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ScienceDirect

Catalysis Communications 8 (2007) 967–970

CATALYSIS COMMUNICATIONS

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Trimerization of isobutene over zeolite catalysts: Remarkable performance over a ferrierite zeolite

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Received 9 June 2006; received in revised form 4 October 2006; accepted 5 October 2006

Abstract

Oligomerization of isobutene has been investigated using several zeolites in order to produce triisobutenes that are useful chemical feedstocks for heavy alkylates and neo-acids. Stable isobutene conversion and high selectivity for trimers are obtained over a ferrierite zeolite at high temperature and low space velocity. Trimers selectivity increases with increasing isobutene conversion. Isobutene is quantitatively oligomerized over a ferrierite catalyst with selectivity for trimers higher than 60% up to 50 h at high isobutene WHSV of 10 h^{-1}. Moreover, a deactivated catalyst can be regenerated easily by calcining in flowing air. The ferrierite zeolite is one of the potential catalysts for the isobutene trimerization showing high stability, quantitative conversion, high selectivity and easy regeneration.

Keywords: Ferrierite; Isobutene; Trimerization; Zeolite

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1. Introduction

Recently, trimerization of light olefins has attracted considerable attention as a method for the production of fuel additives [1] and separation of isoolefins from other olefins [2]. Moreover, triisobutenes, for example, are considered to be highly useful for the synthesis of specialty chemicals including neo-acids [2]. Heavy alkylates containing C_9 or higher carbons are used as additives for kerosene and jet fuel [3] and as premium solvents (odorless solvents due to absence of aromatics). Heavy alkylates can be produced by the hydrogenation of olefin oligomers such as triisobutenes.

The blending of MTBE (methyl-*tert*-butyl ether) in gasoline has been banned in California [4] since 2004 due to contamination caused by the dissolution of MTBE in underground water. The surplus of isobutene is, therefore expected because it is one of the main raw materials for the synthesis of MTBE.

Hence, the trimerization is a very promising reaction not only for the utilization and separation of isobutene but also for the production of isobutene trimers and heavy alkylates (after hydrogenation of oligomers). Nevertheless, the trimerization of isobutene has not received adequate attention in comparison with the dimerization of olefins [5–10]. Several solid acid catalysts such as sulfated titania [1,11,12], cation exchange resins [2,13], heteropoly acid [14] and zirconia [15] have been suggested for the trimerization. Very recently, ZSM-22 has been used to produce mono-branched trimers of propene due to shape selective catalysis because of the uniform tubular pore (10-memebered ring) of ZSM-22 [16].

To the best of our knowledge, there has been no report for the utilization of zeolites in the isobutene trimerization reaction even though they are well-known acid catalysts. We, therefore, have undertaken the present work with an

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doi:10.1016/j.catcom.2006.10.006

objective to study the isobutene oligomerization reaction over highly potential zeolite catalysts in order to produce isobutene trimers.

2. Experimental

Trimerization of isobutene (99%, Rigas Korea) was carried out in the liquid phase using a fixed bed continuous flow reactor (OD 3/8 in., stainless steel 316) equipped with a back pressure regulator (Tescom). The reaction temperature and pressure used for the reaction were 40–100 °C and 15 bar, respectively. The reactor temperature was maintained constant by a water jacket in which water, kept at constant temperature, was flowing continuously with the help of a circulator. The reactant (isobutene) and a diluent (*n*-butane, 99%, Rigas Korea) were continuously fed by using liquid mass flow controllers (Bronkhorst HI-TEC). The space velocity of isobutene, WHSV (weight-hourly space velocity, g-isobutene/g-catalyst/h) was varied between 2.5 h^{-1} and 20.0 h^{-1} by controlling the flow rates of isobutene and *n*-butane. The feeding rates of the isobutene and the diluent were equal (50 wt%/50 wt%). Unless otherwise specified, the reaction temperature, pressure and space velocity (isobutene WHSV) were 70 °C, 15 bar and 10 h^{-1}, respectively.

