RESEARCH ARTICLE

The effect of doping and steam treatment on the catalytic activities of nano-scale H-ZSM-5 in the methanol to gasoline reaction

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Abstract In the transformation of methanol to gasoline (MTG), the selectivity to gasoline and the aromatic content in the produced gasoline are important factors. The catalytic activities of steam-treated and non-steam-treated nano-scale H-ZSM-5 (NHZ5) catalysts impregnated with Ag(I), Zn(II) or P(V) have been investigated in a continuous flow fixed bed reactor. The NH_3-TPD results showed that after impregnation, the Ag/NHZ5, Zn/NHZ5 and P/NHZ5 catalysts contained comparatively more strong, medium-strong and weak acid sites, respectively. Treatment with steam decreased the number of acid sites in all the catalysts, but the pore volumes in the catalysts were larger which improved carbon deposition resistance resulting in prolonged lifetimes. After 6 h of MTG reaction, the selectivity to gasoline for the steam-treated catalysts, Ag_{H_2O}/NHZ5, Zn_{H_2O}/NHZ5 and P_{H_2O}/NHZ5 were 70.5, 68.4 and 68.7 wt-%, respectively, whereas their respective aromatic contents in the produced gasoline were 61.9, 55.4 and 39.0 wt-%. Thus P_{H_2O}/NHZ5 is the most promising catalyst for MTG applications which can meet the China IV gasoline standard that the amount of aromatics in gasoline should be less than 48 wt-%.

Keywords MTG, nano-scale H-ZSM-5, steam treatment, gasoline, selectivity to gasoline

1 Introduction

Petroleum, natural gas and coal are the primary sources of energy in the world today and they account for about 80%

of global energy consumption [1]. With the continuous increase of motor vehicles and the rapid development of the global economy, the worldwide demand for energy is growing fast. One method to help to solve these energy demands is to develop new energy resources from non-fossil fuel sources such as methanol [2]. Methanol can be synthesized via the Lurgi and Imperial Chemical Industries (ICI) processes at low pressures from synthesis gas (H_2 and CO), which is obtained from biomass [3]. The produced methanol can then be further converted to high octane gasoline using the methanol to gasoline (MTG) technology [4]. The gasoline synthesized from the MTG process not only has a high octane value, but also contains low amounts of undesirable materials like chlorine and sulfur. The selection of an efficient catalyst is key for the MTG process. The H-ZSM-5 catalyst has attracted a great deal of attention since Mobil developed the MTG process with this catalyst in the 1970s [5]. The three-dimensional network in H-ZSM-5 is composed of 10 ring channels running parallel (5.6 nm × 5.3 nm), and these are intersected by 10 sinusoidal ring channels (5.5 nm × 5.1 nm) [6]. This catalyst has been widely used for converting methanol to olefins and aromatics and it produces gasoline with high octane numbers.

The crystal size of the zeolite is an important factor in the transformation of methanol to gasoline [7]. When the crystal size of H-ZSM-5 catalyst is reduced to the nano-scale, the catalyst not only has a high activity and a good stability, but also it effectively alleviates carbon deposition on the active sites in H-ZSM-5 [8]. Firoozi et al. [9] showed that nano-sized H-ZSM-5 (NHZ5) has the higher activity and stability than micro-sized H-ZSM-5 in the transformation of methanol to propane and propylene (MTP). Saxena et al. [10] also found that the gasoline yield increased three fold for NHZ5 compared with that for the

micro-sized H-ZSM-5. There has been much effort devoted to improving the catalytic activity and the carbon deposition resistance of MTG catalysts [11–13]. Loading H-ZSM-5 catalysts with metal or non-metal species generally improves their catalytic activity. For example, Ono et al. [14] showed that a H-ZSM-5 catalyst loaded with Zn(II), prepared via an ion-exchange method, had enhanced selectivity to aromatics during the conversion of methanol. Li et al. [15] deposited $Ga(NO_3)_3$ on H-ZSM-5 and found that the selectivity to aromatics and C_{5+} aliphatics increased during the conversion of methanol. Dyballa et al. [16] reported that a H-ZSM-5 catalyst impregnated with $NH_4H_2PO_4$ enhanced the selectivity to C_2-C_4 alkenes. In addition, introduction of metal and non-metal species also influences the acidity of H-ZSM-5 which can enhance the formation of target compounds [17]. The micropores in pure H-ZSM-5 give rise to diffusion limitations, which results in coking [18]. Several modification methods including steaming and chemical treatments have been used to improve the carbon deposition resistance of H-ZSM-5 catalysts [19]. Aramburo et al. [20] showed that a mild steam treatment of H-ZSM-5 at 500 °C prolonged the lifetime of H-ZSM-5, but did not cause changes in activity and selectivity to aromatics in methanol to hydrocarbon (MTH) reactions. Ni et al. [21] used 0.25 mol/L NaOH to modify H-ZSM-5 and observed that the lifetime of the modified zeolite was 2.2 times longer than that of the pure H-ZSM-5 in the MTH reactions. MTG catalysts also need to produce gasoline with an appropriate amount of aromatics. For instance, the state IV gasoline standard in China states that the amount of aromatics in gasoline should be less than 48 wt-% [22] since an excess amount of aromatics makes it difficult to further treat the products [23].

In this work, nano-scale H-ZSM-5 was modified to improve the lifetime and catalytic activity of the catalysts in the MTG reactions. The H-ZSM-5 was doped with $AgNO_3$, $Zn(NO_3)_2$ and $(NH_4)_2HPO_4$ salts and then subsequently treated with steam. The physical properties of the modified catalysts were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM), Brunauer-Emmett-Teller (BET) method and temperature programming desorption of NH_3 (NH_3-TPD). In addition, the conversion efficiency of methanol to gasoline as well as the selectivity to aromatics were investigated for these modified catalysts.

