

Double-bond isomerization of hexadecenes with solid acid catalysts



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ABSTRACT

The positional isomerization of hexadecenes was investigated using the following catalysts: perfluorinated ion exchange resins (Nafion®) supported on SiO₂ or Al₂O₃, sulfonated poly(styrene-co-divinylbenzene) resins (PS-DVBs), tungstated zirconias, and acidic zeolites. Acid sites were characterized by propan-1-amine (1-PA) temperature programmed desorption, wet titration, and decomposition of sulfonate groups. Catalysts were evaluated in a packed bed reactor at 130 °C for 3 h with flowing hexadecenes. Active Nafion/Al₂O₃ catalysts were synthesized by wet impregnation and, in one case, such a catalyst was selective for double-bond isomerization, although less active than silica-supported Nafion. Selected catalysts underwent lifetime studies to examine the effects of structure and acid strength on deactivation. We found that oversulfonated PS-DVBs (e.g., Amberlyst 35) were reasonably selective with long lifetimes, only gradually deactivating due to poisoning by surface oligomers. Amberlyst 70, Amberlyst XN1010, ZSM-35 and SAPO-11 were evaluated because of their lower acid site densities and (for the Amberlysts) varying degrees of crosslinking. None of these catalysts were optimal for various reasons. Beneficial cooperative effects arising from the close proximity of acid sites in certain catalysts were observed.

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1. Introduction

Internal, long-chain alkenes (>C₁₀) are feedstocks in the manufacture of paper sizing agents and deep-sea drilling fluids [1,2]. Alkenyl succinic anhydrides (ASA), common sizing agents, are synthesized by reacting maleic anhydride with a long-chain alkene. The sizing properties of ASA increase with extent of olefin double-bond isomerization [1], so there is interest in methods that maximize internal alkenes. Practical methods include isomerization by either solid acids [3], organometallic “chain-walking” catalysts [4], or metathesis [4].

We have evaluated solid acid catalysts for the selective double-bond isomerization of hexadecenes (C₁₆). Sulfonated poly(styrene-co-divinylbenzene) (PS-DVB), perfluorinated ion exchange resins, and acidic zeolites are most frequently used [2,5–9]. Both skeletal isomerization (branching) and oligomerization compete with positional (double bond) isomerization. Oligomerization is slower with internal alkenes when using weaker, primarily Lewis acid, catalysts [10,11]. Selectivity to internal alkenes decreases with respect to both increasing temperature (usually at >150 °C) and acid strength [12,13].

Perfluorinated polymers with pendant sulfonic acid groups (e.g., Nafion®) are of interest as catalysts for these and other acid-catalyzed reactions such as alkylation and Claisen condensation. These catalysts are characterized by high acid strengths and thermal stability up to 280 °C [14]. However, given their inherently low surface areas, the polymers must be supported, usually on SiO₂. The silica-polymer composites are weaker acids than Nafion itself, with relatively low crush strengths [15–17]. Interaction of the sulfonic acid groups with the silanols can have other malign effects, such as increasing deactivation rates [15]. Using both a higher crush strength and a more amphoteric support (e.g., certain catalytic aluminas) may improve catalyst lifetime. We note that Harmer et al. reported difficulties in distributing Nafion in porous silica by wet impregnation [18], and that Bringue et al. found that a Nafion/Al₂O₃ had at least some catalytic activity for the dehydration of 1-pentanol [19].

In this work, the activity of materials prepared by various methods of impregnation of Nafion/Al₂O₃ was investigated. These new Nafion materials were compared directly to the presumably weaker sulfonated PS-DVBs, and to commercial Nafion/SiO₂. We also tested commercial zeolites and tungstated zirconia (WZ), comparing both selectivity to internal alkenes and turnover frequency. Lifetime studies and acid site characterizations were performed to elucidate how the structure and acid strengths of the active sites may contribute to the catalyst deactivation.

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2. Experimental procedures

2.1. Catalyst preparation

Commercial catalysts were provided by several manufacturers: the PS-DVBs were Amberlyst 15 (AM-15, Dow), Amberlyst 35 (AM-35, Dow), Amberlyst 70 (AM-70, Dow), Amberlyst XN1010 (AM-XN1010, Dow) and Lewatit K2620 (K2620, Sybron). The supported Nafion/SiO₂ was SAC-13, provided by BASF. The tungstated zirconia was XZO 1251, provided by Magnesium Elektron. The zeolites included SAPO-11 (6C USA) and ZSM-35 (Alfa Aesar). Prior to use, SAPO-11 and ZSM-35 were calcined in flowing air for 3 h at 450 °C and cooled under N₂. XZO 1251 was calcined in flowing air at 800 °C for 3 h. The PS-DVBs and supported Nafion catalysts were dried for 16 h under vacuum at 90 °C and 110 °C, respectively.

Nafion/Al₂O₃ catalysts were prepared by wet impregnation in two ways starting with Nafion NR50 beads (Ion Power, 1100 EW). For the preparation of BCPR5, the Nafion was first dissolved (1 L 316SS autoclave, overnight, 220 °C, 500 rpm) in water/propan-2-ol (50% v/v) to a 0.8 wt% solution, then 225 mL of solution was contacted with 15 g Al₂O₃ (Engelhard Al-3945 E, 2.1 mm) in a rotary evaporator under 5.0 mbar pressure for 6 h. For BCPR4, an Al₂O₃ support (LaRoche A 201 5 × 8 alumina spheres, 15 g) was wet impregnated overnight in the 1 L autoclave concurrent with the Nafion dissolution (750 mL of the 0.8 wt% solution, 220 °C, 100 rpm). All Nafion/Al₂O₃ catalysts underwent filtration and three separate ion exchanges with 125 mL of 0.05 M HCl for 2 h. Catalysts were then washed with DI water, dried at 110 °C, and vacuum dried for 3 h at 120 °C. Nafion content was determined by thermogravimetric analysis (TGA). A Perkin Elmer TGA-7 was ramped from 50 to 550 °C in flowing He.

