Supporting Information

Study of the CA-treated ZSM-22 zeolite with enhanced catalytic performance in the hydroisomerization of long-chain *n*-dodecane

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1. Preparation of Pt/HZSM-22 catalyst

The parent ZSM-22 sample was treated by ion-exchange with 1.0 M NH_4NO_3 solution twice at 80 °C for 4 h (20 mL/g sample), followed by drying at 100 °C overnight and then calcination at 500 °C for 4 h. Finally, the H-typed ZSM-22 sample was obtained, denoted as HZSM-22. Next, the Pt catalyst on HZSM-22 (Pt/HZSM-22) was prepared by the same method in the text, and the Pt loading was 0.5wt.%. After placing at room temperature and dried at 100 °C for 12 h, respectively, the Pt/HZSM-22 catalyst was shaped to 40-60 mesh, and further calcined at 450 °C for 3 h.

2. Figures

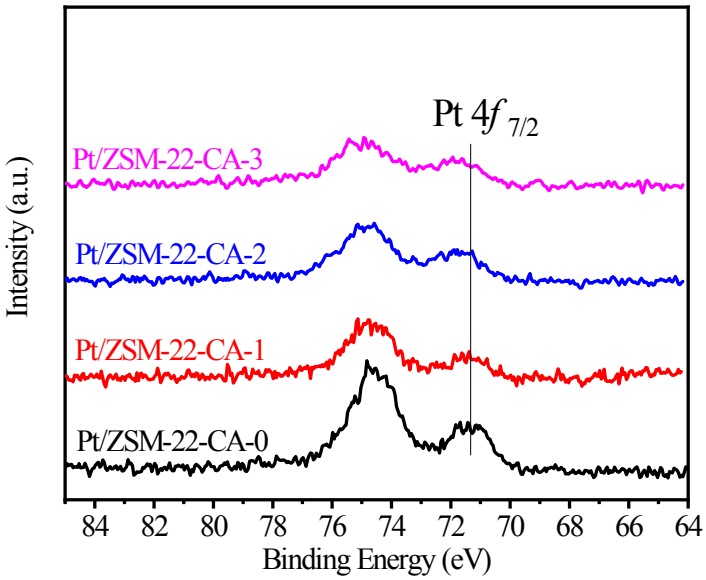
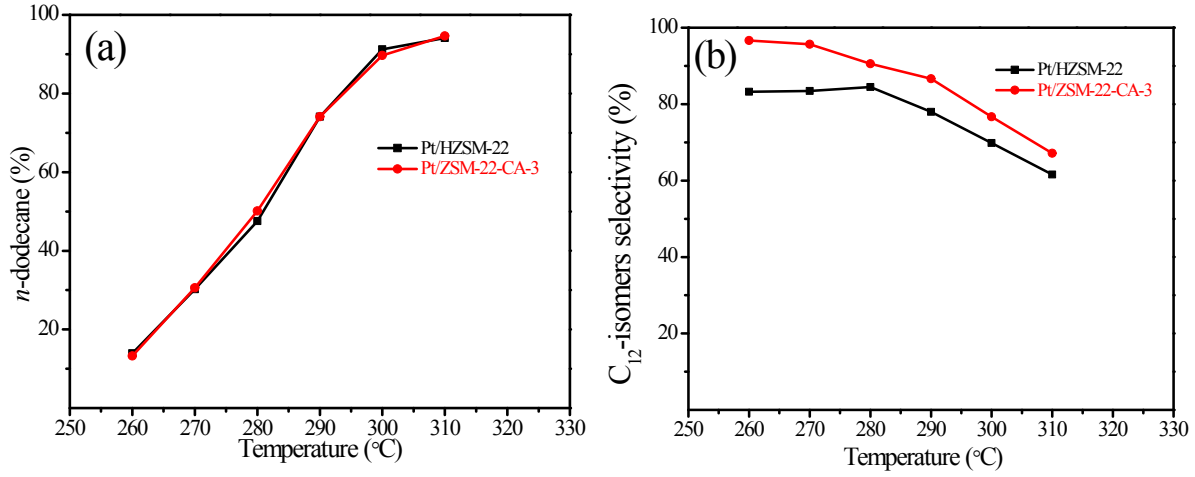


Figure S1 Pt 4*f* XPS spectra of Pt/ZSM-22-CA-x (x=0-3) catalysts.

Discussion: Because the binging energy region of Pt $4f_{5/2}$ and Al 2*p* were seriously overlapped, then the Pt $4f_{7/2}$ was mainly referenced. Typically, the binding energy of the metallic Pt $4f_{7/2}$ was 71.0 eV. While this value for the Pt $4f_{7/2}$ on the series of Pt/CA-ZSM-22-x catalysts was in the range of 71.0-71.8 eV, demonstrating a shift to higher binding energy for the Pt $4f_{7/2}$. This phenomenon could be related to the change in the acidity of the CA-treated ZSM-22 zeolites. The close contact between the acidic sites and Pt clusters on the ZSM-22-based catalyst made the electron withdraw from the Pt atoms, leading to a higher binding energy of 71.8 eV for Pt $4f_{7/2}$ on the Pt/ZSM-22-CA-3 catalyst.



