Available online at www.sciencedirect.com

ScienceDirect

Microporous and Mesoporous Materials 104 (2007) 192–198

MICROPOROUS AND MESOPOROUS MATERIALS

www.elsevier.com/locate/micromeso

Comparison of butene skeletal isomerization selectivity over a pair of commercial H-ferrierites

György Onyestyák

Institute of Surface Chemistry and Catalysis, Chemical Research Center, Hungarian Academy of Sciences, P.O. Box 17, H-1525 Budapest, Hungary

Received 11 October 2006; received in revised form 23 January 2007; accepted 2 February 2007
Available online 8 February 2007

Abstract

The conversion of butenes to isobutene was compared at atmospheric pressure and 250–350 °C over two commercial H-ferrierite catalysts having different chemical compositions, crystal morphologies, and diffusional resistance (DR). The Si/Al ratio affects the number of Brönsted acidic (BA) sites but not their intrinsic acid strength. These equally strong BA sites are thought to be active sites for the skeletal isomerization. Catalyst selectivity seems mainly depend on the diffusional resistance of micropores and the reaction conditions. The DR is affected by the presence of extra-framework species in the 10MR channels of the zeolite which might include charge compensating cations, Al-containing species, and coke. To see their effect on the selectivity for i-butene versus oligomerization products we tested zeolites with basic exchanged cations and removed Al-containing debris from the transport channels with EDTA solutions. A proper balance of the extra-framework species and the reaction conditions allowed nearly 100% isobutene selectivity at relatively high branched butene yield.

Keywords: H-Ferrierite; Butenes; Skeletal isomerization; Diffusion; EFAl

1. Introduction

Isobutene is used in many important chemical processes including the production of methyl-*tert*-butyl-ether (MTBE) and alkylation of C_4-hydrocarbons to boost the octane number of gasoline. The current isobutene supply seems not to be enough to satisfy the increasing interest for introducing new, isobutene based technologies. This supply can be increased by the skeletal isomerization of butenes. The proton-exchanged ferrierite seems to be an effective commercial catalyst for this process hence numerous studies have been carried out to understand the origin of its remarkable catalytic properties [1,2]. It has been found that the micropore structure of this zeolite plays a crucial role in the catalytic selectivity [3] but some authors still emphasize the exclusive effect of acidity as a function the Si/Al ratio [4,5]. There is only scarce information available in the literature how various steric factors affect the intra-crystalline diffusional resistance and the selectivity of this catalyst [1–3].

The exceptional selectivity and stability of ferrierite in the butene skeletal isomerization was discovered by Shell workers in the 1990s [6]. They showed that this catalyst becomes selective only after reaching a certain degree of deactivation. Most researchers agree that the increase in selectivity and yield to isobutene are related to the formation of carbonaceous deposits (coke) on the zeolite although the exact role of coke is heavily debated [2]. The observed product distribution over a fresh catalyst points to bimolecular reaction mechanism involving successive steps of dimerization, isomerization and cracking whereas the high selectivity to isobutene over an aged catalyst seems to be typical of a monomolecular reaction pathway which has been confirmed with experiments with ^{13}C labeled *n*-butene [7,8]. The formation of carbonaceous deposits coincides with the increase of selectivity. Since after a short time-on-stream (TOS) the pore system of

---

E-mail address: ony@chemres.hu

1387-1811/$ - see front matter © 2007 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2007.02.004

ferrierite is largely filled with coke it has been speculated that this might play a role in boosting catalyst selectivity [9] because it is believed that the production of isobutene occurs at the pore mouth of the 10MR channels [2]. IR spectroscopy showed that with TOS carbonaceous deposits are slowly converted from hydrogen-rich alkyl-aromatics into hydrogen-poor cyclopenta-fused-alkyl-aromatics, which reduces by-product formation and therefore enhances isobutene selectivity [9].

Meriaudeau et al. [10] tried to elucidate the role of coke by varying the pore volume and number of protons with lithium or cesium exchange-cations by "mimic" of carbonaceous deposits. The selectivity was found to be significantly improved in cesium-exchanged zeolite due to the restricted channel dimensions. However these results obtained only with "bracketing technique" minimized the role of aging cannot be extended and confirmed on the final activity of the catalyst [11].