2.2. Catalyst characterization

Acid sites were characterized by both wet titration and TPD of propan-1-amine (1-PA, Alfa Aesar 99+%). Wet titration was performed by stirring 0.1 g catalyst overnight in 20 mL of 2 M NaCl followed by titration with 0.01 M NaOH to a phenolphthalein endpoint. For TPD (Perkin Elmer TGA-7), the 1-PA was adsorbed at 50 °C for 15 min, then held at 50 °C until constant weight, then ramped to 300 °C at 5 °C/min. Samples of effluent gas were analyzed by GC/MS (HP 5890 Series II/5927 MSD). The components were separated by an SP-1000 column (Supelco, 30 m, 0.32 mm ID). The surface area and pore volume of each catalyst was calculated by N₂ physisorption. Adsorption/desorption isotherms at -196 °C were measured using a Quantachrome Autosorb 1 porosimeter.

2.3. Isomerization studies

The positional isomerization of C₁₆ alkenes was studied in packed bed reactors (316 SS, 12.7 mm ID, 0.36 m long) at 130 °C except where noted. Each reactor was filled with 20 mL of catalyst with α -alumina as bed support. After drying under N₂ flow at 130 °C overnight, the reactor was fed with 1 mL/min [LHSV ~3 mL feed/(h mL catalyst)] of partially isomerized feedstock (~70 wt% 1-, 2-, and 3-C₁₆). Samples were collected every hour for 3 h.

Lifetime studies were performed on selected catalysts in a larger but otherwise similar reactor at the same LHSV (15.5 mm ID, 0.61 m length, 30 mL catalyst). Samples were collected every 12 h. Catalysts were regenerated where necessary by pumping solvent (50 vol% propan-2-ol/50% m-xylene) through the system.

Product samples were analyzed by GC/FID. An HP 5890 GC equipped with an SP-1000 column (Supelco, 30 m, 0.32 mm ID) was used. The initial temperature of 70 °C was increased 15 °C/min to 145 °C, then 2 °C/min to 160 °C with a final hold time of 2.5 min.

Industrial olefin mixtures (see Supporting Information) were used as analytical standards.

Gel Permeation Chromatography (GPC) was used to measure dimer content. A 20–50 mg sample was dissolved in HPLC-grade THF (Fisher) and analyzed in an Agilent 1100 HPLC with THF carrier using an Agilent 1200 DRI detector. The column was a Phenogel 10 μ m, 7.8 mm ID × 300 mm length (Phenomenex). The solvent flow rate was set to 1.0 mL/min with each test lasting 20 min. Each sample was run at least twice.

Solvents used in catalyst regenerations were analyzed by matrix-assisted laser desorption ionization (MALDI) MS (Bruker Omniflex), with α -cyano-4-methoxycinnamic acid (Aldrich) as the target.

3. Results and discussion

3.1. Catalyst characterization

The Nafion loadings (by TGA) and acid site densities (by 1-PA TPD) of three representative Nafion/Al₂O₃ catalysts are listed in Table 1, along with those of SAC-13. The Nafion polymer in SAC-13 decomposed between 305 and 355 °C and 410 and 510 °C (Fig. 1), corresponding to desulfonation and depolymerization, respectively [14–17,20]. The total weight loss for both regions (13 wt%) exactly matched the reported Nafion loading. It can be seen from Fig. 1 that the alumina-supported Nafion materials underwent similar transitions but at a slightly higher desulfonation temperature range.

For the supported Nafion catalysts, the acid site densities varied according to the method of impregnation. The GC/MS samples taken during the 1-PA TPD established that the desorption peak centered between 130 and 140 °C for SAC-13 (Fig. 2) was associated with Hofmann elimination, giving propene and NH₃. This reaction is generally considered diagnostic for Brønsted sites [21,22], with lower temperature features associated with desorption of 1-PA. The

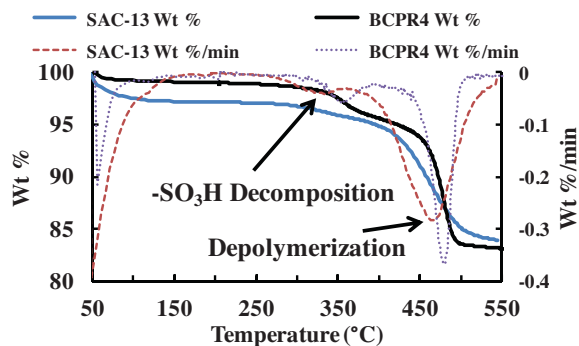


Fig. 1. Thermal analysis of supported Nafion resins, SAC-13 and BCPR4.

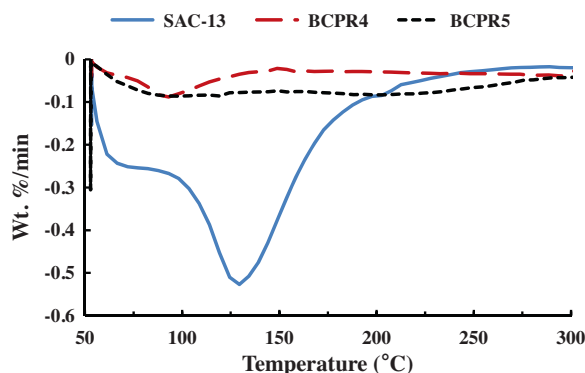


Fig. 2. Propan-1-amine (1-PA) TPD for SAC-13 and two Nafion/Al₂O₃ catalysts.

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