



Article Acid Site Density as a Kinetic Descriptor of Catalytic Reactions over Zeolites

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Abstract: A mathematical framework for the quantitative description of site density dependence of catalytic data (activity and selectivity) was developed considering that changes in the electrostatic contribution to the Gibbs energy of an elementary reaction on the acid sites in zeolites depend on the proximity of these sites. For the two-step sequence with the most abundant surface intermediate, an expression for turnover frequency explicitly containing the acid site density was derived. The treatment was extended to linear sequences of elementary reaction and analysis of the acid site density on selectivity in parallel and consecutive reactions, allowing to quantitatively relate the ratio between products for such reactions. Experimental data on Prins condensation of isopulegol with acetone and transformations of syngas over mesoporous H-ZSM-5 supported cobalt nanoparticles to a mixture of iso- and normal hydrocarbons were used as a show case.

Keywords: acid site density; zeolites; kinetics



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1. Introduction

Solid Brønsted acid catalysts, such as zeolites, are of immense importance for oil refining and transformations of chemicals [1–3]. Significant efforts have been made on the development of novel materials and mechanistic interpretation of catalytic data. Several parameters, including the structure, morphology and the Si/Al ratio, presence of various ions, etc., can be used to fine-tune the number, nature, strength and distribution of acid sites [4–7].

Kinetic analysis of catalytic reactions over zeolites often is limited by only considering the acid sites as isolated and noninteracting with each other, allowing to apply the classical approaches of heterogeneous catalytic kinetics [8–10]. On the other hand, there is a little doubt that active sites in zeolitic materials possess different acid strength and thus activity, which is manifested by analysis of acidity with ammonia or pyridine [11–13] or calorimetry [14].

One of the descriptors, which can be used to reflect the complexity of catalytic reactions over zeolites, is the acid site density [15,16], as the dependence of turnover frequency (TOF) as a function of this parameter indicates a structure sensitivity similar to the dependence of TOF vs. the metal dispersion in the case of catalysis over supported metals. Recently, it was demonstrated that TOF calculated per proton can be independent of the acid site density, decrease, or even pass through the maximum [15,17–19]. Moreover, in [19], it was shown that for the Prins cyclization of (-) isopulegol with acetone, also selectivity, expressed as the ratio of products, depends on the acid site concentration.

2. Site Density Dependence for Adsorption

An explanation proposed for the maxima in TOF vs. the acid site density was related [17] to changes in the ionic strength depending itself on the volumetric densities of hydronium ions, and thus on the concentration of Brønsted acid sites. The general applicability of the Debye–Hückel or the semi-empirical Truesdell–Jones equations to the nanoconfined space of zeolites might be questionable [20], and thus an alternative approach to account for the spatial constraints in such a nanoconfined space was proposed [21].

More precisely, along the nonelectrostatic contribution to the Gibbs energy of the solid surface with acid sites, also the electrostatic one was considered:

$$\Delta G_{es} = \frac{N_A Z_{H^+} Z_{H^+} e^2}{4\pi\varepsilon_0 \varepsilon d_{ave,H^+ - H^+}} = \frac{\varphi Z_{H^+} Z_{H^+}}{d_{ave,H^+ - H^+}}$$
(1)

where Z_{H^+} is the charge of acid sites/hydronium ions, d_{ave,H^+-H^+} is the average distance between these ions/acid sites, ε_0 is the permittivity in vacuum, ε dielectric constant, e is the charge of the electron, N_A is Avogadro's number, and φ is lumped constant $\varphi = N_A e^2 / 4\pi\varepsilon_0 \varepsilon$.

Changes in the electrostatic contribution to the Gibbs energy upon adsorption on the acid sites with a partial donation of protons to the adsorbate were expressed [21] as

$$\Delta G_{ads} = \Delta G_{ads,nes}^0 + \delta_{Z_{H^+}} \frac{\varphi}{d_{ave,H^+ - H^+}}$$
(2)

where $\delta_{Z_{H^+}}$ is the increment of the electrostatic contribution to the Gibbs energy upon adsorption on the acid sites. From Equation (2), changes in the electrostatic contribution depend on proximity of sites or the average distance between the acid sites d_{ave,H^+-H^+} . From the relationship between the Gibbs energy and the equilibrium constant the equilibrium constant for adsorption can be easily expressed:

$$K_{ads,0} = e^{-\frac{\Delta G_{ads}^0}{RT}} e^{-\delta_{Z_{H^+}} \varphi/d_{ave,H^+ - H^+}}$$
(3)

Further linking the rate constant *k* with the equilibrium constants *K* through the linear free energy relationship [22] the rate constant of adsorption takes the form

$$k = gK^{\alpha} = k_0 e^{-\alpha \delta_{Z_{H^+}} \varphi / d_{ave, H^+ - H^+}}$$
(4)

where α is the Polanyi parameter ($0 < \alpha < 1$). The average distance between acid sites can be calculated through the density of acid sites ρ_{H^+} (mol/g) defined via the overall surface area divided by the effective area around the surface site. This effective area in the simplest case is taken as a circle with the diameter equal to the average distance between acid sites giving, thus,

$$\rho_{H^+} = \frac{S_{N_2}}{\frac{\pi d_{ave,H^+ - H^+}^2}{4}N_A}$$
(5)

and subsequently

$$d_{ave,H^{+}-H^{+}} = \sqrt{\frac{4S_{N_{2}}}{\pi\rho_{H^{+}}N_{A}}}$$
(6)

