Unraveling How the H\textsubscript{2} Treatment Helps Improve the Performances of Cu and Ag Loaded Y Zeolites for Adsorptive Desulfurization

Zhengjian Hou, Ling Wei, Xinyuan Feng, Neng Qin, Huijie Wei, Yanyan Xi, * Xufeng Lin, * and Chuangye Wang

ABSTRACT: This work seeks for a better understanding on how the gas treatment process affected the structure of metal loaded zeolite Y (MY, M = Ag, Cu) adsorbents and how the structural changes affected the performances of the adsorbents for adsorptive desulfurization. A series of characterization tools including solid-state nuclear magnetic resonance were employed. Compared to the N\textsubscript{2} treatment, the H\textsubscript{2} treatment on the MY adsorbents led to the reduction of the loaded M components to their metallic state and, consequently, brought several structural changes to the zeolitic framework. The structural changes brought by the H\textsubscript{2} treatment can be accounted for the decreased Brønsted acidity over the Lewis acidity of the adsorbents and thus helped in improving their adsorption capacity. This paper provides new insights on how the zeolitic framework changes affected the sulfur adsorption capacity of MY, which is helpful for designing better adsorbents for sulfur removal from oil.

1. INTRODUCTION

Deep desulfurization for producing ultra-low-sulfur transportation fuel is a topic of important concerns with the increasingly more stringent environmental regulations in the world.\textsuperscript{1} For instance, the latest National (VI) standard for fuel oil in China requires that the sulfur concentrations in gasoline and diesel should be less than 10 and 15 parts per million on weight basis (ppmw),\textsuperscript{2–5} respectively. Removal of the original sulfur compounds, such as thiophene (TP), benzothiophene and their derivatives, etc., from diesel and gasoline is still a big challenge in petroleum refining. In recent decades, the hydrodesulfurization (HDS) process has been established to be an effective way for removal of sulfides, disulfides, and thiols and has been widely applied in industrial oil refinery. However, it is difficult to remove the original sulfur compounds in FCC naphtha with HDS since HDS requires rather high cost including large hydrogen consumption, high reaction pressure and temperature, and sacrificial unsaturated hydrocarbons.\textsuperscript{6–8} Therefore, attention has been paid to develop other processes for deep desulfurization in order to meet the growing demand of ultra-low-sulfur transportation fuels such as oxidative desulfurization, membrane separation, bio-desulfurization, ionic liquid desulfurization, adsorptive desulfurization,\textsuperscript{9–13} etc. Among these new methods, adsorptive desulfurization has several advantages like ease of operation and being able to acquire deep sulfur removal under mild conditions. Obviously, one essential factor affecting the competitiveness of the adsorptive desulfurization method is the performance of adsorbents, including adsorption capacity and adsorption selectivity.

Presently, a variety of adsorbents have been developed by researchers.\textsuperscript{14–21} Most adsorbents are metal loaded activated carbon, alumina, zeolites, mesoporous materials, and metal–organic frameworks. However, it is still a big challenge to obtain high adsorption selectivity to sulfur compounds over olefins and aromatics for an absorbant when maintaining desirable adsorption capacity. From the point of view of this requirement, Y-type zeolites modified with metal-ion exchange were found to have rather high adsorption capacities and high sulfur-removal selectivity\textsuperscript{19–21} compared to other types adsorbents.

Besides the great effort taken by the researchers to the exploratory searches for high-performance sulfur-removal adsorbents, effort has also been taken to the understanding of the sulfur-removal mechanisms in the adsorption systems. It
is obviously helpful for designing high-performance adsorbents to deeply understand the key adsorption sites and the key processes occurring on these sites. However, such understandings are still quite poor in the literature for the zeolitic adsorbents in general and for zeolite Y-based adsorbents for removing TP and its analogues in particular.

Zeolite Y modified with metal-ion exchanges often show a desirably large S adsorption capacity, especially Cu(I)-Y obtained by reduction.\textsuperscript{21-23} For zeolites modified with ion exchange, a number of researchers have reported that the Lewis acidic sites were active adsorption sites, which adsorb TP molecules through π-interaction or S-M interaction.\textsuperscript{16,24,25} After comparing the sulfur removal performance of zeolite Y ion-exchanged with different types of metal, Yang et al.\textsuperscript{19,25} proposed that Cu(I)-Y showed excellent adsorption capacity via a π-complexation between the Cu\textsuperscript{+} ion and the thiophenic aromatic rings.

