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Reply to Letter to the Editor

Comment on the paper "Diffusion and adsorption selectivities of hydrocarbons over FCC catalysts" by A.M. Ávila, C.M. Bidabehere and U. Sedran [Chem. Eng. J. 132 (2007) 67–75]

In a letter by Kärger [1] about our paper on the assessment of the diffusivities in fluid catalytic cracking (FCC) catalysts [2], it is mentioned that diffusivities calculated by different methods (macroscopic in one case, or from pulsed field gradient (PFG) NMR technique in the other) are different. It is also pointed out that the results of diffusivities for a given compound obtained from different macroscopic techniques are not explained satisfactorily. Both facts are true. We understand that the letter is not only a valuable contribution to the field, considering its large and laborious data collection, but also an incentive for the search of a better comprehension of the mechanisms controlling the FCC process. Most importantly, the differences observed should not hamper experiments with macroscopic techniques nor lead to disregard results suspected of mass and/or heat transfer limitations. It is important to recognize them as enriched by other type of information, and that they become necessary as design tools. By these reasons, and considering that not too much can be added to the details depicted in Ref. [1], we believe it would be useful to clarify some issues, mainly pointing to a distinct approach in the interpretation of the data.

The diffusivities of diverse hydrocarbons in the Y zeolite component of FCC catalysts obtained using different macroscopic techniques such as the analysis of transient responses in zero length column (ZLC), uptake, stirred reactors, etc., use to differ significantly. The discrepancies are more perceptible if the comparisons are performed with results from transient response of a mixer [2] and from microscopic methods such as PFG NMR [3,4]. The letter by Kärger [1] shows them clearly and includes abundant references. In order to facilitate comparisons and perceive information more clearly, many of these data and some additions to illustrate our views are presented in Fig. 1, where the values of diffusivities and diffusion coefficients are shown as a function of temperature.

One of the issues to clarify is the statement by Kärger that our data (see Table 1 in Ref. [1]) "*contradict* in two important items the evidences of direct diffusion measurements by the PFG NMR technique". That is not strictly correct. The contradictions mentioned were:

(i) The diffusivity of unsaturated hydrocarbons (like toluene) in FAU-type zeolites (NaX,Y), as measured by PFG NMR, is lower than that of saturated hydrocarbons (*n*-hexane), at least one order of magnitude. Also macroscopic measurements of benzene diffusivity in FAU-type zeolites are found smaller than those of saturated hydrocarbons of comparable molecular weight. As it can be seen in Fig. 1, the diffusivity of hexane is slightly larger than that of toluene in Ref. [2].

(ii) The absolute values of the intracrystalline diffusivities of the *n*-alkanes in zeolite NaY as resulting from the PFG NMR measurements are extremely larger than the data we obtained. Also discrepancies result in the comparison of our data for the unsaturated hydrocarbons with the diffusivities for *n*-octane [3] measured by PFG NMR. Furthermore, Kärger pointed out that the correctness of NMR data was confirmed by numerous checks of self-consistency and cross-checks, including validation by agreement with the evidence of "macroscopic" measurements when applied to macroscopic systems, for example, for the adsorption of hydrocarbons on 5A zeolite.

In this context, the term *contradict* in the statement previously mentioned may lead to incorrect ideas, like assuming that it is reasonable to expect that any difference between results from macroscopic and microscopic methods imply a necessary contradiction. In general, it is not correct to state that the values of diffusivities assessed from macroscopic techniques (like, e.g. in Ref. [2]), must be the same as diffusion coefficients that can be assessed directly with microscopic techniques (e.g. [4]); they are not necessarily the same, given that the physical meaning of each parameter can be different.

Diffusion coefficients from microscopic NMR experiments correspond to genuine self-diffusion coefficients. When diffusion proceeds via a known mechanism and it is possible to establish a model at the molecular level, then it allows the theoretical estimation of the diffusion coefficient. In these cases, then, the agreement between theoretical and experimental values is not only to be expected but also confirmed. For this reason, as mentioned in Ref. [1], PFG NMR data can be confirmed by the results of molecular modeling, and there is agreement between some macroscopic results in systems where diffusion can be explained with a configurational mechanism, like those of adsorption of *n*-alkanes on 5A zeolite.

Intracrystalline diffusivities are not but mere adjusting parameters in the zeolite crystal's mass balance, where a transport model was assumed. If the assumptions both in this balance and that of the gas phase surrounding the zeolite particles are proper, and the experimental conditions chosen are correct in the sense of having good parametric sensitivity and minimum correlation between parameters, then the values of intracrystalline diffusivities are apparent diffusivities. They are not necessarily the same as diffusion coefficients obtained at similar temperatures and, of course, as those extrapolated from experiments at very dissimilar temperatures, like those in PFG NMR experiments.