Finally, the rate of adsorption can be expressed via the Brønsted acid site density:

$$k = k_0 e^{-\alpha \varphi \delta_{Z_{H^+}} \sqrt{\frac{\pi \rho_{H^+} N_A}{4S_{N_2}}}} = k_0 e^{-\alpha \varphi' \sqrt{\rho_{H^+}}}$$
(7)

where

$$\varphi' = \varphi \delta_{Z_{H^+}} \sqrt{\frac{\pi N_A}{4S_{N_2}}} = \frac{\delta_{Z_{H^+}} N_A e^2}{4\pi \varepsilon_0 \varepsilon} \sqrt{\frac{\pi N_A}{4S_{N_2}}}$$
(8)

3. Two-Step Sequence

Quite often, heterogeneous catalytic kinetics is expressed by the two-step mechanism with two kinetically significant steps [23,24], and one most abundant surface intermediate *I*:

$$\frac{1.* + A_1 \leftrightarrow *I + B_1}{2.*I + A_2 \leftrightarrow * + B_2}$$

$$(9)$$

$$\frac{A_1 + A_2 \leftrightarrow B_1 + B_2}{4 + A_2 \leftrightarrow B_1 + B_2}$$

where A_1 and A_2 are reactants, B_1 , and B_2 are products, * is the surface vacant site, and *I* is an adsorbed intermediate.

The reaction rate for this mechanism being well-known is presented below for turnover frequency per acid site [25]:

$$TOF_{[H^+]} = \frac{k_{+1}C_{A_1}k_{+2}C_{A_2} - k_{-1}C_{B_1}k_{-2}C_{B_2}}{k_{+1}C_{A_1} + k_{+2}C_{A_2} + k_{-1}C_{B_1} + k_{-2}C_{B_2}}$$
(10)

where C_{A1} , etc., are concentrations of reagents, and k_i is the rate constants.

The rate constant for the first step in mechanism (9) directly follows from Equation (7), namely,

$$k_{+1(H^+)} = k_{+1} e^{-\alpha_1 \varphi' \sqrt{\rho_{H^+}}}$$
(11)

where α_1 is the Polanyi parameter of the first step. Similarly, for the backward reaction of the second step, one obtains

$$k_{-2(H^+)} = k_{-2} e^{-\alpha_2 \varphi' \sqrt{\rho_{H^+}}}$$
(12)

The rate constant for the backward reaction of the first step is obtained from Equation (11) and the acid site density dependence of the adsorption equilibrium constant:

$$K_{H^+} = K_0 e^{\varphi' \sqrt{\rho_{H^+}}}$$
(13)

leading to

$$k_{-1(H^+)} = k_{-1} e^{(1-\alpha_1)\varphi'\sqrt{\rho_{H^+}}}$$
(14)

Analogously, it holds for the forward reaction of the second step:

$$k_{+2(H^+)} = k_{+2} e^{(1-\alpha_2)\varphi'\sqrt{\rho_{H^+}}}$$
(15)

The TOF per acid site can be expressed subsequently:

$$TOF_{H^+} = \frac{(k_{+1}C_{A_1}k_{+2}C_{A_2} - k_{-1}C_{B_1}k_{-2}C_{B_2})e^{(1-\alpha_2-\alpha_1)\varphi'\sqrt{\rho_{H^+}}}}{k_{+1}C_{A_1}e^{-\alpha_1\varphi'\sqrt{\rho_{H^+}}} + k_{+2}C_{A_2}e^{(1-\alpha_2)\varphi'\sqrt{\rho_{H^+}}} + k_{-1}C_{B_1}e^{(1-\alpha_1)\varphi'\sqrt{\rho_{H^+}}} + k_{-2}C_{B_2}e^{-\alpha_2\varphi'\sqrt{\rho_{H^+}}}}$$
(16)

When both steps are irreversible, Equation (16) can be transformed into

$$TOF_{H^+} = \frac{k_{+1}C_{A_1}k_{+2}C_{A_2}e^{(1-\alpha_1-\alpha_2)\varphi'\sqrt{\rho_{H^+}}}}{k_{+1}C_{A_1}e^{-\alpha_1\varphi'\sqrt{\rho_{H^+}}} + k_{+2}C_{A_2}e^{(1-\alpha_2)\varphi'\sqrt{\rho_{H^+}}}}$$
(17)

Or

$$TOF_{H^+} = \frac{k_{+2}C_{A_2}e^{(1-\alpha_2)\varphi'\sqrt{\rho_{H^+}}}}{1 + \frac{k_{+2}C_{A_2}}{k_{+1}C_{A_1}}e^{(1-\alpha_2+\alpha_1)\varphi'\sqrt{\rho_{H^+}}}} = \frac{\omega_{+2}e^{(1-\alpha_2)\varphi'\sqrt{\rho_{H^+}}}}{1 + \frac{\omega_{+2}}{\omega_{+1}}e^{(1-\alpha_2+\alpha_1)\varphi'\sqrt{\rho_{H^+}}}}$$
(18)

where ω_{+2} is the acid site density independent frequency of steps [25]:

$$\omega_{+1} = k_{+1}C_{A_1}; \\ \omega_{+2} = k_{+2}C_{A_2};$$
⁽¹⁹⁾

It can be demonstrated that Equation (18) exhibits a maximum of TOF as a function of the acid site density. To illustrate this, a minimum of the reciprocal value of TOF can be determined by taking $d(1/TOF)/d \rho_{H^+atmax}$ equal to zero:

$$d(1/TOF_{H^+})' = \left(\frac{e^{(\alpha_2 - 1)\varphi'\sqrt{\rho_{H^+}}}}{\omega_{+2}} + \frac{e^{\alpha_1\varphi'\sqrt{\rho_{H^+}}}}{\omega_{+1}}\right)' = 0$$
(20)

