available at www.sciencedirect.com journal homepage: www.elsevier.com/locate/chnjc

Article

The effect of P modification on the acidity of HZSM-5 and P-HZSM-5/CuO-ZnO-Al₂O₃ mixed catalysts for hydrogen production by dimethyl ether steam reforming

Jianhui Lü, Shuang Zhou, Kui Ma, Ming Meng*, Ye Tian #

Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin Key Laboratory of Applied Catalysis Science and Engineering, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, China

ARTICLE INFO

Article history:

Received 21 March 2015

Accepted 24 April 2015

Published 20 August 2015

Keywords:

HZSM-5 zeolite

Phosphorus modification

Acidity

Deposition of coke

Dimethyl ether steam reforming

Hydrogen production

ABSTRACT

Dimethyl ether steam reforming (DME SR) was catalyzed by a CuO-ZnO-Al₂O₃ (CuZnAlO) catalyst mixed with P-modified HZSM-5 for the production of H₂. The effect of P modification on the acidity and activity of the P-HZSM-5/CuZnAlO mixed catalyst for DME SR was investigated. P-HZSM-5/CuZnAlO gave a higher CO₂ selectivity and also higher stability during DME SR compared to the mixed catalyst with HZSM-5. N₂ desorption, X-ray diffraction, temperature-programmed oxidation (TPO), NH₃ temperature-programmed desorption (NH₃-TPD), Fourier transform infrared spectroscopy (FT-IR), and solid-state ³¹P magic angle spinning nuclear magnetic resonance (³¹P MAS NMR) were used for catalyst characterization. NH₃-TPD results showed that both the acid quantity and strength of HZSM-5 were significantly changed after P modification. With increased P content, the density of strong acid sites decreased, while the weak acid sites changed little. TPO results indicated that catalyst deactivation was mainly caused by the deposition of coke. The catalyst with 5% P exhibited much better stability than the parent HZSM-5 due to the disappearance of strong acid sites after P modification. The FT-IR spectra of pyridine adsorption clearly revealed that with increased P content, there was an obvious decrease of Lewis acid sites and slight decrease of Brønsted acid sites. From the results of ³¹P MAS NMR, NH₃-TPD and FT-IR of adsorbed pyridine, a description of the effect of phosphorus modification on HZSM-5 was proposed.

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

The increasing consumption of fossil fuels has led to the energy crisis and various environmental pollutions. Thus, it is necessary to search for clean and sustainable energy sources. As a new clean energy, H₂ is getting more attention from world governments and researchers [1,2]. In the past several years,

H₂-based fuel cells such as the proton exchange membrane fuel cells have become research hotspots due to their high efficiency in chemical-to-electric energy conversion [3]. However, as a renewable gaseous energy source, H₂ is hard to be stored, compressed and transported [1], which restricts the wide application of H₂-based fuel cells on vehicles. So, techniques for onboard H₂ production from H₂-rich carriers must be devel-

* Corresponding author. Tel: +86-22-27892275; E-mail: mengm@tju.edu.cn

Corresponding author. Tel: +86-22-27405297; E-mail: tianye@tju.edu.cn

This work was supported by the National Natural Science Foundation of China (21276184, U1332102, 21476160), the Specialized Research Fund for the Doctoral Program of Higher Education of China (20120032110014), the Natural Science Foundation of Tianjin (12JCZDJC14000, 15JCZDJC37400), and the Program for Introducing Talents of Discipline to Universities of China (B06006).

DOI: 10.1016/S1872-2067(15)60883-X | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 36, No. 8, August 2015

oped. Recently, dimethyl ether (DME) as a potential onboard H₂ source material has attracted increasing attention due to its intrinsic advantages such as a high H/C ratio, high energy density, no toxicity and no carcinogenicity [4]. DME can be stored and handled like liquid petroleum gas (LPG) because of their similar physical properties. By using reforming techniques, DME can be efficiently converted to H₂. The reforming techniques include partial oxidation reforming, autothermal reforming, dry reforming and steam reforming (SR). SR can produce the largest amount of H₂ per mole DME due to the additional utilization of the hydrogen available in water. So, DME SR is now regarded as a promising route for onboard H₂ production and supply for H₂-based fuel cells.

The overall reaction of DME SR can be expressed as Eq. (1), which consists of two successive moderately endothermic reactions: DME hydrolysis to methanol (Eq. (2)) catalyzed by a solid acid catalyst and the subsequent steam reforming of methanol to H₂ and CO₂ (Eq. (3)) catalyzed by a metal catalyst.

