.

Table 5a Textural properties of Pd zeolite and spent Pd zeolite

Sample	V _{pore} (cm ³ . g ⁻¹) ^a	V _{micro} (cm ³ . g ⁻¹) ^b	S _{micro} (m ² . g ⁻¹) ^b	S _{BET} (m ² . g ⁻¹) ^c	S _{External} (m ² . g ⁻¹) ^c
PdZSM-5	0.215	0.133	326.9	378.3	51.4
PdZSM-5-S	0.199	0.107	265.0	308.0	43.0
Pdβ	0.555	0.140	350.9	529.2	178.3
Pdβ-S	0.489	0.090	220.0	395.1	175.0
PdY	0.478	0.276	610.3	709.1	98.9
PdY-S	0.388	0.204	491.5	590.6	99.1

a. Measured V_{ads} at p/p⁰ = 0.98.

b. t-plot method.

c. BET method.

“S” means “spent”

Table 5b The reduction rate of physical properties in spent Pd modified zeolite

Sample	dV _{pore} /V _{pore} %	dV _{micro} /V _{micro} %	dS _{micro} /S _{micro} %	dS _{BET} /S _{BET} %	dS _{External} /S _{External} %
PdZSM-5-S	7.4	19.5	18.9	18.6	16.3
Pdβ-S	11.9	35.7	37.3	25.3	1.9
PdY-S	18.8	26.1	19.5	16.7	~0

Note: $dX/X = (X_0 - X_i)/X_0$, which means the reduction rate of the samples' physical properties. X₀ means the property value of fresh catalyst; X_i means the property value of spent catalyst.

As shown in Figure 5, obvious CO₂ and H₂O signals were detected by mass spectrometer (MS) in the three spent Pd modified zeolites (PdZSM-5-S, Pdβ-S and PdY-S), especially in Pdβ-S and PdY-S. Only the weakest H₂O and CO₂ signals were detected over PdZSM-5-S which was consistent with good stability of CZA/PdZSM-5. TPO-MS data shows three CO₂ peaks for PdZSM-5-S while two peaks for both Pdβ-S and PdY-S. N₂ physical adsorption data (see Table 5a) show that the total pore volume of the three spent Pd-zeolites is decreased. The order of reduced volume is PdZSM-5-S < Pdβ-S < PdY-S which is in line with the results of TPO-MS. Table 5b shows that the reduction rate order of external surface is PdY-S < Pdβ-S < PdZSM-5-S. In contrast, the reduction rate order of volume is PdZSM-5-S < Pdβ-S < PdY-S. The results of TPO-MS and N₂ physical adsorption techniques indicate that external coke was formed over PdZSM-5, while higher hydrocarbons were formed within the micropores of Pdβ and PdY during syngas conversion reactions. These trapped higher hydrocarbons became carbonaceous compounds and blocked the pores, especially micropores, of Pd-zeolites. The first peak at about 300°C belongs to the calcinations of external coke while peaks greater than 400°C belong to the calcinations of internal coke. Table 3 shows that both Hβ and HY contain a 12-ring opening channel system and a cavity while HZSM-5 contains a 10-ring opening channel system but no cavity. The pore sizes of the three Pd-zeolites are 0.53×0.56 nm for PdZSM-5, 0.67×0.66 nm for Pdβ and 0.74×0.74 nm for PdY, respectively. The large cavity of PdY (1.3 nm) and Pdβ (1.0 nm) can provide a much bigger space for the following chain growth reactions to form higher hydrocarbons like polymethylbenzene. Many hexamethylbenzene were detected over CZA/Pdβ. From the

literature, we know that the kinetic diameter of hexamethylbenzene is approximately 0.72 nm³⁰, which is bigger than the pore size of Pdβ. The formation of hexamethylbenzene should happen in the cavity of Pdβ. As the chemical bond in zeolite framework is elastic and vibrational³¹, the hexamethylbenzene could also diffuse out from the large pores of Pdβ. That's why we detected hexamethylbenzene over CZA/Pdβ. The cavity size of Pdβ (~1.0 nm) is smaller than the cavity size of PdY (~1.3 nm). The maximal size of hydrocarbons formed in the cavities of PdY should be larger than that formed in the cavities of Pdβ. Thus, the formed hydrocarbons in the cavities of PdY might be higher aromatics with 2-ring and 3-ring (Polycyclic aromatic hydrocarbons, PAHs). The formed higher aromatics in cavities were trapped into the pores of zeolites which become the precursors of coke. For PdZSM-5, the chain growth reactions were limited for its narrow pore size. The formation of higher aromatics was restrained in PdZSM-5. However, there were also carbonaceous compounds deposited over the external surface of PdZSM-5. In general, the blockage of micropores by hydrocarbon-type coke caused the deactivation of hybrid catalysts.