Giving then

$$\frac{1}{\omega_{+2}}e^{(\alpha_2-1)\varphi'(\sqrt{\rho_{H^+}})_{\max}}\frac{(\alpha_2-1)\varphi'}{2(\sqrt{\rho_{H^+}})_{\max}} + \frac{1}{\omega_{+1}}e^{(\alpha_1)\varphi'(\sqrt{\rho_{H^+}})_{\max}}\frac{\alpha_1\varphi'}{2(\sqrt{\rho_{H^+}})_{\max}} = 0$$
(21)

Equation (21), after some manipulations, is

$$\frac{\alpha_2 - 1}{\omega_{+2}} e^{(\alpha_2 - 1)\varphi'(\sqrt{\rho_{H^+}})_{\max}} + \frac{\alpha_1}{\omega_{+1}} e^{\alpha_1 \varphi'(\sqrt{\rho_{H^+}})_{\max}} = 0$$
(22)

$$e^{(\alpha_2 - \alpha_1 - 1)\varphi'(\sqrt{\rho_{H^+}})_{\max}} = \frac{\alpha_1 \omega_{+2}}{(1 - \alpha_2)\omega_{+1}}$$
(23)

and

$$(\alpha_2 - \alpha_1 - 1)\varphi'(\sqrt{\rho_{H^+}})_{\max} = \ln \frac{\alpha_1 \omega_{+2}}{(1 - \alpha_2)\omega_{+1}}$$
(24)

can rewritten in a form allowing to obtain an explicit expression for the acid site density at which the maximum in TOF is observed:

$$(\rho_{H^+})_{\max} = \left[\frac{\ln\frac{\alpha_1\omega_{+2}}{(1-\alpha_2)\omega_{+1}}}{(\alpha_2 - \alpha_1 - 1)\varphi'}\right]^2$$
(25)

When the Polanyi parameters of the steps are equal to each other, Equation (25) can be simplified:

$$\left(\rho_{H^{+}}\right)_{\max} = \left[\frac{\ln\frac{(1-\alpha)\omega_{+1}}{\alpha\omega_{+2}}}{\varphi'}\right]^{2}$$
(26)

Figure 1 illustrates that the value of the acid site density at which maxima in the TOF are observed depends on the values of the Polanyi parameter and the frequencies of steps. The latter implies that not only the rate constants vary depending on the catalyst, but also the concentrations of reagents can have an impact on the experimentally observed values of the acid site density corresponding to the maxima in TOF. For high values of the Polanyi parameter (e.g., 0.75), such dependence will be less pronounced.

Comparison of the experimental data for reactions occurring over catalysts with different acid site density is typically performed at the same values of the reaction parameters (i.e., temperature and concentration of reagents). The current theoretical analysis highlights that the acid site density, at which TOF exhibits a maximum, is a function not only on the catalyst, but the process parameters as well. This apparently urges a detailed experimental exploration of this hypothesis.



Figure 1. Dependence of $(\rho_{H^+})_{max}(\varphi')^2$ as a function of the ratio of the frequencies of the first and second steps in the forward direction according to Equation (26).

4. Christiansen Sequence

An extension of the reaction mechanism discussed above is a Christiansen sequence containing a linear step of isomerization in the adsorbed state [26]:

$$1.* + A_1 \leftrightarrow *I_1 + B_1$$

$$2.* I_1 \leftrightarrow *I_2$$

$$3.* I_2 + A_2 \leftrightarrow * + B_2$$

$$A_1 + A_2 \leftrightarrow B_1 + B_2$$
(27)

Such a type of generic mechanism can be relevant in the context of skeletal isomerization, cracking or alkylation reactions. In a simplified treatment of this reaction mechanism, it can be assumed that $\delta_{Z_{H^+}}$ or the increment of the electrostatic contribution to the Gibbs energy upon adsorption on the acid sites is the same for both intermediates I_1 and I_2 .

The equilibrium constant of the first step is then

$$K_1 = k_{+1} e^{-\alpha_1 \varphi' \sqrt{\rho_{H^+}}} / k_{-1} e^{(1-\alpha_1)\varphi' \sqrt{\rho_{H^+}}} = K_{1,0} e^{-\varphi' \sqrt{\rho_{H^+}}}$$
(28)

For the third step of Equation (27), it can be written as

$$K_3 = k_3 e^{(1-\alpha_3)\varphi'\sqrt{\rho_{H^+}}} / k_{-3} e^{-\alpha_3\varphi'\sqrt{\rho_{H^+}}} = K_{3,0} e^{\varphi'\sqrt{\rho_{H^+}}}$$
(29)

As the overall constant $K = K_1 K_2 K_3$ does not depend on the acid site density, it is apparently clear that for the isomerization step 2 in (27), the equilibrium constant does not depend on the acid site density either.

