

Zeolite-based catalysts for microwave-induced transformations of hydrocarbons

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Ferrierite-based catalysts have been evaluated in 1-butene isomerization using a continuous flow reactor operating under microwave and conventional heating conditions. The key feature of this study is the application of a single-mode microwave cavity, which can considerably enhance the heating efficiency compared to traditional microwave ovens. Our results demonstrate that the transformations of low polarity organic compounds over siliceous zeolites can be induced by microwave radiation. Despite the high power density in the utilized single-mode system, no structural degradation of the catalysts has been detected using FTIR and XRD. Our catalytic data confirm that medium-pore ferrierite is an effective isomerization catalyst providing high selectivity towards isobutene, particularly under conditions favoring the monomolecular reaction mechanism. The catalytic performance of ferrierite in the reactions carried out under microwave and conventional heating is very similar, although under the microwave irradiation this zeolite demonstrates a slightly higher yield and selectivity towards isobutene.

KEY WORDS: microwave-induced catalysis; isomerization of 1-butene; ferrierite.

1. Introduction

A significant impact on the development of new environmentally benign chemical technologies is expected from non-traditional approaches to catalysis and the availability of novel catalytic materials. For instance, new opportunities in heterogeneous catalysis are associated with the use of microwave radiation [1–4], which is already widely employed in communication technology and medicine as well as for fast heating, digestion and drying. In chemistry and materials science, microwave radiation can also be used in the preparation of new materials, for the enhancement of reaction rate and selectivity and for microwave plasma generation. Although the acceleration of chemical reactions under microwave heating has attracted considerable research interest, particularly in organic synthesis and drug discovery [5–7], its application in heterogeneous catalysis has been limited. From the fundamental and practical viewpoints, the mechanisms of the influence of microwave radiation on catalytic systems are not fully understood. The preferential heating of the supported active phase, the formation of hot spots, changes in the adsorption–desorption equilibrium and active site modification have been suggested as primary reasons for possible microwave effects [1,2,4,8].

The main objective of our research in this field is to utilize a microwave catalytic system for the evaluation of zeolites and ordered mesoporous materials. Based on

the nature of the catalyst and the substrate, the following areas of interest can be outlined: (i) catalytic transformations of hydrocarbons over H-forms of siliceous (low polarity) zeolites; (ii) catalytic conversion of polar compounds on high silica zeolites (e.g., methanol on ZSM-5); (iii) catalytic reactions on “polar” microporous materials (high alumina zeolites and aluminophosphates); (iv) bifunctional catalysis on metal clusters supported on zeolites and ordered mesoporous oxides; and (v) the application of tunable microwave reactors for selective activation of reacting species.

This study is focused on the microwave-induced isomerization of 1-butene over a zeolite-based catalyst. Isobutene is an important chemical for the production of diisobutylene, butyl rubber and copolymer resins with butadiene and acrylonitrile. In addition, it is used in the synthesis of methyl-*t*-butyl ether (MTBE, a somewhat controversial oxygenate in reformulated gasoline). In the late 1990s, the demand for isobutene outstripped the supply from conventional fluid and steam cracking units in refineries. New methods of isobutene production have been developed therefore, and the use of solid acid catalysts under conventional heating in these processes has been the subject of considerable research [9,10]. Although excellent catalytic performance in butene isomerization has been achieved over medium-pore molecular sieves, such as ferrierite and SAPO-11, a considerable effort is still devoted to the optimization of the existing catalysts. This reaction involving transformations of largely non-polar species takes place under relatively mild conditions. In addition, one of the best

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performing zeolites for this process is a siliceous ferrierite of low polarity. Since microwave heating is most effective for polar and ionic compounds, it is interesting to explore the possibility of carrying out 1-butene isomerization over ferrierite under the microwave heating conditions.

