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Dehydroisomerization of butane into isobutene on Pt–Sn intermetallic compounds supported on H-SAPO-11

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Abstract

The dehydroisomerization of butane to form isobutene was carried out on Pt-based bimetallic catalysts supported on zeolite. Among various zeolites, Si-rich H-SAPO-11 was most appropriate for obtaining high selectivity to isobutene at higher butane conversions. The acid sites of Si-rich H-SAPO-11 were characterized by ammonia adsorption, ^{29}Si MAS NMR, and the cracking of cumene. The addition of second elements, such as Sn, Pb, Zn and In, onto Pt/H-SAPO-11 retarded the hydrogenolysis activity of Pt, resulting in decreased methane selectivity. Among the second elements, tin was the most effective additive for obtaining higher isobutene selectivity. The formation of Pt–Sn intermetallic compounds, Pt_3Sn, PtSn, and $PtSn_2$, was revealed by XRD. The surface of Pt–Sn bimetallic particles was characterized through the dispersion of Pt and IR spectra of adsorbed CO. The formation of surface intermetallic compounds is proposed to retard hydrogenolysis by the ensemble effect.

Keywords: Dehydroisomerization; Butane; Isobutene; Intermetallic compound; Platinum; Tin; Silicoaluminophosphate; SAPO-11; Ensemble effect

1. Introduction

Isobutene is one of the key intermediates in the petrochemical industry for the production of methyl methacrylate, polybutene, etc. An FCC process has supplied isobutene as a part of C_4 fractions. An increasing demand for isobutene has stimulated the development of a new route to obtain isobutene from butane. This process is composed of two-step reactions; the isomerization of butane into isobutane and subsequent dehydrogenation of isobutane or the dehydrogenation of butane into 1- and 2-butenes and subsequent isomerization into isobutene. Recently, some researches on the one-step formation of isobutene from butane through the dehydroisomerization using bifunctional catalysts have been reported. Platinum supported on zeolite is widely studied, such as Pt/ZSM-5 [1–3], Pt/MFI-ferrisilicate [4], and Pt/MCM-22 [5].

Because the dehydrogenation of alkane requires high temperatures, the dehydroisomerization of butane was carried out usually at high temperatures around 800 K. The strong Brønsted acid sites on zeolites often catalyze the undesirable cracking, hydride transfer, aromatization, and coke formation as well as isomerization at high temperatures. Therefore, molecular sieves with weaker acid sites have been applied as the isomerization catalyst combined with metal catalysts. Wei et al. [6] studied the catalytic properties of Pd supported on silicoaluminophosphate (SAPO) with AEL, AFI, and CHA framework types. They reported that Pd/SAPO-5 and Pd/SAPO-34 were not effective catalysts because of the insufficient acid strength and too small pore diameters, respectively, and that Pd/SAPO-11 was the best catalyst for the formation of isobutene. They further studied the effect of Si content on the catalytic performance of Pd/SAPO-11 and found that the increased Si content resulted in the increased butane conversion and decreased isobutene selectivity [7]. Vieira et al. [8] studied the effect of Mn on the catalytic properties of Pt/$AlPO_4$-11. When Mn was introduced into the framework of $AlPO_4$-11 to form MnAPO-11, the resultant Brønsted acid sites effectively catalyzed the isomerization, whereas Pt on Mn-impregnated $AlPO_4$-11 was not effective like Pt/$AlPO_4$-11 because of their insufficient acidity. On the active Pt/MnAPO-11, a part of Mn was dispersed as extra-framework species and located on Pt particles to reduce the undesirable hydrogenolysis catalyzed by Pt through the ensemble effect [9].

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To increase the selectivity to isobutene, the hydrogenolysis catalyzed by metal particles must be suppressed. In the case of alkane dehydrogenation, the addition of tin into Pt-catalysts has been reported to be effective in suppressing the hydrogenolysis by Pt particles to increase alkene selectivity [10–13]. The effect of tin in such Pt–Sn bimetallic catalysts would result from the ensemble effect [10,11,14] or a significant ligand effect [15]. For the dehydroisomerization of butane, copper was impregnated on Pt/H-MCM-22, demonstrating that copper suppressed hydrogenolysis by reducing the size of the Pt ensembles at the surface of Pt particles [16]. The hydrogenolysis activity of Pt particles in Pt/H-Y was retarded by co-impregnation of tin [17]. The IR spectra of adsorbed CO indicated that tin apparently was dispersed onto Pt to reduce the large ensemble of Pt active for the hydrogenolysis. In these reports, the state of the second element (Cu or Sn) was not clearly determined, however.

