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### Non-mercury catalytic acetylene hydrochlorination over the NH<sub>4</sub>F-Urea-modified Pd/HY catalyst for vinyl chloride monomer production

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Pd/HY zeolite catalyst modified by ammonium fluoride and urea (Pd/NH<sub>4</sub>F-Urea-HY) was efficient applied in acetylene hydrochlorination reaction and had an enhanced catalytic performance compared to untreated Pd/HY catalyst, which was attributed to the presence of ammonium fluoride and urea partly inhibited carbon deposition and Pd<sup>2+</sup> reduction.

Vinyl chloride monomer (VCM) is primarily manufactured from a cetylene hydrochlorination by the mercuric chloride (HgCl<sub>2</sub>) catalysts, which are highly toxic and cause serious environmental problems<sup>1</sup>. In addition, mercury resources are in short supply and the application of mercuric chloride will be forbidden over the world in the future<sup>2</sup>. Hence, it is imperative to explore efficient nonmercuric catalysts for the acetylene hydrochlorination reaction.

At present, More than 30 non-mercuric metal chlorides (including Au<sup>III</sup>, Pt<sup>II</sup>, Pd<sup>II</sup>, Rh<sup>III</sup>, Ru<sup>III</sup>, Bi<sup>III</sup>, Cu<sup>II</sup>, etc.) supported carbon have been carried out for acetylene hydrochlorination and AuO<sub>3</sub> may be the best for this process<sup>3</sup>. Up to now, most researches have demonstrated that metal chloride catalysts were often encountered with rapid deactivation problems because that some metallic cations were readily reduced to zero-valent metal by acetylene during the reaction<sup>4-6</sup>. But for Pd-based catalysts, which also could obtain the good catalytic activity in acetylene hydrochlorination, the valence states of Pd species and their changes during the reaction were still not dear<sup>5d,7</sup>. In addition, the weak interaction between active species and supports was also resulted in loss of activities of catalysts<sup>4a,4b,4e,4f</sup>. To address the problem, many other (SiO<sub>2</sub>, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, CNTs, etc.) supports have been investigated for acetylene hydrochlorination in recent years besides activated  $\mathsf{carbon}^{\mathsf{5b},\mathsf{6a-6d}},\!\mathsf{which}$  is the most common support in reaction and easily crushed and pulverized under reaction conditions<sup>5d</sup>. For example, the Au-Bi/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst was reported and it had the stronger mechanical strength and regeneration capacity than those of the traditional Au-based/active carbon catalyst<sup>6d</sup>. These previous work mentioned above inspired us to consider that the support might play a notable role in the overall reaction. Nowadays, zeolites

have been applied as catalyst supports for various catalytic reactions because of their unique properties, such as high surface area, well-defined microporosity, high thermal stability and controlled density of acid sites<sup>6e</sup>. Compared with  $SiO_2$ ,  $TiO_2$  supports<sup>4a</sup> in the acetylene hydrochlorination reaction, the initial activity and selectivity of zeolites catalysts were higher but they were still easily deactivated for the carbon deposition and the Pd species loss<sup>5d</sup>. In our work, we have reported the Pd/HY catalyst could be applied in acetylene hydrochlorination reaction and the appropriate modification could affect the activities of catalysts, but the changes of Pd states during the reaction were still not discussed<sup>7</sup>. These results have promoted us to study the states of Pd species in depths in the Pd/HY catalyst for acetylene hydrochlorination.

Meanwhile, many nitrogen or phosphorus-doped Au/AC catalysts have been reported recently and N,P-doped carbon supports could activate a cetylene and HC molecules, which was believed to stabilize metal components<sup>5a-5c</sup>. Recently, non-metallic catalysts including carbon nitride have been developed as new catalytic systems for a cetylene hydrochlorination<sup>5b,6c</sup>. Despite the significant improvements for this transformation, it remained a great challenge to develop a new, active and stable catalytic system for a cetylene hydrochlorination. So in this work, an improved Pd/HY zeolite catalyst modified by a mmonium fluoride and urea had been synthesized by ultrasonic wave-assisted techniques, and its catalytic activity for a cetylene hydrochlorination had been studied compared to untreated the Pd/HY catalyst. Finally, the effects of a mmonium fluoride and urea modification on the catalyst performance were also investigated.

