

The role of zeolites in oil refining

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During the past few decades, researchers have made significant contributions to the oil refining and petrochemistry. Current innovation in this field is largely based on the use of zeolites or more broadly molecular sieves (also called ‘solid acids’ in refinery process) as catalysts.¹ The refining processes are mainly light naphtha isomerization, olefin alkylation, reforming, cracking and hydrocracking (**Figure 1**). The extensive consumption of energy is majorly based on the combustion of fossil fuels provided by refining.² There is much interest in replacing as a primary energy resource fossil fuels by alternative renewable energy sources from sustainability and environment protection point of view.³ However, there are several reasons to continue with this conventional energy source such as the discovery of new oil fields, modern extraction technologies⁴ and efficiency in the use of oil and the difficulty in developing on a massive scale other energy sources.

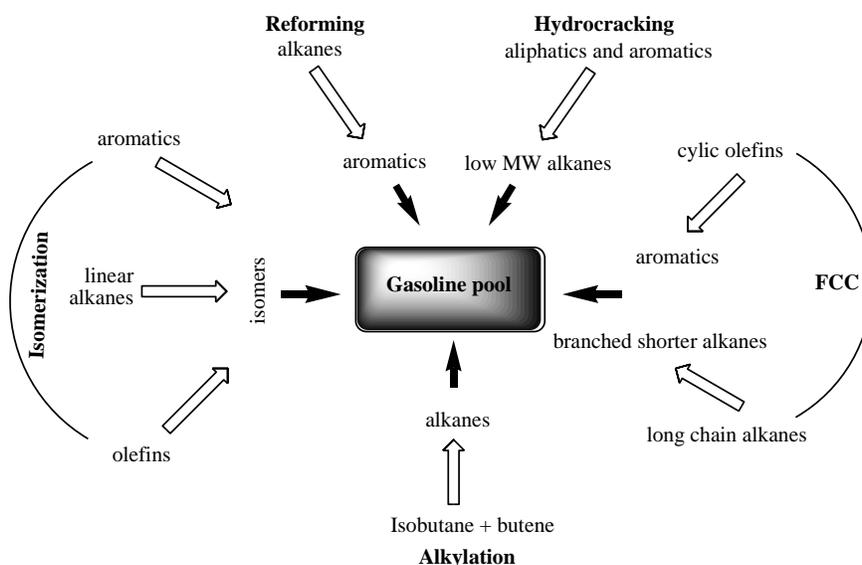


Figure 1. Major processes of oil refining

The advantage with zeolites as a catalyst is their large surface area in heterogeneous catalysis. Zeolites, as defined are crystalline, porous aluminosilicates having primary building blocks TO_4 tetrahedra with Si^{4+} or Al^{3+} cation (T atoms) at the center and four oxygen atoms at the corners. Each corner is shared by two TO_4 units forming a tridimensional framework consisting of micropores. The porosity allows the mass transfer from the exterior to the interior of the zeolite particle and the intracrystalline diffusion of molecules smaller than the micropore dimensions. Zeolites can be classified depending on the pore size as small, medium and large pore size zeolites when the openings of the micropores are constituted by rings of eight, ten or twelve oxygen atoms. Many properties of the zeolites are controlled by the aluminum content by having a large influence on their catalytic activity. The aluminum content may vary from one

Al atom per Si atom (zeolite X) to the case of all-silica zeolite (silicalite) with complete absence of aluminum (zeolite Y). Due to the different charge of Al^{3+} and Si^{4+} , the TO_4 tetrahedra can have a net negative charge (AlO_4) or can be neutral (SiO_4). The presence of Al^{3+} in framework positions generates an equivalent number of negative charges which have the presence of cations. These charge-balancing cations occupy the micropore and are bonded to the lattice by Coulombic forces, therefore, can be totally or partially exchanged by different cations.