DME SR:

DME hydrolysis:

MeOH SR:

During DME SR, the formation of CO cannot be avoided due to the presence of reverse water gas shift reaction (r-WGS) shown as Eq. (4).

r-WGS:

It was reported that DME hydrolysis was the rate limiting step for DME SR in many catalytic systems [5–7], so, the acceleration of this step is significant for the increase of the overall reaction rate. DME hydrolysis is usually catalyzed by a solid acid catalyst such as γ -Al₂O₃ and zeolites. Up to now, γ -Al₂O₃ has been studied extensively due to its good activity and stability for DME hydrolysis and it has few side reactions. However, γ -Al₂O₃ needs a high operating temperature (300–400 °C) for DME hydrolysis, leading to the sintering of Cu species and deactivation of Cu-based catalysts [7]. Compared to γ -Al₂O₃, zeolites have much stronger acidity and can catalyze DME hydrolysis at a lower temperature (< 300 °C) [8,9]. Nevertheless, the strong acid sites on zeolites also result in the formation of coke [10,11], thus decreasing the performance of the catalyst. So, the modification of the acidity of the zeolite is necessary. Based on this analysis, the present research aims to tune the acidity of zeolite HZSM-5 to remove the unnecessary strong acid sites.

The H-type of the zeolite HZSM-5 has been widely employed in many catalytic reactions due to its high activity and low cost [12–15]. In order to further improve the performance of HZSM-5, many elements or compounds have been employed to modify the structure and acidity of HZSM-5, such as La [10,16], Mg [17], Ga [18], B [15] or P [14,19–21] and an alkaline treatment [22]. After P modification of H-ZSM-5, the coke deposition in many reactions was dramatically decreased [14,23]. So, in this work, phosphorus was selected and added to HZSM-5 for the optimization of its acidity. It is found that the

CuO-ZnO-Al₂O₃ (CuZnAlO, CuO/ZnO/Al₂O₃ mass ratio was 3/1/6) catalysts mixed with the modified P-HZSM-5 exhibited higher activity and also better stability and higher CO₂ selectivity in DME SR compared to those consisting of CuZnAlO and pure HZSM-5. By using ³¹P magic angle spinning nuclear magnetic resonance (³¹P MAS NMR), NH₃ temperature-programmed desorption (NH₃-TPD) and Fourier transform infrared spectroscopy (FT-IR), the catalysts were well characterized, and the relationship between the catalyst structure and catalytic performance was clearly revealed.

2. Experimental

2.1. Catalyst preparation

HZSM-5 with a SiO₂/Al₂O₃ molar ratio of 25 was purchased from the Catalyst Co. Ltd of Nankai University and calcined at 550 °C for 3 h to remove impurities. The P modified samples (P/HZSM-5 mass ratios: 1%, 3%, 5% or 7%) were prepared by impregnating the HZSM-5 zeolite in an aqueous solution of diammonium hydrogen phosphate with the desired concentration. After evaporating at 50 °C and drying at 120 °C for 12 h, the dry precursor was obtained, which was further calcined in air at 500 °C for 4 h. The final solid acid catalysts were denoted as xP/HZSM-5, where x represents the mass ratio of P to HZSM-5. Before use in the DME SR reaction, the solid acid catalyst was mechanically mixed with a CuZnAlO reforming catalyst (mass ratio: 1/1) and made into particles of 40–60 mesh. The details for the preparation of the CuZnAlO catalyst (CuO/ZnO/Al₂O₃ mass ratios are 3/1/6) by the co-precipitation method can be found elsewhere.

2.2. Catalyst characterization

The specific surface area and pore structure of the catalysts were determined by N₂ adsorption at –196 °C on a volumetric adsorption apparatus (Quantachrome QuadraSorb SI instrument). The specific surface area of the catalyst was calculated according to BET equation. The average pore diameter was measured by the BJH method.

The X-ray diffraction (XRD) patterns were recorded on a D8 diffractometer (Bruker Company) using a cobalt anode X-ray tube (Cu K α radiation, λ = 0.15418 nm) operated at 40 kV and 40 mA. Diffraction data in the range of 2 θ from 10° to 50° were collected with a step size of 0.02°.

Before the NH₃-TPD test, the catalyst (100 mg each time) was first pretreated at 500 °C for 1 h in He (99.999%, 80 mL/min). The sample was cooled to 100 °C in the same atmosphere. Then, the atmosphere was switched to 5% NH₃ in N₂ for 2 h NH₃ adsorption at 100 °C. After flushing with pure He, the NH₃-TPD test was carried out in the range of 100–600 °C at a heating rate of 10 °C/min. The signal was monitored by a gas chromatograph equipped with a TCD detector (XianQuan TP-5079 instrument).

Temperature-programmed oxidation (TPO) was performed on the spent catalysts using the same XianQuan TP-5079 instrument. Each time, 100 mg spent catalyst was heated from

room temperature to 700 °C at a heating rate of 10 °C /min in the atmosphere of 6% O₂/He (20 mL/min).