2 Experimental

2.1 Materials

All the reagents were of analytical grade or higher purity and were used without further purification. The $Zn(NO_3)_2$, $AgNO_3$ and $(NH_4)_2HPO_4$ were purchased from Tianjin

Huadong Reagent Factory, Aladdin Reagent Factory and Tianjin Fengchuan Chemical Reagent Factory, respectively. Pseudoboehmite was obtained from Nankai University Catalyst Factory. The NHZ5 zeolite with a Si:Al ratio of 25 was also obtained from Nankai University Catalyst Factory.
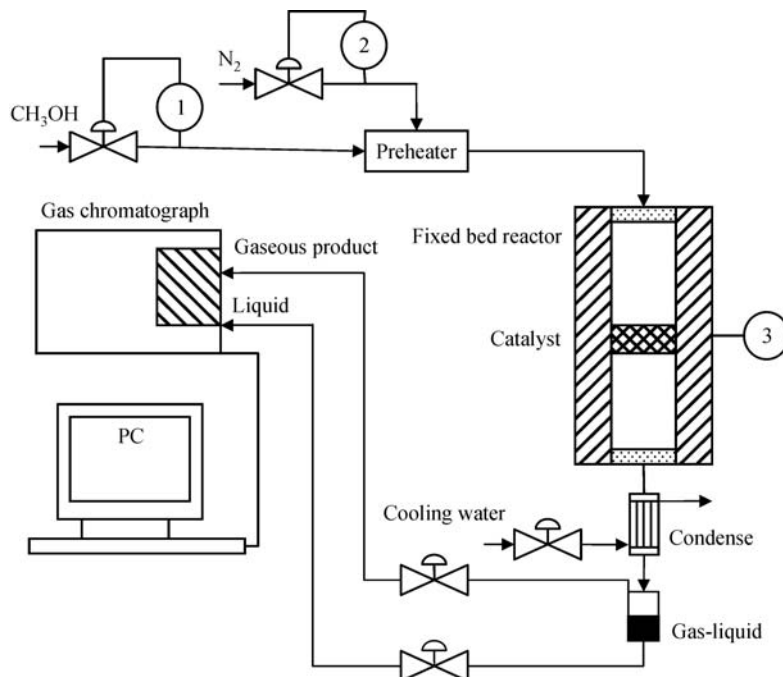
2.2 Preparation of the catalysts

The modified NHZ5 was prepared via an incipient wetness impregnation method. As an example, for the Ag/NHZ5 catalyst (4.0 wt-% Ag_2O), 0.27 g $AgNO_3$ was dissolved in 17.2 g H_2O, and then 10 g NHZ5 was added into the $AgNO_3$ solution. The mixture was then stirred at room temperature for 12 h. After impregnation, the mixture was dried at 110 °C for 12 h, and then calcined in air at 550 °C for 3 h. Finally the Ag/NHZ5 catalyst was mixed with 2.0 g pseudoboehmite binder and then bars (2 mm in diameter) were extruded. The Zn/NHZ5 (4.0 wt-% of ZnO) and P/NHZ5 (4.0 wt-% of P_2O_5) catalysts were prepared using the above procedure except appropriate amounts of $Zn(NO_3)_2$ or $(NH_4)_2HPO_4$ were used instead of $AgNO_3$.

The steam treatment was carried out in a fixed bed reactor heated by an electric furnace. The zeolite sample (20 g) was heated to 500 °C at a heating rate of 10 °C·min^{-1}, and this temperature was maintained for 4 h while a flow of pure steam with a constant mass space velocity of 3 h^{-1} was flowed over the sample. The Ag/NHZ5, Zn/NHZ5 and P/NHZ5 samples treated by steam are denoted as Ag_{H_2O}/NHZ5, Zn_{H_2O}/NHZ5 and P_{H_2O}/NHZ5, respectively.

2.3 Catalytic activities of MTG reaction

The MTG reaction was conducted in a continuous flow fixed-bed reactor (Scheme 1) with a diameter of 15 mm and a length of 1200 mm. The reactor was loaded with 10 g of catalyst and the catalyst was activated by air for 2 h before reaction. In each test, the modified NHZ5 was crushed into 40–60 mesh pieces. The reaction temperature was maintained at 400 °C. Liquid methanol was then introduced into the reactor using a metering pump. The weight hourly space velocity (WHSV) was kept constant at 6.7 h^{-1}. The products from the reactor were passed through the condenser where the liquid and gas products were separated. The gas products were analyzed online by a SP6890 gas chromatograph, equipped with a capillary column (HP-PLOTQ, 30 m × 0.32 mm with a flame ionization detector (FID)). The liquid products were physically separated into water- and oil- phase products, and these products were analyzed by a GC9790 gas chromatograph equipped with a packed-column (GDX-502, 3 m × 2 mm with a thermal conductivity detector (TCD)) and a SP6890 gas chromatograph equipped with

Scheme 1　MTG reaction unit 1, 2: Flow rate controller; 3: Temperature controller

the capillary column (FFAP, 60 m × 0.32 mm with FID), respectively.

2.4　Characterization of the catalysts

XRD analysis was conducted on a D/max-2550 advance diffractometer using Cu Kα (λ = 1.5418 Å) irradiation at 40 kV and 100 mA in the 2θ range of 2°–50° with a scanning rate of 4°/min and a step size of 0.02°. The morphology and elemental distribution of zeolite was determined using a scanning electron microscopy (Nanosem 430, America), coupled with an energy dispersive X-ray spectroscopy analyzer. The NH_3-TPD experiments were carried out on a TP5079 automatic adsorber instrument. The sample was activated by raising the temperature to 550 °C for 1 h and then the sample was cooled to 80 °C. NH_3 adsorption was then carried out before using N_2 (40 mL·min^{-1}) to remove the physically adsorbed NH_3 at 80 °C. After that, the samples were heated from 80 to 650 °C at a rate of 15 °C·min^{-1}. The effluent was continuously monitored by TCD to determine the desorption rate of NH_3. The BET surface areas of the zeolites were determined by a Micromeritics Tristar-3000 apparatus.

3　Results and discussion

3.1　Characterization of the catalysts

The morphologies of the pristine NHZ5 and the doped

samples were characterized by SEM and the results are shown in Fig. 1. The NHZ5 sample contains (Fig. 1(a)) rectangular-shaped particles with lengths of about 100–200 nm. However the particles are agglomerated to form larger particles with diameters of ca. 1 μm. The particles in the doped samples (Figs. 1(b–d)) are composed of larger and more irregular agglomerates. EDX analysis of the samples confirms the presence of Si, Al and O in all samples and the presence of Zn, P and Ag in the three modified samples, respectively (Figs. 1(e–g)). However, the Si:Al ratios from the EDX analysis do not match the known HZSM-5 Si:Al ratio of 25. This is because the addition of the pseudoboehmite binder to the catalysts increased the Al content in each sample.