However, the potential effect of the Brönsted acidic sites in the zeolitic framework, which can be generated during the reduction process after ion-exchange did not cast enough attention by Yang et al.\textsuperscript{25} Actually, the Brönsted acidic sites were found to be active to catalyze some conversion reactions of TP or TP derivatives, such as protonation, oligomerization, cleavage, etc.\textsuperscript{2,24,26,27} For example, Song et al.\textsuperscript{2} reported that the protonation reactions of TP can be catalyzed by the Brönsted acid sites, in particular, the \ensuremath{\equiv}\text{Si—OH—Al\equiv} sites, in HY and CeY. The protonation and the subsequent oligomerization of TP lead to the blockage of zeolitic holes, which can significantly cut the sulfur removal amount of the zeolitic adsorbents.

When a transition metal cation occupying a zeolitic cationic site is reduced by H\textsubscript{2}, the microstructure of the nearby tetrahedral (Si or Al) sites can also be significantly changed. Such changes include those of Si—OH groups and Brönsted acid sites, and in principle such changes may significantly affect the sulfur removal performance of the zeolitic adsorbents.\textsuperscript{2,24—27} However, few people paid attention to the role of such changes. In particular, the reason for why Cu(I)-Y has large S adsorption capacity is still far from clear.

This paper aims to shed more light on how the H\textsubscript{2}-reduced metal loaded Y zeolite (MY, where M = Cu or Ag in this work) enhances its adsorption capacity for TP compared to the unreduced MY. To achieve this goal, the differences between reduced and unreduced MY were systematically analyzed, and how these differences were associated with the sulfur removal performances was proposed through employing a series of characterization tools including solid-state nuclear magnetic resonance (NMR). A mechanistic scheme was proposed for explaining how the H\textsubscript{2} reduction led to the changes of the zeolitic tetrahedral sites and thus the improvement of

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**Figure 1.** X-ray diffraction patterns of different adsorbents including NaY (black), CuY-N\textsubscript{2} (blue), CuY-H\textsubscript{2} (green), AgY-N\textsubscript{2} (red), and AgY-H\textsubscript{2} (dark yellow) as indicated in the figure.

**Figure 2.** (a) N\textsubscript{2} adsorption isotherms of NaY (black), CuY-N\textsubscript{2} (blue), CuY-H\textsubscript{2} (green), AgY-N\textsubscript{2} (red), and AgY-H\textsubscript{2} (dark yellow). (b) Corresponding HK micropore size distributions of these adsorbents.
adsorption performance. The mechanistic insights provided in this paper may help people design better zeolitic adsorbents for sulfur removal from oils.

2. RESULTS AND DISCUSSION

2.1. Adsorbent Characterization. 2.1.1. Basic Physicochemical Properties. Figure 1 shows the XRD patterns of NaY, Cu-Y-N2, Cu-Y-H2, Ag-Y-N2, and Ag-Y-H2. All of these samples showed a crystalline faujasite structure, with peaks located at 6.18°, 10.12°, 11.89°, 15.63°, 20.32°, 23.66°, 27.03°, and 21.43° assigned to (111), (220), (311), (331), (440), (533), (642), and (555) planes, respectively. Compared to NaY, Cu-Y-N2, and Cu-Y-H2, a slight decrease was observed for the intensity of the above characteristic peaks in the patterns of Ag-Y-N2 and Ag-Y-H2. The peak intensity decrease reflected a slight loss of crystallinity of Ag-Y-N2 and Ag-Y-H2 partly due to the sintering of the loaded metal component. Furthermore, there were two additional peaks for both Cu-Y-H2 and Ag-Y-H2 over other zeolites. Peaks located at 43.2° and 50.4° for Cu-Y-H2 can be assigned to the Cu(0) crystalline phases, and peaks at 38.1° and 44.3° for Ag-Y-H2 can be assigned to Ag(0) crystalline phases. The appearance of these peaks showed that after being calcined in H2, the Cu(0) and Ag(0) components can be significantly generated from Cu(II) and Ag(I) on zeolite Y.

Figure 2 shows the 77 K N2 adsorption–desorption isotherm and the pore size distribution of NaY, Cu-Y-N2, Cu-Y-H2, Ag-Y-N2, and Ag-Y-H2. For all samples, the isotherms can be identified as a type I isotherm, which is typical for microporous solids. The absence of hysteresis loop in these isotherms suggested that there were no noticeable mesopores. The surface area and pore volumes of these adsorbents are shown in Table 1. It can be seen that the surface area and pore volume decreased obviously, from 682 m²/g and 0.34 cm³/g for NaY to 533 m²/g and 0.27 cm³/g for Ag-Y-N2, and to 622 m²/g and 0.33 cm³/g for Cu-Y-N2, respectively. These decreases can be due to the crystallinity decrease of the adsorbents, in particular, for the Ag case, after the metal loading, as reflected by the XRD results (see Figure 1). Similar trends were observed for the surface area and pore volume of Cu-Y-H2 and Ag-Y-H2 compared with those of NaY. The mild loss of the surface area and pore volume observed for Ag-Y-H2 can be partly due to the structural damage caused by the aggregation of metallic Ag, as reflected by the XRD results.