The catalytic performances of the Pd/HY and Pd/NH<sub>4</sub>F-Urea-HY catalysts were shown in Fig. 1. The acetylene conversion of the Pd/HY catalyst decreased from 98% to 19% after running for 2.5 h, indicating that Pd/HY was rapidly deactivated under this reaction condition. As a comparison, the Pd/NH<sub>4</sub>F-Urea-HY catalyst showed a better stability (the acetylene conversion was over 99% in running for 8 h and decreased 33% after 12 h), which was also much better than single NH<sub>4</sub>F or urea modified Pd/HY catalysts (from Fig.S1). These facts revealed that the Pd/NH<sub>4</sub>F-Urea-HY catalyst had much slower deactivation rate than that of the Pd/HY catalyst, and both

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the catalytic activity and stability of the Pd/  $NH_4F$ -Urea-HY catalyst were enhanced in the acetylene hydrochlorination reaction.

From XRD patterns (Fig. 2), the characteristic peaks at 6.3°, 15.9° and 24.0° were known to the reflection of the (111), (133) and (266) planes of Y-zeolite lattices<sup>8</sup> and the NH<sub>4</sub>F-Urea-HY support kept few changes about the diffraction peaks. Moreover, the Pd/HY catalysts were better crystallized than the Pd/NH<sub>4</sub>F-Urea-HY catalysts. Apart from the diffraction peaks of the zeolite matrix, no visible characteristic peaks of Pd species were identified in Pd-based catalysts, regardless of great efforts (adding greater Pd concentration) were done, indicating that high partide dispersion<sup>4b,5d</sup> or Pd species were supposed to be of a small partide size<sup>9</sup>. According to TEM results (from Fig. S2), It was found that the Pd dispersion was changed by NH<sub>4</sub>F and urea modification and the estimated size of detected Pd particles was about 5-20 nm in Pd/NH<sub>4</sub>F-Urea-HY catalyst.

Pd<sup>0</sup> under the reaction conditions, resulting the the teactive to a solution of the teactive teacher and the teacher and Pd-based catalysts. Comparing with the Pd/HY catalyst, the binding energy of Pd 3d<sub>5/2</sub> of the fresh Pd/NH<sub>4</sub>F-Urea-HY catalyst showed the obvious negative shift (about 0.8 eV) and the interaction between Pd and NH<sub>4</sub>F-Urea-HY support was a considerable reason. In combination with the catalytic performance of catalysts (Fig.1), it was reasonable to condude that the enhanced catalytic performance in the Pd/NH<sub>4</sub>F-Urea-HY catalyst was attributed to the presence of nitrogen and fluorine (from Fig. S3), which affected the interaction between Pd and NH<sub>4</sub>F-Urea-HY support, increased the electron density of Pd<sup>2+</sup> and inhibited the Pd<sup>2+</sup> reduction. Besides the surface characterization of XPS analysis, the actual Pd content in the fresh and used Pd-based catalysts were also measured by ICP in Table 1. It was obviously indicated that the loss ratio of Pd in the Pd/HY catalyst was 47.4% and that in the Pd/NH<sub>4</sub>F-Urea-HY catalyst was 44.7% in the reaction process. It was suggested that Pd loss remained one reason for catalyst deactivation and the Pd catalyst with the NH<sub>4</sub>F-Urea-modified HY support could inhibit Pd loss.

Pd/NH₄F-Urea-HY catalyst. It was likely that Pd<sup>2+</sup> was reduced into







The XPS region spectra of Pd 3d in the fresh and used Pd-based catalysts were measured to further investigate the valence state and relative amount of the active Pd species in Fig. 3. It should be noted that all of the Pd (3d) signals had been divided into two components responding to metallic Pd<sup>0</sup> and Pd<sup>2+</sup> species<sup>10</sup>. Curve fitting were employed to analyze the ratio of Pd<sup>0</sup> and Pd<sup>2+</sup> species and the results were calculated in Table 1. According to the data, the relative content of Pd<sup>2+</sup> was 42.5% presented in the fresh Pd/HY catalyst, and the relative content of Pd<sup>2+</sup> was 49.4% observed in the fresh Pd/NH<sub>4</sub>F-Urea-HY catalyst. However, the relative content of Pd<sup>2+</sup> was 26.9% for the used Pd/HY and 37.6% for the used



Fig.3 XPS Pd 3d profiles of the Pd-based catalysts Table 1 The relative content of Pd species in the fresh and used catalysts determined by XPS, and the actual Pd content determined by ICP.