The crystalline structure of the catalysts was further investigated by the XRD analysis (Fig. 2). The XRD peaks at 2θ = 7.86°, 8.78°, 23.10°, 23.78°, 24.38° and 29.91° can be attributed to the characteristic peaks of NHZ5 (PDF No.44-0003) [24]. The presence of these peaks in all the samples indicates that the crystalline structure of the modified NHZ5 did not change after any modification. There are no diffraction peaks detected for Ag_2O, ZnO or P_2O_5 in any of the modified samples. This is because the content of these components is too low to be detected. However, the modifications do cause changes in the peak intensities. The peak intensities of P/NHZ5, Zn/NHZ5 and Ag/NHZ5 are all lower than those in NHZ5 and after the treatment with steam, the peak intensities of the catalysts are even lower. This is due to the extraction of aluminum atoms from the tetrahedral zeolite framework [25].

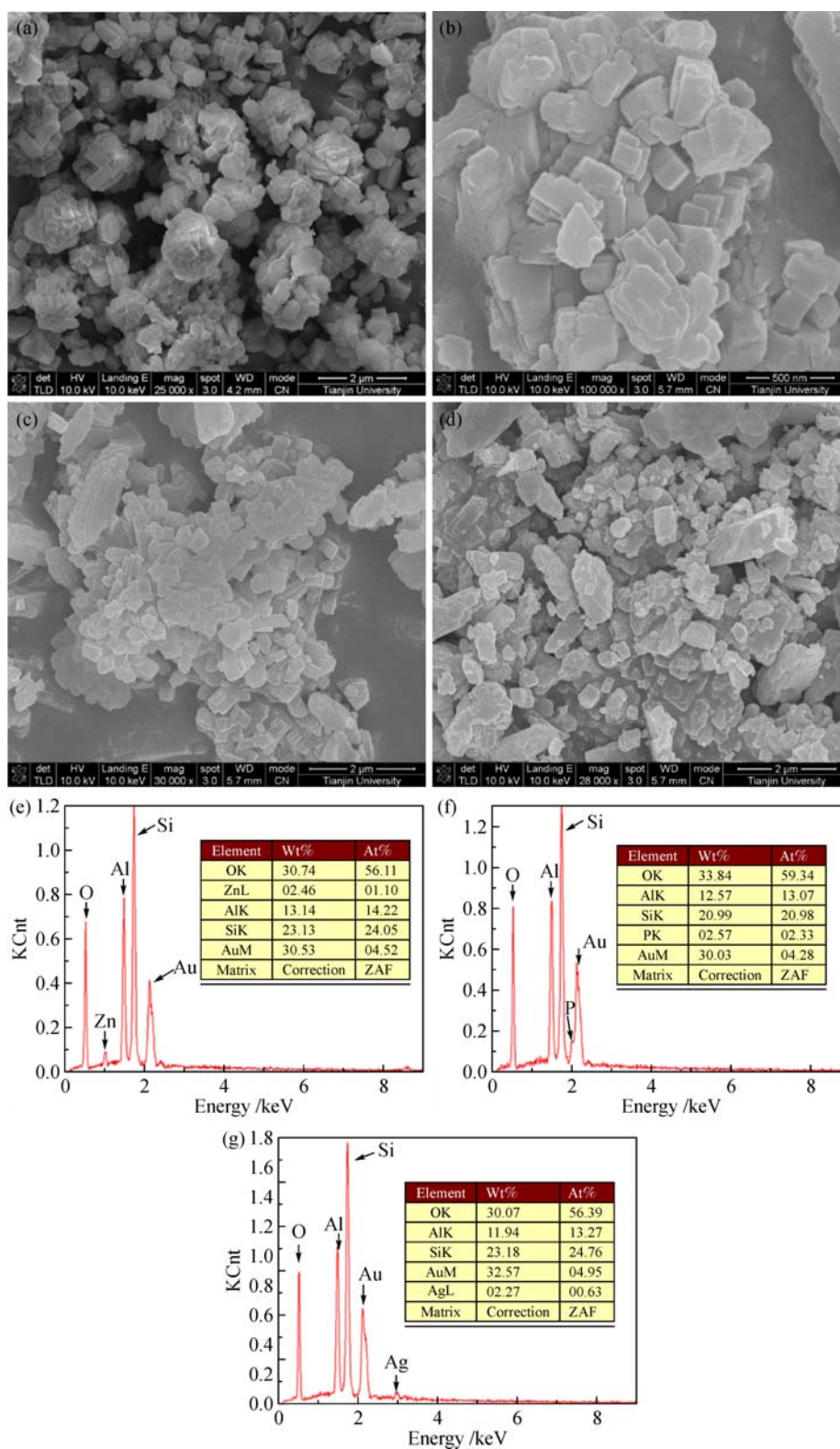A volumetric adsorption method was used to determine

Fig. 1   SEM images of (a) HZSM-5, (b) Zn/NHZ5, (c) P/NHZ5 and (d) Ag/NHZ5, as well as EDX analysis of (e) Zn/NHZ5, (f) P/NHZ5 and (g) Ag/NHZ5
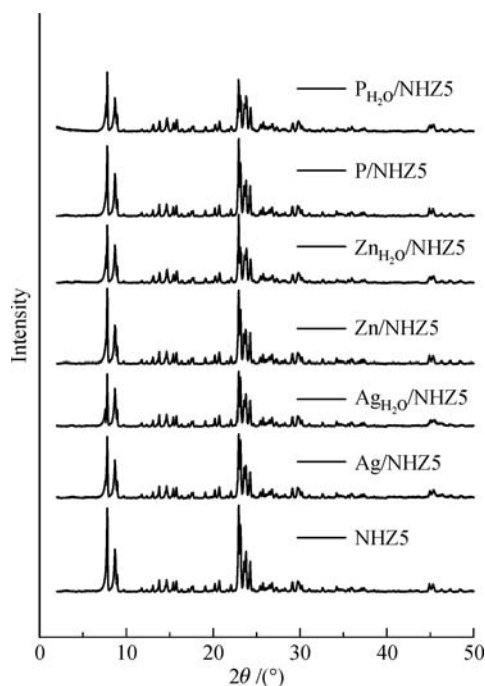
Fig. 2   The XRD patterns of NHZ5 and the modified samples

