

Communication

# A Novel Catalyst for Isobutene Oligomerization to High Quality Gasoline

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**Dimerization of isobutene in liquid state to form high-octane value gasoline components was investigated over a homemade novel ion exchange resin, SPPEsk, which shows high activity and selectivity in isobutene dimerization under mild conditions.**

**Keywords** isobutene, oligomerization, gasoline, resins

Gasoline reformulation is an important way to improve the capability of fuel. Methyl-*tert*-butyl ether (MTBE) has been used as standard high-octane value gasoline components for years, but for environmental reason, it will be phased out in the US from the beginning of 2003.<sup>1</sup>

Branched saturated hydrocarbons appear to be the substitute and they can be obtained in different ways, such as isomerization of alkanes, alkylation or dimerization of propene and butenes. Light paraffin (C<sub>4</sub>—C<sub>8</sub>) skeletal isomerization usually occurs at the temperature as high as 300—500 °C and the research octane number (RON) for the obtained products is lower than 88.

Alkylate is a good gasoline blending, which has higher-octane value (> 90) and low volatility. However, in the process of alkylation, highly hazardous hydrofluoric acid or corrosive sulfuric acid is usually used as catalyst, and large amount of acid mud will be produced.

Dimerization of isobutene and further hydrogenation to form iso-octane is another way to obtain high-octane value gasoline. The reaction may occur over various catalysts, such as phosphoric acid,<sup>2</sup> aluminosilicate,<sup>3,4</sup> zeolite<sup>5</sup> and ion exchange resins.<sup>6-8</sup> Though the widely used commercial phosphoric acid catalyst gives high conversion and fully branched dimers under conditions of 200—300 °C and 3—

10 MPa, it is crumbly and difficult to handle.

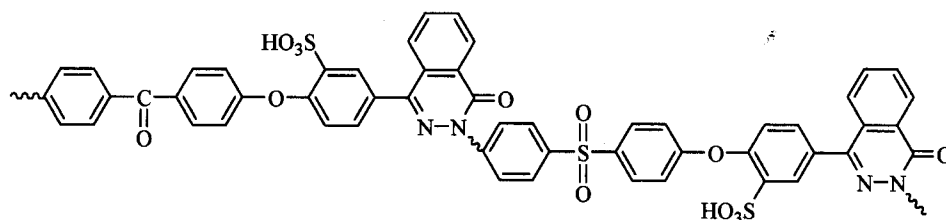
Acidic ion exchange resins may be the alternative of the present used catalysts for this purpose. Amberlyst resins have been proved to exhibit high catalytic activity. However, the selectivity to dimer is about 50% in these cases, so the processes have to be accompanied by adding alcohols to improve selectivity to C<sub>8</sub>.<sup>6,9</sup> It has been found that oligomerization of isobutene over Amberlyst-15 in mixed gas-liquid phase gives a triisobutene yield of higher than 80% under conditions of 90—110 °C and normal pressure.<sup>10</sup> In this communication, a novel catalyst, sulfonated poly(phthalazinone ether sulfone ketone) (SPPEsk), which has high selectivity to dimer and relatively high thermal stability was reported.

SPPEsk was prepared by homogeneous sulfonation of poly(phthalazinone ether sulfone ketone) (PPEsk)<sup>11</sup> with 30%—50% fuming sulfuric acid (*ca.* 5 mL/g PPEsk) at 60 °C for 3 h (chloroform used as solvent, 10 mL CHCl<sub>3</sub>/g PPEsk).<sup>12</sup> The chemical structure of SPPEsk is as follows (Scheme 1).<sup>13</sup>

NKC-9, a kind of macroporous styrene-divinylbenzene copolymers with sulfonic groups (product from Chemical Factory of Nankai University, similar to Amberlyst-15) was selected for comparison in the experiments. It was used without further treatment, and its acid capacity is higher than 4.7 mmol H<sup>+</sup>/g.

The reaction was carried out in a fixed bed reactor made of stainless steel (55 cm length, 1.2 cm O.D) at LHSV 2 h<sup>-1</sup>, 1.8 MPa (catalyst 4 mL). The products were separated in a glass gas-liquid separator. The gas

Scheme 1

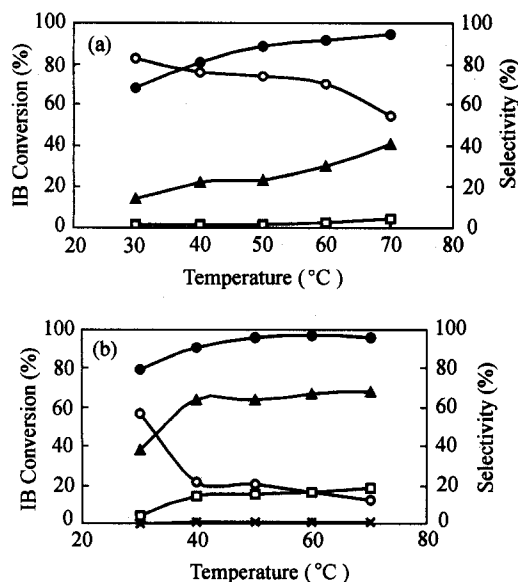


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phase was analyzed using GC100 (Shanghai Analytical Instrument Factory) equipped with an  $\text{AgNO}_3$  column and FID for calculation of the conversion of isobutene; the liquid phase was analyzed using GC 8A (Shimadzu Company) equipped with an OV-17 column (FID detection). In the later case temperature programming was adopted with an initial temperature of 40 °C, a final temperature of 200 °C and a programmed temperature rate of 5 °C/min.

Fig. 1(a) shows the dependence of the activity of the novel catalyst on the reaction temperature. It can be seen that with increasing the reaction temperature, conversions of the isobutene and the trimer increase, but the selectivity to dimer decreases. Even so the main product is dimer in the range of reaction temperatures (30–70 °C), especially at low temperature over SPPEK. For instance the selectivity to dimer is 83% at 30 °C.

Corresponding experimental data on commercially available resin, NKC-9, are given in Fig. 1(b). It can be seen from this figure that the dependence of conversion on reaction temperature for NKC-9 is similar to that for SPPEK, and this resin is more active than our homemade novel catalyst, but it should be emphasized that the main product in this case is triisobutene at the temperatures higher than 40 °C.



**Fig. 1** The effect of reaction temperature on the isobutene (IB) conversion and product distribution for (a) SPPEK and (b) NKC-9. ●—conversion; ○—dimer; ▲—trimer; □—tetramer; ×—pentamer.

Obviously, our homemade novel catalyst shows very good selectivity to dimer, compared with NKC-9 at the si-

milar isobutene conversion. For example, as SPPEK is used as catalyst, the selectivity to dimer is higher than 69% at the isobutene conversion of 91.4% (60 °C), while the selectivity to dimer is only 21.2% at the isobutene conversion of 90.8% on NKC-9 (40 °C).

The stability of the SPPEK catalyst has been tested at 40 °C for more than 200 h. The results indicate that the activity of the catalyst increases gradually in the first 20 h, then reaches a nearly steady state both in conversion and selectivity. This is similar to other ion exchange resin catalysts used in this kind of reactions.

In summary, SPPEK catalyst shows quite high activity, stability and selectivity to dimer in oligomerization of isobutene under mild conditions. Apart from this, as a kind of resins, it may be an environmentally-friendly catalyst, and has the potential to be widely used in isobutene oligomerization to produce high-octane value gasoline components.

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