An expression for the three-step Christiansen sequence with linear steps is well-known [25,27]:

$$TOF = \frac{\omega_{+1}\omega_{+2}\omega_{+3} - \omega_{-1}\omega_{-2}\omega_{-3}}{\omega_{+2}\omega_{+3} + \omega_{-3}\omega_{+2} + \omega_{-3}\omega_{-2} + \omega_{+3}\omega_{+1} + \omega_{-1}\omega_{+3} + \omega_{-1}\omega_{-3} + \omega_{+1}\omega_{+2} + \omega_{-2}\omega_{+1} + \omega_{-2}\omega_{-1}}$$
(30)

With the frequencies of steps in the particular case of the three-step reaction on acid sites,

$$\omega_{+1} = k_{+1}e^{-\alpha_{1}\varphi'}\sqrt{\rho_{H^{+}}}C_{A_{1}}; \omega_{-1} = k_{-1}e^{(1-\alpha_{1})\varphi'}\sqrt{\rho_{H^{+}}}C_{B_{1}};
\omega_{+2} = k_{+2}; \omega_{-2} = k_{-2};
\omega_{+3} = k_{+3}e^{(1-\alpha_{3})\varphi'}\sqrt{\rho_{H^{+}}}C_{A_{2}}; \omega_{-3} = k_{-3}e^{-\alpha_{3}\varphi'}\sqrt{\rho_{H^{+}}}C_{B_{2}}$$
(31)

When in the reaction mechanism all steps are irreversible Equation (30) can be further simplified to

$$TOF_{H^+} = \frac{k_{+1}k_{+2}k_{+3}e^{(1-\alpha_3-\alpha_1)\varphi'\sqrt{\rho_{H^+}}}C_{A_1}C_{A_2}}{k_{+2}k_{+3}e^{(1-\alpha_3)\varphi'\sqrt{\rho_{H^+}}}C_{A_2} + k_{+1}k_{+3}e^{(1-\alpha_3-\alpha_1)\varphi'\sqrt{\rho_{H^+}}}C_{A_1}C_{A_2} + k_{+1}k_{+2}e^{-\alpha_1\varphi'\sqrt{\rho_{H^+}}}C_{A_1}}$$
(32)

Often, the value of the Polanyi parameter is equal to 0.5 [25], implying that $\alpha_1 = \alpha_3 = \alpha = 0.5$ and

$$TOF_{H^+} = \frac{k_{+1}k_{+2}k_{+3}C_{A_1}C_{A_2}}{k_{+2}k_{+3}e^{(1-\alpha)\varphi'\sqrt{\rho_{H^+}}}C_{A_2} + k_{+1}k_{+2}e^{-\alpha\varphi'\sqrt{\rho_{H^+}}}C_{A_1} + k_{+1}k_{+3}C_{A_1}C_{A_2}}$$
(33)

The acid site density can be determined in a similar fashion as for the two-step sequence (Equation (20)), giving

$$d(1/TOF_{H^+})' = \left(\frac{e^{(1-\alpha)\varphi'\sqrt{\rho_{H^+}}}}{\omega_{+1}} + \frac{e^{-\alpha\varphi'\sqrt{\rho_{H^+}}}}{\omega_{+3}}\right)' = 0$$
(34)

Thus,

$$\frac{(1-\alpha)}{\omega_{+1}}e^{(1-\alpha)\varphi'(\sqrt{\rho_{H^+}})_{\max}} - \frac{\alpha}{\omega_{+3}}e^{-\alpha\varphi'(\sqrt{\rho_{H^+}})_{\max}} = 0$$
(35)

leading to an expression of the acid site density at the maximum TOF when the Polanyi parameters are equal to 0.5.

$$\rho_{H^+\max} = \left[\frac{\ln\frac{\alpha\omega_{+1}}{(1-\alpha)\omega_{+3}}}{\varphi'}\right]^2 = \left[\frac{\ln\frac{\omega_{+1}}{\omega_{+3}}}{\varphi'}\right]^2 \tag{36}$$

Similar to the treatment above, the acid site density, at which TOF exhibits a maximum, depends on the frequencies of steps and thus process parameters.

The treatment above considered that the increment of the electrostatic contribution to the Gibbs energy of adsorbed species is the same, which should not be necessarily the case upon adsorption on the acid sites for both intermediates I_1 and I_2 .

In such an instance, instead of Equation (8), the relevant expressions for intermediates I_1 and I_2 will be

$$\varphi_{I_1}' = (\delta_{Z_{H^+}})_{I_1} \frac{N_A e^2}{4\pi\varepsilon_0 \varepsilon} \sqrt{\frac{\pi N_A}{4S_{N_2}}}; \varphi_{I_2}' = (\delta_{Z_{H^+}})_{I_2} \frac{N_A e^2}{4\pi\varepsilon_0 \varepsilon} \sqrt{\frac{\pi N_A}{4S_{N_2}}}$$
(37)

resulting in the expressions for turnover frequencies of steps 1 and 3 of the reaction mechanism (27):

$$\omega_{+1} = k_{+1}e^{-\alpha_1\varphi_{I_1}'\sqrt{\rho_{H^+}}}C_{A_1}; \omega_{-1} = k_{-1}e^{(1-\alpha_1)\varphi_{I_1}'\sqrt{\rho_{H^+}}}C_{B_1}; \omega_{+3} = k_{+3}e^{(1-\alpha_3)\varphi_{I_2}'\sqrt{\rho_{H^+}}}C_{A_2}; \omega_{-3} = k_{-3}e^{-\alpha_3\varphi_{I_2}'}\sqrt{\rho_{H^+}}C_{B_2}$$
(38)

Considering the modified equilibrium constant of these steps,

$$K_1 = K_{1,0} e^{-\varphi_{I_1}' \sqrt{\rho_{H^+}}}; \ K_3 = K_{3,0} e^{\varphi_{I_2}' \sqrt{\rho_{H^+}}}$$
(39)

An expression for the equilibrium constant of the second step is

$$K_{2} = K/K_{1}K_{3} = Ke^{(\varphi_{I_{1}}' - \varphi_{I_{2}}')\sqrt{\rho_{H^{+}}}}/(K_{1,0}K_{3,0}) = K_{2,0}e^{(\varphi_{I_{1}}' - \varphi_{I_{2}}')\sqrt{\rho_{H^{+}}}}$$
(40)