2.1.2. Characterization of the Transition Metal States with XPS. Auger parameters and 3d spectra are often used by researchers to analyze the valence of transition metals in an XPS measurement. Figure 3a,b presents the Ag 3d and Ag MNN Auger XPS spectra of Ag-Y-N2 and Ag-Y-H2, respectively. The binding energy (BE) of Ag 3d having two peaks at 369.4 and 375.8 eV and the kinetic energy (KE) of Ag MNN Auger structure having two peaks at 347.9 and 352.8 eV can be assigned to the Ag(I) cations occupying the zeolitic cationic sites in Ag-Y-N2. In contrast, the BE of Ag 3d having two peaks at 368.2 and 374.5 eV and the KE of Ag MNN Auger structure having two peaks at 351.6 and 357.6 eV for the case of Ag-Y-H2 show that most the Ag component was reduced to the atomic Ag(0) state. When the Ag(I) ions at the cationic sites were reduced, in principle, the atomically dispersed Ag atoms were generated. Then, part of the atomically dispersed Ag atoms tended to aggregate, which was reflected by the new XRD features (2θ of 37 and 44° in Figure 1) of Ag-Y-H2.

Figure 3c,d shows the Cu 2p detailed photoelectron XPS region and MNN Auger structure of Cu-Y-N2 and Cu-Y-H2, respectively. The peaks at the BE of 935.7 and 944.3 eV in Cu-Y-N2 can be assigned to a Cu(II)/(OH)-O-zeolite structure according to the work of Tannenbaum et al.,39 where they showed that Cu(OH)+ occupied the zeolitic cationic sites after the ion-exchange step. The band at 933.5 eV can be ascribed to Cu(I) generated from auto-reduction of Cu(OH)-O-zeolite when calcined at a high temperature. The BE of Cu 2d of 944.3 and 957.5 eV disappeared, showing that almost all Cu(II) components were reduced for the Cu-Y-H2 adsorbent. The BE of 932.5 eV for Cu-Y-H2, slightly lower than 933.5 for Cu-Y-N2, can be assigned to mixing chemical state of Cu(0) and Cu(I), as reported by Zhang et al.35 As described above, the XRD result for Cu-Y-H2 (Figure 1) showed that at least part of the Cu component existed in the metallic Cu(0) state.

2.1.3. Acidic Site Characterization. The DFTIR spectra of pyridine adsorbed on zeolite Y adsorbents are presented in Figure 4. In all of the spectra, two peaks located at ~1450 and ~1540 cm⁻¹ can be clearly observed, and the assignments of these two peaks have been well established in the literature. Pyridine adsorption on a Brønsted acid site leads to the ~1540 cm⁻¹ peak assigned to the ring deformation vibration of pyridine. Meanwhile, pyridine adsorption on a Lewis acid site leads to the ~1450 cm⁻¹ peak assigned to the deformation vibration of C−H bonds. Although the quantitative determination of the amount of acid sites with different types was not available at present, the relative ratio of the amount of Lewis acid sites over that of Brønsted acid sites (L/B ratio) can be estimated by the relative area of the ~1450 cm⁻¹ band over the ~1540 cm⁻¹ one. Table 2 collects the L/B ratios of the different zeolitic Y adsorbents. It can be seen from Table 2 that the L/B ratio was increased for all the Cu/Ag loaded zeolite Y compared to the starting material of NaY. Interestingly, the H2 treatment led to a further higher L/B ratio than the N2 treatment for both of the Cu and Ag loaded zeolites. As described in section 1, Lewis acid sites can adsorb TP and Brønsted acid sites can catalyze the protonation and the subsequent oligomerization. Therefore, the L/B ratio of the adsorbents studied may be highly associative with their performances of sulfur adsorption.