Table 1   Characterization of the pristine and the modified NHZ5

Samples	$S_{BET}/(m^2 \cdot g^{-1})$		$V_{pore}/(cm^3 \cdot g^{-1})$	
	S_{total}	S_{mseo}	V_{tot}	V_{mseo}
NHZ5	445.4	168.5	0.437	0.321
Ag/NHZ5	387.6	142.7	0.373	0.259
Zn/NHZ5	418.5	152.7	0.402	0.285
P/NHZ5	322.1	102.3	0.244	0.125
Ag_{H_2O}/NHZ5	517.7	201.5	0.767	0.655
Zn_{H_2O}/NHZ5	544.8	221.3	0.834	0.715
P_{H_2O}/NHZ5	556.7	235.8	0.872	0.737

the BET surface area and the pore volume of the catalysts and the results are shown in Table 1. The BET surface area and the pore volume are important factors impacting the lifetime and structural molecule shape selectivity of zeolite. In general, doping metal or non-metal has an effect on the surface area and pore volume due to the pore blockage and metal sintering during the calcination step [26]. When phosphorus was incorporated in NHZ5, the BET surface area decreased from 445.4 to 322.1 $m^2 \cdot g^{-1}$ and the total pore volume decreased from 0.437 to 0.244 $cm^3 \cdot g^{-1}$. However after the steam treatment, both the BET surface area and the total pore volume of P_{H_2O}/NHZ5 increased to 556.7 $m^2 \cdot g^{-1}$ and 0.872 $cm^3 \cdot g^{-1}$, respectively. The same changes were found in other modified zeolite. The pore volume and the BET surface area of Zn/NHZ5 and Ag/NHZ5 both decreased after the NHZ5 was doped with Ag and Zn species and then increased after the steam treatment. For all three samples (P_{H_2O}/NHZ5, Zn_{H_2O}/NHZ5 and Ag_{H_2O}/NHZ5), the volumes of mesopores significantly increased after steam treatment.

In order to investigate changes in the acidity of the catalysts, NH_3-TPD analysis was carried out and the results are shown in Fig. 3. In NHZ5, the peaks at 200 and 420 °C represent the weak and strong acid sites, respectively [29]. In Ag/NHZ5, the weak acid peak shifts to 260 °C and the strong acid peak shifts to 460 °C. The both shifts suggest that some of the H in the zeolite has been displaced by Ag(I) [27]. This results in an increase in the acid strength of Ag/NHZ5 compared to NHZ5. After

treatment by the 500 °C steam, for the Ag_{H_2O}/NHZ5 the low temperature desorption peak is at 230 °C and high temperature desorption is at 430 °C (Fig. 3(a)), indicating that Ag_{H_2O}/NHZ5 is a weaker acid than Ag/NHZ5, but is stronger than NHZ5. This is because some of the Ag(I) in Ag_{H_2O}/NHZ5 is reduced to Ag(0) by the steam [28] which causes a decrease in the acid strength.

The NH_3-TPD results for Zn/NHZ5 show that there are fewer strong acid sites and more weak acid sites in Zn/NHZ5 compared to NHZ5 (Fig. 3(b)).The Zn/NHZ5 curve also has a shoulder at 270 °C which is due to the medium acid sites. These are produced by the reaction of $Zn(NO_3)_2$ with some of the strong acid sites [29]. After Zn/NHZ5 was treated by steam, the position of desorption peaks remains unchanged, suggesting that the addition of Zn improves the hydrothermal stability of the zeolite.

The results for P/NHZ5 (Fig. 3(c)) show that compared with NHZ5, the position of desorption peaks of P/NHZ5 and P_{H_2O}/NHZ5 remains unchanged, suggesting that the type of acid strength of three samples (NHZ5, P/NHZ5 and P_{H_2O}/NHZ5) is the same.

In addition, compared with NHZ5, P/NHZ5 has fewer strong acid sites and significantly more weak acid sites. This is because phosphate reacts with the strong acid sites to generate new weak acid sites [29]. The number of weak acid sites in Ag/NHZ5 almost remains unchanged and the number of strong acid sites increases, whereas the number of both strong and weak acid sites decreases and additional medium strong acid appears. In contrast, Ag/NHZ5 has the most strong acid sites, and Zn/NHZ5 has the most medium strong sites. The number of both weak and strong acid sites decreases in steamed samples compared with doped ones. The catalytic activity of a material is closely related to the type of acid sites it has.

3.2   Catalytic activities of NHZ5 and the doped NHZ5

Figure 4 shows the catalytic activities of the pristine and the doped catalysts for the MTG reaction as a function of time. For all the catalysts, there is initially a relatively stable conversion of methanol but at longer times on
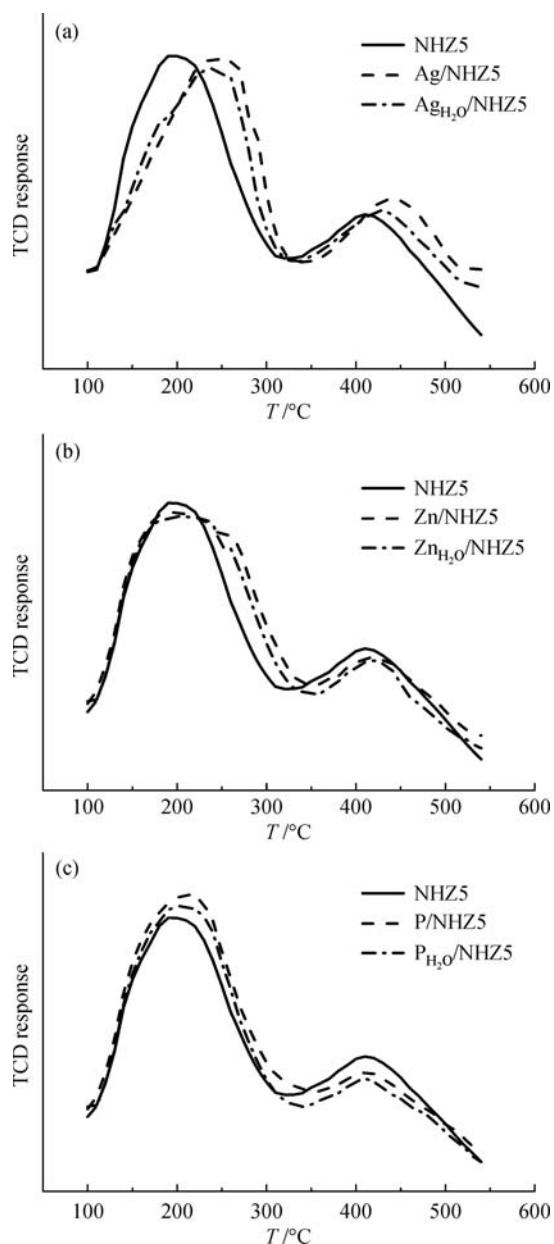
Fig. 3   NH$_3$-TPD patterns of NHZ5 and modified samples