The aim of this work is to investigate the effects of microwave heating on the catalytic performance of ferrierite, on its structural integrity, on coke formation and catalyst deactivation. Isomerization of 1-butene is carried out utilizing a microwave catalytic reactor and a ferrierite-type zeolite selected as a model system. The reaction is performed at 300 °C under conventional heating and under microwave irradiation with an on-line analysis of the reaction products. Zeolite-based catalysts are characterized before and after the reaction studies employing infrared spectroscopy, X-ray diffraction and thermal analysis. These results are correlated with the data obtained previously on the ferrierite family of zeolites, and the possible effects of microwave irradiation on their catalytic performance, on deactivation in the course of the reaction and on their structural properties are discussed.

2. Experimental

A sample of ferrierite (FER, Si/Al = 9.8) obtained from Zeolyst was calcined and ion-exchanged. Catalytic experiments were carried out in a continuous flow reactor at WHSV = 1.5–2.0 h⁻¹, using a 5% 1-butene in nitrogen gas mixture over 100 mg of catalyst. The reaction studies were performed at 300 °C under conventional heating and under microwave irradiation at a power setting corresponding to the same temperature. The conventional furnace was controlled with an accuracy of 1 °C using a Eurotherm temperature programmer. For the microwave-induced reactions, a variable power 300 W generator operating at 2460 MHz (SAIREM, model GMP 03 K/SM) and a single-mode cavity (SAIREM, model DO280) were utilized. For these experiments, the reactor temperature was controlled with an accuracy of 5 °C and no coupling between a shielded thermocouple and the electromagnetic field was found in blank experiments and when using additional infrared temperature sensors. On-line product analysis was performed with a Pye Unicam P4500 gas chromatograph equipped with a flame ionization detector and a 30-m PLOT/Al₂O₃ column. Transmittance FTIR spectra of self-supported zeolite disks activated at 450 °C were collected at a resolution of 2 cm⁻¹ using a Nicolet Protege 460 spectrometer. Thermal analysis of the samples (both thermal gravimetric analysis, TGA, and differential scanning calorimetry, DSC) following the catalytic experiments was undertaken in flowing air with a temperature ramp of 10 °C/min on a STA-1500 Rheometric Scientific

instrument. XRD characterization (2θ range from 7–40°, $\sim 1^\circ/\text{min}$) of the samples exposed to microwave radiation was carried out employing a Philips 1710 diffractometer.

3. Results and discussion

Recent research interest in ferrierite type catalysts is associated with their high selectivity in isomerization of linear butenes [9–11 and references therein], a reaction that is carried out as an important industrial process. Catalytic performances of the medium-pore molecular sieves in this reaction are based on a delicate balance of the reaction conditions and the zeolite structural properties. The performance of ferrierite, in particular, its shape selective properties, can be related to its structural characteristics. As shown in figure 1, ferrierite features 10-, 8-, 6- and 5-membered rings in the framework forming 10-ring channels parallel to [001] and 8-ring channels parallel to [010] [12–14]. One of the main factors governing the isobutene selectivity is believed to be the restricted transition state shape selectivity (see review [10] for a detailed discussion of the reaction mechanism).