2.1.4. Si/Al Site Characterization by Solid-State NMR. Figure 5 shows the 29Si MAS NMR spectra of the Cu and Ag loaded Y zeolites with different post-treatments. In order for a better description, the notation of Si-n(OAl) is used to represent a Si site in the zeolitic framework hereafter, where the integer n (in the range of 0–4) is the number of Al atoms connected to this Si site through an oxygen bridge (Al−O−Si).
In principle, a “Al−O−Si” bridge should have a cationic site connecting to the bridging O atom, which can be occupied by a metal cation like Na⁺ or a Brønsted acid site, i.e., H⁺. The chemical shifts located at 89, −94, −100, and −105 ppm can be assigned to Si-3(OAl), Si-2(OAl), Si-1(OAl), and Si-0(OAl) sites, respectively. The Si-4(OAl) sites were not detected. In principle, since the Si-0(OAl) sites did not have cationic sites, they can be considered as keeping intact during the ion-exchange and gas treatment processes, compared to other Si sites. In NaY, the Si-2(OAl), Si-1(OAl) sites contributed to most of the Si sites, and their contributions were comparable to each other. Comparison between the 29Si-MAS NMR spectra of NaY and AgY-N₂ showed that the structural environment of the Si site did not have an observable change when Na⁺ was exchanged with Ag(I) (Figure 5a). However, further inspection of the two spectra of AgY-N₂ and AgY-H₂ showed that the H₂ reduction treatment led to a mild decrease in the amount of the Si-2(OAl) sites over that of the metal cation like Na⁺ or a Brønsted acid site, i.e., H⁺. The chemical shifts located at 89, −94, −100, and −105 ppm can be assigned to Si-3(OAl), Si-2(OAl), Si-1(OAl), and Si-0(OAl) sites, respectively. The Si-4(OAl) sites were not detected. In principle, since the Si-0(OAl) sites did not have cationic sites, they can be considered as keeping intact during the ion-exchange and gas treatment processes, compared to other Si sites. In NaY, the Si-2(OAl), Si-1(OAl) sites contributed to most of the Si sites, and their contributions were comparable to each other. Comparison between the 29Si-MAS NMR spectra of NaY and AgY-N₂ showed that the structural environment of the Si site did not have an observable change when Na⁺ was exchanged with Ag(I) (Figure 5a). However, further inspection of the two spectra of AgY-N₂ and AgY-H₂ showed that the H₂ reduction treatment led to a mild decrease in the amount of the Si-2(OAl) sites over that of the metal cation like Na⁺ or a Brønsted acid site, i.e., H⁺.
Si-0(OAl) ones, and a dramatic decrease for the Si-3(OAl) case.

Different to the case of AgY-N2, it can be clearly seen that the contributions of the Si-3(OAl) and Si-2(OAl) sites over those of the Si-0(OAl) ones were obviously decreased from the NMR spectra of CuY-N2 (see the middle curve in Figure 5b). The H2 treatment led to a further decrease in the contribution of the Si-2(OAl) sites.

For zeolitic materials, 27Al MAS NMR spectra may provide important supplementary information to 29Si MAS NMR spectra for understanding the behaviors of the tetrahedral sites (Si or Al) in the zeolitic framework. Figure 6 shows the 27Al MAS NMR spectra with Cu and Ag loaded zeolite Y with that of the starting material of NaY. The main peak located at the chemical shift of 60 ppm was a typical feature from the framework Al in zeolite Y42 for all adsorbents studied. AgY-N2 did not show noticeable features of new Al species,42 and CuY-N2 only showed a rather slight feature at ~0 ppm, indicating that there was no significant dealumination during both of the ion-exchange processes and the N2-treatment processes.

Different from the case of N2-treated zeolites, the feature (at 0 ppm) assigned for the extra-framework Al species was observed on the spectrum of H2-treated zeolites. This feature was mildly slight for CuY-H2 (while larger than the case of CuY-N2) and obvious for AgY-H2. Therefore, the H2 treatment not only resulted in the reduction of the chemical state of

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**Figure 5.** 29Si MAS NMR spectra for zeolite Y-based adsorbents as indicated in the figure. (a) Comparisons of AgYs with NaY. (b) Comparisons of CuYs with NaY.

**Figure 6.** 27Al MAS NMR spectra for zeolite Y-based adsorbents as indicated in the figure. (a) Comparisons of CuYs with NaY. (b) Comparisons of AgYs with NaY.
loaded metals but also dealuminization in some extent. Both ²⁹Si and ²⁷Al MAS NMR spectra showed that CuY-H₂ had less extra-framework aluminum than AgY-H₂. This trend was consistent with the XRD results shown in Figure 1, which shows that the metallic Cu features in CuY-H₂ were less obvious than the metallic Ag features in AgY-H₂. The reduction of Ag(I) to Ag(0) was easier than the reduction of Cu(II)/Cu(I) to Cu(0), which led to easier sintering and agglomeration of Ag, resulting in a larger loss in the specific surface area and pore volume for the Ag cases (see Table 2).

