1. Introduction

Mono-olefins and di-olefins are important feedstocks for the industrial production of synthetic resins, synthetic rubbers, plastics, and other chemical products, and increased demand of these feedstocks, combined with higher cost of naphtha cracking, has resulted in greater motivation for developing processes for the production of olefins by the dehydrogenation of light alkanes. In particular, increased demand from the automotive industry has led to increased investments in n-butane dehydrogenation processes. Noble-metal-based and metal-oxide-based catalysts have been extensively studied for the direct dehydrogenation as well as oxidative dehydrogenation of alkanes to the corresponding olefins. Moreover, isolated metal species including Zn and Co species can act as the active sites for the direct dehydrogenation of alkanes instead of bulk metal oxides. Formation of isolated metal species can be achieved on zeolites because metal cations can be individually located in the cationic positions of the zeolite through the conventional ion-exchange technique. Indeed, zinc-modified zeolites prepared by hydrothermal treatment in the absence of alkali cations showed significantly higher yields of 1,3-butadiene compared to ZnO loaded on silicalite-1 by impregnation.

2. Experimental

2.1. Catalyst Preparation

Zn(NO₃)₂ · 6H₂O, Cu(NO₃)₂ · 3H₂O, Fe(NO₃)₃ · 9H₂O, In(NO₃)₃ · nH₂O, Ni(NO₃)₂ · 6H₂O, SnCl₄ · 5H₂O, NH₄VO₃, (NH₄)₂MoO₄·2H₂O, and Co(NO₃)₃ · 6H₂O were used as the metal sources. Metal-containing MFI-type zeolites were prepared as follows. Tetraethyl orthosilicate (TEOS) was added to an aqueous solution containing tetrapropylammonium hydroxide (TPAOH, 20-25 wt% in water). The resulting mixture was stirred at 353 K for 24 h. Then, an aqueous solution of Zn(NO₃)₂ and Ti into the zeolite framework leads to the formation of isolated metal oxide (i.e., [Si-O-Al-O]) with specific catalytic properties, which are quite different from those of metal oxides such as Al₂O₃ and TiO₂, in acid-catalyzed reactions and oxidation. Therefore, isolated metal species active for the dehydrogenation of alkanes should be formed by the introduction of metal species into zeolite. In addition, the synthesis of zeolite in the absence of Al species would result in absence of strong Brønsted acid sites, resulting in the suppression of the formation of by-products by the cracking and isomerization.

In this study, we directly synthesized metal-containing MFI-type zeolites in the absence of both Al species and alkali cations and used for the direct dehydrogenation of n-butane to evaluate the catalytic properties. Zn-, Fe-, and Ni-containing MFI zeolites exhibited high catalytic activities, and predominantly produced 1,3-butadiene. Furthermore, Zn-containing MFI zeolites prepared by hydrothermal treatment in the absence of alkali cations showed significantly higher yields of 1,3-butadiene compared to ZnO loaded on silicalite-1 by impregnation.

Keywords

MFI-type zeolite catalyst, Metal-containing, 1,3-Butadiene, n-Butane, Dehydrogenation

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containing the metal salt was added to the mixture, and the prepared starting gel with a molar composition of 1SiO2 : 0.0125-0.1Metal : 0.26TPAOH : 12H2O was hydrothermally treated at 448 K for 24 h. The resultant solid was recovered by centrifugation, washed with deionized water, and dried at 363 K. The obtained product was calcined in air at 823 K for 8 h to remove TPA cations.

The prepared zeolite catalysts were characterized using X-ray diffraction (XRD) and X-ray fluorescence (XRF).

2.2. n-Butane Dehydrogenation

The dehydrogenation of n-butane was carried out in a 6-mm outside diameter quartz tubular flow reactor loaded with 100 mg of zeolite pellets formed without a binder. The catalyst was calcined at 873 K for 1 h in air flow prior to the reaction, and then the catalyst was cooled down to the desired reaction temperature in nitrogen flow. The partial pressure of n-butane was set at 1.0 kPa. Nitrogen was used as the carrier. The catalyst weight to the flow rate ratio (W/Fn-butane) was 65 g-cat h (moln-butane)–1, which corresponded to the weight hourly space velocity of n-butane (WHSV) of 0.89 h⁻¹. The reaction products were analyzed with an on-line gas chromatograph (Shimadzu GC-2014) equipped with a flame ionization detector and a capillary column (HP-PLOT).