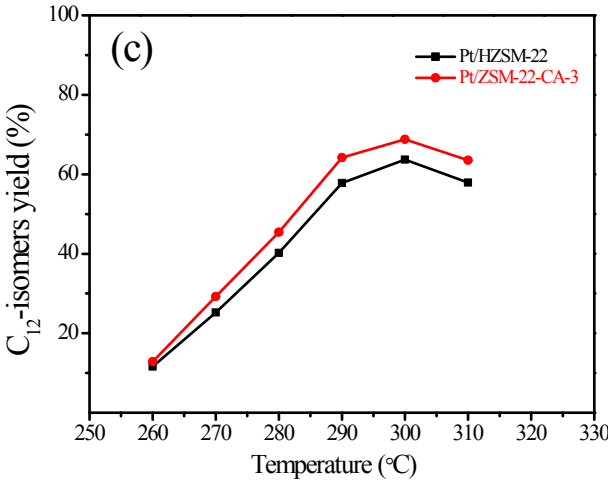


Figure S2 The (a) *n*-dodecane conversion, (b) C_{12}-isomers selectivity and (c) C_{12}-isomers yield over Pt/HZSM-22 and Pt/ZSM-22-CA-3 catalysts as a function of temperature. (Reaction conditions: temperature of 260-310 °C, a total pressure of 2.0 MPa, a weight hourly space velocity of 2.3 h^{-1}, and a hydrogen-to-*n*-dodecane volume ratio of 600)

Discussion: For comparison, the catalytic data for Pt/ZSM-22-CA-3 catalyst was also given in the same figure. Obviously, the Pt/HZSM-22 and Pt/ZSM-22-CA-3 catalysts exhibited similar *n*-dodecane conversion at the reaction temperature. But the Pt/ZSM-22-CA-3 catalyst had a better advantage than Pt/HZSM-22 in terms of the C_{12}-isomers selectivity, and correspondingly, the Pt/ZSM-22-CA-3 catalyst showed higher yield of C_{12}-isomers than Pt/HZSM-22 catalyst. For example, the Pt/ZSM-22-CA-3 catalyst had optimal C_{12}-isomers yield of 68.8%, higher than Pt/HZSM-22 catalyst (63.7%). Considering the similar textural parameters for the two catalysts, the difference in isomers yields could be related to the acidity property of the catalysts, as discussed below.

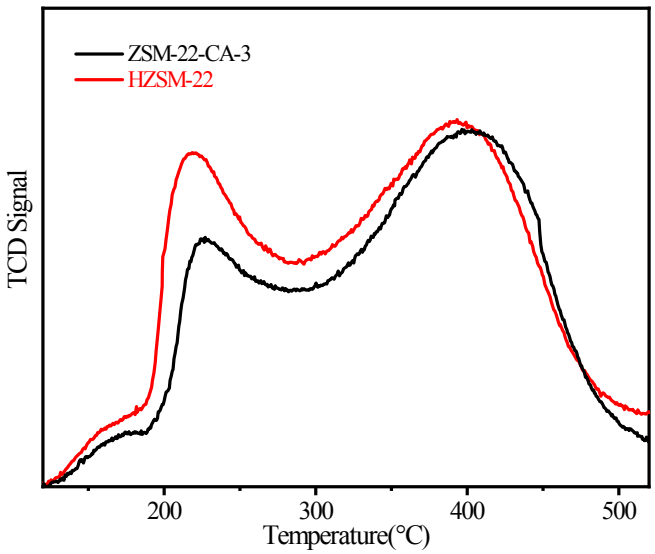


Figure S3 the NH_3-TPD result for ZSM-22-CA-3 and HZSM-22 samples.

Discussion: The desorbed peaks at temperature region of 150~200 °C, 200~300 °C, and 300~500 °C were assigned to the weak acidic sites, medium-strong acidic sites, and strong acidic sites, respectively[1]. As shown in **Figure S3**, the HZSM-22 sample had similar strong acidic sites to ZSM-22-CA-3 sample, but more medium-strong acidic sites than ZSM-22-CA-3 sample, which may lead to the further cracking of the C_{12}-isomers.

Reference

[1] S. Liu, J. Ren, S. Zhu, H. Zhang, E. Lv, J. Xu, Y.-W. Li, Synthesis and characterization of the Fe-substituted ZSM-22 zeolite catalyst with high n-dodecane isomerization performance, J. Catal. 330 (2015) 485-496.