The FT-IR spectra of the catalysts after pyridine adsorption were recorded on a Nicolet Nexus IR spectrometer to characterize the surface acid sites (Brönsted or Lewis). Fresh catalyst (30 mg) was ground and pressed into a very thin wafer, which was placed in a quartz IR cell with CaF₂ windows. The sample was evacuated at 300 °C for 1 h to remove impurities adsorbed on the catalyst. The catalyst was exposed to pyridine under a N₂ stream at room temperature until the adsorbed amount of pyridine reached saturation. Finally the IR cell was evacuated at 150 and 300 °C for 30 min for the collection of IR spectra at these two temperatures.

The spectra of ³¹P MAS NMR were recorded on a Varian InfinityPlus 300 NMR spectrometer at 121.38 MHz with a spinning rate of 8.0 kHz. The pulse width and pulse delay were 1.0 μs and 35.0 s, respectively.

2.3. Catalyst activity and stability evaluation

The activity of the catalysts (500 mg) for DME SR was measured in a fixed-bed continuous flow reactor with a constant space velocity of 12000 mL/(h·g_{cat}) at atmospheric pressure. Prior to each test, the mixed catalyst was reduced at 300 °C for 1 h in 10% H₂/N₂ mixture gas. After the temperature dropped to 200 °C, the stream was switched to the feed gas consisting of 10% DME, 40% N₂ and 50% H₂O (g) (S/C = 2.5), and kept at this same temperature for 0.5 h, and the DME SR activity was evaluated at different temperatures with an interval of 25 °C. The effects of external and internal mass transfer limitation on the catalytic reaction were confirmed as excluded by varying the linear flow rate over the catalyst and the catalyst particle size, respectively. The products were analyzed using an online gas chromatograph (Agilent 7890A) equipped with PoraPak N, molecular sieve 5A and PoraPak Q capillary columns.

DME conversion and selectivity to C₁ species were defined as follows:

$$\text{DME conversion} = (F_{\text{DME,in}} - F_{\text{DME,out}}) / F_{\text{DME,in}} \times 100\%$$

$$\text{Selectivity to } C_i \text{ species} = F_{C_i} / \sum F_{C_i} \times 100\%$$

where F_{DME} and F_{C_i} are the effluent molar flow rates of DME and C₁-containing products (CH₄, CO and CO₂), respectively.

Hydrogen yield was defined as the ratio of the molar amount of DME converted to hydrogen to the total molar amount of DME fed to the reactor, and was calculated using

$$\text{H}_2 \text{ yield} = F_{\text{H}_2} / 6F_{\text{DME,in}} \times 100\%$$

where F_{H_2} is the molar flow rate of H₂.

The catalytic stability of HZSM-5 or 5%P-modified HZSM-5 mixed with CuO/ZnO/Al₂O₃ for DME SR was investigated by a continuous isothermal activity measurement at 350 °C for 8 h.

3. Results and discussion

3.1. Texture data

The specific surface area, pore volume and pore diameter of P-modified HZSM-5 are summarized in Table 1. With the in-

Table 1

Specific surface area, pore volume and pore diameter of P-modified HZSM-5.

P content (wt%)	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Pore diameter (nm)
0	333.5	0.087	1.361
1.0	284.6	0.061	1.358
3.0	224.8	0.042	1.352
5.0	194.5	0.039	1.356
7.0	163.0	0.021	1.335

crease of P content, both the BET surface area and total pore volume of the modified HZSM-5 samples gradually decreased. However, there was no significant difference in the pore diameter among all the catalysts, which suggested no pore blocking by the added P.

3.2. XRD

The XRD patterns of the P-modified samples are shown in Fig. 1. The P-modified catalysts displayed similar diffraction peaks at the same positions as pure HZSM-5, suggesting the maintaining of the framework structure of HZSM-5 zeolite. However, the intensity of the diffraction peaks of the P-modified catalysts gradually decreased with the increase of P content, which may be due to the decreased crystallite size of the HZSM-5 zeolite. In addition, after P modification, no diffraction peak of P species was observed even for the sample containing 7%P, which reflects the high dispersion of the P species.

3.3. NH₃-TPD

The NH₃-TPD profiles of the parent HZSM-5 and P-modified HZSM-5 are presented in Fig. 2. There were two desorption peaks for the parent HZSM-5. The peak at high temperature corresponded to strong acid sites and can be attributed to the desorption of NH₃ from bridging hydroxyl groups (Si-OH-Al) on the zeolite. The other peak at low temperature correspond-

Fig. 1. XRD patterns of the parent HZSM-5 and the P-modified HZSM-5 catalysts. (1) HZSM-5; (2) 1%P/HZSM-5; (3) 3%P/HZSM-5; (4) 5%P/HZSM-5; (5) 7%P/HZSM-5.

