

Distinguishment and fabrication of the active sites species in Y zeolites and application in selective adsorption desulfurization and catalytic reaction

Yun Zu^a, Yu Hui^a, Yucai Qin^a, Xiaotong Zhang^a, Zhaolin Sun^{a, b, *}, Lijuan Song^{a, b, *}

^a Key Laboratory of Petrochemical Catalytic Science and Technology, Liaoning ShiHua University, Fushun 113001, Liaoning Province, P. R. China

^b College of Chemistry and Chemical Engineering, China University of Petroleum (East China), Qingdao 266555, Shandong Province, P. R. China

*Corresponding author: lsong56@263.net, zlsun56@263.net, zuyun1990@126.com

Abstract: The dynamic chemical transformation processes of framework and extra-framework species, (e.g. cerium species and copper species) during the metal modified Y zeolites as a function of temperature, atmosphere (N₂, O₂, air and vacuum), Si/Al, Ce/Al and Cu/Al ratio, *etc.*, were accurately distinguished by using *in situ* FT-IR with various probing molecules, solid-state NMR, XRD Rietveld refinement, TPD-MS, Raman spectroscopy and XPS techniques. Accordingly, the performance of the SADS, OATS, olefin isomerization, catalytic cracking reactions was effectively promoted or restricted by changing a chemical speciation of the abovementioned species at a certain stage.

Keywords: Y zeolites, Active sites species, Chemical speciation, Catalytic reaction.

1. Introduction

Over the years, Y zeolites have shown an excellent adsorption and catalytic performance in the fields of catalytic cracking reaction, selective adsorption desulfurization (SADS) and olefinic alkylation of thiophenes (OATS), *etc.* [1]. Universally, the adsorption and catalytic conversion behaviors of different adsorbates on the active sites of the catalysts or adsorbents are the key issues for the catalytic processes. Initially, lots of studies of this research area have focused on the subject of the analysis of the Brønsted or Lewis acid sites in the Y zeolites. Obviously, the above analysis is far from enough. Several studies have begun to speculate the possible active sites species structure in terms of the initial and eventual chemical speciation of the metal modified Y zeolites. However, the present researching results are still difficult to meet for the recognition of the adsorption or catalytic cracking mechanisms. Therefore, the goal of the present work is to accurately distinguish the dynamic chemical transformation of the active sites species during the modification. Besides, the fabrication of some effective active sites species is successfully applied in the catalytic cracking reaction, olefin isomerization, OATS and SADS. The achievements of this study can provide a good theoretical fundamental in modulating other catalytic reaction and fabricating the ideal and effective active sites in the catalysts or adsorbents in the future.

2. Experimental

A series of Y zeolites (NaY, HY, CeY, CuY) with different loading, calcined temperatures and atmosphere, were utilized as the researching objects. The textural properties of the samples were characterized by the XRD, SEM, TEM, and Ar adsorption. The chemical component of the samples was obtained by employing the XRF and ICP-AES. The acidic properties were measured by NH₃-TPD, Py-FTIR, solid-state NMR. The dynamic chemical transformation of the active sites species in the modified Y zeolites were studied by *in situ* FTIR with various probing molecules, XPS, solid-state NMR, and Raman spectroscopy. The adsorption and catalytic conversion behaviors of the adsorbates (thiophene, 1-hexene, 1,3,5-triisopropylbenzene, *etc.*) were analyzed using *in situ* FTIR, TPD-MS transient response, GC-SCD, and GC-MS, molecular simulation technique.

3. Results and discussion

Figure 1A and 1B give the TG-DTG curves and the hydroxyls IR spectra during the temperature programmed desorption from the 12CeY (hydrated), respectively. Four chemical transformation processes of the Ce species can be speculated through four stages of the weight loss (%) and the variation of the bands at