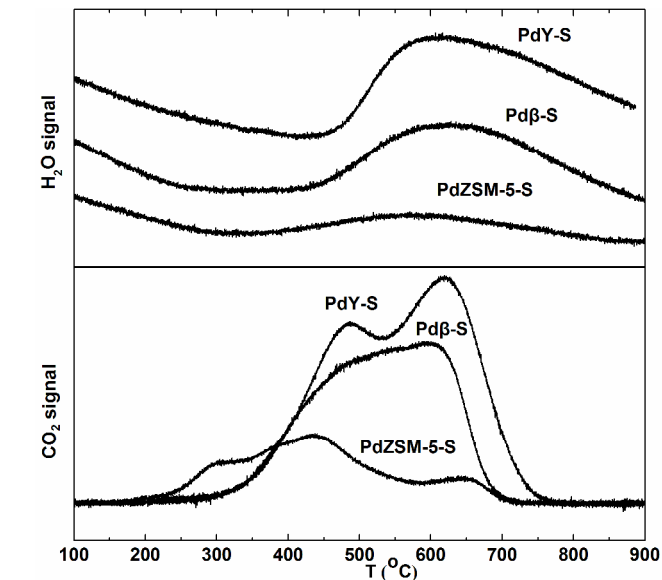


Figure 5. TPO-MS spectrum of spent PdZSM-5-S, Pdβ-S and PdY-S zeolite.

Conclusion

Synthesis gas could be converted into different hydrocarbon fractions over hybrid catalyst composed of Cu-ZnO-Al₂O₃ methanol synthesis catalyst and Pd modified zeolite. The results indicate that the intermediate step of DME dehydration to hydrocarbons mainly happened on the Brönsted acid sites while methanol could be effectively converted into DME on the weak Lewis acid sites. Additionally, hydrocarbon distribution and carbonaceous compound formation had a close relationship with the topology and the acidity of Pd modified zeolite. More C₄+ hydrocarbons were formed over hybrid catalyst of CZA/Pd-β and CZA/Pd-Y due to their large pore and cavities. However, the cavity also provided enough space for the formation of higher

aromatics which would block the micropores of Pd modified zeolite in hybrid catalyst and cause the activity loss of the hybrid catalyst. For CZA/PdZSM-5, the formation of higher aromatics was restrained because of the narrow pores in PdZSM-5. Carbonaceous compounds were deposited on the external surface of PdZSM-5 because of its strongest acid sites. The compositions of C₅-C₁₂ were rich in gasoline-type branched paraffins. There is still much work left to increase the content of liquid fuels in hydrocarbon products over a hybrid catalyst, improve the stability of the hybrid catalyst and promote the efficiency of carbon conversion into hydrocarbons.

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Notes and references

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‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