Fig. 2. NH_3 -TPD profiles of the different catalysts. (1) HZSM-5; (2) 1%P/HZSM-5; (3) 3%P/HZSM-5; (4) 5%P/HZSM-5; (5) 7%P/HZSM-5.

ed to the desorption of NH_3 from silanol groups or extra framework aluminum species [24]. After modification by P, the low temperature desorption peaks showed small changes in position and intensity. The high temperature desorption peaks were much decreased. Moreover, as the P content increased to 5%, the high temperature desorption peak almost disappeared. In order to give the acid amounts on these catalysts, we calculated the amounts of desorbed NH_3 from the desorption peaks areas, as listed in Table 2. It is clear that the P modification mainly reduced the amounts of strong acid sites, which is favorable for catalyst stability in the DME SR reaction because strong acid sites catalyze the formation of coke. By careful observation, it was also found that with the increase of P content, the desorption peak of weak acid sites slightly shifted to lower temperature, implying the subtle weakening of the acid strength.

Based on these results, a schematic model for P-modified HZSM-5 was proposed and shown in Fig. 3. As the content of P increased, the strong acid sites decreased sharply and the weak acid sites increased slowly. When the amount of P reached 5%, the strong acid sites had almost disappeared. Further increase of P content to 7% resulted in the decrease of the weak acid sites as reflected by the decreased intensity of the desorption peak below 300 °C.

3.4. O_2 -TPO

To investigate the correlation between P modification and coke formation during DME SR, O_2 -TPD tests were performed

Table 2

Amount of desorbed NH_3 of parent and P-modified HZSM-5 catalysts calculated from the NH_3 -TPD profiles.

Sample	Amount of desorbed ammonia (mmol/g)		
	Weak acid	Strong acid	Total acid
HZSM-5	445	386	831
1%P/HZSM-5	440	246	686
3%P/HZSM-5	459	155	614
5%P/HZSM-5	533	—	533
7%P/HZSM-5	448	—	448

Fig. 3. Schematic model of P-modified HZSM-5.

on the spent catalysts. The results are presented in Fig. 4. With the increase of P content, the amount of coke on the catalyst surface sharply decreased, suggesting the obvious decrease of strong acid sites as confirmed by NH_3 -TPD. It is known that the coke formed can cover both the metal sites and the acid sites, leading to the decrease of the catalytic activities for DME hydrolysis and the following methanol reforming. The P induced decrease or disappearance of strong acid sites is helpful for catalytic activity and catalyst stability.

3.5. FT-IR

Because NH_3 -TPD cannot distinguish Brönsted acid sites and Lewis acid sites, the FT-IR spectra of the catalysts after pyridine adsorption were collected. Fig. 5(a) shows the FT-IR spectra of pyridine adsorbed on the parent HZSM-5 and P-modified HZSM-5 at 150 °C. Both the bands at 1450 cm^{-1} corresponding to Lewis acid sites and that at 1540 cm^{-1} corresponding to Brönsted acid sites [25,26] were clearly identified. By calculating the areas of these two peaks, the relative amounts of Lewis acid sites and Brönsted acid sites as well as the ratios of Lewis acid sites to Brönsted acid sites (L/B) were obtained, as listed in Table 3. As the P content increased, both the Lewis acid sites and Brönsted acid sites decreased. Mean-

Fig. 4. O_2 -TPO profiles of spent catalysts. (1) HZSM-5; (2) 1%P/HZSM-5; (3) 3%P/HZSM-5; (4) 5%P/HZSM-5; (5) 7%P/HZSM-5.

Fig. 5. FT-IR spectra after pyridine adsorption on the parent and P-modified HZSM-5 recorded at different temperatures. (a) 150 °C; (b) 300 °C. (1) HZSM-5; (2) 1%P/HZSM-5; (3) 3%P/HZSM-5; (4) 5%P/HZSM-5; (5) 7%P/HZSM-5.

Table 3

Amounts of Lewis acid sites, Brönsted acid sites and total acid sites calculated from the FT-IR spectra of pyridine adsorption at 150 and 300 °C.

