But-1-ene isomerization over Nafion® resin/silica composite catalyst

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But-1-ene isomerization to but-2-enes at 50 °C to near thermodynamic equilibrium is observed over a novel high surface area Nafion® resin/silica composite solid acid catalyst at a mass hourly space velocity (MHSV) of but-1-ene of 2.5 h^{-1}.

Traditionally, alkene isomerization and alkylation, important reactions in petroleum refineries, are catalysed by mineral acids like H_2SO_4, HF or $AlCl_3$. Environmental concerns associated with corrosive mineral-acid catalysts have encouraged process changes and the development of solid-bed catalytic processes. It is very desirable to convert but-1-ene to but-2-enes for the HF catalysed alkylation process because the quality of the alkylates from but-2-enes feed [96–98 research octane number (RON)] is significantly better than that from the but-1-ene (87–89 RON).[1] Various solid-acid catalysts and even amorphous silica–alumina catalyse the but-1-ene isomerization to but-2-enes at near ambient temperatures, but rapid deactivation is frequently encountered.[2–6] Perfluorinated sulfonic acid resin (*e.g.* Nafion® resin), is another possible solid-acid alternative.[7] However, owing to its extremely low surface area (*ca.* 0.02 m^2 g^{-1}),[8] Nafion® resin is not an effective catalyst for gas- or liquid-phase reactions where the reactant or solvent could not swell the framework of Nafion® resin. Recently, Harmer has developed a highly active high surface area Nafion® resin/silica composite material (surface area ≈ 350 m^2 g^{-1})[9] where small Nafion® resin particles (< 100 nm average diameters) have been entrapped in the porous silica framework during a sol–gel preparation.[10]

In the current study, a 13 mass% Nafion® resin/silica composite was used as a catalyst for the but-1-ene isomerization and comparisons were made with pure Nafion®–NR50 beads, Amberlyst-15® resin, HZSM-5, and amorphous silica–alumina catalysts.

Solid-acid catalysed but-1-ene isomerization to *cis*-but-2-ene, *trans*-but-2-ene and 2-methylpropene was carried out in the temperatures range 23–250 °C and ambient pressure in a 1/2″ stainless-steel reactor. Typically, 2.5–5.0 g of catalyst were loaded in the reactor. Prior to the reaction, Nafion® resin-based catalysts were dried in a vacuum oven at 150 °C overnight, Amberlyst-15® resin was dried at 110 °C overnight, HZSM-5 and silica–alumina were calcined at 400 °C for 2 h. The reactant but-1-ene was diluted with helium. The reaction mixture was analysed by an on-line GC equipped with an FID detector and a 25 m plot column coated with Al_2O_3/KCl.

The 13 mass% Nafion® resin/silica composite is a very effective catalyst for the but-1-ene to but-2-enes isomerization reaction under mild conditions. Even at 50 °C, near thermodynamic equilibrium values are obtained, which at 50 °C are 4.1, 70.5 and 25.4% for but-1-ene, *trans*-but-2-ene, and *cis*-but-2-ene, respectively,[11] and the experimental data are 6.6, 66.9 and 26.5%, respectively at MHSV of but-1-ene of 1 h^{-1} as shown in Fig. 1. The formation of 2-methylpropene and oligomers is negligible below 100 °C. The effective activation energy for but-1-ene isomerization to but-2-enes was determined to be 16.0 kcal mol^{-1} (cal = 4.184J) over this 13 mass% Nafion® resin/silica composite. Although no catalyst deactivation was observed over more than 12 hours for the but-1-ene isomerization to but-2-enes, at temperatures > 100 °C the formation of 2-methylpropene and oligomers decreased rather rapidly with time on stream.

On the other hand, over the Nafion®–NR50 beads but-1-ene conversion was < 1% at 50 °C (Table 1). But-1-ene conversion increased gradually with increased reaction temperature up to 200 °C. At the temperature where Nafion® resin effectively catalyses the but-1-ene isomerization, *ca.* 200 °C, significant yields of oligomers of butene (C_8^+ hydrocarbons) and the cracking products of oligomers (C_1–C_7 hydrocarbons) were also formed. In all cases, 2-methylpropene formation was negligible. A significantly greater amount of oligomers formed over the gel-type Nafion®–NR50 beads relative to the composite catalyst under the same reaction conditions.