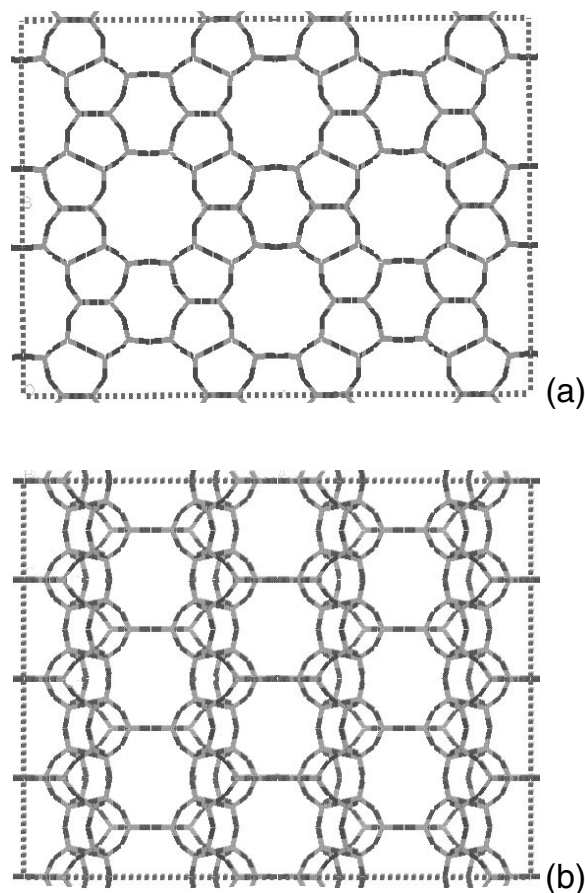


Figure 1. Skeletal structure of ferrierite: (a) view along [001], (b) view along [010]. The 10-ring channels viewed along [001] are $4.2 \times 5.4 \text{ \AA}$, and 8-ring channels viewed along [010] are $3.5 \times 4.8 \text{ \AA}$.

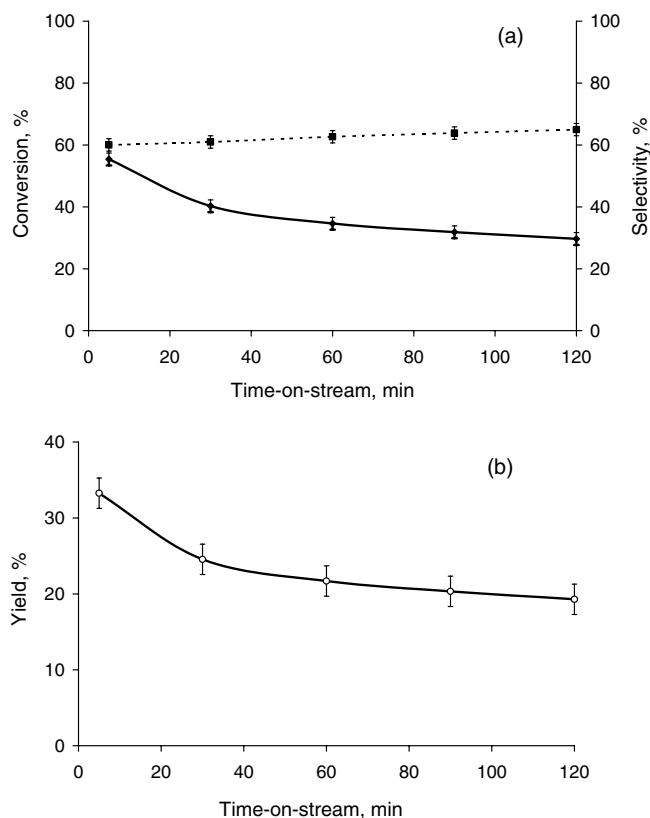


Figure 2. (a) Conversion of 1-butene and selectivity for isobutene, (b) yield of isobutene as a function of time-on-stream for 1-butene isomerization carried out at 300 °C under conventional heating.

Catalytic data obtained using a continuous flow microreactor at 300 °C are presented in figure 2. Overall, medium-pore ferrierite is an effective catalyst with both high *n*-butene conversion and selectivity to isobutene formation. In agreement with the previous data for this material obtained utilizing conventional heating [10,11,15,16], the selectivity to isobutene significantly increases and the conversion of 1-butene is falling with time-on-stream. Such catalytic performance has previously been attributed to the pore narrowing by coke deposits formed during the reaction and to the increasing role of the monomolecular mechanism of butene isomerization. These data also agree with our results on the accessibility of acid sites in ferrierite [16,17]. A greater number of acid sites accessible for the reacting species leads to a higher activity of the zeolite-based catalyst but also favors the non-selective bimolecular isomerization mechanism. However, the pore system of ferrierite facilitates the monomolecular mechanism of the reaction, particularly for longer reaction times when the pores become partially blocked because of coke deposition. The coke formation results in a decreasing number of acid sites participating in the reaction and additional steric restrictions leading to a greater contribution from the monomolecular reaction mechanism, and consequently, to lower activity and higher selectivity of the ferrierite-based catalyst.