In fact Weisz [5] explained by means of a critical analysis of the mass balances in the crystals (the so-called Fick's second law, that

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Nomenclature

C	concentration in the gas phase (gmol/m^3)
D	diffusivity (m^2/s)
E_d	energy of activation for diffusion
ΔH	enthalpy change (kJ/mol)
K	Henry's constant (dimensionless)
q	concentration in the solid phase, adsorbed species (mol/m^3)
r_c	crystal radius (m)
R	catalyst particle radius (m)
T	temperature (K)
Greek symbols	
ε_m	micropore void fraction in the crystal (dimensionless)
τ	time constant (s)
Subscripts	
c	crystal
i	system component (i)
m	mobile species within the macropores
o	diluted conditions
p	particles

defines intracrystalline diffusivity) the differences over five orders of magnitude found between *o*-xylene diffusivities associated to the molecular movement (the so-called corrected diffusivity) and apparent intracrystalline diffusivities from uptake studies in ZSM-5 zeolite. The reasoning followed by Weisz has an interesting analogy with the explanation found in classical books on the subject (e.g. [4,6]) in respect to the case of control of the process by mass transfer limitations in the macropores rather than within the crystals: in this case the apparent intracrystalline diffusivity depends on parameters associated to two different processes: diffusion of mobile molecules in the crystal's pores and adsorption equilibrium on the crystals' surfaces. Weisz [5] clearly pointed out that, in systems where it is possible to distinguish between an immobilized phase on the surface and a mobile phase diffusing in the macropores, and where sorption/desorption equilibrium between these phases is attainable on the micropore surface, significant discrepancies between apparent intracrystalline diffusivity and mobile phase diffusivity can be predicted. Other authors considered that, besides configurational diffusion, an activated Knudsen type flow also exists [7,8].

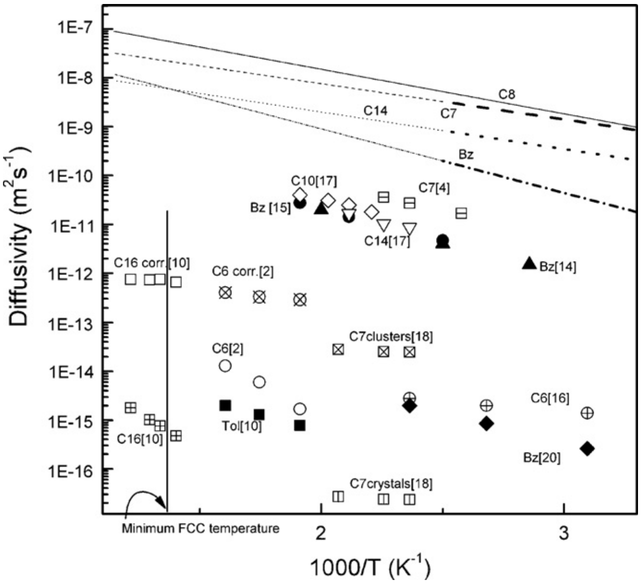

Fig. 1. Diffusivities and diffusion coefficients as a function of 1000/*T*, taken from various references as indicated. Lines represent results from NMR technique; thick lines cover the region of experiments; thin lines represent extrapolations (see ref. [20]).

In our paper [2] that originated the letter by Kärger [1], this possibility was explored for the three hydrocarbons studied. In that case, for linear adsorption processes, the mass balance can be described by means of

$$\frac{\partial C_i}{\partial t} = \frac{\varepsilon_m}{\varepsilon_m + K'_i} D_{m,i} \nabla^2 C_i \tag{1}$$

And if it is compared with a configurational diffusion process under dilute conditions,

$$\frac{\partial q_i}{\partial t} = D_{0,i} \nabla^2 q_i \tag{2}$$

then it is possible to find the relation between microporous diffusivity D_m and intracrystalline diffusivity at zero coverage D_0 to be

$$D_{0,i} = \frac{\varepsilon_m}{\varepsilon_m + K'_i} D_{m,i} \tag{3}$$

Moreover, considering that $K'_i = K_i(1 - \varepsilon_m) >> 1$ and that for Y zeolite ε_m is about 0.5 [9], then

$$D_{0,i} = \frac{D_{m,i}}{K} \tag{4}$$

In the case of saturated hydrocarbons, corrections in the diffusivities (see Figure 6 in Ref. [2]) lead to values up to three orders of magnitude higher than those in Table 1 in Ref. [1]. This is in agreement with results obtained for the diffusion of *n*-hexadecane in equilibrium FCC catalysts at high temperatures [10] (refer to Figure 2). Since the functionality of $D_{m,i}$ with temperature is much less sensitive than that of K'_i, the energy of activation of $D_{0,i}$ would be indeed near that of the adsorption heat. This would be suggesting that a mechanism different from purely configurational applies to the diffusion of *n*-paraffins at high temperatures above 250 °C. This possibility has been examined extensively in the literature, as indicated by, for example, in Refs. [5,11–13].

