Chapter 2
Model Catalysts

Abstract The idea is to understand of the physical-chemical properties of a catalytic process that allows making the choice of a catalyst presenting the best activity and desired product selectivity.

Keywords Model catalyst • Reaction mechanism • Selection of a catalyst

The idea is if we have the understanding of the physical-chemical properties of a catalytic process, then it may be possible to choose a catalyst presenting the best activity and desired product selectivity. If the process is thermodynamically possible, then it may be possible to preview the reaction behavior and the catalytic performance, as well as an understanding of the reaction mechanism, which explains the intrinsic activity and product distribution or selectivity of a desired product. We may select the most efficient catalyst of a desired process based on empirical experiments; however, with this idea, one can find novel catalysts of a chemical process or of an inefficient existing process in the industry.

For a better comprehension of this model, we started with a well-known process: the production of aromatics from propene, involving different reaction mechanisms, like cyclization, oligomerization, and dehydrogenation reactions resulting in aromatics. In this process, there are several other secondary reactions, such as carbonization and cracking [1–9].

The principal reaction and the secondary reactions are presented in Fig. 2.1 [1].

The principal reaction is thermodynamically possible and favored at high temperatures, around 300 °C, and at atmospheric pressure.

It is noteworthy that dimerization occurs in the first step, followed by the cyclization and dehydrogenation in steps 2 and 3, respectively. There are still undesired side reactions, such as dimerization and branched coking.

On the other hand, we may classify these reactions in different families. From the empirical experiments, it may be possible to select a catalyst for the specific reaction, tested separately, verifying the catalytic performance of activity and selectivity or product distribution. Depending of the reactions, the selection of a catalyst can be found through many attempts, but a general choice is practically unviable.

The dehydrogenation reaction occurs preferentially on metallic sites. The competition of molecules on sites depends on the geometrical and electronic structures;
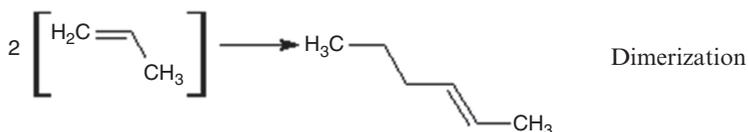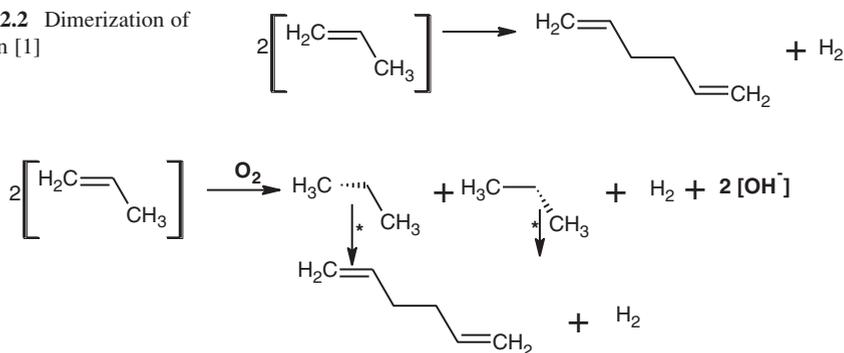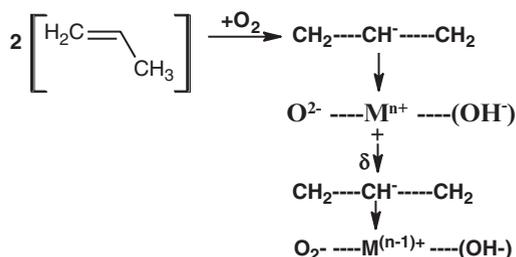
Principal reaction

Secondary reaction

Dimerization
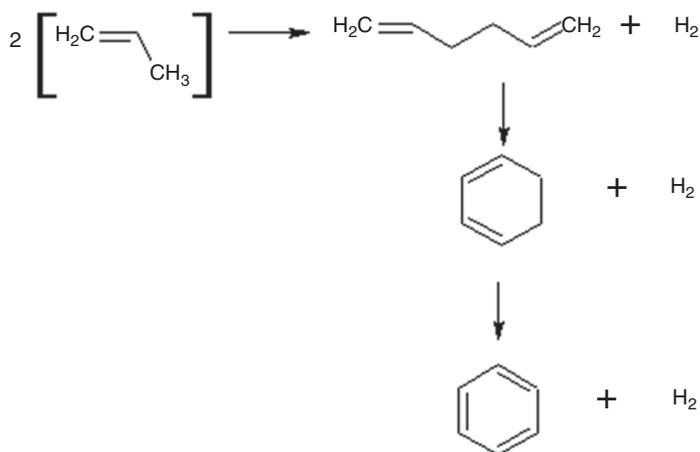
Carbonization

Fig. 2.1 Reaction pathway: production of aromatics from propene [1]

however, the determining step depends also on other factors which will be focused in this model. The usual metals are Ni, Co, W, Cr, Fe, Pd, Pt, and Rh, which in many cases favor coke formation. Otherwise, the cyclization and olygomerization reactions occur on acid sites or metallic oxides, such as zeolites and GaO_2 and ZnO, respectively. The protonic H-ZSM5 zeolite is the most recommended; however, supported metal oxides on zeolites are bifunctional catalysts, occurring in the dehydrogenation or hydrogenation, cyclization, and oligomerization reactions simultaneously. Specifically for aromatization of propane or propylene, Pt/HSM5, Cu/HSM5, Ga/HSM5, and Ge/HSM5 [1, 4], which have well-dispersed metallic sites and acidic sites, were done successfully.

