Hydroisomerization of Hexane over Pt modified H-Beta Zeolite Extrudate Catalysts: Bifunctional Catalysis and Reaction Mechanisms

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Highlights

o Synthesis of extrudate shaped catalysts H-Beta-Bentonite, Pt-H-Beta-Bentonite

o Physico-chemical characterizations using several techniques

o Evaluation of catalytic properties in hydrosiomerization of hexane

o Highest selectivity to dimethyl butane was obtained over Pt-H-Beta-25-Bentonite extrudate

1. Introduction

Bifunctional catalysis using transitional, noble metals, Brønsted and Lewis acid sites are important for production of fuel components, pharmaceuticals, fine and speciality chemicals. Alumina, silica, zirconia, microporous zeolites and mesoporous materials supported with Pt, Pd, Ru, Ni, Zn, Cu and Co have been reported for applications in several industrial processes for production of fuel components, fine and speciality chemicals. Microporous zeolites with well defined Brønsted and Lewis acid sites have attracted attention of researchers in academia and industry for synthesis of transition and noble metals modified bifunctional catalysts in hydroisomerization reactions. In this research we report Pt modified Beta-25 zeolite extrudate shaped catalysts for hexane hydroisomerization reaction.

2. Methods

Extrudate shaped Beta zeolite catalyst was prepared using bentonite as binder. Pt modified H-Beta-25 zeolite catalyst was synthesized using post synthesis modifications of Pt-H-Beta-25 extrudate using evaporation impregnation method. Physico-chemical characterizations of the pristine H-Beta-25-Bentonite and Pt-modified H-Beta-25-Bentonite extrudatee were carried out using nitrogen physisorption for the measurements of the surface area, pore volume, and pore size distributions. The structural features and phase purity of the pristine H-Beta-25-Bentonite and Pt modified H-Beta-25 extrudates were performed using X-ray powder diffraction. Pt nanoparticle size was determined using transmission electron microscopy. Morphological properties such as shape, size and distributions of crystals were measured using scanning electron microscopy. The amounts of Brønsted and Lewis acid sites in the pristine H-Beta-25-Bentonite and Pt modified Beta zeolite extrudates were measured using FTIR-pyridine. The evaluation of catalytic properties in hydroisomerization of hexane was carried out in a fixed bed reactor. Amount of catalyst used for evaluation of hexane hydroisomerization reaction was 3g, at reaction temperature 205 – 358 ^{0}C, pressure 17 bar, hydrogen flow 180 ml/min and hexane flow rate 0.24 ml/min. Prior to evaluation, the reduction of Pt-H-Beta-25-Bentonite extrudate in flow of hydrogen was carried out at 350 ^{0}C for 60 min.

3. Results and discussion

The scanning electron micrographs of H-Beta-25-Bentonite and Pt-H-Beta-25-Bentonite extrudates exhibited presence of typical crystal shapes of Bentonite and Beta zeolite. Transmission electron micrograph applied to study the Pt nanoparticle size distributions in the Pt-H-Beta-25-Bentonite extrudate exhibited highly dispersed Pt nanoparticles (Figure 1). The Pt content measured was 2.3 wt % using Energy dispersive X-ray micro analysis. The smallest Pt nanoparticle measured was 1.6 nm and largest Pt nanoparticles 7.4 nm. Brønsted and Lewis acid sites measured using FTIR-Pyridine exhibited decrease in acid sites for Pt-Beta-25-Bentonite extrudate as compared to the pristine H-Beta-25-Bentonite extrudate. The conversion of hexane and selectivity to high octane number component 2,2 dimethylbutane increased with increase in temperature (Figure 2). The highest selectivity to i-C6 (branched isomers methyl pentane and dimethyl butane) was obtained at 250 ^{0}C using Pt-H-Beta-25-Bentonite extrudate catalyst. The highest selectivity to dimethylbutane (2,3 dimethyl butane and 2,2 dimethyl butane) was also obtained for the Pt-H-Beta-25-Bentonite extrudate catalyst (Figure 2). Pt-H-Beta-25-Bentonite extrudate catalyst exhibited stability during the hexane hydroisomerization reaction, however H-Beta-25-Bentonite extrudate showed deactivation due to coke formation. Methods of introduction of Pt such as evaporation impregnation and *in-situ* Pt modifications influenced the conversion of hexane and selectivity to 2, 2 dimethyl butane during the hydroisomerization reaction. Furthermore, amounts of Bronsted acid sites in pristine H-Beta-25-Bentonite and Pt-H-Beta-25-Bentonite played a significant role in the formation of branched isomers and decrease the formation of cracking products.