The acidity of catalysts is an extremely important property for refining since many of the processes⁵ such as the generation of carbocations and proteolytic C–C bond cleavages. Apart from that, hydrogenation/dehydrogenation efficiency of catalysts is another important part of the refining process. The problem with acid zeolites is that they are not hydrogenation catalysts. Therefore, this functionality has been provided to these solids by adding suitable metals, such as Ni, Pd or Pt. These bifunctional zeolites act as a solid support with a large surface area to highly dispersed metal nanoparticles in the isomerization of linear alkanes and hydrocracking of heavy oil fractions.

Fluid catalytic cracking (FCC):

The zeolite catalysts have been largely used in fluid catalytic cracking process. The process is an occurrence of several molecular transformations such as C–C bond breaking in long chain linear alkanes, isomerization of linear into branched alkanes and dehydrogenation of cyclic olefins into aromatic naphthenes, during which, vacuum gasoil converts into gasoline. The FCC catalyst contains a solid matrix (between 50 and 90% of the total) which has the zeolite (10 to 50 wt%) dispersed on it. The purpose to have the solid matrix is to provide physical and mechanical resistance and embedding the active component (zeolite) with some additives that increase the tolerance of the zeolite against deactivation by poisoning. As a catalyst, large pore zeolites (dealuminated zeolite containing rare earths) are preferred. The dealumination process enhances the activity of the zeolite. Steam treatment of zeolites is performed to reduce framework Al and produce an ultrastable Y (USY)-type zeolite with high structural stability. At the same time, the mesoporosity of the crystallites increases due to the partial damage of the zeolite particles which is also beneficial for the activity and stability of the zeolite by favoring intracrystalline diffusion of substrates and products. The crystal size of the USY zeolite is a key for controlling the activity and selectivity, which, in general increase with a decrease in average crystal size. However, this fraction contains a large extent of sulfur which is mainly present in the form of dialkylsulfides, mercaptans, thiophenes, benzothiophene and dibenzothiophenes. Therefore, desulfuration post-treatments are required such as the selective liquid-phase oxidation of thiophene and similar compounds under mild conditions, using *tert*-butyl hydroperoxide or H_2O_2 as the oxidizing reagent. This process oxidizes the sulfur atom into sulfoxide or sulfone, which indeed increases the water solubility and boiling point of the sulfur compounds and allows their easier separation from the fuel.

Isobutane–butene alkylation:

About 12% of the blend in the gasoline pool may come from butene alkylation. Classical alkylation processes are based on the use of homogeneous liquid acids and particularly HF and H_2SO_4 . However, safety measures and their corrosiveness are the major disadvantages associated with such methods. One alternative to the use of liquid acids is the use of solid acids. Amorphous silica–alumina has been used as solid catalyst, but zeolites have the advantage of a higher activity and durability. Some noble or transition metals associated with the catalyst allow the regeneration step by using the hydrogen in gasification and hydrocracking of coke which may neutralize the acid sites and thus deactivate the catalyst by pore blocking. By the hydrogenation process, noble metals convert the coke into gaseous hydrocarbons and retain

the zeolite activity. A Ni/mordenite catalyst converts C2–C5 olefins to gasoline, kerosene, and distillate at high pressures (10–50 bar) and low temperatures (200–280 °C).

Linear paraffin (naphtha) isomerization:

As we know, the octane number decreases with an increase in the number of carbons of linear alkanes. Therefore, the long-chain linear compounds (mainly C7 and C8) should be isomerized to branched alkanes. In the process, a bifunctional zeolite or an acid metal oxide both containing noble metals is preferred, as the conventional zeolites face deactivation due to the presence of sulfur in the stream. Mordenite is a monodirectional zeolite with twelve membered ring channels. The acidity of mordenite is increased by dealumination to reach the optimal Si/Al ratio (around 16), obtained by a combination of steaming and acid washing. These modified zeolites are more efficient for light straight run naphtha isomerization. Pt supported on dealuminated zeolite provides higher sulfur tolerance of the catalyst. However, Pt supported on sulfated zirconia (a super acid solid) was proposed as an alternative to zeolites for light straight run paraffin isomerization, which could perform isomerization of linear alkanes at temperatures between 150 and 200 °C unlike zeolites (from 240 to 280 °C). Unfortunately, Pt supported on sulfated zirconia has a low stability in the presence of sulfur and water. For this reason, zeolites are preferred for this process. Pt nanoparticles supported on nanocrystalline Beta (ncBeta) zeolite has been considered as a convenient catalyst for co-processing linear alkanes and benzene. A comparative study of the conversion of *n*-alkanes into the corresponding isoalkanes in the presence of benzene showed that the Pt-ncBeta is more stable and efficient than Pt-mordenite. Additionally, Pt-ncBeta was able to perform simultaneous hydrogenation of benzene to provide a mixture of cyclohexane and methylcyclopentane with complete conversion under these conditions.

Reforming:

Reforming is one of the most important processes in refining as it converts the heavy naphtha fraction into mixtures of aromatic compounds with lower molecular weight such as benzene, toluene and xylenes. The purpose to obtain these aromatics by dehydrogenation is that they display octane numbers over 100 and their addition into the gasoline pool increases the octane number of the blend. As the dehydrogenation process proceeds with the hydrogen evolution, acidic zeolites are not necessary as the catalyst. Therefore, the noble metals with high hydrogenation/dehydrogenation activity form the main active component and most of the commercial reforming catalysts contain Pt supported on non-acidic zeolites or metal oxides with large surface area.

Hydrocracking:

The process of converting the heavier fractions into the mixtures of hydrocarbons with lesser carbons accompanied by the hydrogenation is called hydrocracking. It requires the presence of hydrogen as well as the metal catalysts for hydrogenation to minimize the deactivation of the zeolite catalyst by the formation of coke and carbonaceous residues. Hydrocracking is performed on a large scale to transform the gasoil from coke into the lighter compounds. There are two types of hydrocracking processes (i) single-stage hydrocracking, where the fractionating unit is located after the hydrocracker (ii) two-stage hydrocracking, having the main fractionating unit located between two hydrocrackers. In later process, the first reactor is used to perform hydrotreatment of the feed to eliminate sulfur, nitrogen, oxygen and metals with a light hydrocracking of the alkanes. The second reactor predominantly upholds the effective shortening of the average number of chain carbons. Hydrocracking requires bifunctional catalysts with ability to promote hydrogenation of olefins and cracking of alkanes. During the dehydrogenation at the metal

sites, the *n*-paraffin forms *n*-olefins which get protonated by the acid sites of zeolite to form secondary carbenium ions. These ions further rearrange into more stable tertiary carbenium ions which may form cracked products through β -scission at the carbocation center or form isomerized alkanes after the hydrogenation of iso-olefins.

In the modern times, the large consumption of fossil fuels as the energy source for electricity production and transportation continues. In the leading areas, zeolite catalysts for light paraffin–olefin alkylation remain in center of attraction to the researchers. The major problem of zeolites as catalysts is the impeded diffusion of large molecules through the internal pores, as the catalytic activity of Ni-Y zeolite decreases with increasing alkane chain length.^{1a} However, in fluid catalytic cracking, zeolite Y and its variants USY and REY remain the catalysts of choice in future because of their low cost and versatility. Zeolite-Y-based bifunctional hydrocracking catalysts are extremely valuable with high levels of basic nitrogen or high levels of sulfur poison. Although, new catalytic processes to further reduce the sulfur content below the legal limits is a challenge. The refinery–petrochemical interface is believed to have better opportunity. The processes to maximize olefins and aromatics with clean fuels production are the points of attraction to refiners. The metal-supported zeolites with a combination of micro and mesopores are expected to contribute to the refining process with consideration to the nature of biomass derived molecules.

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