Fig. 4   Methanol conversions over NHZ5 and the doped NHZ5 catalysts as a function of time. Reaction conditions: WHSV, 6.7 h^{-1}; temperature, 673 K; reaction pressure, 0.1 MPa; catalyst loading, 10 g

stream the conversion decreases rapidly, suggesting deactivation of all the catalysts. The methanol conversions over NHZ5, Ag/NHZ5 and Zn/NHZ5 were all more than 94% in the initial stages whereas that over P/NHZ5 was only 88.6%. After 26 h of reaction, the conversions drop to 50.7%, 56.7%, 65.3% and 78.7%, respectively. Ag/NHZ5 and Zn/NHZ5 have higher initial methanol conversions than P/NHZ5 because Ag and Zn increase the acidity of the catalysts more than P does (Fig. 3). The interactions between the strong acid sites and phosphate does not change the acid strength in P/NHZ5. In addition, compared with Ag/NHZ5 and Zn/ NHZ5, P/NHZ5 had the lowest surface area and pore volume (Table 1) which reduces the adsorption rate of methanol onto the acid sites.
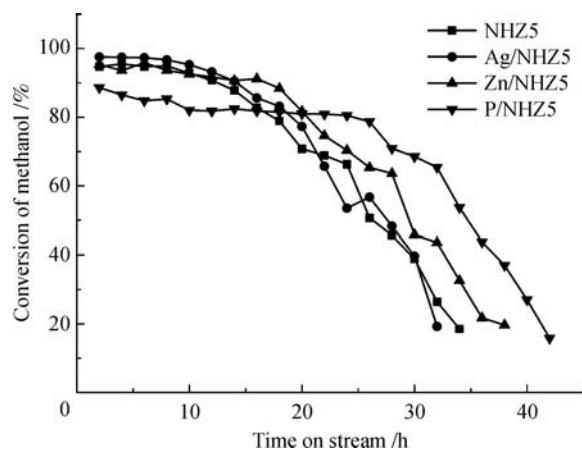
However, as shown in Fig. 4, the lifetime of P/NHZ5 is longer than those of NHZ5, Ag/NHZ5 and Zn/NHZ5. This suggests the modification with phosphate makes the catalyst more stable. Zhang et al. [31] showed that strong acid sites are active for hydrogen transfer reactions and they accelerate the formation of aromatics and coke. Compared to NHZ5, P/NHZ5 has fewer strong acid sites and more weak acid sites (Fig. 3(c)) and these are responsible for the higher catalyst stability of P/NHZ5.

Table 2 shows the distribution of products produced over NHZ5, Ag/NHZ5, Zn/NHZ5 and P/NHZ5 at 6 h. Compared with NHZ5, the selectivity to aromatic hydrocarbons significantly increased to 53.5% and 45.6% for the Ag/NHZ5 and Zn/NHZ5 catalysts, respectively, whereas the selectivity to light hydrocarbon (C$_2$-C$_4$) decreases to 28.8% and 33.5%, respectively (Table 2). On the other hand, the selectivity to aromatic hydrocarbons for P/NHZ5 decreased to 14.3%, but the selectivity to light hydrocarbon (C$_2$-C$_4$) increased to 59.7%. The selectivity to aromatic hydrocarbons therefore follows the order Ag/NHZ5 > Zn/NHZ5 > NHZ5 > P/NHZ5, whereas the selectivity to light hydrocarbons follows the order P/NHZ5 > NHZ5 > Zn/NHZ5 > Ag/NHZ5.
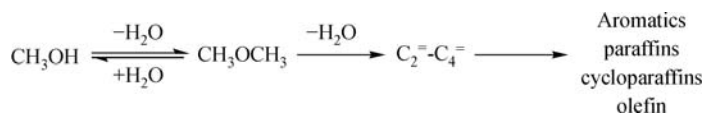
The mechanism for the formation of various types of hydrocarbons in MTG processes is summarized in Scheme 2 [32]. First some of the methanol is converted to dimethyl ether (DME) and H$_2$O, and the strong acid sites (Bronsted acid) on H-ZSM-5 further facilitates dehydration of DME to alkenes. After that, a series of reactions including cyclization, oligomerization and hydrogen transfer reactions take place to transform the produced alkenes to paraffins and aromatics, which are the primary products of gasoline.