The conversion of isobutene was determined by analyzing frequently the composition of the off-gas stream by using a GC equipped with a TCD and an alumina column (J&W Scientific, 30 m × 0.53 mm). The conversion was cross-checked by measuring the total flow rates of isobutene and the diluent, after condensing liquid products, with a mass flow meter (Brooks, 5850 E). Liquid products were analyzed by a FID GC containing a PONA column (HP, 50 m × 0.20 mm). The detailed analysis conditions were reported elsewhere [13]. In this study, the selectivity for dimers, trimers and tetramers is described in wt%.

Several commercial zeolites such as ferrierite (Zeolyst-914C, ammonium form, $SiO_2/Al_2O_3 = 20$, surface area = 400 m^2/g), ZSM-5 (Zeolyst-CBV5524, ammonium form, $SiO_2/Al_2O_3 = 50$, surface area = 425 m^2/g) and mordenite (Zeocat-FM-8H, proton form, SiO_2/Al_2O_3 =2 5, surface area = 500 m^2/g) were used in this study without further purification. The ferrierite and ZSM-5 were calcined at 550 °C for 8 h in a muffle furnace to convert an ammonium form into a proton form. Prior to the commencement of the reaction, the zeolites loaded in the reactor were dehydrated at 300 °C for 10 h under the flow of nitrogen.

3. Results and discussion

Fig. 1 compares the isobutene oligomerization over three catalysts such as ZSM-5, mordenite and ferrierite. The conversion decreases sharply with time on stream over the mordenite and ZSM-5 as has been observed in the dimerization of isobutene [17]. However, the ferrierite shows very stable catalytic performances up to 12 h. Moreover, the selectivity for trimers over the ferrierite is very high compared with that over mordenite and ZSM-5 (Fig. 1b).

The oligomerizations were conducted in wide reaction conditions, such as reaction temperature and space velocity (isobutene WHSV), over the ferrierite catalyst. As shown in Fig. 2a, the reaction conversion is nearly quantitative even at low temperature of 40 °C. The conversion and selectivity for trimers increase steadily with increasing temperature. On the contrary, the selectivity for dimers decreases slightly with the increase of the reaction temperature. The conversion is nearly complete when the isobutene WHSV is up to 10 h^{-1}. However, the conversion decreases steadily with the reaction time after 20 h when the WHSV is 20 h^{-1}, representing the deactivation of the catalyst with high conversion of isobutene or with excessive contact to hydrocarbons. As shown in Fig. 2c, the selectivity for trimers is low when WHSV is high due to low conversion.

Fig. 3 shows the dependences of selectivities with the change of isobutene conversions obtained in various reaction conditions over the three catalysts. As the conversion increases, the trimers selectivity increases irrespective of the catalysts similar to the results observed in cation exchange resins [13] because the oligomerization reaction is a consec-

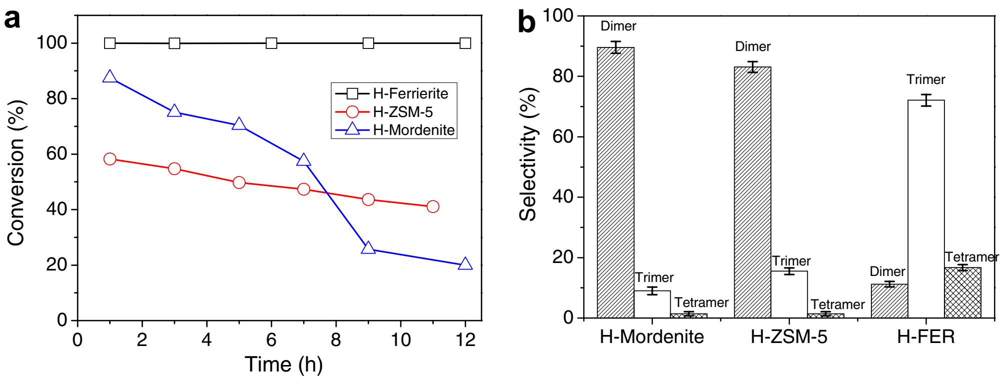

Fig. 1. Catalytic activities and selectivities over zeolite catalysts for oligomerization of isobutene: (a) catalytic activities as a function of reaction time and (b) selectivities for oligomers after 10 h on stream.