Implying that

$$\omega_{+2} = k_{+2} e^{(1-\alpha_2)(\varphi_{I_1}' - \varphi_{I_2}')\sqrt{\rho_{H^+}}}; \\ \omega_{-2} = k_{-2} e^{-\alpha_2(\varphi_{I_1}' - \varphi_{I_2}')\sqrt{\rho_{H^+}}}$$
(41)

For the three-step catalytic sequence of all irreversible steps, it holds that

$$TOF_{H^{+}} = \frac{k_{+1}k_{+2}k_{+3}C_{A_{1}}C_{A_{2}}e^{(-\alpha_{1}\varphi_{I_{1}}'+(1-\alpha_{3})\varphi_{I_{2}}'+(1-\alpha_{2})(\varphi_{I_{1}}'-\varphi_{I_{2}}'))\sqrt{\rho_{H^{+}}}}{k_{+2}k_{+3}C_{A_{2}}e^{((1-\alpha_{2})(\varphi_{I_{1}}'-\varphi_{I_{2}}')+(1-\alpha_{3})\varphi_{I_{2}}')\sqrt{\rho_{H^{+}}}} + k_{+3}k_{+1}C_{A_{1}}C_{A_{2}}e^{((1-\alpha_{3})\varphi_{I_{2}}'-\alpha_{1}\varphi_{I_{1}}')\sqrt{\rho_{H^{+}}}} + k_{+1}k_{+2}C_{A_{1}}e^{(-\alpha_{1}\varphi_{I_{1}}'+(1-\alpha_{2})(\varphi_{I_{1}}'-\varphi_{I_{2}}'))\sqrt{\rho_{H^{+}}}}$$
(42)

which for $\alpha_1 = \alpha_2 = \alpha_3 = \alpha = 0.5$ is simplified to

$$TOF_{H^+} = \frac{k_{+1}k_{+2}k_{+3}C_{A_1}C_{A_2}}{k_{+2}k_{+3}C_{A_2}e^{0.5\varphi_{I_1}'\sqrt{\rho_{H^+}}} + k_{+3}k_{+1}C_{A_1}C_{A_2}e^{0.5(\varphi_{I_2}'-\varphi_{I_1}')\sqrt{\rho_{H^+}}} + k_{+1}k_{+2}C_{A_1}e^{(-0.5\varphi_{I_2}')\sqrt{\rho_{H^+}}}$$
(43)

Apparently, Equation (43) also exhibits a maximum in TOF as a function of the acid site density, the determination of which requires solving the following rather complex equation:

$$d(1/TOF_{H^+})' = \left(\frac{e^{(0.5)\varphi_{I_1}'\sqrt{\rho_{H^+}}}}{\omega_{+1}} + \frac{e^{0.5(\varphi_{I_2}'-\varphi_{I_1}')\sqrt{\rho_{H^+}}}}{\omega_{+2}} + \frac{e^{(-0.5\varphi_{I_2}')\sqrt{\rho_{H^+}}}}{\omega_{+3}}\right)' = 0$$
(44)

5. Parallel Reactions: Coupling between Cycles

The conceptual ideas in the analysis above can be applied to elucidation of the influence of acid site density on selectivity in parallel and consecutive reactions.

First, the case of kinetic coupling between catalytic cycles will be considered with a joint reaction intermediate:

The reaction scheme in Equation (47) reflects two reaction routes, $N^{(1)}$ and $N^{(2)}$, taking place simultaneously. On the right-hand side of the equations for the steps, the respective stoichiometric (Horiuti) numbers are given, which should be multiplied by the equations of steps to yield the chemical equations along the different routes. For example, after multiplying the equations of the first and the second steps in Equation (45) by unity and the third step by zero and summing up all concentrations on the left and right sides, concentrations of the surface species are cancelled, giving the equation for the first route, i.e., $A_1 + A_2 \leftrightarrow B_1 + B_2$.

A chemical example of such a mechanism can be the formation of carbocations in the first step with the subsequent splitting of different carbon–carbon bonds. For the sake of simplicity, just the irreversible steps in Equation (45) are considered. It can be easily demonstrated using the steady-state approximation,

$$dI_1/dt = 0 \tag{46}$$

that

$$r_1 = r_2 + r_3$$
 (47)

leading subsequently to

$$r_{B_2} = \frac{\omega_{+1}\omega_{+2}}{\omega_{+1} + \omega_{+2} + \omega_{+3}} = \frac{k_{+1}C_{A_1}k_{+2}C_{A_2}}{k_{+1}C_{A_1} + k_{+2}C_{A_2} + k_{+3}C_{A_3}}$$
(48)

$$r_{B_3} = \frac{\omega_{+1}\omega_{+3}}{\omega_{+1} + \omega_{+2} + \omega_{+3}} = \frac{k_{+1}C_{A_1}k_{+3}C_{A_3}}{k_{+1}C_{A_1} + k_{+2}C_{A_2} + k_{+3}C_{A_3}}$$
(49)

The overall rate is

$$-r_{A_1} = \frac{\omega_{+1}(\omega_{+2} + \omega_{+3})}{\omega_{+1} + \omega_{+2} + \omega_{+3}}$$
(50)

Selectivity to a product B₂ can be easily obtained from Equations (48) and (49), giving

$$S_{B_2} = \frac{r_{B_2}}{r_{B_2} + r_{B_3}} = \frac{k_{+2}C_{A_2}}{k_{+2}C_{A_2} + k_{+3}C_{A_3}}$$
(51)