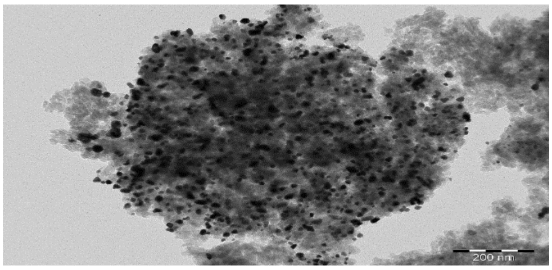

Figure 1. TEM Pt-H-Beta-25-Bentonite extrudate catalyst.

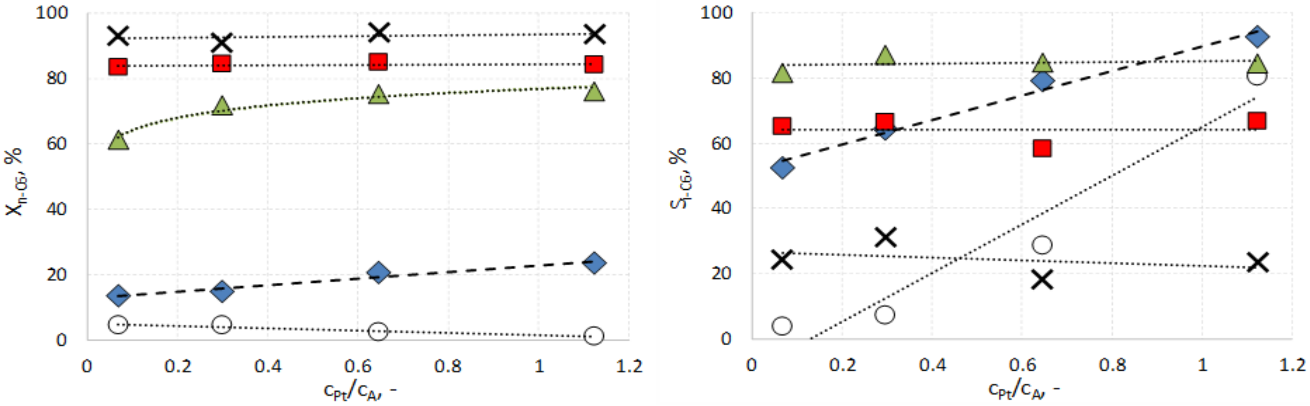

Figure 2. Isomerization of n-hexane as a function of cPt/cA ratio a) conversion; b) selectivity to C6 isomers. Legend: 200 °C (white circle); 250 °C (blue diamond); 300 °C (green triangle); 330 °C (red square); 350 °C (black cross), Pt-H-Beta-25-Bentonite extrudate catalyst.

4. Conclusions

The hexane hydroisomerization reaction proceeds via bifunctional reaction mechanism. Conversion of hexane and formation of branched isomer products are attributed to active sites, Pt nanoparticles and Brønsted acid sites. Pt nanoparticle size, dispersion, amounts of Brønsted and Lewis acid sites were observed to influence the conversion of hexane and formation of hexane isomers.

References

1. Z. Vajglova, N. Kumar, M. Peurla, L. Hupa, K. Semkin, D. Sladkovskiy, D. Yu. Murzin, Ind. Eng. Chem.Res 2019, 58, 10875-10885.
2. Z. Vajglova, N. Kumar, M. Peurla, L. Hupa, K. Semkin, D. Sladkovskiy, D. Yu. Murzin, Journal of Chemical Technology & Biotechnology 2021, 1645-1655.
3. Z. Vajglova, M. Navas, P. Mäki-Arvela, M. Peurla, K. Eränen, D. Yu. Murzin, Chemical Engineering Journal, 2022, 429, 132190.

Keywords Extrudates, hydroisomerization, hexane, isomers