Catalysts	Pd <sup>0</sup> (area%)		Pd <sup>2+</sup> (area%)	
Fresh Pd/HY	57	7.5	42.5	
Used Pd/HY	73.1		26.9	
Fresh Pd/NH <sub>4</sub> F-Urea-HY	50.6		49.4	
Used Pd/ NH <sub>4</sub> F-Urea-HY	62.4		37.6	
Catalysts	Total Pd (wt%)		Loss ratio of Pd	
catalysis	Fresh	Used	- (%)	
Pd/HY	0.95	0.50	47.4	
$Pd/NH_4F$ -Urea-HY	1.23	0.68	44.7	

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SEM results (from Fig. S4) indicated that the presence of NH₄F and urea did not changed the surface morphology of the HY support and the agglomeration was occurred in used Pd NH<sub>4</sub>F-Urea-HY catalyst. BET results (Table 2) showed that BET surface areas of the fresh Pd/HY and Pd/NH<sub>4</sub>F-Urea-HY catalysts were decreased and the average pore diameter of them were increased due to the blocking of pores of Pd addition. After reaction, a significant loss of surface a reas of Pd/HY (from 333 to 21 m<sup>2</sup>/g) and Pd/NH<sub>4</sub>F-Urea-HY (from 255 to 39 m<sup>2</sup>/g) might be ascribed to carbon deposition  $\frac{4e,4f}{2}$ which were certified by TGA results. It can be seen from Fig.4, neither the fresh nor used Pd-based catalysts had a visible loss of mass before 150 °C, indicating minor water adsorption on the surface of catalysts. In the range of 150-450 °C, the fresh Pd/HY showed a slow weight loss, reaching 3.85%. While the fresh Pd/NH<sub>4</sub>F-Urea-HY had a significant weight loss (21.10%), which was associated with the loss of frame water and the breakdown of active components linked the Si-O-Si bond. When the temperature above 450 °C, the weight of used Pd/HY (11.70%) and Pd/NH<sub>4</sub>F-Urea-HY (23.21%) catalysts decreased rapidly due to oxidation of carbon deposition. The amount of carbon deposition on the Pd/NH<sub>4</sub>F-Urea-HY catalyst could be calculated as 2.11%, which was less than that in the used Pd/HY catalyst (7.85%)<sup>4a,4b,4f,5d</sup>. Combined with BET and TGA results, it could be inferred the better catalytic performance of the Pd/NH<sub>4</sub>F-Urea-HY catalysts was attributed to inhibiting the carbon deposition.

Samples	<sup>a</sup> S <sub>BET</sub> (m <sup>2</sup> /g)	<sup>b</sup> V(cm <sup>3</sup> /g)	۵D(nm)
HY	505	0.11	1.03
NH <sub>4</sub> F-Urea/HY	296	0.28	2.57
Fresh Pd/HY	333	0.23	1.24
Used Pd/HY	21	0.07	2.92
Fresh Pd/NH <sub>4</sub> F-Urea-HY	255	0.20	2.28
Used Pd/NH <sub>4</sub> F-Urea-HY	39	0.06	2.30

<sup>a</sup> Surface area; <sup>b</sup> Total pore volume;<sup>c</sup> Average pore diameter.



Fig.4 TG profiles of Pd-based catalysts.

Generally, the surface functional groups and acidic properties on zeolites can affect the catalytic performance of zeolite-based catalysts<sup>11a-11d</sup>. We compared the FT-IR (Fig.5a) and  $NH_3$ -TPD (Fig.5b)

profiles of Pd-based catalysts. From Fig. 5a, it can be observed that there was no significant band position shift, which That the zeolite framework remained intact after NH₄F and Urea modification. This result supported the earlier dissection on XRD. Compared with the fresh Pd/HY catalyst, the intensities of the hydroxyl groups (including Si-OH, Al-OH and H-bonded hydroxyl groups) at 4000 to 3000 cm<sup>-1</sup> were reduced in the fresh Pd/NH<sub>4</sub>F-Urea-HY catalyst, due to Pd cations interacting with hydroxyl groups of NH<sub>4</sub>F-Urea-HY support<sup>11a-11e</sup>. After reaction, the band at 3450 cm<sup>-</sup> was disappeared due to the formation of carbon deposition coating the effective acidic sites on the catalyst surface, resulting in decreasing the performance of catalyst. NH<sub>3</sub>-TPD images in Fig. 5b could further provide evidence to analyze changes of acidic properties on Pd-based catalysts. Two desorption peaks of ammonia at low (~100 °C) and moderate temperatures (350~500 °C) were ascribed to weak acid sites and media strong acid sites, belonged to the original HY zeolites<sup>11d</sup>. After modification by NH<sub>4</sub>F and Urea, the range of peak corresponds to weak acid sites at around 100 °C from the surface hydroxyl groups shifted to the lower temperature, which were consistent with the FT-IR results discussed previously. Compared with fresh Pd/HY, the media strong acid sites slightly increased, shifting to the higher temperature, and induced a new acid site in the fresh Pd/NH<sub>4</sub>F-Urea-HY, which was a considerable reason for improving the catalytic performance of catalysts.