As seen from Table 2, the aromatic selectivity over Ag/NHZ5 is higher than those of the other catalysts. This is because Ag(I) reacts with the strong acid sites to generate

Table 2   Product distribution over the pristine and the modified NHZ5[a]

| Samples	Yields /%								SOA /wt-%	SOG /wt-%	COA /wt-%
	CH_4	C_2-C_4	C_{5+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	$C_{10}H_{14}$			
NHZ5	2.1	38.0	28.4	0.4	3.9	13.5	9.4	5.6	32.8	61.2	50.7
Ag/NHZ5	2.4	28.8	15.3	1.3	5.5	12.8	25.4	8.5	53.5	68.4	76.2
Zn/NHZ5	1.9	33.5	18.7	0.9	6.8	16.2	13.4	8.3	45.6	64.3	69.1
P/NHZ5	1.5	59.7	24.1	0.5	1.8	6.5	3.3	2.2	14.3	38.4	36.3

a) SOA, SOG and COA represent the selectivity to aromatics, the selectivity of gasoline, and the content of aromatics in gasoline, respectively

$$CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftharpoons}} CH_3OCH_3 \xrightarrow{-H_2O} C_2^= \text{-} C_4^= \longrightarrow \begin{array}{l} \text{Aromatics} \\ \text{paraffins} \\ \text{cycloparaffins} \\ \text{olefin} \end{array}$$

Scheme 2   Reaction mechanism of MTG

even stronger acid sites on the catalyst. When $Zn(NO_3)_2$ is introduced into the zeolite framework, it interacts with a fraction of the strong acid to form medium-strong acid sites. Biscardi et al. [33] suggested that introducing Zn $(NO_3)_2$ into H-ZSM-5 enhances the dehydrognation reaction and facilitates the formation of aromatics and C_{5+} aliphatics. The selectivity to aromatics over P/NHZ5 is lower than those over the other modified catalysts whereas the selectivity to C_{5+} aliphatics over P/NHZ5 is higher than those over the other modified catalysts. The reduction of the strong acid sites in P/NHZ5 was more significant than those in Ag/NHZ5 and Zn/NHZ5, indicating that the phosphate reacts with the strong acid sites to generate weak acid sites. Weak acid sites inhibit the hydrogen transfer reaction between alkenes and aliphatics over P/NHZ5 resulting in the formation of fewer aromatics and more aliphatics [34]. On the other hand, phosphate reduces the pore volumes in the zeolite (from 0.321 to 0.125 $cm^3 \cdot g^{-1}$, Table 1) [29] which limits diffusion of the reactants and decreases the selectivity to aromatics.

Figure 5 shows the selectivity to aromatics for the pristine and the doped catalysts as a function of time. The catalytic activities of all catalysts gradually decreased with time which is due to the accumulation of carbon deposits. Compared with NHZ5, both Ag/NHZ5 and Zn/NHZ5 had significantly better selectivity to aromatics in the first 2 h of reaction (30.5% *versus* 50.6% and 45.2%, respectively). In contrast, the selectivity to aromatic hydrocarbons over P/NHZ5 was only 13.8% in the first 2 h. The selectivity to aromatic hydrocarbons follows the order Ag/NHZ5 > Zn/NHZ5 > NHZ5 > P/NHZ5. After 30 h, the selectivity to aromatics dropped to 33.6% and 29.6% for Ag/NHZ5 and Zn/NHZ5 respectively and was only 9.0% for P/NHZ5. As explained earlier, the lower performance for P/NHZ5 is due to the smaller pores and the presence of more weak acid sites.

Figure 6 shows the selectivity to gasoline for the catalysts as a function of time. In the first two hours of
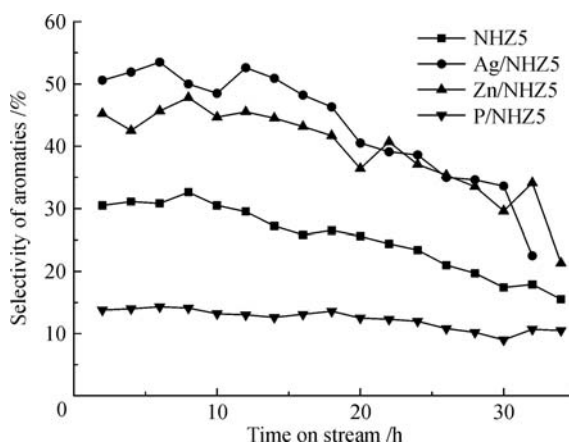
Fig. 5   The selectivity to aromatics with time over NHZ5 and the doped NHZ5. Reaction conditions: WHSV, 6.7 h^{-1}; temperature, 673 K; reaction pressure, 0.1 MPa; catalyst loading 10 g
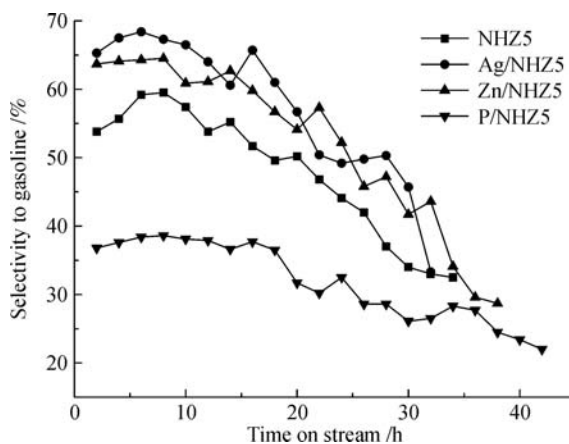
Fig. 6   The selectivity to gasoline with time over NHZ5 and the doped NHZ5. Reaction conditions: WHSV, 6.7 h^{-1}; temperature, 673 K; reaction pressure, 0.1 MPa; catalyst loading 10 g

reaction, the selectivity to gasoline over Zn/NHZ5 and Ag/NHZ5 are comparable (63.7% and 65.3%, respectively) whereas that for P/NHZ5 is only 36.8%. The selectivity to gasoline therefore follows the order Ag/NHZ5 > Zn/NHZ5 > NHZ5 > P/NHZ5. The poor performance of P/NHZ5 suggests the importance of the strong acid sites (which are comparative fewer in P/NHZ5) for the hydrogen transfer reactions since these facilitate the formation of aromatics [31] which account for most of the gasoline's compositions. Also the loading of phosphate narrows the pore volumes, which also inhibits the formation of aromatics. As with the aromatics, the selectivity to gasoline decreased with time on stream for all the catalysts and at 30 h was only 45.7%, 41.7% and 26.1% for Ag/NHZ5, Zn/NHZ5 and P/NHZ5, respectively.