2.2. Study of the Adsorptive Desulfurization Systems. 2.2.1. Desulfurization Performance. The desulfurization performance of different adsorbents is shown in Table 3. It can be seen from Table 3 that both CuY-N₂ and AgY-N₂ showed improved adsorption capacity for TP removal compared to NaY. CuY-N₂ had a better adsorption capacity than AgY-N₂ (79% vs 61%). The adsorbents with H₂ treatment had a substantially higher sulfur capacity than the one with N₂ treatment (about 79% vs 93 for the Cu case and 61% vs 75% for the Ag case).

The above adsorption capacities and the observed order were consistent with the results reported by Yang et al. Through a quantum chemical computation work, they showed that the adsorption energy of TP on Cu(I)-Y and Ag(I)-Y was rather strong and stronger than that of benzene. The desired adsorption energy of Cu(I) was due to its specific electronic configuration ([Ar]3d¹⁰4s⁰). However, these understandings were rather insufficient to explain the experimental data. For example, Ag(I) has a similar electronic configuration ([Kr]4d¹⁰⁵s⁰) as Cu(I), and the sulfur removal rate of AgY-N₂ was between those of NaY and CuY-N₂, even being closer to that of NaY. This question became severe when it was considered that only part of Cu was in the status of Cu(I) from the XPS results (Figure 3c,d). Another interesting question calls for a better understanding of the case that when Ag(I) was reduced to Ag(0) (Figure 3a,b) and part of the metallic Ag components aggregated (Figure 1), the sulfur removal rate increased. A similar question can be raised for the CuY case. Putting together the experimental observations, one has to consider that the zeolitic framework itself had a significant contribution to the overall sulfur removal rate. The H₂-reduction process, which led to the reduction of the transition metal components, also brought several changes of the zeolitic framework. In this context, how the changes of the zeolitic framework brought by the H₂-reduction process influenced on the sulfur removal rate should be further investigated.

2.2.2. TP-Adsorption Systems Studied by In Situ DRIFT Study. The in situ diffuse-reflectance infrared Fourier Transformation (DRIFT) spectra of TP adsorbed on different zeolite Y-based adsorbents are presented in Figure 7. The 1460 cm⁻¹ peak can be assigned to the deformation vibration of a CH₂ group around sulfur (−CH₂−S) or near the double bond (CH₂−C≡C). This peak was obvious on NaY and AgY-N₂, slight on CuY-N₂, and nearly not observable on CuY-H₂ and AgY-H₂. Since there was no CH₂ group in an intact TP molecule, the appearance of the 1460 cm⁻¹ peak was proposed to be an indication of the CH₂ formation due to the protonation of TP at its α-C site. The 1421 cm⁻¹ peak belonged to the CH₂ group bending in the TP oligomers as reported by Song et al. The band at 1504 cm⁻¹ was also related to the TP oligomers, showing that oligomerization of TP occurred on absorbents. Compared to the case of N₂-treated MY adsorbents, the intensities of bands at 1421 and 1460 cm⁻¹ were near not observable in the cases of H₂-treated MY adsorbents. The absence of these two IR bands in CuY-H₂ and AgY-H₂ indicated that the protonation and the subsequent oligomerization of TP, occurring on other adsorbents, were dramatically suppressed in these two adsorbents. This suppression can be accounted for the decreased amount of Brønsted acid sites over that of Lewis ones (see Table 2) since, in principle, the protonation and the subsequent oligomerization of TP were always triggered by the Brønsted acid sites. The band at 1396 cm⁻¹ was assigned to the perturbed symmetric stretching vibration of C≡C in the fundamental ring of TP adsorbed on the Y zeolites, which had a 13 cm⁻¹ red shift compared with the case of TP weakly adsorbed on ZMS-5. The 3100 cm⁻¹ peak was assigned to the =C−H stretching of TP, and the 2946 cm⁻¹ peak was assigned to aliphatic C−H vibrations after the protonization of TP, as reported by Chen et al. The presence of the 2946 cm⁻¹ peak on the cases of NaY, AgY-N₂, and CuY-N₂ and the absence of this peak on the cases of AgY-H₂ and CuY-H₂ further supported that the above hypothesis made from the 1421 and 1460 cm⁻¹ peaks.