Fig.5 FT-IR (a) and NH<sub>3</sub>-TPD (b) profiles of Pd-based catalysts.

In summary, we demonstrated the Pd/NH<sub>4</sub>F-Urea-HY catalyst can be effective to apply for a cetylene hydrochlorination. The modification of NH<sub>4</sub>F and Urea in Pd/HY catalyst could significantly enhance the catalytic performance, maintaining a good catalytic performance with a cetylene conversion (99 %) and a selectivity to vinyl chloride (99%) for over 8 h. It was illustrated that the enhanced catalytic performance was attributed to the NH<sub>4</sub>F and Urea modification, which decreased the Pd loss, changed the surface acidity of catalysts, prevented the Pd reduction and inhibited the carbon deposition.

#### **Experimental section**

The HY modified by ammonium fluoride and urea (denoted as  $NH_4F$ -Urea-HY) support was synthesized by the HY zeolites (purchased by Nankai university, Si/Al =9) to a mixture of  $NH_4F$  and urea under stirring in 100 mL distilled water, so as to modulate a

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mass ratio of NH<sub>4</sub>F/Urea keeping 2/1. After stirring 4 h at 298 K, the mixture was filtered and washed thoroughly with distilled water until the filtrate was neutral. Then it was dried at 353 K for 10 h. Pd-based catalysts using the prepared NH<sub>4</sub>F-Urea-HY support or original HY support were prepared by ultrasonic-assisted and incipient wetness impregnation technique<sup>7</sup>. The Pd loading was 0.9 wt% and the obtained catalysts were denoted as Pd/HY and Pd/NH<sub>4</sub>F-Urea-HY catalysts, respectively. The single NH<sub>4</sub>F or urea modified Pd/HY catalysts was prepared by the same method as shown above.

Activity tests of catalysts were evaluated in a fixed-bed quartz tube reactor (i.d. 10 mm) at atmospheric pressure. A premixed hydrogen chloride (99.99%) and a cetylene (98%) stream with a volume ratio of 1.25 were fed into a heated reaction containing 4 g catalysts, keeping a C<sub>2</sub>H<sub>2</sub> gas hourly space velocity (GHSV) of 110 h<sup>-1</sup> and a reaction temperature of 160 °C. The exit gas mixture from the reactor was passed through an aqueous NaOH solution to remove untreated HC before being set into a gas chromatography (GC 2010, Shimadzu) to analyzed the conversion of a cetylene (X<sub>A</sub>) and the selectivity of the selectivity of VCM (S<sub>vC</sub>) immediately.

Scanning electron microscopy (SEM) was performed using a LEO1450VP detector and transmission electron microscopy (TEM) was tested with H-600-II electron microscope from Hitachi Co. LTD at an accelerating voltage of 200 KV. Palladium contents were detected using an inductively coupled plasma (ICP-6300) instrument. X-ray diffraction (XRD) data were acquired using a M18XHF22-SRA diffractometer operating at 50 kV, 100 mA with Cu-K  $\alpha$  irradiation in the scan range of  $2\theta$  between 5°-80°. X-ray photoelectron spectroscopy (XPS) data were executed by AXIS ULTRA spectrometer (Kratos Analytical Ltd) and binding energies are referred to the C1s line at 284.8 eV. Fourier Transform Infrared Spectrometer (FTIR) was analyzed on a EQUINOX-55 (Bruker Company, Germany) experiment and temperature programmed decomposition (TPD) was determined using a TP-5080 adsorption instrument over a temperature ramp of 0-900 °C, ramp rate of 10 °C min<sup>-1</sup>, flow of 100 mL min<sup>-1</sup>. Brunauer-Emmett-Teller (BET) surface area data were collected using a Barrett-Joyner-Halenda (BJH) desorption branch analysis. A thermogravimetric (TG) analysis was performed by the TG-DSC simultaneous thermal analyzer (NETZSCH SAT 449F3 Jupiter, Germany), air atmosphere, flow rate of 100 mL  $min^{-1}$ , heating rate of 10 °C  $min^{-1}$ .

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#### **Graphical abstract:**

# Non-mercury catalytic acetylene hydrochlorination over the NH<sub>4</sub>F-Urea-modified Pd/HY catalyst for vinyl chloride monomer production

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 $8 \text{ cm} \times 4 \text{ cm}$ 

The modification of  $NH_4F$  and urea significantly enhances the stability of Pd/HY catalyst for acetylene hydrochlorination.