3. Results and Discussion

3.1. Synthesis of Metal-containing MFI-type Zeolites

Figure 1 shows XRD patterns of the calcined products prepared with different metal species. All samples exhibited XRD patterns typical of the MFI structure. The preparation with higher Si/Metal molar ratios in the starting gel than as described in Fig. 1 formed crystalline products with the MFI structure irrespective of the metal species, indicating that MFI zeolite can be synthesized with many different metal species and metal contents even in the absence of Al species and alkali cations through heating at low temperature followed by hydrothermal treatment. In contrast, the preparation with Fe, Sn, or Co with lower Si/Metal molar ratios in the starting gel, which corresponds to larger metal amounts in the starting gel, than as described in Fig. 1 formed an amorphous phase or a mixture of the MFI phase and amorphous phase.

The metal content of the samples was evaluated by XRF analysis. The Si/Metal molar ratios were 8, 9, 24, 20, 8, 98, 251, 6486, and 8 for the Zn-, Cu-, Fe-, In-, Ni-, Sn-, V-, Mo-, and Co-containing catalysts, respectively. Since In and Sn cations are much larger than Si cations, smaller In and Sn contents than those in the starting gel would be introduced into the catalysts. V and Mo species were little introduced into the zeolite by hydrothermal treatment. In contrast, the Si/Co molar ratio in the catalyst was higher than that in the starting gel. The use of Co species as a metal source resulted in slow crystallization of the MFI zeolite, suggesting that silica sources persisted in the gel.

3.2. n-Butane Dehydrogenation over Metal-containing MFI-type Zeolites

The synthesized metal-containing MFI-type zeolites were used to catalyze the dehydrogenation of n-butane. The results obtained after the reaction time of 1 h at 873 K are shown in Fig. 2. The Zn-, Fe-, and Ni-containing zeolite catalysts showed the highest yields of 1-butene, trans-2-butene, and 1,3-butadiene among the zeolite catalysts. Interestingly, 1,3-butadiene was predominantly produced with trans-2-butene over the three
zeolites, suggesting that the dehydrogenation of 1-butene to 1,3-butadiene was enhanced over the metal-containing zeolites. Methane, ethene, and propene were produced in quite small amounts over the three catalysts, while no aromatic compound was formed. In contrast, the zeolite catalysts prepared with the other metal species showed very low or negligible activities for the dehydrogenation of \( n \)-butane, although Sn species is, in particular, used as a key element of catalysts for the dehydrogenation of alkanes \(^{12-14}\). Moreover, no C4 olefin was produced over the zeolites containing V, Mo, or Co species.

Since Zn-containing MFI zeolite, [Zn]-MFI, specifically produced 1,3-butadiene in the dehydrogenation of \( n \)-butane among the zeolite catalysts, the catalytic properties of [Zn]-MFI were investigated in detail. [Zn]-MFI catalysts were synthesized using the starting gel with different Si/Zn molar ratios by the same method. The Zn content of the [Zn]-MFI catalysts was estimated by XRF analysis. The Si/Zn molar ratios were 8, 16, 25, and 66 for the catalysts prepared using the starting gel with the Si/Zn molar ratios of 10, 20, 30, and 50, respectively. Figure 3 shows the results of the dehydrogenation of \( n \)-butane at 873 K over the [Zn]-MFI catalysts with different Si/Zn molar ratios. The yield of butenes increased with a decrease in the Si/Zn molar ratio, which corresponded to an increase in the Zn content in the zeolite. Moreover, 1,3-butadiene was selectively produced followed by trans-2-butene irrespective of the Zn content. Therefore, the Zn species in [Zn]-MFI clearly acted as the active sites on the dehydrogenation, and the Zn species were important in the selective production of 1,3-butadiene in the dehydrogenation of \( n \)-butane. In addition, since the [Zn]-MFI catalysts showed similar product ratios, the Zn species in the [Zn]-MFI catalysts were presumably present in similar states independent of the Zn content.

