

Moreover, they are less robust than the zeolitic catalysts operating at higher temperature (see below). Very recently, it was announced that LPI-100, a sulfated metal oxide (non-chlorinated) catalyst, has been commercialized by UOP (basis earlier work at Cosmo Oil and Mitsubishi Heavy Industries), which is about 80°C more active than the zeolitic ones but does not have the contaminant sensitivity of chlorinated catalysts, and has already been in commercial operation since December 1996 [128, 143].

### 7.5.3.2

#### Isomerization over Zeolitic Catalysts

Zeolitic paraffin isomerization catalysts are less active than the amorphous ones, and as a consequence have to be operated at higher temperatures, i.e., at about 250°C, with the inherent disadvantages of a lower maximum conversion per pass and of a lower content of dibranched species that can be obtained. These disadvantages are, however, offset by their much lower sensitivity to poisons, and hence these catalysts have found wide use, both in the dedicated Shell-developed Hysomer process, and in the UOP process, with the I-7 catalyst. These processes are often coupled with an i/n-separation process, such as Isosiv developed by Union Carbide, with recycle of the normal paraffins. Thus the Hysomer/Isosiv combination is called the Total Isomerization Process (TIP) (see Fig. 7.44 [112]); while Hysomer alone can raise the research octane number to about 80, with the Isosiv process values of 90 are achieved [112]. The preferred catalysts are based on mordenite, which is first converted into the acid form and then acid-leached to increase the silica/alumina ratio [112, 144, 145]. Indeed, the value of the silica/alumina ratio which gives maximum activity observed by Guisnet et al. (about 20) is close to the value expected for isolated aluminum atoms;

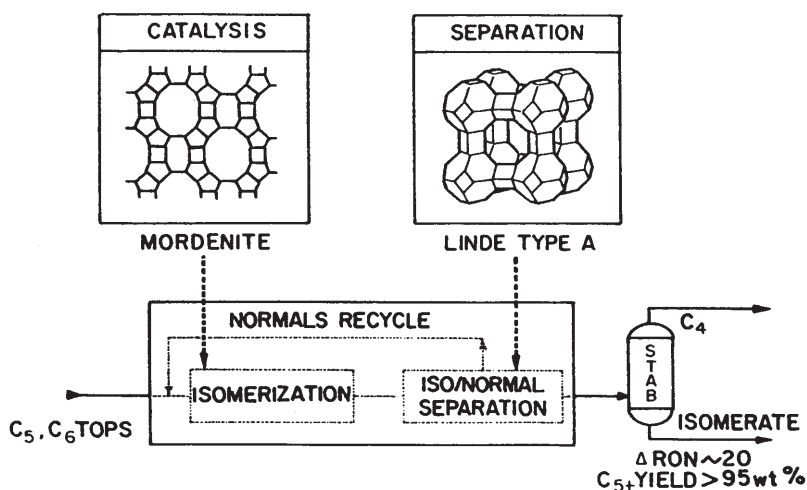


Fig. 7.44. Paraffin Total Isomerization Process (TIP) [112]

a higher silica/alumina ratio merely leads to a decreased number of sites, whilst a lower ratio leads to next nearest neighboring Al atoms, which are known to be less acidic [146]. These authors also report higher stability at the higher silica/alumina ratio, with high-alumina catalysts even benefiting from increased hydrogen pressures [147], and some speculations on the origin of the effects have been made. The final calcination temperature of the mordenite catalyst was reported to be important [148], which is not surprising. Some studies on isomerization catalysts based on other zeolites than mordenite have been published recently, dealing with Pd/USY (Pd particle size effects) [149, 150], with zeolite omega [151, 152] and with zeolite beta [133–135, 153]; a detailed discussion is beyond the scope of this review.

One can expect the isomerization area to remain important, and the challenge is to isomerize also the higher paraffins. In the conventional bifunctional catalysis, mechanistic considerations indicate, however, that the selectivities that can be attained will be clearly lower than with C<sub>5</sub>–C<sub>6</sub> isomerization. Possibly the high i/n ratios that are obtained in hydrocracking can be of value to obtain suitable C<sub>7+</sub> streams.