Sample	Acid amounts measured at 150 °C				Acid amounts measured at 300 °C			
	L acid sites	B acid sites	Total acid sites	L/B	L acid sites	B acid sites	Total acid sites	L/B
HZSM-5	370	517	887	0.72	153	436	589	0.35
1%P/HZSM-5	303	488	791	0.62	128	347	475	0.37
3%P/HZSM-5	187	452	639	0.41	58	224	282	0.26
5%P/HZSM-5	96	394	490	0.24	15	100	115	0.15
7%P/HZSM-5	25	159	184	0.15	11	68	79	0.16

while, the L/B ratios also decreased sharply, which means the larger decreasing extent of Lewis acid sites, as depicted in Fig. 6(a). The FT-IR spectra of pyridine adsorption at the higher temperature of 300 °C were also recorded. The results are shown in Fig. 5(b), Table 3 and Fig. 6(b). By a comparison of the data in Table 3, it is found that as the content of P increased, both the Brönsted acid sites and Lewis acid sites decreased quickly. The remaining band at 1540 cm⁻¹ in Fig. 5(b) corresponded to the strong Brönsted acid sites because adsorbed pyridine on weak Brönsted acid sites can be removed by vacuum evacuation at 300 °C. For the samples containing 1% to

5% P, the quantities of strong Brönsted acid sites measured at 300 °C decreased rapidly with the increase of P content, while the quantity of total Brönsted acid sites measured at 150 °C changed little. Further increase of P content to 7% decreased both the strong acid sites and weak acid sites. Based on these results, it is suggested that the strong Lewis acid sites can be readily covered by P, while the strong Brönsted acid sites can be modulated by P and were transformed to weak acid sites, as demonstrated by the increasing difference of Brönsted acid sites listed in Table 3.

In order to reveal the potential change of the acidity of these

Fig. 6. Acid sites of P-modified HZSM-5 catalysts measured by pyridine IR at different temperatures. (a) 150 °C; (b) 300 °C. (1) L acid sites; (2) B acid sites; (3) Total acid sites.

Fig. 7. FT-IR spectra of pyridine adsorption over fresh or spent 5%P/HZSM-5 at 150 or 300 °C. (1) Fresh, 150 °C; (2) Spent, 150 °C; (3) Fresh, 300 °C; (4) Spent, 300 °C.

catalysts during reactions, the FT-IR spectra of pyridine adsorbed on the spent 5%P-HZSM-5 catalysts at different temperatures were also recorded and compared with those for the fresh catalysts, as shown in Fig. 7. It was found that the quantities of the acid sites on this catalyst decreased after use in the DME hydrolysis reaction, especially the strong acid sites, which was reflected by the obvious difference in the spectra measured at 300 °C. This accounts well for the decrease of catalytic activity.

It is well known that a progressive dehydration of acidic solid catalysts can occur during heating, inducing the consequent transformation of Brönsted acid sites to Lewis acid sites, as described by the following reaction [25]:

However, in the presence of H₂O, the reverse chemical reaction can also occur. So, to reveal the influence of steam (one of the reactants) on the acid sites of the catalysts, the FT-IR spectra of pyridine adsorption on 5% P-modified HZSM-5 previously treated by steam at 350 °C for 0.5 h were collected, as displayed in Fig. 8. By the comparison with the spectra of the untreated samples, it was found that steam treatment increased the Brönsted acid sites but decreased the Lewis acid sites for both the parent HZSM-5 and P-modified HZSM-5. So it was deduced that during the DME SR reaction, most of the Lewis acid sites were transformed to Brönsted acid sites due to the presence of the large amount of steam in the feed and the long reaction time. In other words, the Brönsted acid sites play the major role for DME hydrolysis during the DME SR reaction.

3.6. Solid-state ³¹P MAS NMR

Fig. 9 shows the ³¹P MAS NMR spectra of the P-modified HZSM-5 catalysts. The resonance peak at the chemical shift position of $\delta = 0$ corresponds to the free monomeric [PO₄] orthophosphate species group [19]. From the signal at $\delta = 0$, it can

Fig. 8. FT-IR spectra of pyridine adsorption at 150 °C over fresh HZSM-5 (1), HZSM-5 treated by steam for 0.5 h (2), fresh 5% P-modified HZSM-5 (3), and 5% P-modified HZSM-5 treated by steam for 0.5 h (4).

be inferred that as 1% or 3% P was added to HZSM-5, few free monomeric [PO₄] orthophosphate species were formed, while the addition of larger amounts of P resulted in a remarkable increase of such species. The other two peaks at $\delta = -6$ and -12 can be attributed to the terminal P atoms in pyrophosphoric acid species, and the middle P atoms in polyphosphates or some polymerized short-chain polyphosphates, respectively, according to the assignments in the literature [20,21,27]. The characteristic resonance peaks at $\delta = -20$ and -24 corresponding to the bidentate middle chain groups of polyphosphates with an Al–O–P structure [27] were also observed. The resonance peak at $\delta = -40$, which increased with the increase of P content in HZSM-5, can be assigned to the groups in highly condensed branching polyphosphates like P₄O₁₀, and it was also correlated well with aluminum [27]. The above pyridine FT-IR results indicated that the modification of HZSM-5 by the increased amounts of P gradually modulated the strong Brönsted acid sites to form weak acid sites. So, by combining the results of ³¹P MAS NMR and pyridine FT-IR, a mechanism

Fig. 9. ³¹P MAS NMR spectra of the P-modified HZSM-5 catalysts. (1) HZSM-5; (2) 1%P/HZSM-5; (3) 3%P/HZSM-5; (4) 5%P/HZSM-5; (5) 7%P/HZSM-5.