Both activity and selectivity of zeolite samples in 1-butene isomerization have been found to depend on the activation procedure. The highest activity and the lowest selectivity have been obtained for samples activated at 400–500 °C. Either an increase or a decrease in the activation temperature leads to a higher selectivity and lower activity of the catalyst. These observations can be related to the increase in the concentration of Brønsted acid sites in ferrierite as the activation temperature is rising up to ~450 °C followed by its reduction resulting from the partial dehydroxylation and dealumination of the zeolite structure.

XRD patterns of the parent ferrierite and of this material activated in a microwave reactor at temperatures between 300 and 500 °C are presented in figure 3. The data demonstrate no detrimental effect on the structure after a prolonged high-temperature zeolite pretreatment in a microwave cavity. Figure 4 shows IR spectra of the ferrierite samples activated under conventional and microwave heating. In agreement with [17], the spectra display an intense asymmetric peak at 3600 cm⁻¹, which corresponds to the overlapping OH bands of Si(OH)Al groups present in different channels of the zeolite framework, as well as a weaker band at 3745 cm⁻¹ and a shoulder around 3650 cm⁻¹, which can be attributed to Si-OH and Al-OH groups respectively. In agreement with the XRD data, no evidence of degradation or dealumination of the catalyst exposed to microwave radiation has been observed. In addition, Py adsorption studies indicate no change in the concentration of Lewis acid sites, peak at 1455 cm⁻¹, or in the accessibility of the acid sites in ferrierite samples pretreated in the microwave reactor.

Catalytic results acquired under the microwave heating conditions are summarized in figure 5, whereas figure 6 shows a comparison of the selectivity data obtained using a microwave and a conventional reactor. Similar patterns of catalytic performance are observed for the reactions carried out under microwave (MW) and conventional heating (CH). In the former case, however, both the conversion of 1-butene, 33% (MW) versus 30% (CH), and the selectivity for isobutene, 69% (MW) versus 65% (CH), are slightly higher after 2 h of time-on-stream. As a result, the yield of isobutene is also higher under microwave irradiation, 22% compared to 19% under conventional heating. The product distributions obtained for 1-butene isomerization with microwave and conventional heating are very similar, with isobutene featured as the major product. The isobutene selectivity is slightly lower under conventional heating conditions, whereas the selectivities for propylene, *n*-butane and C₆₊ products are slightly higher. The increased formation of these hydrocarbons may reflect a greater contribution of secondary reactions and of the bimolecular mechanism of isomerization.

Several effects can be considered to account for these differences in the catalytic behavior of ferrierite. Firstly,

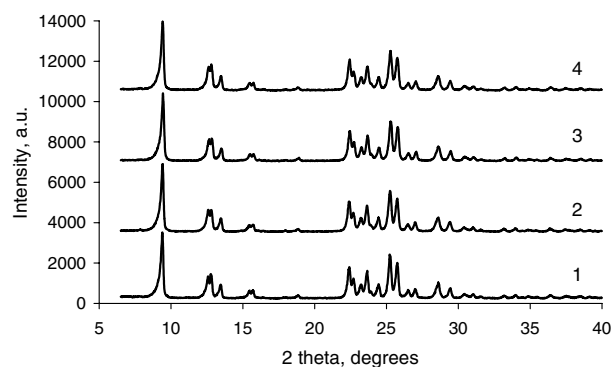


Figure 3. XRD patterns of the parent ferrierite (1) and of ferrierite samples activated in a microwave reactor at 300 (2), 400 (3) and 500 °C (4).

the intermediate species with higher polarity and polarizability would be interacting strongly with the electromagnetic field. This should, however, depend on their lifetime, and for short-lived species such as carbenium ions the effect should not be significant. Secondly, the formation of hot spots and preferential heating of the active phase are frequently invoked in the literature [2,4,8], although some authors have found no significant temperature gradients studying supported Pt