3634, 3626, 3616, 3574, 3550, 3528 and 1637 cm^{-1} , as the schematic diagram shown in Figure 1C. In 120~250°C region, the $\text{Ce}(\text{H}_2\text{O})_3^{3+}$ species are transformed into the $\text{Ce}(\text{OH})^{2+}\cdot\text{H}_2\text{O}$ in the supercages. Subsequently, the $\text{Ce}(\text{OH})^{2+}$ species are formed through the $\text{Ce}(\text{OH})^{2+}\cdot\text{H}_2\text{O}$ with $1\text{H}_2\text{O}$ loss in the range of 250~350°C and migrate into the SOD cages. The temperature increases from 350 to 550°C, the $\text{Ce}(\text{OH})^{2+}$ species transform into di-nuclear octahedral Ce species in the SOD cages. Besides, the chemical transformation processes of Ce species are associated with Ce loading, calcined atmosphere. In conclusion, the $\text{Ce}(\text{OH})^{2+}$ species (~ 250°C, N_2 , 12Ce/u.c.) in the supercages are the efficient adsorption sites in the SADS. The formation of the di-nuclear octahedral Ce species (~ 550°C, N_2 or air, 12Ce/u.c.) is the essence of improving the (hydro)thermal of the Y zeolites and increase the strength of Brönsted acid sites in the supercage that can enhance the catalytic cracking performance [2].

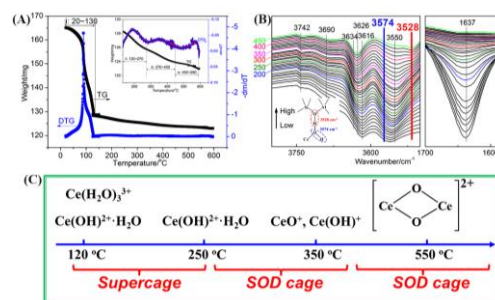


Figure 1. TG-DTG curve (A) and hydroxyls IR spectra of the 12CeY (hydrated), schematic diagram of the chemical transformation of the Ce species in various stages (C).

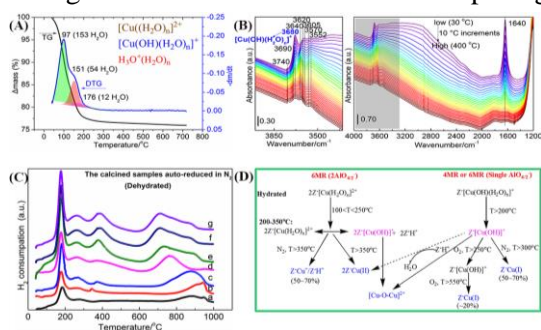


Figure 2. TG-DTG curve (A) and hydroxyls IR spectra of the 13CuY (hydrated) and H_2 -TPR (C) of CuY with different loading, schematic diagram of the chemical transformation of Cu species in various stages (D).

Cu^+ species located in the SII and SIII' of Y zeolites are in favor of capturing thiophene and prompting the OATS performance. Oppositely, the CuO_x and $[\text{Cu-O-Cu}]^{2+}$ reduce effective adsorption sites (e.g. the Cu^+ species and Brönsted acid sites) and hinder the occurrence of the above reaction.

To sum up, the adsorption and catalytic mechanisms of thiophene and/or 1-hexene on the active sites species in the CeY and CuY zeolites are acquired (cf. Figure 3). The results show that oligomerization, alkylation of thiophene with 1-hexene or isomerization of 1-hexene are prompted under the synergism between $\text{Si}(\text{OH})\text{Al}$ groups active sites and the $\text{Ce}(\text{OH})^{2+}$ species active sites located in the supercage[2]. Surprisingly, the oligomerization of thiophene can be restricted in the present of the Cu^+ species. While, the thiophene alkylation with 1-hexene is enhanced [1].

4. Conclusions

The dynamic chemical transformation processes of cerium species and copper species in the modified Y zeolites on the dependent of temperature and atmosphere, were accurately distinguished. Naturally, the performance of the SDAS, OATS, olefin isomerization, catalytic cracking reactions could be effectively modulated by changing a chemical speciation of the abovementioned species at some stage.

References

1. Y. Zu, Y. Qin, X. Gao, H. Liu, X. Zhang, J. Zhang, L. Song, Appl. Catal. B-Environ. 203 (2017) 96-107.
2. L. Zhang, Y. Qin, D. Ji, G. Chu, X. Gao, X. Zhang, L. Song, J. Rare. Earth. 35 (2017) 791-799.

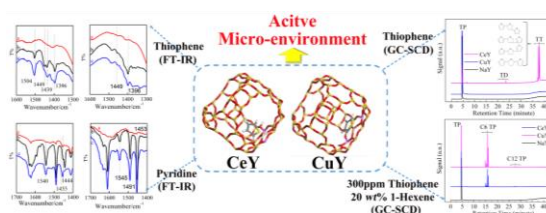


Figure 3. The adsorption and catalytic mechanisms of thiophene and/or 1-hexene on the active sites species in the CeY and CuY zeolites.