The inverted peaks appeared in the spectral region of 3600−3800 cm⁻¹ also provided interesting information about the interaction of the TP with the sites on all of the adsorbents examined in this work. The DRIFT spectra of all adsorbents showed a strong peak at 3698 cm⁻¹ assigned to the residue water loss after TP adsorption and a weak peak at 3750 cm⁻¹ assigned to TP interaction with the non-acidic terminal silanol (Si−OH) sites. The 3640 cm⁻¹ inverse peak was assigned to the bridging hydroxyls (≡Al−OH−Si≡), i.e., the Brønsted acid sites in the zeolitic framework. As proposed by Song et al., the bridging OH sites are mainly responsible for the protonation reaction of the adsorbed TP. The intensity of the 3640 cm⁻¹ peak was obviously decreased in the CuY-H₂ and AgY-H₂ zeolites compared to the CuY-N₂ and AgY-N₂. This decreasing trend was highly associative with the decrease in the peak intensity at 1460 and 1421 cm⁻¹, both being accounted for the decreased protonation and thus decreased oligomerization.

A. Proposed Picture of the Active Sites on Metal Loaded Y Zeolite for Adsorptive Desulfurization. Put together all of the above-described results about both of the Ag and Cu loaded Y zeolites and their TP adsorption systems, one can found several relationships. These relationships will be

| adsorbents | sulfur content (ppmw) | removal efficiency (%) | adsorption capacity (mg S g⁻¹ adsorbent) |
|------------|-----------------------|------------------------|----------------------------------------|
| NaY        | 258                   | 48.3                   | 12.1                                   |
| CuY-N₂     | 102                   | 79.6                   | 19.9                                   |
| AgY-N₂     | 194                   | 61.3                   | 15.3                                   |
| CuY-H₂     | 35.2                  | 93.0                   | 23.2                                   |
| AgY-H₂     | 122                   | 75.7                   | 18.9                                   |

*The initial sulfur content was 500 ppmw. See section 4 for more details.*

Metal contents measured by XRF.

Table 3. Desulfurization Performances of Different Zeolite Y-Based Adsorbents for Removing TP from the Model Fuel Oil

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described as follows in forms of comparisons of the H$_2$-treated MY adsorbents with the N$_2$-treated ones:

(i) On the basis of sulfur adsorption capacity, the H$_2$ treatment led to a significant increase in TP removal percentage compared to the N$_2$ treatment (see Table 3).

(ii) The H$_2$ treatment led to more reduced oxidation state of the loaded metal on the adsorbents (Figure 3).

(iii) The H$_2$ treatment led to a decreased contribution of Brønsted acid sites to the overall acid sites (Table 2). Correspondingly, TP adsorption on the H$_2$-treated metal loaded Y zeolites presented a nearly non-observable IR signal of TP oligomerization as well as that of TP-Brönsted OH interaction (Figure 7).

(iv) The H$_2$ treatment led to much more obvious changes in zeolitic Si sites, in particular in that the contribution of the Si-3(OAl) sites was decreased (Figure 5). At the same time, the H$_2$ treatment led to the formation of extra-framework Al species.

(v) Accompanied with the decrease in the 3640 cm$^{-1}$ peak assigned to the Brønsted acid sites, the intensity of the 3675 cm$^{-1}$ shoulder peak appeared in the CuY-H$_2$ and AgY-H$_2$ zeolites, which was absent in the CuY-N$_2$ and AgY-N$_2$ zeolites, as well as in the original NaY zeolite (Figure 7).

Interestingly, the above relationships stood for both of the AgY and CuY adsorbents. Further inspection of these relationships showed that they can be further associated with each other, and according to such associations, the schematic illustrations for how a representative zeolitic cationic sites, i.e., \(\equiv \text{Si} - \text{O}(-\text{cation}) - \text{Al}\equiv\), changed in different steps of preparation are presented in Scheme 1 for both of the Ag (Scheme 1a) and Cu (Scheme 1b) loaded zeolite Y.

2.3.1. The Proposed Changes of a Zeolitic Cationic Site in the MY Adsorbents. Scheme 1 shows the illustration of the possible evolvement of a zeolitic cationic site, i.e., \(\equiv \text{Si} - \text{O}(-\text{cation}) - \text{Al}\equiv\), during the preparation of the AgY (Scheme 1a) and CuY (Scheme 1b) adsorbents. Panel (i) in Scheme 1 shows a structure of a zeolitic cationic site in the starting material of NaY, where the cationic site is Na$^+$ or H$^+$, with the former having a predominant contribution. When this site is occupied by H$, this site shows Brønsted acidity. In principle, the O$^-$Al bond in panel (i) is a coordination bond, and this site can be also existed as in the structure shown in panel (ii), where the Al site shows the Lewis acidity.