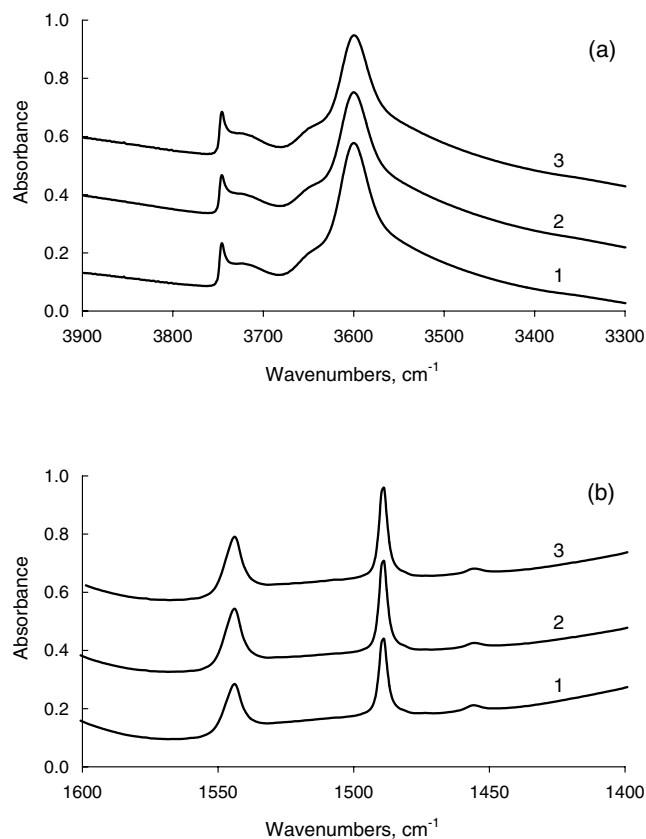


Figure 4. FTIR spectra of the parent ferrierite (1) and of ferrierite samples pretreated in a microwave reactor at 300 (2) and 500 °C (3); (a) OH region for samples activated at 450 °C in the infrared cell prior to the data acquisition, (b) Py region following this probe molecule adsorption at 150 °C.

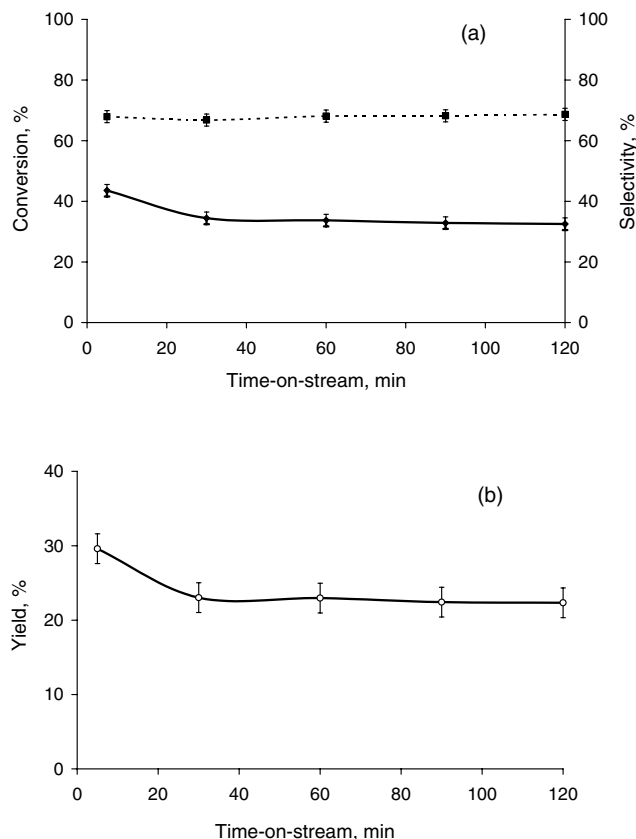


Figure 5. (a) Conversion of 1-butene and selectivity for isobutene, (b) yield of isobutene as a function of time-on-stream for 1-butene isomerization carried out at 300 °C under microwave heating.

catalysts [18,19]. The fast uniform heating under microwave irradiation in most systems is generally attributed to dielectric polarization and ionic conduction. The latter effect can be excluded for high silica zeolite samples studied in this work. Preferential heating of bridging OH groups, which are polar and which are the active sites of the isomerization reaction, is possible. However, our infrared data do not provide any support for this hypothesis. It is also difficult to offer a mechanism for the possible conversion of the electromagnetic radiation into heat for well-separated structural OH groups of the ferrierite with Si/Al ratio close to 10. Finally, the influence of microwave heating on coking and catalyst deactivation should be considered.

