



# Influence of crystal size on the uptake rate of isooctane in plain and hollow silicalite-1 crystals



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## ABSTRACT

The sorption kinetics of isooctane at 150 °C over a series of silicalite-1 materials comprising small and large crystals and their corresponding hollow forms were followed by *in situ* diffuse reflectance FT-IR spectroscopy. The results suggest that sorption rate was mostly limited by surface effects in the case of small (i.e. 100 nm diameter) crystals, while this was not the case for much larger crystals.

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## 1. Introduction

MFI-type materials (e.g. ZSM-5, silicalite-1, TS-1) are crystalline microporous silica-based solids extensively used in industrial catalytic and adsorption/separation processes [1,2]. The intrinsic microporosity of these solids often imposes molecular diffusion limitations due to hindered access and slow intra-crystalline transport. This leads to a substantial under-utilization of the potential of zeolites in catalytic applications by limiting the corresponding activity, selectivity, and catalyst lifetime [3]. Hierarchical (or mesoporous) zeolites can alleviate these issues by adding to the native microporosity an auxiliary network of inter- and/or intra-crystalline mesopores. The added mesoporosity increases the number of accessible micropores and effectively shortens the average path length to the active sites, hereby increasing their catalytic performance [4–9].

Diffusion studies have traditionally focused on large crystals [10–15]. The present work reports an investigation on the sorption uptake properties in silicalites-1 crystals of very different crystal sizes. Examining both small and large crystals is worthwhile because large crystals are often used as model systems exhibiting reasonably well-defined geometric forms and sizes, while small crystals are of more practical importance. The sorption of isooctane

(i.e. 2,2,4-trimethylpentane, also noted here iC8), which exhibits a kinetic diameter similar to that of silicalite-1 pore size, was monitored.

Uptake methods may evidence the influence of pore entrance effects [16,17], which can be determining the sorption rate of the substrate. Lercher and co-workers proposed that the transport limiting step was actually different in the case of large and small ZSM-5 crystals [18]: intracrystalline diffusion was rate-determining for large particles, while for the small particles the diffusion was controlled by surface effects. Similar observations were reported by Geudré et al. on silicalite-1 crystals [17].

To our knowledge, measures of the sorption rate of a large hydrocarbon on hollow silicalite-1 single crystals with different sizes have never been reported and are presented here for the first time. Such hollow crystals were shown to exhibit near-ideal sieving properties in the case of the hydrogenation of arenes carried out over encapsulated metal nanoparticles, suppressing the hydrogenation of mesitylene, while that of toluene was unhindered [19,20].

## 2. Experimental

### 2.1. Synthesis of silicalite-1 nanocrystals

In a typical synthesis, 0.1 mol of tetraethyl orthosilicate (TEOS) was mixed with 27 mL of TPAOH (1 M solution in water). After 15 min, 61.5 mL of H<sub>2</sub>O were added and the mixture was heated at 35 °C for 5 h under stirring. Then, the clear gel was crystallized

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under static conditions for 3 days at 170 °C. After recovering by centrifugation and drying, the product was calcined in air at 540 °C for 6 h. The sample is further denoted “SP” for Small Plain crystals.

For large silicalite-1 crystals, the synthesis method was adapted from one of our previous publications [21]. Typically, tetraethyl orthosilicate was hydrolyzed in a mixture of tetraethylammonium (TEAOH) and tetrabutyl phosphonium (TBPOH) hydroxides (TEAOH/(TBPOH + TEAOH) = 0.25) and crystallized under static conditions at 170 °C for 4 days. The crystals obtained were recovered by centrifugation and further denoted “LP” for Large Plain crystals.

## 2.2. Alkaline treatment

For both SP and LP zeolites, alkaline treatment was performed with 0.3 M TPAOH at 170 °C under stirring for 72 h [22] After centrifugation and drying, samples were calcined at 540 °C for 6 h and denoted “SH” and “LH” for Small Hollow and Large Hollow crystals, respectively.

## 2.3. X-ray diffraction

X-ray Diffraction patterns were recorded on a Bruker D5005 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Spectra were recorded over a  $2\theta$  range of 4°–80° with a step size of 0.02° and 1 s per step.

## 2.4. Electron microscopy

Transmission electron microscopy (TEM) images were taken on JEOL 2010 LaB6 at an acceleration voltage of 200 kV. Samples were prepared by plunging carbon-coated copper grids into ethanol solutions of the samples followed by drying at room temperature. Scanning electron microscopy (SEM) images were taken on a FEI ESEM-XL30 microscope.

## 2.5. N<sub>2</sub> isotherms

N<sub>2</sub> isotherms were measured on Belsorp mini. First, samples were degassed in vacuum ( $P/P_0 < 10^{-7}$ ) at 300 °C overnight. The total surface area was calculated using the Brunauer–Emmett–Teller (BET) method and the t-plot method was used to differentiate microporosity and mesoporosity.