When the ion-exchange was carried out, the cationic site can had the structure shown in panels (iii) and (iv) in Scheme 1, where an Ag(I) ion occupied the cationic site. This site was unchanged during N$_2$ treatment (as reflected by the XPS results shown in the upper curves in Figure 3a,b). When the AgY adsorbent was treated in H$_2$, Ag(I) was reduced to form metallic Ag(0) (see the lower curves in Figure 3a,b), residing near to the O$^-$Al moiety as shown in panels (v) and (vi).

The evolvement of the cationic site in the CuY case can be similar as, but somewhat more complicated than, that in the

Figure 7. In situ DRIFT spectra of TP adsorbed on NaY (black), AgY-N$_2$ (red), CuY-N$_2$ (blue), AgY-H$_2$ (green), and CuY-H$_2$ (dark yellow).
Scheme 1. Schematic Diagrams for Illustration of the Evolvement of a Zeolitic Cationic Site of \( \equiv \text{Si} - \text{O}(\text{cation}) - \text{Al} \equiv \) during the Preparation of the (a) AgY and (b) CuY Adsorbents (See More Details in the Text)
3(OAl) site shown in Scheme 2 can also explain how the Brønsted acidity was decreased during the H₂ treatment process (see Table 2 and Figures 4 and 7). As is known for an ion-exchange process for zeolite, not all the cations occupying the cationic sites will be replaced by the ions in the solution. For the example of NaY ion-exchanged with AgNO₃ in this work, there is always part the original cations (most of them being Na⁺ and a small portion of them being H⁺) occupying the cationic sites remaining unchanged during the ion-exchange process. In order to represent this property of ion-exchange in Scheme 2, when the cationic site shown with an asterisk 

\[ \ast \]

mark is occupied by H⁺ [see panels (i) and (ii)], this site could be unchanged [see the \( \ast \) marks in panels (v) and (vi)] after NaY transformed to AgY-N₂. The Brønsted acidity of this site could be unchanged during the whole treatment. In contrast to that, when NaY was transformed to AgY-H₂, the reduced metallic Ag(0) atoms [see in panel (x)] and small Ag(0) clusters near the −OAl− moieties may hinder the formation of the Al···O bond, cutting down the Brønsted acidity of this site. More importantly, formation of the Ag(0) clusters and the extra-framework Al species makes the Si site isolated from the Al sites, and this Brønsted acid site is completely transformed to a Si−OH group [see the \( \ast \) marks in panels (xii) and (xiii)].

It has been well established in the literature that a Brønsted acid site, owing to its rather strong acidity, may trigger protonation of TP. Our results also reinforced this point of view by the 1421 and 1461 cm⁻¹ peaks in Figure 7. As is known, the oligomerization of TP is obviously disadvantageous to the TP adsorption capacity since the oligomerization products can easily block the zeolitic pore. Therefore, on one hand, our results reinforced that the Brønsted acid sites on the MY adsorbents catalyzed the protonation and oligomerization of TP, thus were disadvantageous to the S adsorption capacity of the adsorbents. On the other hand, the insight was provided that the H₂ treatment, through affecting on the Si-2(AlO) and Si-3(OAl) sites, in particular the latter ones, led to the decrease in the Brønsted acidity over the Lewis acidity and finally helped improve the sulfur removal performance of the MY adsorbents.

### 3. CONCLUSIONS

Through a systematic characterizations of metal loaded zeolite Y (MY, M = Ag, Cu) adsorbents and the TP-adsorbent systems, this work provides the following major findings in understanding how the gas treatment processes affected the S adsorption capacity of the adsorbents:

1. Compared to the N₂ treatment, the H₂ treatment on the MY adsorbents led to the reduction of the loaded M components to their metallic state, and consequently, the reduction process brought several structural changes on the zeolitic framework. These changes included decreased contributions of the zeolitic Si-2(OAl) and Si-
3(OAl) sites (in particular the latter ones) and generation of extra-framework Al species, as observed by the NMR spectroscopic measurements.

(2) Compared to the \( \text{N}_2 \) treatment case, the decreased Brønsted acidity over Lewis acidity observed by the Py-DRIFT and TP-DRIFT experiments can be well explained by the changes of the zeolitic framework brought by the \( \text{H}_2 \) treatment.