Analogously, it holds for the forward reaction of the second and third steps similar to Equation (15) that

$$k_{+2(H^+)} = k_{+2} e^{(1-\alpha_2)\varphi'\sqrt{\rho_{H^+}}}; \ k_{+3(H^+)} = k_{+3} e^{(1-\alpha_3)\varphi'\sqrt{\rho_{H^+}}}$$
(52)

Dependence of selectivity on the acid site density for the simplified case of three irreversible steps is thus

$$S_{B_2} = \frac{k_{+2}e^{(1-\alpha_2)\varphi'\sqrt{\rho_{H^+}}}C_{A_2}}{k_{+2}e^{(1-\alpha_2)\varphi'\sqrt{\rho_{H^+}}}C_{A_2} + k_{+3}e^{(1-\alpha_3)\varphi'\sqrt{\rho_{H^+}}}C_{A_3}} = \frac{1}{1 + \frac{k_{+3}C_{A_3}}{k_{+2}C_{A_2}}e^{(\alpha_2-\alpha_3)\varphi'\sqrt{\rho_{H^+}}}}$$
(53)

while the ratio between the products is defined as

$$\frac{r_{B_3}}{r_{B_2}} = \frac{k_{+3}C_{A_3}}{k_{+2}C_{A_2}} e^{(\alpha_2 - \alpha_3)\varphi'\sqrt{\rho_{H^+}}}$$
(54)

The latter equation can be linearized as

$$\ln \frac{r_{B_3}}{r_{B_2}} = \ln \frac{k_{+3}C_{A_3}}{k_{+2}C_{A_2}} + (\alpha_2 - \alpha_3)\varphi'\sqrt{\rho_{H^+}}$$
(55)

allowing to relate the rates and subsequently the ratios between products with the square root of the acid site density. Figure 2 illustrates the successful implementation of Equation (55) to treat the experimental ratio of 4R and 4S chromenols obtained from the Prins cyclization of (-)isopulegol with acetone [19] as a function of the square root of the total acid site density.



Figure 2. The ratio of reaction products in the Prins condensation of isopulegol with acetone as a function of the total concentration of acid sites. Points—experimental data from [19], calculations—Equation (55). The calculated values of $\ln(k_{+3}C_{A_3}/k_{+2}C_{A_2})$ and $(\alpha_2 - \alpha_3)\varphi'$ are respectively 0.50338 ± 0.46502 and 0.13566 ± 0.03495.

6. Parallel Reactions: Separate Cycles

The mechanism given by Equation (45) represents an example of a catalytic sequence with a joint edge connecting the nodes of the graph (Figure 3a) using the formalism of the graph theory [27]. One route shown in Figure 3 comprises steps 1 and 2, while in the second route besides step 1 common for both routes, step 3 is involved.

On the contrary, in the mechanism with two parallel routes featured in Figure 3b, there is only one common node corresponding to the vacant acid site and separate cycles with stepss 1, 2 and 3, 4. Subsequently, in the most general case, the reaction mechanism can be written in the following way:

$$1.^{*} + A_{1} \leftrightarrow {}^{*}I_{1} + B_{1} \qquad 1 \quad 0$$

$$2.^{*}I_{1} + A_{2} \leftrightarrow {}^{*} + B_{2} \qquad 1 \quad 0$$

$$3.^{*} + A_{1} \leftrightarrow {}^{*}I_{2} + B_{3} \qquad 0 \quad 1$$

$$4.^{*}I_{2} + A_{3} \leftrightarrow {}^{*} + B_{4} \qquad 0 \quad 1$$

$$N^{(1)}: A_{1} + A_{2} \leftrightarrow B_{1} + B_{2}; N^{(2)}: A_{1} + A_{3} \leftrightarrow B_{3} + B_{4}$$
(56)

There are obviously many variations of the mechanism in Equation (56), such as the cases when A_2 is the same as A_3 reflecting for example different adsorption modes through different functional groups, or when B_1 is the same as B_3 . The corresponding equations can be easily derived from a more general consideration.



Figure 3. Mechanisms of parallel reactions: (**a**) with kinetic coupling and a joint edge, (**b**) with one joint node. A_1, A_2, A_3, A_4 —reactants, B_1, B_2, B_3, B_4 —products.

For the sake of simplicity, steps 2 and 4 are considered irreversible, giving

$$\theta_{I_1} = \frac{k_{+1}C_{A_1}}{k_{-1}C_{B_1} + k_{+2}C_{A_2}} \theta_0; \ \theta_{I_2} = \frac{k_{+3}C_{A_1}}{k_{-3}C_{B_3} + k_{+4}C_{A_3}} \theta_0$$
(57)

where θ_0 is the coverage of vacant site and θ_{I_1} , θ_{I_2} are coverages of respective intermediates. The rates along different routes can be calculated considering the site balance resulting this in

$$r^{N(1)} = r_{+2} = \frac{k_{+1}C_{A_1}k_{+2}C_{A_2}}{k_{-1}C_{B_1} + k_{+2}C_{A_2}} \frac{1}{D}; \ r^{N(2)} = r_{+4} = \frac{k_{+3}C_{A_1}k_{+4}C_{A_3}}{k_{-3}C_{B_3} + k_{+4}C_{A_3}} \frac{1}{D}$$
(58)

with

$$D = 1 + \frac{k_{+1}C_{A_1}}{k_{-1}C_{B_1} + k_{+2}C_{A_2}} + \frac{k_{+3}C_{A_1}}{k_{-3}C_{B_3} + k_{+4}C_{A_3}}$$
(59)