The extra-framework aluminum (EFAl) species can also control the available space around the active centre and affect the mass transport dynamics in the 10MR transport pores [12]. It is well known that EFAL species can easily form in zeolites during the hydrothermal synthesis or dealumination of zeolites, however the literature did not focused on correlation between different EFAl contents and catalytic behaviors.[5,13,14]. Therefore we investigate in this paper the effect of the EFAl species in the zeolite channel, which change the pore dimensions but only slightly affect the Bronsted acidity. We study and compare here two commercial synthetic ferrierites with significantly different EFAl contents to contribute to the understanding of the most important governing factors for the isobutene selectivity.

2. Experimental

2.1. Sample preparation

NH_4-ferrierites with 10.0 (CP 914C) and 27.5 (CP 914) nominal Si/Al ratios were obtained from Zeolyst International and denoted in this paper as FER(10) and FER(28), respectively. Some of their characteristics are shown in Table 1. The extra-lattice nature of a significant part of Al in FER(10) was also confirmed by ^{27}Al NMR and nearly the same framework Si/Al ratio was obtained. Note that Zeolyst ferrierites have been studied in the literature before but their EFAL content has not been considered in those studies [9,4,15,16].

Five grams ammonium-exchanged FER(10) was boiled twice in 100 mL 5 M hydrochloric acid under reflux for 8 h to remove EFAl. After the first step EFAl decreased to 0.51 mmol/g and further decrease was not observed during the second treatment. Three grams FER(10) was also refluxed in a solution of 0.33 g EDTA (ethylenediaminetetraacetic acid) and 100 cm^3 water for 8 h three times. This procedure reduced its EFAl content to 0.29 mmol/g. An identical EDTA treatment reduced the EFAl of FER(28) to 0.10 mmol/g.

Li- and Cs-exchanged ferrierite samples were made by conventional aqueous ion-exchange from 5 g of the ammonia-exchanged zeolites at room temperature for 8 h with 0.1 M aqueous solutions of the corresponding alkaline chlorides. By calculating from the residual ammonium contents of zeolites, the exchange level was around 75% for both ions and both zeolites (in the case of the Li-form repeated process was needed). Solid state ion-exchange [17] was also carried out with calculated amounts of LiCl resulting in 25%, 50% and 75% exchange level on proton-exchanged FER(10). At 450 °C in nitrogen flow for an hour the proposed exchange could be attained.

2.2. Characterization

The morphology of zeolite powders was examined using a Hitachi SEM-570 type scanning electron microscope. Transmission infrared (IR) spectroscopic measurements were made on self-supporting wafers in a stainless steel home-made UHV cell using a Nicolet Impact 300 type spectrometer. Spectra were recorded at room temperature after *in situ* heat treatments for 20 min in nitrogen flow at various temperatures from 100 °C to 550 °C. The diffusional resistance of degassed ferrierite crystals was tested with adsorbing pyridine probe molecule and after heat treatment at $<10^{-5}$ mbar at different temperatures. Adsorbed N_2 was studied at room temperature and 9 bar pressure in a SpectraTech type DRIFT spectroscopic cell in a Nicolet 5PC FT-IR spectrometer. The intrinsic acid strength of Brønsted acidic sites was characterized by the

Table 1
Characterization of the ferrierite samples

Product designation[a]	Si/Al ratio[b] bulk	CEC[c] (mmol/g)	Al[d] (mmol/g)	EFAl[e] (mmol/g)	Si/Al ratio[f]framework
FER(10) [CP 914C]	10	0.92	1.56	0.64	17
FER(28) [CP 914]	27.5	0.40	0.55	0.15	38

[a] Zeolyst's commercial names are given in brackets.

[b] Zeolyst's nominal values.

[c] Cation exchange capacity (CEC) calculated from the NH_3 released up to 630 °C during the calcination of the NH_4-exchanged zeolite; CEC can be considered to measure the number framework aluminum atoms.

[d] Total Al, determined by chemical analysis.

[e] Extra-framework aluminum (EFAl), obtained as difference of total and framework Al.

[f] True values calculated from framework Al.