Scheme 1. A mechanism for the modification of HZSM-5 by phosphorus.

for the modification of HZSM-5 by phosphorus can be derived, which is similar to that reported in the literature [27], as shown in Scheme 1.

3.7. Catalyst activity and stability

The catalytic activity of the catalysts including DME conversion and H_2 yield are shown in Fig. 10(a) and (b). Both DME conversion and H_2 yield increased with the increase of reaction temperature. The modification with P exhibited different influence on the catalytic performance in different temperature regions. Below 290 °C, the DME conversion and H_2 yield decreased with the increase of P content. Above 300 °C, P modification showed a positive influence on the DME SR performance of the catalysts with the amounts of P between 1% and 5%. Further increase of P content to 7% led to decreased DME conversion and H_2 yield. At the lower temperature below 290 °C, the DME SR performance was mainly determined by the DME hydrolysis activity of the solid acid catalyst. Since the parent HZSM-5 has a larger amount of acid sites than the catalysts modified by P, it naturally exhibited better performance for

DME hydrolysis. As a result, better DME SR performance including higher DME conversion and higher H_2 yield were achieved over this sample. However, at relatively higher temperatures (> 300 °C), DME hydrolysis is not the determining step for DME SR. In this situation, the catalytic performance of the catalysts was mainly determined by methanol reforming over the Cu-based metallic catalyst. The NH_3 -TPD and pyridine FT-IR results indicated that the densities of strong acid sites decreased with the increase of P doped in HZSM-5, which is favorable for the inhibition of coke formation. Nevertheless, an excessive amount of P in HZSM such as 7% would result in too weak acidity and too low activity of the catalyst for DME hydrolysis, thus decreasing the whole DME SR performance. So, the optimized content of P in HZSM-5 is 5%.

Fig. 10(c) and (d) illustrates that as the reaction temperature increased, the CO_2 selectivity decreased and the CO selectivity increased, which were caused by the side reactions including the r-WGS reaction, DME decomposition, MeOH decomposition and DME to syngas reforming at high temperatures. From this figure, it was also found that at 275 °C or higher, the sample containing 5% P exhibited the lowest CO selectivity.

As mentioned above, acid sites facilitate DME hydrolysis, increasing the DME SR reaction rate. However, the acidity also enhanced the formation of coke, decreasing the catalytic performance of the catalysts. To evaluate the catalytic stability of the P-modified HZSM-5 catalysts, the parent HZSM-5 and 5%P-modified HZSM-5 were selected for an 8 h durability test

Fig. 10. DME SR performance of the P-modified HZSM-5 catalysts mixed with the CuZnAlO catalyst. (a) DME conversion; (b) H_2 yield; (c) CO selectivity; (d) CO_2 selectivity. (1) HZSM-5; (2) 1%P/HZSM-5; (3) 3%P/HZSM-5; (4) 5%P/HZSM-5; (5) 7%P/HZSM-5.

Fig. 11. Time-on-stream stability tests on HZSM-5 (1) and 5% P-modified HZSM-5 (2) catalysts.

at 350 °C. The results are displayed in Fig. 11. DME conversion over HZSM-5 decreased quickly in the first 4 h, which resulted from coke formation or the transformation of strong acid sites to weak acid sites in the presence of steam. After modification by P, the decline of DME conversion over 5%P-modified HZSM-5 was effectively inhibited. In the whole process, 5% P-modified HZSM-5 displayed higher catalytic stability.

4. Conclusions

Compared to HZSM-5, a 5% P-modified HZSM-5 catalyst mixed with CuZnAlO exhibited higher CO₂ selectivity and better catalytic stability for DME SR due to the presence of the appropriate amounts of P and strength of acidity. The framework structure of H-ZSM-5 was maintained after P modification. As the P content increased, the strong acid sites decreased sharply. 5 wt% P in HZSM-5 can completely cover the strong acid sites, transforming them to weak acid sites. On the basis of ³¹P MAS NMR and pyridine FT-IR data, a mechanism of P modification on the acidity of HZSM-5 was derived. HZSM-5 modified by 5% P exhibited better stability due to less coke deposition.