In order to investigate the effects of the state of Zn species in zeolite on the catalytic properties, the dehydrogenation of \( n \)-butane was conducted over catalysts containing Zn species introduced by different methods. Figure 4 shows the results of the dehydrogenation of \( n \)-butane over various Zn-containing catalysts at 873 K. The Zn content in the catalysts was evaluated by XRF analysis. The [Zn]-MFI catalysts, in which the Zn species were introduced by hydrothermal treatment (HT), showed the highest dehydrogenation activities and yields of 1,3-butadiene among the catalysts. In contrast, [Zn]-MFI prepared in the presence of sodium cations with a Na/Zn molar ratio of 2 showed quite low catalytic activity, although the Si/Zn molar ratio of 22 was similar to that of 16 for the [Zn]-MFI catalyst prepared in the absence of sodium cations. Therefore, sodium cations adjacent to Zn species suppressed the dehydrogenation activity of Zn species. Zn species were also loaded on silicalite-1, which was prepared without metal salts using the same procedure as that for metal-containing zeolites, by the impregnation method (IMP) with a Zn(NO\(_3\))\(_2\)-6H\(_2\)O aqueous solution. The catalysts (IMP) also exhibited lower catalytic activities than the [Zn]-MFI catalysts prepared in the absence of sodium cations, although the catalysts (IMP) had similar Zn contents to those of the [Zn]-MFI catalysts. Isolated Zn species like Zn(OH)\(^+\) are much more active for the dehydrogenation in the conversion of propane compared to agglomerated forms of ZnO \(^{6-7}\). In the case of the impregnation method, Zn species on silicalite-1 would aggregate to form bulk ZnO after the calcination, leading to low activities for the dehydrogenation of \( n \)-butane. Considering our findings above, it is assumed that Zn species would be highly dispersed in...
zeolite through the hydrothermal treatment to form isolated Zn species, leading to the capacity for the alkane dehydrogenation in the [Zn]-MFI catalyst.

Changes in the product distribution affected by reaction conditions were examined over [Zn]-MFI prepared with the Si/Zn molar ratio of 10 at various reaction temperatures (Fig. 5). As the reaction temperature was increased from 723 to 873 K, the yield of butenes increased because higher temperatures are favorable for the dehydrogenation of n-butane on the basis of the thermodynamic equilibrium. 1,3-Butadiene was predominantly produced with the selectivity of more than 50 %, independent of the reaction temperature. Formation of only 1,3-butadiene and trans-2-butene was observed at lower temperatures, while 1-butene was also detected together with 1,3-butadiene and trans-2-butene at higher temperatures. Considering that both 1,3-butadiene and 2-butenes are produced from 1-butene, the transformation of 1-butene would occur faster than the dehydrogenation of n-butane to 1-butene. Furthermore, the dehydrogenation of 1-butene to 1,3-butadiene would preferably proceed over [Zn]-MFI compared to the structural change of 1-butene to 2-butenes.

The effect of the contact time on the product distribution was investigated over [Zn]-MFI prepared with the Si/Zn molar ratio of 10 at various WHSVs at 873 K (Fig. 6). The yield of the products was increased with lower WHSVs, whereas the selective production of 1,3-butadiene was maintained. Moreover, iso-butene was detected at a WHSV of 0.45 h⁻¹, indicating that the isomerization of hydrocarbons proceeded with higher contact frequency of n-butane and products with the catalyst.

4. Conclusions

Metal-containing MFI-type zeolites without Al species were synthesized with Zn, Cu, Fe, In, Ni, Sn, V, Mo, or Co species through heating at low temperature followed by hydrothermal treatment. Zn-, Fe-, and Ni-containing MFI zeolites showed high catalytic activities and predominant production of 1,3-butadiene in the direct dehydrogenation of n-butane. Zn-containing MFI zeolites selectively produced 1,3-butadiene from n-butane, independent of reaction conditions. Furthermore, the Zn-containing MFI zeolite catalyst exhibited significantly higher yields of butenes than ZnO loaded on silicalite-1 by impregnation, probably because of the formation of isolated Zn species, which are active for the dehydrogenation of alkanes, in the zeolite.

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要 旨

金属含有ゼオライト触媒を用いたn-プロタン脱水素による1,3-ブタンジエンの選択的合成

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n-プロタンの直接脱水素による1,3-ブタンジエンの一段合成を目指して、金属含有ゼオライト触媒の開発を行った。Zn, Cu, Fe, In, Ni, Sn, V, Mo または Co を金属源として用い、低圧での加熱攪拌と続く水熱合成により、Al 塩およびアルカリ金属カチオンを共存させずに金属含有 MFI 型ゼオライトの直接合成に成功した。本調製法では、広範な金属量でのゼオライトの直接合成を可能にした。合成した金属含有 MFI 型ゼオライトのうち、Zn, Fe または Ni を含有するゼオライト触媒が n-プロタンの脱水素に高い活性を示し、さらに1,3-ブタンジエンを選択的に生成した。また、Zn 含有ゼオライトは、silicalite-1に ZnO を合浸担持した触媒に比較し、高い脱水素活性および 1,3-ブタンジエン収率を示すことを見出した。これは、Zn がパラク体の ZnO とは異なる状態でゼオライト中には分散していること、また Al 種を含まないことから強酸点が発現せず、クラッキングや異性化などの副反応が抑制されたことに由来すると推測される。

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