- W. Maqbool and E. S. Lee, *Chem. Eng. Technol.*, 2014, **37**, 995-1001.
- J. R. Rostrup-Nielsen, *Catal. Today*, 2002, **71**, 243-247.
- P. Tunå and C. Hultberg, *Fuel*, 2014, **117**, Part B, 1020-1026.
- N. Tsubaki, Y. Yoneyama, K. Michiki and K. Fujimoto, *Catal. Commun.*, 2003, **4**, 108-111.
- H. M. Torres Galvis, J. H. Bitter, C. B. Khare, M. Ruitenbeek, A. I. Dugulan and K. P. de Jong, *Science*, 2012, **335**, 835-838.
- K. Fujimoto, H. Saima and H.-o. Tominaga, *Bull. Chem. Soc. Jpn.*, 1985, **58**, 3059-3060.
- N. V. Kolesnichenko, L. E. Kitaev, Z. M. Bukina, N. A. Markova, V. V. Yushchenko, O. V. Yashina, G. I. Lin and A. Y. Rozovskii, *Kinet. Catal.*, 2007, **48**, 789-793.
- C. Wang, D. Zhang, C. Fang, Q. Ge and H. Xu, *Fuel*, 2014, **134**, 11-16.
- Q. Zhang, K. Cheng, J. Kang, W. Deng and Y. Wang, *ChemSusChem*, 2014, **7**, 1251-1264.
- J. Sun, C. Xing, H. Xu, F. Meng, Y. Yoneyama and N. Tsubaki, *J. Mater. Chem. A*, 2013, **1**, 5670-5678.
- J. Kang, K. Cheng, L. Zhang, Q. Zhang, J. Ding, W. Hua, Y. Lou, Q. Zhai and Y. Wang, *Angew. Chem.*, 2011, **123**, 5306-5309.
- S. Sartipi, K. Parashar, M. Makkee, J. Gascon and F. Kapteijn, *Catal. Sci. Technol.*, 2013, **3**, 572-575.
- R. A. Dagle, J. A. Lizarazo-Adarme, V. Lebarbier Dagle, M. J. Gray, J. F. White, D. L. King and D. R. Palo, *Fuel Process. Technol.*, 2014, **123**, 65-74.
- X. Ma, Q. Ge, C. Fang, J. Ma and H. Xu, *Fuel*, 2011, **90**, 2051-2054.
- K. Fujimoto, *J. Jan. Petrol. Inst.*, 2004, **47**, 394-402.
- Q. Ge, Y. Lian, X. Yuan, X. Li and K. Fujimoto, *Catal. Commun.*, 2008, **9**, 256-261.

- C. D. Chang, W. H. Lang and A. J. Silvestri, *J. Catal.*, 1979, **56**, 268-273.
- T. Ma, H. Imai, Y. Suehiro, C. Chen, T. Kimura, S. Asaoka and X. Li, *Catal. Today*, 2014, **228**, 167-174.
- J. G. van Bennekom, R. H. Venderbosch, J. G. M. Winkelman, E. Wilbers, D. Assink, K. P. J. Lemmens and H. J. Heeres, *Chem. Eng. Sci.*, 2013, **87**, 204-208.
- T. Ogawa, N. Inoue, T. Shikada and Y. Ohno, *J. Nat. Gas Chem.*, 2003, **12**, 219-227.
- M. Behrens, F. Studt, I. Kasatkin, S. Kühl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B.-L. Knief, M. Tovar, R. W. Fischer, J. K. Nørskov and R. Schlögl, *Science*, 2012, **336**, 893-897.
- K. M. V. Bussche and G. F. Froment, *J. Catal.*, 1996, **161**, 1-10.
- M. Xu, J. H. Lunsford, D. W. Goodman and A. Bhattacharyya, *Appl. Catal. A*, 1997, **149**, 289-301.
- M. Niwa, K. Suzuki, N. Morishita, G. Sastre, K. Okumura and N. Katada, *Catal. Sci. Technol.*, 2013, **3**, 1919-1927.
- S. Fathi, M. Sohrabi and C. Falamaki, *Fuel*, 2014, **116**, 529-537.
- M. Guisnet, *J. Mol. Catal. A: Chem.*, 2002, **182**, 367-382.
- M. Guisnet and P. Magnoux, *Appl. Catal.*, 1989, **54**, 1-27.
- B. Paweewan, P. J. Barrie and L. F. Gladden, *Appl. Catal. A*, 1999, **185**, 259-268.
- M. Guisnet, L. Costa and F. R. Ribeiro, *J. Mol. Catal. A: Chem.*, 2009, **305**, 69-83.
- Q. Zhu, J. N. Kondo, T. Tatsumi, S. Inagaki, R. Ohnuma, Y. Kubota, Y. Shimodaira, H. Kobayashi and K. Domen, *J. Phys. Chem. C*, 2007, **111**, 5409-5415.
- Liu Yi and G. Zi, *Acta Petrolei Sinica(Petroleum Processing Section)*, 1996, **12**, 35-40.