The ratio between the rates along different routes is thus

$$\frac{r^{N(1)}}{r^{N(2)}} = \frac{k_{+1}k_{+2}C_{A_2}}{k_{-1}C_{B_1} + k_{+2}C_{A_2}} \frac{k_{-3}C_{B_3} + k_{+4}C_{A_3}}{k_{+3}k_{+4}C_{A_3}}$$
(60)

The expressions for the rate constants as a function of the site density follow from the general considerations discussed above, giving

$$k_{+1} = k'_{+1}e^{-\alpha_1\varphi_{I_1}'\sqrt{\rho_{H^+}}}; k_{-1} = k'_{-1}e^{(1-\alpha_1)\varphi_{I_1}'\sqrt{\rho_{H^+}}}; k_{+2} = k'_{+2}e^{(1-\alpha_2)\varphi_{I_1}'\sqrt{\rho_{H^+}}}; k_{+3} = k'_{+3}e^{-\alpha_3\varphi_{I_2}'\sqrt{\rho_{H^+}}}; k_{-3} = k'_{-3}e^{(1-\alpha_3)\varphi_{I_2}'\sqrt{\rho_{H^+}}}; k_{+4} = k'_{+4}e^{(1-\alpha_4)\varphi_{I_2}'\sqrt{\rho_{H^+}}};$$
(61)

The ratio of rates takes a relatively complicated form:

$$\frac{r^{N(1)}}{r^{N(2)}} = \frac{k'_{+1}k'_{+2}e^{(1-\alpha_2-\alpha_1)\varphi_{I_1}'\sqrt{\rho_{H^+}}}C_{A_2}}{k'_{+3}k'_{+4}e^{(1-\alpha_4-\alpha_3)\varphi_{I_2}'\sqrt{\rho_{H^+}}}C_{A_3}}\frac{k'_{-3}e^{(1-\alpha_3)\varphi_{I_2}'\sqrt{\rho_{H^+}}}C_{B_3} + k'_{+4}e^{(1-\alpha_4)\varphi_{I_2}'\sqrt{\rho_{H^+}}}C_{A_3}}{k'_{-1}e^{(1-\alpha_1)\varphi_{I_1}'\sqrt{\rho_{H^+}}}C_{B_1} + k'_{+2}e^{(1-\alpha_2)\varphi_{I_1}'\sqrt{\rho_{H^+}}}C_{A_2}}$$
(62)

An expression similar to Equation (54) can be obtained when all steps are irreversible with, however, different dependencies on the concentration of substrates:

$$\frac{r^{N(1)}}{r^{N(2)}} = \frac{k'_{+1}}{k'_{+3}} e^{(\alpha_3 - \alpha_1)\varphi_{I_1}'\sqrt{\rho_{H^+}}}$$
(63)

Equation (63) can be also linearized in the same way as Equation (55).

7. Consecutive Reactions

The last example is related to a network of consecutive reactions as visualized in Equation (64):

$$1.* + A \equiv *A \qquad 1 \qquad 1 \qquad 0$$

$$2.*A \rightarrow *B \qquad 1 \qquad 1 \qquad 0$$

$$3.*B \equiv B + * \qquad 1 \qquad 0 \qquad -1$$

$$4.*B \rightarrow *C \qquad 0 \qquad 1 \qquad 1$$

$$5.*C \equiv \underline{*+C} \qquad 0 \qquad 1 \qquad 1$$

$$N^{(1)}: A \leftrightarrow B; N^{(2)}: A \leftrightarrow C; N^{(3)}: B \leftrightarrow C$$

(64)

To make the illustration more apparent, only two products are considered and moreover steps 1, 3 and 5 are considered to be at quasi-equilibria and steps 2 and 4 are assumed to be irreversible. The expressions for the rate and equilibrium constants naturally follow from the considerations above:

$$K_{1} = K'_{1}e^{-\varphi_{A}'\sqrt{\rho_{H^{+}}}}; K_{3} = K'_{3}e^{\varphi_{B}'\sqrt{\rho_{H^{+}}}}; K_{5} = K'_{5}e^{\varphi_{C}'\sqrt{\rho_{H^{+}}}}$$

$$k_{+2} = k'_{+2}e^{(1-\alpha_{2})(\varphi_{A}'-\varphi_{B}')\sqrt{\rho_{H^{+}}}}; k_{+4} = k'_{+4}e^{(1-\alpha_{4})(\varphi_{B}'-\varphi_{C}')\sqrt{\rho_{H^{+}}}}$$
(65)

It should be noted that the routes $N^{(1)}$ to $N^{(3)}$ are not independent ones, as route $N^{(3)}$ can be obtained by the subtraction of route $N^{(1)}$ from the route $N^{(2)}$ as discussed previously in the literature for similar reaction networks [28]. Subsequently, the reaction network can be described with just two routes having the reaction rates

$$r^{N^{(1)}} = \frac{k_{+2}K_1C_A}{K_1C_A + K_3^{-1}C_B + K_5^{-1}C_C}, \ r^{N^{(2)}} = \frac{k_{+4}K_3^{-1}C_B}{K_1C_A + K_3^{-1}C_B + K_5^{-1}C_C}$$
(66)

which should be solved together with the generation equations for the components

$$-\frac{1}{\rho_{cat}}\frac{dC_A}{dt} = r^{N^{(1)}}; \ \frac{1}{\rho_{cat}}\frac{dC_B}{dt} = r^{N^{(1)}} - r^{N^{(2)}}$$
(67)