We have studied on the catalytic properties of intermetallic compounds, such as CoGe [18], Pt_3Ge [19], Ni_3Sn and Ni_3Sn_2 [20], and $TiPt_3$ [21]. The combination of a transition metal and a typical element resulted in lower activity than the parent transition metal for H_2–D_2 equilibration [18–20] and hydrogenation of acetylene [18,20] and 1,3-butadiene [19], whereas the combination yielded the highly selective catalyst for the partial hydrogenation of acetylene [18,20] and 1,3-butadiene [19]. On the other hand, the compound between two transition metals, $TiPt_3$, showed much higher activity than Pt for the hydrogenation of ethylene [21]. Recently, we prepared the fine particles of intermetallic compounds by supporting them on the surface of silica. The formation of Ni_3Sn particles on SiO_2 was identified by XRD, XPS [22], TPR, IR, and XANES techniques [23]. The resultant Ni_3Sn/SiO_2 had high selectivity to benzene in the dehydrogenation of cyclohexane as in the case of unsupported Ni_3Sn, whereas the decreased particle size enhanced the activity per gram of Ni_3Sn by a factor of 1000 [22]. $RuTi/SiO_2$ was found to be selective for the formation of higher hydrocarbons in FT synthesis compared with Ru/SiO_2, probably because of the weak hydrogenation activity of RuTi in transforming CH_x intermediates into methane [24]. Pt_3Ge/H-ZSM-5 showed higher selectivity to aromatic hydrocarbons in the aromatization of butane through the suppression of the hydrogenolysis by Pt [25]. Clearly, the intermetallic compounds have unique catalytic properties in the reactions of hydrogenation and dehydrogenation.

In this study, we prepared fine particles of Pt–Sn intermetallic compounds on zeolites for the catalyst in the dehydroisomerization of butane into isobutene. The purposes of this study are to clarify the catalytic properties of Pt–Sn intermetallic compounds in the reaction of butane and to obtain the selective catalyst for the formation of isobutene by using acidic silicoaluminophosphate with weak acidity as the isomerization catalyst.

2. Experimental

2.1. Catalyst preparation

Zeolites were prepared by the usual hydrothermal synthesis for ZSM-5 ($Si/Al = 84$), ferrierite (12), MFI-ferrisilicate ($Si/Fe = 42$), and SAPO-5 ($Si/(Si + Al + P) = 0.018$). SAPO-11 with varying Si content was also prepared hydrothermally using aluminum hydroxide (Cataloid AP-1, 71 wt% Al_2O_3, Catalysts and Chemicals Ind.), phosphoric acid, silica (NIPSIL VN3, Nippon Silica Ind.), and di-*n*-propylamine (Kanto Kagaku) as an SDA. SDA was removed by calcination in flowing air at 873 K for 15 h. USY zeolite of $Si/Al = 7.4$ was supplied from Catalysts and Chemicals Ind. All of the zeolites were transformed into H form through ion exchange with 0.1 M aqueous solution of ammonium nitrate at 343 K and a subsequent calcination in air at 773 K for 5 h.

Platinum was supported on zeolites with 1 wt% loading by a usual impregnation method with an aqueous solution of $Pt(NH_3)_4(CH_3COO)_2$. After drying at 403 K overnight, the sample was calcined in air at 573 K for 2 h, at 623 K for 3 h, and at 723 K for 4 h. Pt–M/H-SAPO-11 (M = Sn, Pb, Zn, and In) bimetallic catalysts were prepared by a co-impregnation method. $Sn(CH_3COO)_2$, $Pb(CH_3COO)_2$, $Zn(CH_3COO)_2$, or $In(NO_3)_3$ was dissolved in an acetic acid solution of $Pt(NH_3)_4(CH_3COO)_2$, and H-SAPO-11 was impregnated with the solution to have a Pt loading of 1 wt% and a Pt/M atomic ratio of 1.5. The drying and calcination were carried out similarly to that for Pt/zeolite. Pt–Sn/H-SAPO-11 with varying Sn content was prepared by successive impregnation on Pt/H-SAPO-11 prepared by the above method. A specific amount of $Sn(CH_3COO)_2$ was dissolved in an acetic acid solution. Pt/H-SAPO-11 was put into the solution and dried and calcined under the same conditions as those for Pt/zeolites. The resultant catalyst is expressed as Pt–Sn(*n*)/H-SAPO-11, where *n* represents the Pt/Sn atomic ratio.

2.2. Characterization

The crystal structure of synthesized zeolites and supported metal particles was examined by powder X-ray diffraction (Rigaku, RINT2400). Composition of zeolites was measured by ICP (Rigaku, JY38) after dissolving the zeolites with HF solution or with alkali fusion in the case of SAPO. The amount of adsorbed ammonia was measured by a microbalance. A known amount of sample was put in a quartz basket hanging under a quartz spring. After the sample was evacuated at 773 K for 1 h, ammonia (13 kPa) was introduced at 298 K for 0.5 h. The sample was evacuated at 423 K for 0.5 h, and the weight of the sample was recorded. After the evacuation at 773 K for 1 h, the sample weight was again recorded. The amount of acid sites was obtained from the difference between the sample weights before and after the evacuation at 773 K. ^{29}Si MAS NMR spectra were recorded on a Bruker Avance 400 spectrometer at 79.50 MHz. A total of 2000 scans were accumulated to obtain a satisfactory signal-to-noise ratio, with TMS used as a chemical shift reference.

IR spectra of adsorbed CO were measured with a JASCO FT/IR-430 in transmission mode. A self-supporting wafer (ca. $10\ mg\,cm^{-2}$) of Pt/H-SAPO-11 or Pt–Sn/H-SAPO-11 was placed into a quartz cell with CaF_2 windows. After reduction in flowing hydrogen at 873 K for 1 h and evacuation at 773 K for 0.5 h, the sample was cooled in vacuo to 298 K. CO (5 kPa)