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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]

Ref. [1] reports about the assessment of the diffusivities in fluid catalytic cracking (FCC) catalysts. The procedure is based on the measurement of pressure variation in the atmosphere surrounding the FCC catalyst particles following a pressure step. System evolution is modelled by Fick's 2nd law on the assumption that (i) mass transfer and adsorption in the matrix component of the FCC catalyst particle are negligible in comparison with those in the zeolite component and that (ii) local adsorption equilibrium with the gas phase is instantaneously attained at the surface of the zeolite particles, following a Langmuir-type isotherm. Table 1 (reproduction of Table 3 of Ref. [1]) represents the diffusivities resulting as the best fitting parameters to the experimental data and compares them with literature data obtained by following a similar procedure [2].

These data contradict in two important items the evidence of direct diffusion measurements by the pulsed field gradient NMR technique [3–5]:

(i) In contrast to the data shown in Table 1, the diffusivity of unsaturated hydrocarbons (like toluene) in FAU-type zeolites (NaX,Y) [6] has been found to be exceeded by the diffusivity of saturated hydrocarbons (*n*-hexane) by at least one order of magnitude (see, e.g., Fig. 13.15 of [3] and [7]). These NMR findings are supported by both molecular modelling [8–10] and Quasi-Elastic Neutron Scattering [11].

Most interestingly, also macroscopic (uptake and ZLC [3,12,13]) measurements of benzene in FAU-type zeolites are found to yield notably smaller diffusivities than saturated hydrocarbons of comparable molecular weight (see, e.g., Table 15.2 of [3]), though, with absolute values, partially far below the diffusivities resulting from the microscopic techniques.

(ii) Much more importantly, however, the absolute values of the intracrystalline diffusivities of the *n*-alkanes in zeolite NaY as resulting from the PFG NMR measurements presented in [14] are by more than six (!) orders of magnitude larger than the data of Ref. [1] given in Table 1. Similarly large discrepancies result on comparing the diffusivity data for the unsaturated hydrocarbons of Ref. [1] with the diffusivities directly measured by PFG NMR [7]. The order of magnitude of the PFG NMR diffusivity data for these and similar systems are confirmed by the results of both Quasi-Elastic Neutron Scattering and Molecular Dynamics Simulations [10,15,16].

The correctness of PFG NMR data has been confirmed by numerous checks of self-consistency and cross-checks (see, e.g., Section 7.8 of [3] and [17]), including their validation by their perfect agreement with the evidence of "macroscopic" measurements when applied to macroscopic systems (where any systematic failure in the macroscopic measurements can be excluded) [18,19]. It remains to explain, therefore, why the data resulting from the fitting procedure as presented, e.g., in Refs. [1,2] may deviate so dramatically from the genuine microscopic ones.

Clearly, one always has to be aware of the fact that good fitting results in no way doubtlessly confirm the validity of the underlying model and of the chosen fitting parameters [20]. The discussion of the reliability of the intracrystalline diffusivities of *n*-butane in MFI-type zeolites as deduced from macroscopic TAP experiments [21–24] and of the pitfalls of macroscopic measurements quite in general [12,25] provide prominent examples of this limitation.

Assumption (i) of Ref. [1] is based on an estimate of the time constants of molecular uptake/release of the individual zeolite crystals within the catalyst particle (τ_c) and of the particle as a whole (τ_p). It is interesting to note that exactly this estimate is also made in Ref. [14]. There is, however, an important difference between these two papers. By the application of PFG NMR, in Ref. [14], both relevant diffusivities, namely the intracrystalline diffusivity (which controls τ_c) and the intraparticle diffusivity (which controls τ_p) can be directly measured. It is noteworthy that the intraparticle mean life times calculated in Ref. [1] nicely agree with the order of magnitude of the corresponding data of Ref. [14] calculated from the measured intraparticle diffusivities and the particle sizes. The measured intracrystalline diffusivities, however, yield much smaller intracrystalline mean life times as the estimates given in Ref. [1]. In fact, they turn out to be even notably smaller than the indicated mean life times within the particles. Completely independent from the measurement of intracrystalline diffusion, this conclusion is confirmed by the observation that molecular propagation within the catalyst particle – i.e. propagation with displacements notably exceeding the crystal sizes but still far below the particle sizes – is in complete accordance with the requirements of normal diffusion, exhibiting a Gaussian probability distribution of molecular displacements [26]. Such a behaviour may only result if the molecular exchange time between the individual crystallites is much smaller than the observation time and, hence, than the mean life time within the catalyst particle [27].

As an important technological consequence of this finding, in [14,28] an enhancement of the intraparticle diffusivity was shown to be accompanied by a notable gain in catalytic performance. On comparing the effect of different procedures of catalyst preparation (with composition, zeolite component and overall porosity kept constant), the catalyst particles with largest diffusivities and, hence, largest catalytic activities appeared to exhibit transport

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Table 1

Intracrystalline diffusivities of various hydrocarbons in the zeolite component (NaY) of FCC catalysts at zero loading as following from the model fit in Ref. [1] and comparison with previous literature data [2] at 250 °C (taken from [1])

Hydrocarbon	D ($\times 10^{-15}$ m^2 s^{-1}) [1]	D ($\times 10^{-15}$ m^2 s^{-1}) [2]
n-Hexane	1.70	3.90
n-Decane	0.28	0.20
Toluene	0.79	1.30

pores with the largest pore diameter. This is exactly the behaviour to be expected since, under the regime of Knudsen diffusion as relevant for these studies, the diffusivities increase with increasing pore sizes.

It is interesting to note that, completely correctly, the authors of Ref. [1] take the resulting large values of the apparent activation energies of diffusion as an indication of a possibly dominating role of *inter*crystalline (i.e. *intra*particle) diffusion in the overall transport process. In view of their estimates of the intracrystalline and intraparticle mean life times, τ_c and τ_p, however, they had to abandon this consideration.

Let us now refer to the second assumption, implying immediate equilibration between the surface concentration of each individual crystal and its surrounding atmosphere. This assumption implies infinitely high surface permeabilites, i.e. the absence of any notable surface resistance. Over many years, surface barriers were assumed to be among the main mechanisms giving rise to the discrepancy between microscopic and macroscopic diffusion measurements [29,30]. Today, in addition to these surface barriers, also internal resistances [31–34] have been identified as further sources of impedance of molecular propagation acting in addition to the drag exerted by the genuine pore system. Such resistances have been found to be established during the sorption processes itself by the deposition of admixtures or of by-products [35] or may be related to a partial break down of the host lattice and/or the existence of stacking faults [36]. In fact, as to our knowledge, only with the recently introduced technique of interference microscopy [37] and, so far, for only one particular zeolite specimen [38], the complete absence of any notable surface resistance on a zeolite crystal could be proved.

One can never be sure therefore that, due to the formation of such resistances, the intracrystalline mean life times may in fact attain such large values as the data reported in Ref. [1]. If this would be the case, in view of the large values of the directly measured intracrystalline diffusivities, one may definitely exclude that intercrystalline exchange is limited by intracrystalline diffusion. One has rather to imply the existence of dramatic additional resistances. Their exploration and – eventually – their elimination would open up impressive perspectives for performance enhancement in FCC catalysis.

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