3.3 Activities of the steam treated catalysts

Figure 7 shows the activities of the pristine and the steam-treated NHZ5 for the methanol conversion reaction as a function of time. For NHZ5, the conversion of methanol was more than 94.7% in the first 2 h and then began to drop after 8 h of reaction. For Ag_{H_2O}/NHZ5, Zn_{H_2O}/NHZ5 and P_{H_2O}/NHZ5, the conversions of methanol was over 99.0% in the first 2 h and then started to decrease rapidly after 34,
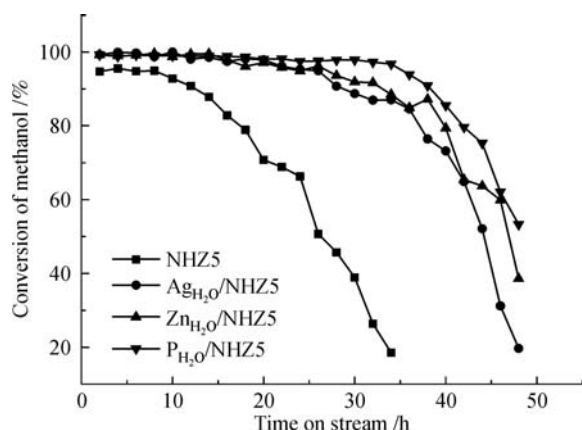

Fig. 7 Methanol conversion with time over the pristine and the steam modified NHZ5 catalyst. Reaction conditions: WHSV, 6.7 h^{-1}; temperature, 673 K; reaction pressure, 0.1 MPa; catalyst loading, 10 g

26 and 26 h, respectively. Compared with NHZ5, the lifetimes of Ag_{H_2O}/NHZ5, Zn_{H_2O}/NHZ5 and P_{H_2O}/NHZ5 were increased by 325%, 225% and 225% (prolonged by 26, 18 and 18 h), respectively. Lucas et al. [34] concluded that treating zeolite with steam generates a secondary pore structure which effectively enhances the deactivation behavior by reducing the diffusion resistance. As shown in Table 1, the pore volumes of Ag_{H_2O}/NHZ5, Zn_{H_2O}/NHZ5 and P_{H_2O}/NHZ5 did increase after the steam treatment. The improved lifetimes of the steam-treated samples can therefore be attributed to the steam treatment creating more resistance to carbon deposition. The initial conversion of methanol over P_{H_2O}/NHZ5 is higher than that over P/NHZ5. This is expected since P_{H_2O}/NHZ5 has a higher surface area and mesoporosity than P/NHZ5, which increases the diffusion rate and speeds up the adsorption and desorption processes of methanol on the zeolite. This result indicates that the pore structure has a more important effect on catalytic activity than the strength of the acid sites.

Table 3 shows the distribution of the products in the effluents at 6 h. The selectivity to gasoline over Ag_{H_2O}/NHZ5 and Zn_{H_2O}/NHZ5 are similar to those for Ag/NHZ5 and Zn/NHZ5 (68.4% vs. 70.5% and 64.3% vs. 68.4%), respectively, whereas their selectivity to aromatics decreased to 44.8% and 38.9% (compared to 53.5% and 45.6%) and their selectivity to C_{5+} aliphatics increased to 25.7 % and 29.5% (compared to 15.3% and 18.7%), respectively. The lower aromatization reactivity of Ag_{H_2O}/NHZ5 and Zn_{H_2O}/NHZ5 is mainly due to the dealumination of NHZ5 that occurs during the steam treatment, which reduces the number of strong acid sites on Ag_{H_2O}/NHZ5 and Zn_{H_2O}/NHZ5 [25]. The selectivity to gasoline over P_{H_2O}/NHZ5 increased to 68.7% (compared to 38.4% for P/NHZ5). This is due to the formation of more C_{5+} aliphatics by the P_{H_2O}/NHZ5 catalyst. The aromatic content in the gasoline produced over P_{H_2O}/NHZ5 was 39.0%, which meets the requirements of the China IV gasoline standard.

Figure 8 shows the selectivity to aromatics of the pristine and the steam-treated NHZ5 as a function of time. In the initial stages of the reaction, the selectivity to aromatic hydrocarbons follows the order Ag_{H_2O}/NHZ5 > Zn_{H_2O}/NHZ5 > NHZ5 > P_{H_2O}/NHZ5. Even though the

Table 3 Product distribution over the pristine and the steam modified NHZ5[a]

Samples	Yields /%								SOA /wt-%	SOG /wt-%	COA /wt-%
	CH_4	C_2-C_4	C_{5+}	C_6H_6	C_7H_8	C_8H_{10}	C_9H_{12}	$C_{10}H_{14}$			
NHZ5	2.1	38.0	28.4	0.4	3.9	13.5	9.4	5.6	32.8	61.2	50.7
Ag_{H_2O}/NHZ5	2.2	26.9	25.7	0.9	5.2	11.2	18.7	7.8	44.8	70.5	61.9
Zn_{H_2O}/NHZ5	2.0	29.3	29.5	0.7	5.7	14.3	11.3	6.9	38.9	68.4	55.4
P_{H_2O}/NHZ5	1.1	29.2	41.2	0.4	3.2	11.0	8.7	4.2	27.5	68.7	39.0

a) SOA, SOG and COA represent the selectivity to aromatics, the selectivity of gasoline, and the content of aromatics in gasoline, respectively
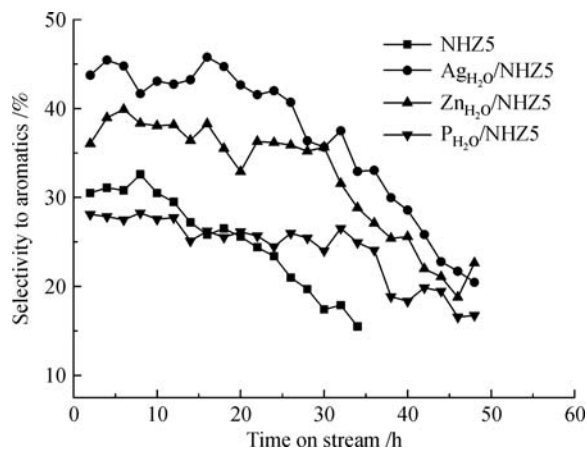
Fig. 8 The selectivity to aromatics with time over NHZ5 and the steamed NHZ5. Reaction conditions: WHSV, 6.7 h^{-1}; temperature, 673 K; reaction pressure, 0.1 MPa; catalyst loading, 10 g