## 2.6. Adsorption measurements

Between 1 and 5 mg of zeolite powder was deposited onto a SiC bed in the crucible of a high temperature-low pressure diffuse reflectance FTIR spectroscopy (DRIFTS) reaction cell from Spectra-Tech described in details elsewhere [23]. The cell was placed in a Collector assembly from Spectra-Tech and fitted in a Nicolet Magna 550 FTIR spectrometer equipped with a MCT detector cooled with liquid nitrogen. A FTIR spectrum recorded over SiC was used as background. The DRIFTS spectra of the zeolites were plotted as  $\log 1/R$ , where R is the sample reflectance. The function  $\log 1/R$  (= pseudo-absorbance) provides better linearity between band intensity against coverage than that given by the Kubelka–Munk function for strongly absorbing media, such as those based on oxides [24].

The reaction cell was modified to eliminate bed by-pass by inserting some PTFE tape between the ceramic crucible and the metallic base plate. The only difference with the cell modifications described in Ref. [23] is that a quartz wool plug was used in place of a metallic mesh to hold the sample bed. High-purity Ar from Air Liquid was fed through low-volume heated stainless-steel lines to the cell and through a saturator kept at 273 K to carry the vapor pressure of iC8 (i.e. 1.75 kPa).

A gas flow rate of 50 mL min<sup>-1</sup> of pure Ar was used to carry the hydrocarbon during the adsorption experiment. The time-resolved adsorption of iC8 was monitored and the exact concentration of the hydrocarbon could be derived from the IR bands corresponding to the C–H stretching vibrations of iC8 and that of the zeolite overtone bands (Fig. 1). The iC8 concentration was determined from a calibration curve measured over the similar MFI-type zeolite using an *in situ* quartz transmission IR cell fitted with KBr windows [8]. The calibration curve was obtained by carrying out titration-type experiments at room temperature over a zeolite wafer of known weight. The samples were first evacuated under secondary vacuum ( $P < 10^{-5}$  torr) at 523 K for 15 min. The hydrocarbon IR signal normalized to that of the zeolite overtones bands (Fig. 1) was then monitored as a function of the number of calibrated pulses sent into the cell. The number of moles in each pulse was determined from the known volume of the injection chamber (2.23 cm<sup>3</sup>) and the pressure in the injection lines read on a Pfeiffer pressure gauge. The calibration plot obtained is shown in Fig. 2. The last data point corresponds to the data reported in Fig. 1. The signal of gas phase iC8 was negligible under the residual equilibrium pressure obtained during the pulse series in the transmission cell.

The ratio of the DRIFTS band of iC8 reported to that of the DRIFTS band of the overtone vibration of the solid, so-called “normalized iC8 uptake” measured over the SP sample was plotted as a function of the square root of time (Fig. 3). The plot showed a typical linear variation at short times, with a non-zero intercept. The non-zero intercept was due to a significant IR absorption from gas-phase iC8 in the DRIFTS cell. This contribution was subtracted by correcting the signal as to force a zero-intercept.

The spectra were recorded with a resolution of 4 cm<sup>-1</sup> and an accumulation of 8 scans initially every 4 s following the introduction of the hydrocarbons. The IR spectra were analyzed using the OMNIC software. The adsorption curves plotted as a function of the square root of time were used to derive the slope of the uptake curve [13].

## 3. Results and discussion

The XRD patterns of the sample corresponded all to the MFI structure only and were highly crystalline (Fig. 4). The peak breadth did not evolve upon the treatment used to create the hollow core. TEM pictures confirmed that SP crystals (Fig. 5A) were short hexagonal prisms of about 150 × 100 × 100 nm in size while LP

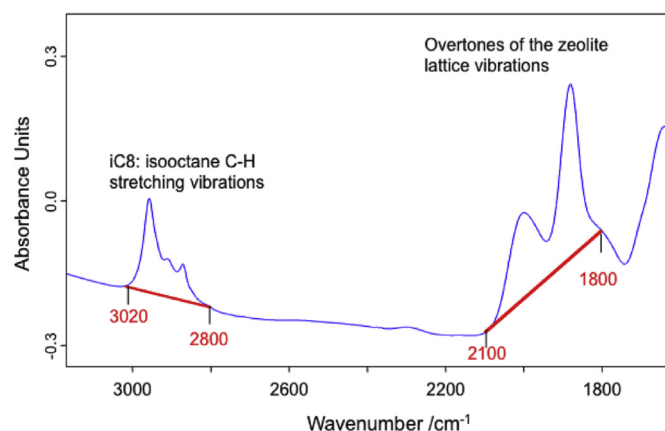


Fig. 1. FT-IR transmission spectrum of ZSM-5 zeolite exposed to iC8, showing the two zones used for normalizing the band area of the adsorbate (region 3020–2800 cm<sup>-1</sup>) to that of the solid (region 2100–1800 cm<sup>-1</sup>). Areas were integrated above the baseline plotted in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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