(3) From the TP-DRIFT experiments, this work reinforced that the Brønsted acid sites on the MY adsorbents catalyzed the protonation and oligomerization of TP, thus were disadvantageous to the S adsorption capacity of the adsorbents. Therefore, this paper provides news insights on how the zeolitic framework changes affected the zeolitic acidic property and thus were closely related to the improvement of the S adsorption capacity of MY.

4. EXPERIMENTAL SECTION

4.1. Preparation of Adsorbents. The zeolite Y-based adsorbents were prepared with the ion-exchange method for metal loading followed by a gas post-treatment. In a typical preparation process, an aqueous slurry having a volume of 150 mL containing 5.0 g of NaY (purchased from Nankai Catalyst Co., and having a molar Si/Al ratio of 2.7, which was confirmed by X-ray fluorescence spectroscopy) and AgNO\(_3\) (Sinopharm Chemical Reagent Co.) was stirred at 343 K for 5 h. Then, the slurry was filtered, and then washed with a large amount of deionized (DI) water. Then, the obtained wet powder was dried at 393 K in an oven for 2 h and further calcinated in an N\(_2\) ow in a quartz tube at 773 K for 4 h. The obtained dry powder is denoted as AgY-N\(_2\) hereafter in this paper.

The preparation of the AgY-H\(_2\) adsorbent had the same procedure as AgY-N\(_2\), with the only difference in that an H\(_2\) ow instead of an N\(_2\) one was used in the preparation. The preparation of the CuY-H\(_2\), CuY-N\(_2\), AgY-H\(_2\), and CuY-H\(_2\) adsorbent was performed with a hemispherical analyzer (111) using Al K\(_\alpha\) (1486.6 eV) radiation (Thermo Escalab 250Xi). The spectra were collected at pass energies of 100 and 0 eV by a 150 W X-ray beam of 400 \( \mu \)m in diameter. The sample was discharged at room temperature at a pressure of \( 10^{-8} \) Pa. The peak positions were internally referenced to the C 1s peak at 284.9 eV.

The \( ^{27}\text{Al} \) nuclear magnetic resonance with magic angle spin (MAS NMR) and \( ^{29}\text{Si} \) MAS NMR spectra of a certain adsorbent were recorded by using a Bruker DRX400 spectrometer. The \( ^{27}\text{Al} \) MAS NMR was the sequence used excitation with a 1 \( \mu \)s pulse (\( \pi/12 \)) length by a small-angle excitation pulse (15\(^{\circ}\)). The sweep time was set to 30 ms, and 1000 sweeps were accumulated. KAl(SO\(_4\))\(_2\)-12H\(_2\)O was used as a reference compound for the chemical shift of \( ^{27}\text{Al} \) at 0.21 ppm. The MAS frequency was kept at 45 kHz during the whole Al-spectrum collection process. The \( ^{29}\text{Si} \) MAS NMR was the sequence used excitation with a 2 \( \mu \)s pulse (hpdcc) length. Kaolinite was used as a reference compound for the chemical shift of \( ^{28}\text{Si} \) at \(-91 \) ppm. The MAS frequency was 125 kHz during the whole Si-spectrum collection process.

4.4. In Situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT). In order to obtain molecular-level information about the adsorption sites on a certain adsorbent, in situ DRIFT experiments were carried out for the adsorption systems of pyridine-adsorbent and TP-adsorbent. All DRIFT spectroscopic measurements were carried out using a Thermo Nicolet Nexus FTIR spectrometer equipped with a mercury cadmium telluride detector cooled with liquid N\(_2\). Each DRIFT spectrum was collected using 128 scans with a resolution of 4 cm\(^{-1}\). Before a DRIFT experiment, a procedure of TP/pyridine absorption on a certain catalyst at room temperature was kept for 12 h, and desorption of the physically adsorbed TP/pyridine was carried out at 120 °C in vacuum for 24 h. The same catalyst without adsorption of adsorbate was used for collecting the background spectrum.

AUTHOR INFORMATION

Corresponding Authors

Yanyan Xi – State Key Laboratory of Heavy Oil Processing and College of Chemical Engineering, China University of Petroleum (East China), Qingdao 266580, P. R. China; Phone: +86-532-86984695; Email: xiyy@upc.edu.cn

Xufeng Lin – State Key Laboratory of Heavy Oil Processing and College of Science, China University of Petroleum (East China), Qingdao 266580, P. R. China; \( \text{orcid.org/0000-0003-0256-9092} \); Email: hattrick2009@upc.edu.cn

Authors

Zhengjian Hou – State Key Laboratory of Heavy Oil Processing and College of Science, China University of Petroleum (East China), Qingdao 266580, P. R. China

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Notes
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