Our catalytic data suggest that deactivation of ferrierite takes place under both microwave and conventional heating. This effect has been further investigated by carrying out a thermal analysis characterization of the zeolites utilized in the reaction for 2 h. Carbon black and soot have been reported to strongly absorb microwave radiation [5,20]. Therefore, one might expect a different coking mode for the catalysts employed under microwave heating conditions. Indeed, our TGA data (figure 7) show a somewhat different weight loss between 20 and 300 °C for the catalysts used in microwave and conventionally heated reactors.

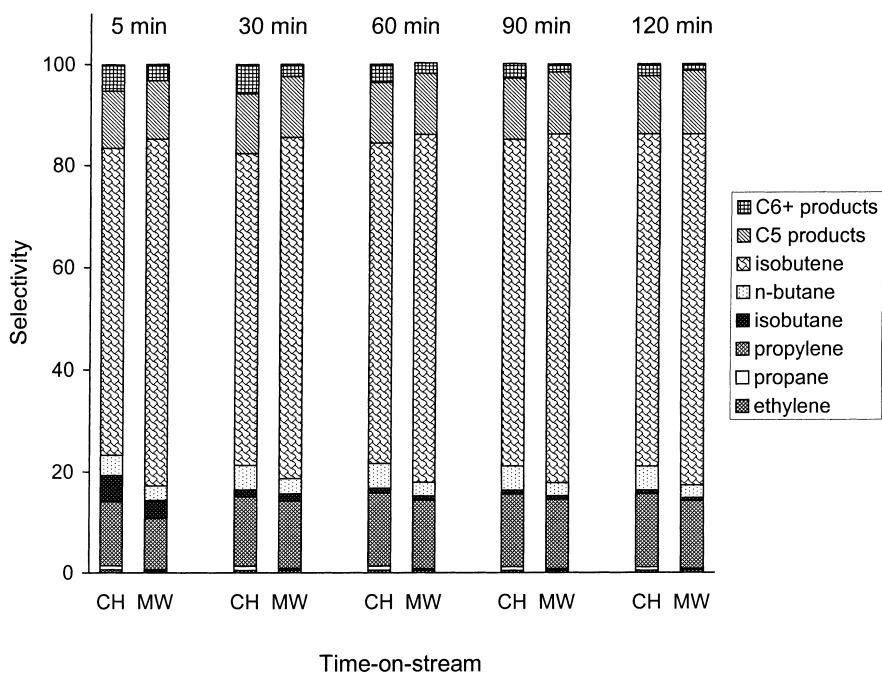


Figure 6. Selectivity for 1-butene isomerization products obtained at 300 °C under conventional heating (CH) and microwave irradiation (MW) conditions as a function of time-on-stream.

However, this can be attributed to the variable quantities of the substrate left in the samples as well as water adsorbed by the samples, and therefore, should not be related to the deactivation of catalysts in the course of the reaction. More importantly, both the pattern and the magnitude of the weight loss above 300 °C are nearly the same for both materials amounting to 5.5%. This weight loss is identified as an exothermic process by DSC, conducted under a flow of air, and is due to the heavier products and carbonaceous deposits, which cannot be removed at the reaction temperature. The relatively small quantities of coke formed on the zeolite catalyst are not sufficient to change its dielectric constant or dielectric loss. Coke deposits [10] after 2 h of the reaction time are mainly aromatic in nature with the H/C ratio of ~ 0.93 . Non-polar aromatics have negligible dielectric loss and therefore do not couple efficiently with microwave radiation [5].