References

- [1] Oriňáková R, Oriňák A. *Fuel*, 2011, 90: 3123
- [2] Qi S T, Li Y Y, Yue J Q, Chen H, Yi C H, Yang B L. *Chin J Catal* (齐随涛, 李迎迎, 岳佳琪, 陈昊, 伊春海, 杨伯伦. 催化学报), 2014, 35: 1833
- [3] Huang Z M, Su A, Hsu C J, Liu Y C. *Fuel*, 2014, 122: 76
- [4] Semelsberger T A, Borup R L, Greene H L. *J Power Sources*, 2006, 156: 497
- [5] Faungnawakij K, Tanaka Y, Shimoda N, Fukunaga T, Kawashima S, Kikuchi R, Eguchi K. *Appl Catal A*, 2006, 304: 40
- [6] Yan C F, Hai H, Hu R R, Guo C Q, Huang S L, Li W B, Wen Y. *Int J Hydrogen Energy*, 2014, 39: 18625
- [7] Zhang Q, Fan F Y, Xu G M, Ye D J, Wang W H, Zhu Z B. *Int J Hydrogen Energy*, 2013, 38: 10305
- [8] Faungnawakij K, Kikuchi R, Matsui T, Fukunaga T, Eguchi K. *Appl Catal A*, 2007, 333: 114
- [9] Vicente J, Ereña J, Oar-Arteta L, Olazar M, Bilbao J, Gayubo A G. *Ind Eng Chem Res*, 2014, 53: 3462
- [10] Ouyang J, Kong F X, Su G D, Hu Y C, Song Q L. *Catal Lett*, 2009, 132: 64
- [11] Tago T, Konno H, Sakamoto M, Nakasaka Y, Masuda T. *Appl Catal A*, 2011, 403: 183
- [12] Pires J, Fernandes A C, Duraiswami D. *Chin J Catal* (催化学报), 2014, 35: 1492
- [13] Yang Q, Zhang H T, Kong M, Bao X X, Fei J H, Zheng X M. *Chin J Catal* (杨琦, 张海涛, 孔猛, 包秀秀, 费金华, 郑小明. 催化学报), 2013, 34: 1576
- [14] Zhang D S, Wang R J, Yang X X. *Catal Lett*, 2008, 124: 384
- [15] Zhang W G, Yu D H, Ji X J, Huang H. *Green Chem*, 2012, 14: 3441
- [16] Zhan N N, Hu Y, Li H, Yu D H, Han Y W, Huang H. *Catal Commun*, 2010, 11: 633
- [17] Long X, Zhang Q J, Liu Z T, Qi P, Lu J, Liu Z W. *Appl Catal B*, 2013, 134-135: 381
- [18] Bigey C, Su B L. *J Mol Catal A*, 2004, 209: 179
- [19] Damodaran K, Wiench J W, de Menezes S M C, Lam Y L, Trebosc J, Amoureux J P, Pruski M. *Microporous Mesoporous Mater*, 2006, 95: 296
- [20] Jang H G, Min H K, Hong S B, Seo G. *J Catal*, 2013, 299: 240
- [21] Zhuang J Q, Ma D, Yang G, Yan Z M, Liu X M, Liu X C, Han X W, Bao X H, Xie P, Liu Z M. *J Catal*, 2004, 228: 234
- [22] Vicente J, Gayubo A G, Ereña J, Aguayo A T, Olazar M, Bilbao J. *Appl*

Graphical Abstract

Chin. J. Catal., 2015, 36: 1295–1303 doi: 10.1016/S1872-2067(15)60883-X

The effect of P modification on the acidity of HZSM-5 and P-HZSM-5/CuO-ZnO-Al₂O₃ mixed catalysts for hydrogen production by dimethyl ether steam reforming

Jianhui Lü, Shuang Zhou, Kui Ma, Ming Meng*, Ye Tian*
Tianjin University

The addition of P can tune the acidity of HZSM-5, increasing both the activity and stability of catalysts in DME steam reforming for H₂ production. The optimized amount of P in HZSM-5 is 5 wt%.