The differences between our observations and those from other microscopic and macroscopic methods in respect to the relative values of the diffusivities for saturated and unsaturated hydrocarbons, should be discussed in the light of the trends of the relative values of *n*-alkanes and aromatic hydrocarbons of similar molecular weight, and of the differences in the energies of activation. At room temperature, the diffusivities of *n*-heptane and *n*-tetradecane are, respectively two and one order of magnitude larger than that of benzene, in all the cases assessed by NMR; but the energies of activation for the diffusion of the unsaturated hydrocarbons are larger ([14,15], Table 3.4 in Ref. [4]). Then, as temperature increases, the differences become smaller. At temperatures that can be considered low or medium (say, from room temperature to about 200 °C), where a comparison between both micro- and macroscopic experimental results can be done, the diffusivities of benzene and toluene keep smaller than the diffusivities of *n*-hexane and *n*-heptane, as it can see Fig. 1, with near one order of magnitude difference between *n*-heptane and benzene in NMR data. The diffusivity of *n*-hexane from other macroscopic methods [16] is still larger than that of benzene, but the differences between them is smaller. At these intermediate temperatures, the diffusivities of *n*-alkanes approximate those of aromatics in all the groups of experiments with macroscopic techniques; particularly for a heavier paraffins (*n*-tetradecane), its diffusivity is similar to that of benzene [14,17]. This is independent from the absolute values of the diffusivities, that differ significantly according to the various experimental conditions (see, for example, *n*-hexane and toluene from Ref. [16]). However, the energies of activation show very slight changes, if any, for the aromatic hydrocarbons, but for linear alkanes with over six carbon atoms per molecule, the apparent energies of activation are higher from macroscopic methods than from microscopic ones. At temperatures higher than 250 °C, the diffusivity for *n*-hexane is still higher than that of toluene [2,16], although the difference between them is somewhat smaller than that at higher temperatures. In this way, it can be seen that the relative values of diffusivities for unsaturated and saturated hydrocarbons of similar molecular weight follow a reasonable trend.

At temperatures typical of the FCC process (see bottom left section of Fig. 1), the slopes of the diffusivities of alkanes as a function of temperature seem to apart from the pattern shown at lower temperatures [1]. However, if corrections are done [5,11] for the case of *n*-hexane, this change is not observed.

Moreover, one the facts that are not mentioned frequently but must be considered carefully, is the difficulty in assessing the crystal size of zeolite crystals in FCC catalysts by, e.g. SEM. Moreover, crystals tend to form clusters with assorted sizes. Since in macroscopic techniques D/r_c^2 is determined, an error in r_c will move D in Arrhenius plots dramatically. For example, it was shown by Cavalcante et al. [18] (see Fig. 1), that the diffusivity of *n*-heptane in USY may be three orders of magnitude larger if clusters with about ten crystals instead of isolated crystals are considered.

It is interesting to notice the coincidence in the energy of activation determined by means of macroscopic methods, and the unexplained discrepancy with the energy of activation from microscopic methods. It can be seen in Figure 13.11 in Ref. [4] that at the same temperature range, the energy of activation from NMR is significantly smaller than that from ZLC for *n*-alkanes with more than seven carbon atoms per molecule.

This is an important issue, if it is considered that the temperature range involved in the various methods is so different: from temperatures well below 0 °C (e.g. up to −117 °C [3]) to 250 °C and above in our work. Changes in the mechanisms of the mass transfer and the control steps are possible if the experimental conditions correspond to different ranges of temperatures.

Finally, it is also mentioned in the letter [1] that it was wrong in our paper to assume that diffusion in the macropores was much faster than diffusion in the macropores, while in Ref. [3], the opposite was observed. In effect, there is no contradiction, because it must be considered that the characteristic time for the case of mass transfer control by diffusion in the macropores is not given by the relationship R^2/D_p, but in diluted systems it is proportional to $R^2/(D_p/K)$ [6]. At so high temperatures as the ones we used in our work, surface diffusion in the macropores walls could be neglected, and D_p has a weak temperature dependence. The relationship τ_p/τ_c, then, will depend on temperature following an exponential function given by the difference between the heat of adsorption and the energy of activation for diffusion; since the first term (ΔH) is higher than the second (E_d), then τ_p/τ_c is very small and the mass transfer control is intracrystalline, or is not controlled by diffusion in the macropores.

As a matter of fact, the error in the estimation of D_p under these circumstances is small [7,19], the value of K was estimated directly in the same experiments, and the time constant for the overall process can be estimated from the transient process in the gas phase. Since the latter was much longer than τ_p, this is a unequivocal confirmation that is it is acceptable to neglect diffusion in the macropores as the controlling process. At low temperatures, however, K is higher, and it is possible to have the mass transfer process controlled by diffusion in the macropores, similar to what happens in experiments with octane at temperatures under 0 °C [3].

The differences in the apparent energies of activation and those from direct diffusion measurements have not been explained completely yet, and point to the coexistence of two worlds apparently separated, but equally needed (macro and micro). Microscopic techniques can be used to determine diffusion coefficients directly, but they cannot be used at temperatures as high as those of the FCC process. Transient methods such as ZLC, uptake, or stirred reactors, can determine design parameters, and give an idea of how far from ideal conditions we are, without being able to explain the reasons for that.

Finally, we fully agree with the comment by Kärger about the technological improvements that can be derived from a more extensive knowledge of the impact of the FCC catalyst properties on the process. In that sense, the neat increase in the use of residual feedstocks raises a number of challenges about the optimization of FCC catalysts.

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