

Deactivation of ferrierite during the skeletal isomerization of linear butenes

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Deactivation of ferrierite during the skeletal isomerization of 1-butene at atmospheric pressure and 0.15 atm 1-butene partial pressure was studied. At 300 °C, the carbon content shows a sharp increase during the first 30 min-on-stream, with a slower growth thereafter. Temperature-programmed oxidation profiles corresponding to different times-on-stream are similar, showing two well-defined combustion peaks centered at about 325 and 640 °C, respectively. When starting the 1-butene feed with the catalytic bed at 100 or 200 °C and then increasing the temperature up to 300 °C, no significant difference is observed, neither in carbon content nor in oxidation profiles. Important differences in the profiles are observed by comparing at the same time at each temperature. The lower the temperature, the higher the reactivity toward oxidation at low temperature. The carbonaceous deposit formed at 100 °C shows the main combustion peak at the lowest temperature (135 °C) and a more olefinic character; it could be related to a strong adsorption of reactant molecules. At 200 °C, the proportion of saturated species associated to oligomers increases; while at 300 °C, coke shows both aromatic and olefinic species.

KEY WORDS: skeletal isomerization; isobutene; ferrierite; deactivation; coke characterization

1. Introduction

In the last few years, the skeletal isomerization of linear butenes has achieved an increasing practical interest as an alternative route for the production of isobutene, which is an important material for the production of methyl *tert*-butyl ether used as a booster of the octane number for reformulated gasolines. That isomerization reaction takes place on acid catalysts. The most suitable zeolitic materials are 10-membered ring molecular sieves with pore diameters between 40 and 55 nm [1,2]. For materials with shape selectivity, some authors consider that pore structure plays a more important role than acidity to improve the isobutene selectivity [1,3]. Ferrierite, a zeolite with a bidimensional pore structure of 10-membered rings (42 × 54 nm) intersected by 8-membered rings (35 × 48 nm), has been presented as one of the best materials [4]. However, ferrierite shows a high activity with a low selectivity to isobutene at short time-on-stream, improving this selectivity when a carbonaceous deposit has been formed [5,6]. This deposit suppresses undesirable side reactions such as dimerization and cracking, thus increasing isobutene selectivity [7]. Between 6 and 10% [7–9], the carbon content reaches significant levels. Characterization of the carbonaceous deposit showed an aromatic nature in essence, although the presence of olefinic species has also been detected [10].

The high activity reached with ferrierite at a short time can be diminished, improving the isobutene selectivity, by starting the 1-butene feed with the catalytic bed at a low temperature and then increasing it up to the reaction one [11]. The carbonaceous deposit thus formed shows a more olefinic than aromatic nature, while coke is more aromatic when the

reactant is directly fed with the bed at the reaction temperature. Catalytic behavior of ferrierite during the 1-butene isomerization at different temperatures and the amount of coke formed [8] as well as the analysis for times between 2 and 18 h [10] and the characterization of adsorbed species at low temperatures [12,13], have been reported. Nevertheless, there are no data available about deactivation and/or characterization of the carbonaceous deposit when reaction starts at different catalytic bed temperatures.

In this paper, ferrierite behavior during the 1-butene isomerization at atmospheric pressure and 0.15 atm 1-butene partial pressure is systematically studied, the alkene feed starting at different bed temperatures. Characterization of the carbonaceous deposit by temperature-programmed oxidation and Fourier transform infrared spectroscopy (FTIR) allows us to analyze the effect of feeding the reactant at different bed temperatures.

2. Experimental

An ammonium ferrierite sample was provided by TOSOH, Japan (sample HSZ-720NHA). The SiO₂/Al₂O₃ molar ratio was 17.8, Na₂O and K₂O concentrations being below 0.05 and 0.10%, respectively. The crystalline structure was characterized by X-ray diffraction using a Rich-Seifert Iso-Debyelex 2002 diffractometer with diffraction spectrum range 0° < 2θ < 60°.

The catalytic behavior during 1-butene isomerization was studied in a continuous down-flow, fixed-bed quartz tubular reactor operated at atmospheric pressure, using 500 mg of catalyst sieved to 35–80 mesh. Samples were heated in a