    These considerations led us to think about how to describe the surface chemical reaction mechanisms. This requires knowledge of the structure of molecules and the

Fig. 2.2 Dimerization of olefin [1]

$$2\left[\ H_2C{=}\!\!\diagdown_{CH_3}\ \right] \longrightarrow H_2C{=}\diagdown\diagup\diagdown{=}CH_2 \quad + H_2$$

$$2\left[\ H_2C{=}\!\!\diagdown_{CH_3}\ \right] \xrightarrow{\ O_2\ } H_3C\overset{\cdots}{\underset{*}{\diagdown}}_{CH_3} + H_3C{-}\overset{\cdots}{\underset{*}{\diagdown}}_{CH_3} + H_2 + 2\,[OH^-]$$

$$H_2C{=}\diagdown\diagup\diagdown{=}CH_2 \quad + \quad H_2$$

Fig. 2.3 Oxidative dehydrogenation [adapted from Trimm, D.L., "Design of Industrial Catalysis" Ed. Elsevier, Scientific Publishing Company, (1980)], where (*asterisk*) represents the active sites

Fig. 2.4 Scheme of the surface mechanism [adapted from Trimm, D.L., "Design of Industrial Catalysis" Ed. Elsevier, Scientific Publishing Company, (1980)]

$$2\left[\ H_2C{=}\!\!\diagdown_{CH_3}\ \right] \xrightarrow{\ +O_2\ } CH_2\text{----}CH^-\text{-----}CH_2$$

$$O^{2-}\text{----}M^{n+}\text{----}(OH^-)$$
$$\overset{+}{\underset{\delta}{\downarrow}}$$
$$CH_2\text{----}CH^-\text{-----}CH_2$$
$$O_2^-\text{----}M^{(n-1)+}\text{----}(OH\text{-})$$

possible adsorption forms, as well as the likely metals and electronic structure of the molecule, known as geometric and electronic effects, which may occur simultaneously or separately [2, 3, 5–8]. As a starting point, one chooses a model surface mechanism for each reaction [1].

According to Trimm [1], starting from the olefin in the first step occurs a linear dimerization with loss of hydrogen (Fig. 2.2).

Trimm [1] suggested that the dehydrogenation at the surface may occur via an oxidative route. In this case, there is formation of intermediate π-allyl with removal of hydrogen by oxygen from the surface of the solid, forming two double bonds (Fig. 2.3).

In this mechanism, it is assumed that the hydrogen of the double bond will be removed by the available oxygen on the surface, forming intermediate π-allyl species in adjacent positions that favor the dimerization. It forms hexadiene that when desorbed releases the active sites of the surface and replenishes the surface oxygen. During the formation of intermediate π-allyl species, there is charge redistribution between the adsorbed complexes, as shown in Fig. 2.4 [1].

If the two allylic species are linked at the same ion to form a dimer, it implies that the metal M is capable of accepting two electrons. If the ion has only two separated valences, the ability of quick transfer of two successive electrons from the same ion is more difficult. Thus, the abstraction of a second electron from a second
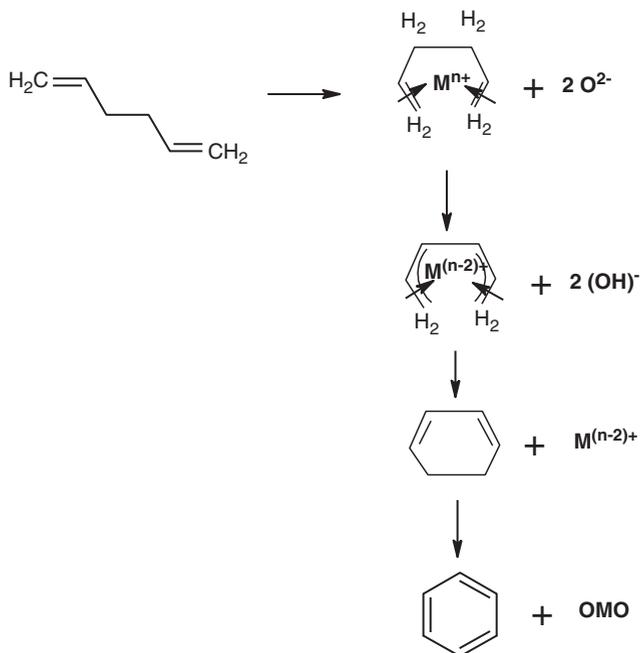
Fig. 2.5 The cyclization mechanism at the surface [adapted from Trimm, D.L., "Design of Industrial Catalysis" Ed. Elsevier, Scientific Publishing Company, (1980)]

adjacent allylic specie is easier, i.e., abstraction of electrons from two adjacent species will favor the dimerization.

Metallic oxides with separated valences in two oxidation states and can adsorb π-allylic species are Sn^{+2}/Sn^{+4} and In^{+1}/In^{+3}. The lower oxidation valence tends to be more stable and increases attraction of electrons [1, 5].

The next steps are the cyclization and dehydrogenation that behave similarly, according to the scheme shown below. During the double cyclization, the adsorbed bindings may cause charge redistribution and electron transfer of these species to the metal ion, allowing the cyclization in adjacent positions and subsequent dehydrogenation and recovery of surface-active sites [1] (Fig. 2.5).

Indeed, the adsorption of π-allylic species is possible on metal ions whose electronic structure is capable to receive electrons (d_1, d_2, d_3, d_8, d_9) and have configurations with geometric structure capable to positioning molecules in adjacent places. These properties will be studied in more detail in later chapters.

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