Overall, the observed changes in catalytic behavior of ferrierite under microwave and conventional heating can be accounted for by the slight variations of the activation and reaction conditions and, as a result, by possible differences in the concentration of the Brønsted acid sites, rather than by special interactions between the electromagnetic field and reacting species. Indeed, in addition to the restricted transition state shape selectivity effects, the increased selectivity to isobutene can result from a significant decrease in the “working” site concentration, which should favor the monomolecular reaction mechanism [16,21]. At the same time, the influence of specific microwave effects cannot be ruled out on the basis of the currently available information.

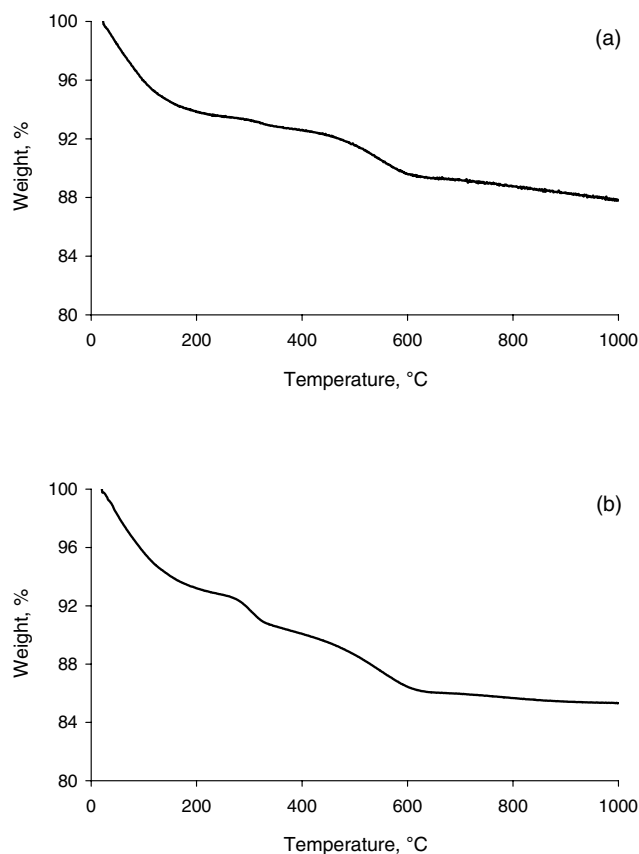


Figure 7. (a) Thermal analysis data for two samples of ferrierite utilized in 1-butene isomerization at 300 °C under the microwave, (b) conventional heating after 2 h time-on-stream.

4. Conclusions

Ferrierite-based catalysts have been evaluated in 1-butene isomerization using a continuous flow reactor operating under microwave and conventional heating conditions. Our study demonstrates that transformations involving low-polarity organic compounds over high silica zeolites can be induced by microwave radiation. The key feature of this study has been the use of a single-mode applicator. Single-mode microwave cavities enhance the heating efficiency by three orders of magnitude compared to multimode microwave ovens. Despite the high power density achieved in our single-mode system, no structural degradation has been detected using FTIR and XRD in the catalysts heated by microwaves up to 500 °C.

The catalytic data confirm that medium-pore ferrierite is an effective isomerization catalyst providing high selectivity towards isobutene. The enhanced selectivity and yield of isobutene originate from the restricted transition state shape selectivity effects and a lowered concentration of the “working” active sites, both of which favor the monomolecular reaction mechanism. The catalytic performance observed for ferrierite in the reactions carried out under microwave and conventional heating is rather similar, although under microwave irradiation this zeolite demonstrates a somewhat higher yield and selectivity towards isobutene. Such differences may be associated with the strong interaction of intermediate species of high polarity and polarizability with the electromagnetic field, with the formation of hot spots and preferential heating of the solid phase and associated shifts in the adsorption–desorption equilibria or with the changing coking mode of the catalyst under the microwave irradiation. However, the observed changes in the catalytic behavior of ferrierite under microwave and conventional heating can be explained by the variations in the activation and reaction conditions resulting in slight differences in the concentration of the acid sites in the zeolite. The effects of microwave radiation on the transformation of organic compounds with low and high polarity over zeolite-based catalysts require further investigation.

Acknowledgments

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