#### 7.5.4

##### Isomerization of Light Olefins

This is a good place to discuss the skeletal isomerization of olefins, a process that in recent years has attracted a lot of attention, also from a mechanistic point of view. With the reduction of the concentration of high octane components such as olefins and benzene in gasoline, a need exists to produce other high octane components. The ethers such as MTBE and TAME have high octane numbers and are therefore of clear interest. With the anticipated rapid increase in demand for these ethers alternative manufacturing routes are of immediate interest. One attractive route for MTBE is the manufacture from isobutene and methanol, and this makes isobutene an attractive raw material. Therefore a selective skeletal isomerization of n-butene into isobutene is clearly attractive, as discussed in [154]. A number of catalyst systems for this reaction are known, such as those based on alumina or silica-alumina (see, e.g., [155]), but in general these exhibit a very short lifetime. In particular the system developed at Shell, Amsterdam, using a particular ferrierite, is very attractive in that it shows both a high selectivity and stability [156], and is the basis of a process developed at Lyondell [157]. The catalytic and mechanistic issues are similar to those in paraffin isomerization: an equilibrium which is better at lower temperatures, the optimum aluminum content of the zeolite, and the issue whether the reaction follows a monomolecular or bimolecular mechanism (a recent reference to this issue, debated by many groups, is given in [158]).

#### 7.5.5

##### Paraffin/Olefin Alkylation

Paraffin/olefin alkylation is a major process for the manufacture of gasoline components, since the formed “C<sub>8</sub>” compounds have a high degree of branching,

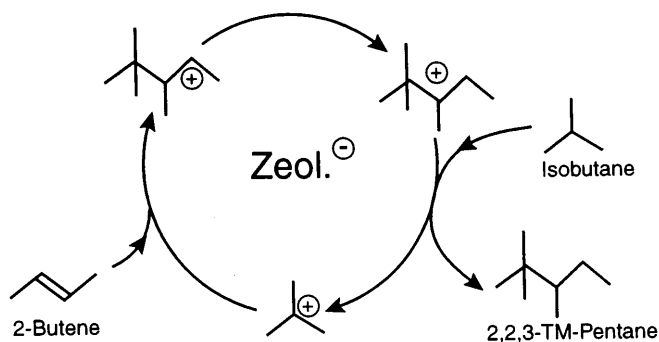


Fig. 7.45. Mechanism of alkylation [159]

and therefore a high octane number. Given the fact that for every olefin molecule used one (often less valuable) isobutane molecule is also used, it is not surprising that this process can be more attractive than olefin oligomerization. Worldwide capacity is high, and has been estimated at 40 million t/a (HF process) and 30 million t/a ( $\text{H}_2\text{SO}_4$  process) [159]. These two existing processes both have their disadvantages as to undesirable chemicals (HF), or waste streams (spent acid,  $\text{H}_2\text{SO}_4$ ). Therefore for a long time a solid, non-toxic, non-corrosive catalyst has been sought. To understand the issues involved it is useful to consider the mechanisms of alkylation (e.g., Fig. 7.45) and olefin oligomerization (Fig. 7.46), as given in [159]. Starting with an adsorbed carbenium ion (e.g., from butene or from isobutane) an olefin is added yielding a branched  $\text{C}_8$  molecule. This molecule can now be desorbed through a hydrogen transfer reaction with isobutane, creating an alkylation cycle. Failure to do this timely will result in oligomerization, instead of alkylation, (the general phenomenon for a deactivated alkylation catalyst) and will also lead to heavy paraffins responsible for

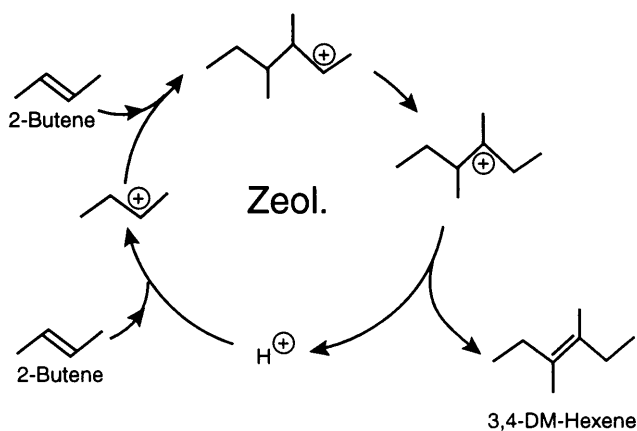


Fig. 7.46. Mechanism of olefin oligomerization [159]