



In situ UV-vis spectroscopic investigation of catalyst deactivation during *n*-butane isomerization

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Introduction

Skeletal isomerization of hydrocarbons is an important step in the production of gasoline from petroleum. Zeolites are discussed as potential, environmentally friendly catalysts for butane isomerization, however, deactivation of the catalyst is a major problem [1]. In the present work, we apply combination of *in situ* UV-vis spectroscopy and on-line GC to investigate the deactivation of H-Mordenite during butane isomerization and the influence of addition of platinum to the catalyst and of H₂ to the feed. Here, we focus on the formation of surface deposits and their effect on the catalyst performance.

Experimental

Two catalysts were used: commercially available mordenite ("H-MOR"; Zeolyst International SiO₂/Al₂O₃ = 20) and Pt/H-mordenite obtained by impregnation of the H-MOR with hexachloroplatinic acid ("Pt/H-MOR"; 0.5 wt.% Pt). The reaction conditions were 15 kPa of *n*-butane at 623 K, with inert gas (He) or H₂ added to reach atmospheric pressure.

In situ diffuse reflectance UV-vis spectroscopy was performed using a PerkinElmer Lambda 950 equipped with a Harrick Praying Mantis™ DRP-P72 accessory and HVC-VUV reaction chamber. Effluent gases were analyzed by on-line GC.

Results and discussion

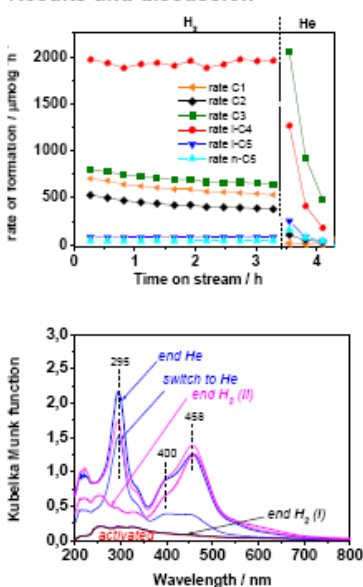


Fig. 1: Catalytic data and UV-vis spectra of Pt/H-MOR during butane conversion at 623 K.

The catalytic performance of Pt/H-MOR and the corresponding spectra for *n*-butane isomerization at 623 K are shown in Figure 1. During reaction in H₂ the catalyst shows high and stable activity with isobutane as the main reaction product in agreement with the literature [2, 3], and no new bands appear in the UV-vis spectra. For H-MOR a slight deactivation is observed in the first hours, and a weak band develops at about 300 nm. After switching the diluent gas to He both catalysts rapidly deactivate. A change in the reaction mechanism is observed with the Pt-promoted catalyst: propane becomes the main product. The simultaneously recorded spectra show for both promoted and unpromoted mordenites intense bands in the range 240-350 and 370-550 nm, assigned to mono- and polyenylic allylic cations, respectively [4, 5]. These bands indicate accumulation of more carbonaceous species on the catalyst in He than in H₂, coupled with stronger deactivation of the catalyst. When H₂ is reintroduced, some deposits disappear; presumably they are hydrogenated by hydrogen activated on platinum.

Conclusions

Diffuse reflectance UV-vis-NIR spectroscopy is a useful tool to follow catalyst deactivation. The influence of the diluent gas on the catalytic activity is confirmed: both catalysts, H-MOR and Pt/H-MOR, show stable activity in H₂ and fast deactivation in inert gas. Formation of unsaturated surface deposits is responsible for the catalyst deactivation.

1. H.S. Cerqueira, C. Sievers, G. Joly, P. Magnoux, J.A. Lercher, *Ind. Eng. Chem. Res.*, 44 (2005) 2069
2. R.A. Asuquo, G. Eder-Mirth, K. Seshan, J.A. Z. Pieterse, J.A. Lercher, *J. Catal.* 168 (1997) 292
3. V. Nieminen, N. Kumar, T. Salmi, D. Yu. Murzin, *Catal. Comm.* 5 (2004) 15
4. A.V. Demidov, A.A. Davydov, *Mater. Chem. Phys.* 39 (1994) 13
5. J.I. Villegas, N. Kumar, T. Heikkilä, V.-P. Lehto, T. Salmi, D. Yu. Murzin, *Chem. Eng. J.* 120 (2006) 83