Fig. 9 The selectivity to gasoline with time over NHZ5 and the steamed NHZ5. Reaction conditions: WHSV, 6.7 h^{-1}; temperature, 673 K; reaction pressure, 0.1 MPa; catalyst loading, 10 g

aromatic selectivity over Ag_{H_2O}/NHZ5 and Zn_{H_2O}/NHZ5 are lower than those over Ag/NHZ5 (43.8% vs. 50.6%) and Zn/NHZ5 (36.0% vs. 45.2%) (Fig. 5) in the first 2 h, they are still significantly higher than that over the pristine NHZ5. In addition, the lifetimes of Ag_{H_2O}/NHZ5 and Zn_{H_2O}/NHZ5 are much longer than that of NHZ5. On the other hand, the selectivity to aromatics over P_{H_2O}/NHZ5 in the first 2 h is much higher than that for P/NHZ5 (28.1% vs. 13.8%). Even though the dealumination in NHZ5 caused by the steam results in a decrease in the number of strong acid sites [25], the selectivity to aromatics still increased because the pore volume has a greater impact on the aromatic selectivity than the strong acid sites. Abubakar et al. [35] also reported that the dealumination of H-ZSM-5 resulted in an increased selectivity to aromatics. The steam-treated NHZ5 maintains a sufficient number of strong acid sites and acidic strength for the formation of aromatics. At 40 h, the selectivity to aromatics over Ag_{H_2O}/NHZ5, Zn_{H_2O}/NHZ5 and P_{H_2O}/N HZ5 decreased to 28.6% and 25.6%, and 18.3%, respectively.

Figure 9 shows the selectivity to gasoline of the pristine and the steam-treated NHZ5 as a function of time. The selectivity to gasoline over both Ag_{H_2O}/NHZ5 and Zn_{H_2O}/NHZ5 are similar to Ag/NHZ5 and Zn/NHZ5 and reached 68.9% and 66.9% in the first 2 h, respectively. The selectivity to gasoline over P_{H_2O}/NHZ5 is the highest and reach 71.6% compared to only 36.8% for P/NHZ5) (Fig. 6). Obviously, the steam treatment has the greatest effect on P/NHZ5. Although the steam-treatment resulted in decreases in the number of acid sites on the catalysts, their selectivity to C_{5+} aliphatic content increased, which is an important factor for high octane gasoline (Table 3). The dealumination after steam-treatment can influence the hydrogen transfer reaction [36], resulting in a higher
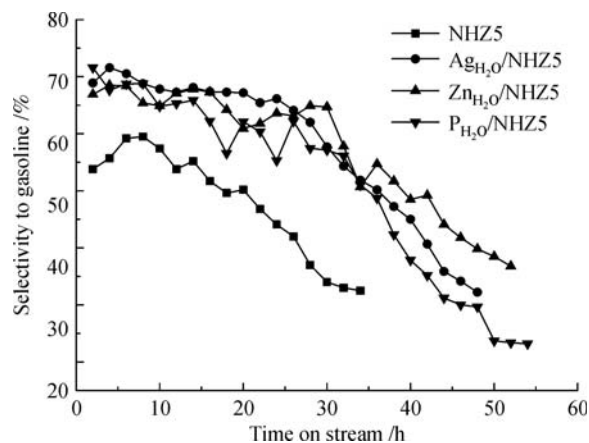
selectivity to C_{5+} aliphatics and a lower selectivity to aromatics. In addition, the higher surface area and mesoporosity after stream treatment also facilitate the formation and diffusion of C_{5+} aliphatics. After 40 h, the selectivity to gasoline over Ag_{H_2O}/NHZ5, Zn_{H_2O}/NHZ5 and P_{H_2O}/NHZ5 decreased to 45.0%, 48.5% and 37.9% respectively. The aromatic content in the gasoline produced over P_{H_2O}/NHZ5 meets the requirement of the China IV gasoline standard (aromatics < 48%).

4   Conclusions

The catalytic activities of the nano-scale H-ZSM-5 catalyst modified with Ag(I), Zn(II), P(V), and treated by steam have been investigated in a continuous flow fixed bed reactor. The XRD results indicated that the crystalline structure of samples did not change after doping. The NH$_3$-TPD results indicated that after doping, Ag/NHZ5 contained more strong acid sites and P/NHZ5 contained more weak acid sites. The selectivity to gasoline depended on the type of acid sites and followed the order Ag/NHZ5 > Zn/NHZ5 > NHZ5 > P/NHZ5, suggesting the importance of the strong acid sites in the aromatization and alkylation reactions. The lifetimes of the Ag/NHZ5 and Zn/NHZ5 catalysts were not prolonged by the doping and the aromatic content in the gasoline produced over these catalysts does not meet China IV standard.

Steam treatment of Ag/NHZ5 and Zn/NHZ5 did not significantly change their selectivities to gasoline but it did have a significant effect on P/NHZ5 (SOG P_{H_2O}/NHZ5 = 71.6% vs. P/NHZ5 = 36.8% in the first 2 h of reaction). Steam treatment also produced a remarkable improvement of C_{5+} aliphatics content in the gasoline produced by all the catalysts. The aromatic contents in the gasoline produced over P_{H_2O}/NHZ5, Zn_{H_2O}/NHZ5 and P_{H_2O}/NH

Z5 were 61.9, 55.4 and 39.0 wt-%, respectively, indicating that only the gasoline produced over P_{H_2O}/NHZ5 can meet the China IV aromatic gasoline standard (less than 48 wt-%). The lifetimes of the steam-treated catalyst were significantly longer than that of NHZ5 with improvements of 325%, 225% and 225% (prolonged by 26, 18 and 18 h) for Ag_{H_2O}/NHZ5, Zn_{H_2O}/NHZ5 and P_{H_2O}/NHZ5 respectively. The NH_3-TPD results indicated that an increase in the pore volumes after steam-treatment improved the carbon deposition resistance of the catalysts and therefore prolonged their lifetimes. Given the low cost of P_{H_2O}/NHZ5, this catalyst should be applicable to the large-scale production of high quality gasoline.

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