- Catal B*, 2013, 130-131: 73
- [23] 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
- [24] Weber R W, Möller K P, O'Connor C T. *Microporous Mesoporous Mater*, 2000, 35-36: 533
- [25] Barzetti T, Selli E, Moschetti D, Forni L. *J Chem Soc, Faraday Trans*, 1996, 92: 1401
- [26] Takahara I, Saito M, Inaba M, Murata K. *Catal Lett*, 2005, 105: 249
- [27] Tian L, Li J W, Li Y X, Chen B H. *Chin J Catal* (田玲, 李建伟, 李英霞, 陈标华. 催化学报), 2008, 29: 889

P改性对HZSM-5酸性及P-HZSM-5/CuO-ZnO-Al₂O₃混合催化剂二甲醚水蒸气重整制氢的影响

吕建辉, 周 双, 马 奎, 孟 明*, 田 野[#]

天津大学化工学院, 天津市应用催化科学与工程重点实验室, 天津化学化工协同创新中心, 天津300072

摘要: 近年来, 氢能作为清洁可再生新型能源越来越受到人们关注. 然而, 氢气储存和运输困难, 制约了其广泛利用. 因此, 寻找一种高效的原位在线制氢技术成为解决这一难题的重要方案之一. 二甲醚作为氢的载体, 具有高H/C比、高能量密度、无毒和无致癌性等优点, 而且二甲醚的物理性质与液化石油气(LPG)相类似, 燃烧时不会产生污染性气体, 且工业上已实现大规模生产. 通过重整技术, 可以使二甲醚有效地转化为H₂. 目前的重整技术主要包括部分氧化重整、自热重整、干重整以及水蒸气重整(SR). 其中二甲醚水蒸气重整(DME SR)技术具有很高的氢气产率, 被认为是一种非常有前途的在线制氢技术.

二甲醚水蒸气重整反应分两步进行, 第一步是固体酸催化剂催化的二甲醚水解反应, 第二步是金属催化剂催化的甲醇水蒸气重整反应. 其中二甲醚水解反应是整个反应的控速步骤. γ -Al₂O₃作为一种最常用的固体酸催化剂, 因其在二甲醚水蒸气重整反应中的良好活性和稳定性, 以及很少的副反应等优点, 得到了国内外研究者的普遍青睐. 但是, γ -Al₂O₃催化二甲醚水解反应的温度较高(300–400 °C), 极易导致用于重整的铜基催化剂烧结和失活. 与 γ -Al₂O₃相比, H型分子筛催化剂(如HZSM-5)酸性较强, 酸性位较多, 催化二甲醚水解反应的温度要低得多(< 300 °C). 然而HZSM-5含有的强酸位在二甲醚水蒸气重整过程中极易导致催化剂因积碳而失活. 因此, 有必要对HZSM-5分子筛进行改性, 去除不必要的强酸位, 以降低积碳, 提高催化剂的活性和稳定性.

本文利用HZSM-5良好的离子交换能力, 在不改变分子筛骨架结构的前提下, 通过一种简单的浸渍法制备了一系列不同P含量的P改性HZSM-5催化剂, 并分别将其与传统的CuO-ZnO-Al₂O₃催化剂机械混合用于二甲醚水蒸气重整制氢. 详细研究了P改性对HZSM-5分子筛酸性以及P-HZSM-5/CuO-ZnO-Al₂O₃混合催化剂二甲醚水蒸气重整制氢活性的影响. 与未改性的HZSM-5相比, P改性的HZSM-5催化剂在重整反应中表现出更高的CO₂选择性和更好的催化稳定性. 通过N₂吸附-脱附、X射线衍射(XRD)、程序升温氧化(TPO)、氨程序升温脱附(NH₃-TPD)、吡啶红外光谱(IR)和³¹P魔角旋转核磁共振光谱(MAS NMR)等技术对催化剂进行了表征. NH₃-TPD结果表明, P改性可以显著影响HZSM-5的酸量和酸强度; 随着P含量的增加, 催化剂的强酸位密度明显降低, 而弱酸量变化不大; 当P含量达到5%时, 催化剂的强酸量几乎消失; 进一步增加P含量, 催化剂的弱酸量也迅速减少. TPO等分析结果表明, 积碳是导致催化剂失活的主要原因. 5% P改性的HZSM-5催化剂由于其强酸位的消失, 在催化反应中表现出更好的稳定性(与未改性的HZSM-5相比). IR结果显示, 随着P含量的增加, 催化剂的L酸量迅速减少, 而B酸量变化相对缓慢. 结合³¹P MAS NMR, NH₃-TPD及IR表征结果, 提出了P改性对HZSM-5酸性修饰的可能机理.

关键词: HZSM-5分子筛; 磷改性; 酸性; 积碳; 二甲醚水蒸气重整; 制氢

收稿日期: 2015-03-21. 接受日期: 2015-04-24. 出版日期: 2015-08-20.

*通讯联系人. 电话: (022)27892275; 电子信箱: mengm@tju.edu.cn

[#]通讯联系人. 电话: (022)27405297; 电子信箱: tianye@tju.edu.cn

基金来源: 国家自然科学基金(21276184, U1332102, 21476160); 高等学校博士学科点专项科研基金(20120032110014); 天津市自然科学基金(12JCYBJC14000, 15JCZDJC37400); 中国大学学科人才引进计划(B06006).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).