where ρ_{cat} is the catalyst bulk density. Subsequently, selectivity toward the product B can be obtained

$$S_B = \frac{r^{N^{(1)}} - r^{N^{(2)}}}{r^{N^{(1)}}} = 1 - \frac{k_{+4}K_3^{-1}C_B}{k_{+2}K_1C_A} = 1 - \frac{C_B}{C_A} \frac{k'_{+2}(K'_3)^{-1}e^{(1-\alpha_2)(\varphi_A'-\varphi_B')}\sqrt{\rho_{H^+}}e^{-\varphi_B'}\sqrt{\rho_{H^+}}}{k'_{+4}K'_1e^{(1-\alpha_4)(\varphi_B'-\varphi_C')}\sqrt{\rho_{H^+}}e^{-\varphi_A'}\sqrt{\rho_{H^+}}}$$
(68)

Or,

$$S_{B} = 1 - \frac{C_{B}}{C_{A}} \frac{k'_{+2} (K'_{3})^{-1}}{k'_{+4} K'_{1}} e^{((1-\alpha_{2})(\varphi_{A}'-\varphi_{B}') - (1-\alpha_{4})(\varphi_{B}'-\varphi_{C}') + (\varphi_{A}'-\varphi_{B}'))\sqrt{\rho_{H^{+}}}}$$
(69)

which can be written in the following way:

$$S_B = 1 - M e^{\lambda \sqrt{\rho_{H^+}}} \frac{C_B}{C_A} = 1 - M' \frac{C_B}{C_A}$$
(70)

With the expressions for constants,

$$M' = \frac{k'_{+2}(K'_3)^{-1}}{k'_{+4}K'_1} e^{\lambda\sqrt{\rho_{H^+}}} = M e^{\lambda\sqrt{\rho_{H^+}}}$$
(71)

$$\lambda = ((1 - \alpha_2)(\varphi_A' - \varphi_B') - (1 - \alpha_4)(\varphi_B' - \varphi_C') + (\varphi_A' - \varphi_B'))$$
(72)

Equation (70) gives a possibility to describe dependence of selectivity to the reactant B concentration as a function of conversion derived previously in the literature for a similar case [29]:

$$S_B = \frac{1}{1 - M'} \frac{1}{\delta} \left[(1 - \delta)^{M'} - (1 - \delta) \right]$$
(73)

where δ is the conversion. Equation (73) can be presented in a more explicit form:

$$S_B = \frac{1}{1 - Me^{\lambda \sqrt{\rho_{H^+}}}} \frac{1}{\delta} \left[(1 - \delta)^{Me^{\lambda \sqrt{\rho_{H^+}}}} - (1 - \delta) \right]$$
(74)

As visible from Figure 4, selectivity declines with an increase in the value of *M*, which reflects in essence how fast the second route is compared to the first one. At the same level of conversion, a higher acid site density will apparently result in low selectivity.



Figure 4. Dependence of selectivity vs. conversion according to Equation (73) for different values of M'.

An analytic expression for the concentration of the intermediate product B in a consecutive reaction network of the type presented in Equation (64) was derived in the literature [29]:

$$C_B = \frac{1}{1 - M'} \left(\frac{C_A^{M'}}{\left(C_A^0\right)^{M' - 1}} - C_A \right)$$
(75)

where C_A^0 is the initial concentration of the reactant *A*. If the initial concentrations of *B* and *C* are equal to zero, the concentration of the component *C* easily follows from the reaction stoichiometry:

$$C_B + C_C = C_A^0 - C_A \tag{76}$$

giving thus an expression for the ratio between the final and the intermediate products:

$$\frac{C_C}{C_B} = \frac{C_A^0 - C_A - \frac{1}{1 - M'} \left(\frac{C_A^{M'}}{\left(C_A^0\right)^{M' - 1}} - C_A\right)}{\frac{1}{1 - M'} \left(\frac{C_A^{M'}}{\left(C_A^0\right)^{M' - 1}} - C_A\right)} = -1 + \frac{(1 - M')\delta}{(1 - \delta)^{M'} - (1 - \delta)}$$
(77)

Equation (77) presents a dependence of the ratio between the final and the intermediate products as a function on conversion δ and can be used in a more explicit form illustrating a dependence on the acid site density:

$$\frac{C_C}{C_B} = -1 + \frac{(1 - Me^{\lambda\sqrt{\rho_{H^+}}})\delta}{(1 - \delta)^{Me^{\lambda\sqrt{\rho_{H^+}}}} - (1 - \delta)}$$
(78)

As an example of Equation (78) utilization to treat the experimental data, the ratio of iso to normal hydrocarbons obtained in transformations of syngas over mesoporous H-ZSM-5 supported cobalt nanoparticles [30] is considered. In that study, the materials were prepared with a different degree of proton exchange, which serves as a proxy for the acid site density. Obviously, the reaction network is much more complicated, but for the illustration properties, the *iso* compounds can be considered the final, while the normal hydrocarbons the intermediate, products. The experimental data in [30] were reported at the same conversion of ca. 30%, thus allowing to probe directly the applicability of Equation (78). The calculations along with the experimental data are presented in Figure 5, clearly confirming that an equation of type (78) can explain the distribution of products in a consecutive reaction in a quantitative way with high precision.



Figure 5. Dependence of the ratio of iso to normal hydrocarbons vs. a degree of proton exchange in transformations of syngas over mesoporous H-ZSM-5 supported cobalt nanoparticles. The experimental data are digitalized from [30].

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