The commercial macroporous Amberlyst-15® resin catalyst (surface area ≈ 45 m^2 g^{-1}) on heating to 100 °C is a quite effective catalyst for the but-1-ene isomerization to the linear but-2-enes. At the conditions employed, He : but-1-ene = 1.2 : 1.0 and MHSV of but-1-ene = 2.5 h^{-1}, a near equilibrium *n*-butene distribution, 8.2, 62.8 and 28.8% for but-1-ene, *trans*-but-2-ene and *cis*-but-2-ene, respectively, was obtained at 100 °C. However, at 50 °C only 31.2% of but-1-ene was converted into but-2-enes. Table 2 compares the catalytic

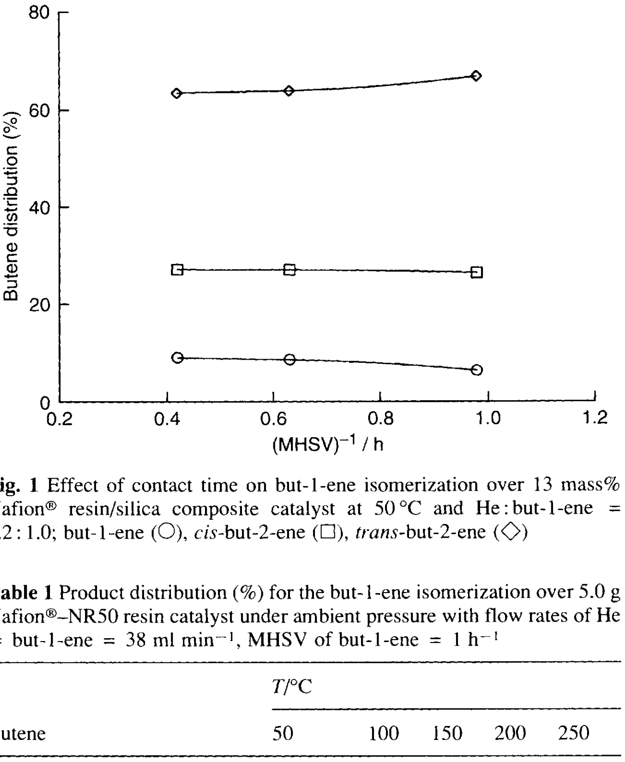

Fig. 1 Effect of contact time on but-1-ene isomerization over 13 mass% Nafion® resin/silica composite catalyst at 50 °C and He : but-1-ene = 1.2 : 1.0; but-1-ene (○), *cis*-but-2-ene (□), *trans*-but-2-ene (◇)

Table 1 Product distribution (%) for the but-1-ene isomerization over 5.0 g Nafion®–NR50 resin catalyst under ambient pressure with flow rates of He = but-1-ene = 38 ml min^{-1}, MHSV of but-1-ene = 1 h^{-1}

	T/°C				
Butene	50	100	150	200	250
But-1-ene	>99.0	86.1	38.1	18.6	24.1
trans-But-2-ene	—	5.8	36.0	48.1	42.9
cis-But-2-ene	< 1.0	8.0	25.7	31.6	31.0
2-Methylpropene	—	0.1	0.2	1.7	3.0
% Oligomers[a]	—	—	*ca.* 9	*ca.* 27	*ca.* 36

[a] Balanced by butenes.

performances of the above three catalysts at 50 °C and same MHSV of but-1-ene. Even though the 13 mass% Nafion® resin/silica composite has a very low acid capacity, 0.12 mequiv. g^{-1} in comparison to the 0.89 mequiv. g^{-1} of Nafion®–NR50 resin and 4.6 mequiv g^{-1} of the Amberlyst-15® resin, it is still a significantly more active catalyst even based on the unit masses.

Although the initial isomerization activity of the HZSM-5 is very high, extremely rapid loss of catalytic activity was observed. At 23 °C and MHSV of but-1-ene of 2.5 h^{-1}, but-1-ene conversion decreased from 48% after 5 min on stream to 5% after 20 min on stream. After being on stream for 30 min at 23 °C, the deactivated catalyst still showed very low activity even at 100 °C, 32% but-1-ene conversion at MHSV = 2.5 h^{-1}. Amorphous silica–alumina shows very low initial activity. No but-1-ene conversion can be realized at 50 °C and but-1-ene MHSV of 2.5 h^{-1}. Even at 100 °C, but-1-ene conversion is only *ca.* 6%.

Table 2 Product distributions (%) for the but-1-ene isomerization over solid-acid catalysts under ambient pressure at 50 °C with He : but-1-ene = 1.2 : 1.0 and MHSV of but-1-ene = 2.5 h^{-1}

	Catalyst		
Butene	Nafion® resin	Amberlyst-15®	13 mass % composite
But-1-ene	> 99.0	69.8	9.2
trans-But-2-ene	—	17.1	63.6
cis-But-2-ene	< 1.0	13.1	27.2

Overall, the extremely low surface area of Nafion®–NR50 beads results in low activity for the but-1-ene isomerization under the reaction conditions employed. However, the intrinsic isomerization activity of the active sites in Nafion® resin is high and when present in a more accessible microstructure it becomes a very effective catalyst. Very high catalytic activity was observed for the 13 mass% Nafion® resin/silica composite material. Equilibrium distribution of *n*-butenes can be readily obtained at 50 °C.

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