

**Faster transport in hollow zeolites**Ana Rita Morgado Prates<sup>a</sup>, Cécile Daniel<sup>a</sup>, Céline Pagis<sup>a,b</sup>, Yves Schuurman<sup>a</sup>, Alain Tuel<sup>a</sup>, David Farrusseng<sup>a</sup>

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**TABLE OF CONTENT**

- 1- Synthesis details
- 2- Characterization of silicalite-1 samples
- 3- Characterization of Beta samples
- 4- ZLC Model
- 5- ZLC set-up
- 6- ZLC Results

## 1. Synthesis details

Table S 1 shows the list of reactants used for the synthesis of the zeolite samples used for this work.

*Table S 1 - Characteristics of the main reactants used for this work.*

Type	Reactants	Composition	Phase	Supplier
Si source	Ludox® HS-30 (SiO <sub>2</sub> )	30 wt. % suspension in H <sub>2</sub> O Na <sub>2</sub> O : 0,4 wt. %	Colloidal	Sigma Aldrich
Si source	Aerosil® 200 (SiO <sub>2</sub> )	> 98,9 wt. %	Solid	Evonik Industries
Al source	Sodium aluminate (NaAlO <sub>2</sub> )	Al <sub>2</sub> O <sub>3</sub> : 50–56 (53 wt. %) Na <sub>2</sub> O : 40–45 (42 wt. %) H <sub>2</sub> O : > 5 wt. %	Solid	Honeywell Riedel-de Haën
Al source	Aluminium powder (Al)	> 99 wt. %	Solid	Sigma Aldrich
Base	Sodium hydroxide (NaOH)	≥ 97,0 wt. %	Solid	Carlo Erba
Base	Ammonium hydroxide (NH <sub>4</sub> OH)	25 wt. % NH <sub>3</sub> in H <sub>2</sub> O	Liquid	Sigma Aldrich
Salt	Sodium chloride (NaCl)	≥ 99,5 wt. %	Solid	Fluka
SDA	Tetraethylammonium hydroxide (TEAOH)	35 wt. % in H <sub>2</sub> O	Liquid	Sigma Aldrich
SDA	Tetramethylammonium bromide (TMABr)	> 98 wt. %	Solid	Sigma Aldrich

**HollowBeta** was first prepared as the hollow Beta crystals in the reference [18]. The calcined crystals were exchanged twice with a 2M NaCl solution, 0.1 gzeol /ml, in order to ensure the greatest elimination of protons. The ion exchange process was carried out at 70 °C for 2h, under vigorous stirring. The dispersion was centrifuged and the solid washed and dried overnight at 80 °C.

**PlainBeta1** was first prepared similarly as reported by Zheng et al.[24]. A gel of Beta zeolite was first prepared with molar composition of the gel: 2.2 Na<sub>2</sub>O : 20 SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> : 4.6 (TEA)<sub>2</sub>O : 2.3 (NH<sub>4</sub>)<sub>2</sub>O : 401 H<sub>2</sub>O. Initially, 0.64 g of NaOH, 18.07 g of TEABr and 1.76 g of NaAlO<sub>2</sub> were dissolved in 36.7 g of distilled water, followed by the addition of 5.63 ml of NH<sub>4</sub>OH. Ludox HS-30 (36.70 g) was added slowly with vigorous stirring. The mixture was stirred at room temperature for 2 h, then transferred into a 100 mL autoclave and kept at 140 °C for 10 days without stirring. The obtained zeolite was filtered, washed with distilled water and dried at 80°C. The as-made crystals were exchanged with a 2M NaCl solution, 0.1 gzeol /ml, similarly to HollowBeta sample. Then, calcination was carried out in air at 550 °C for 4h hours with a heating rate of 87.5 °C/h followed by another ion-exchange with NaCl in similar conditions.

**PlainBeta2** was first prepared similarly as reported by Ding et al.[25]. A gel of Beta zeolite was first prepared with molar composition of the gel: 10.5 TEAOH : 50 SiO<sub>2</sub> : Al<sub>2</sub>O<sub>3</sub> : 750 H<sub>2</sub>O. Initially, 9.6 ml of TEAOH 35% were mixed with 23.6 ml of distilled water. After stirring, the solution is split into solution A and solution B (10 ml of solution). Then, 6.67 g of Aerosil 200 was slowly added to solution A with vigorous stirring. Then, Al powder (0.12 g) were dissolved in solution B, with vigorous stirring for 10 min. Finally, solution A and B are mixed and stirred at room temperature for 4 h. Then the gel was transferred into two 48 mL autoclave and kept at 140 °C for 7 days while stirring. The obtained zeolite was centrifuged, washed with distilled water and dried at 80 °C. Calcination step and ion-exchange step were carried out similarly to HollowBeta sample.

## 2. Characterization of silicalite-1 samples

TEM images of PlainS-1 and HollowS-1 are presented in Figure S 1 and Figure S 2 respectively.

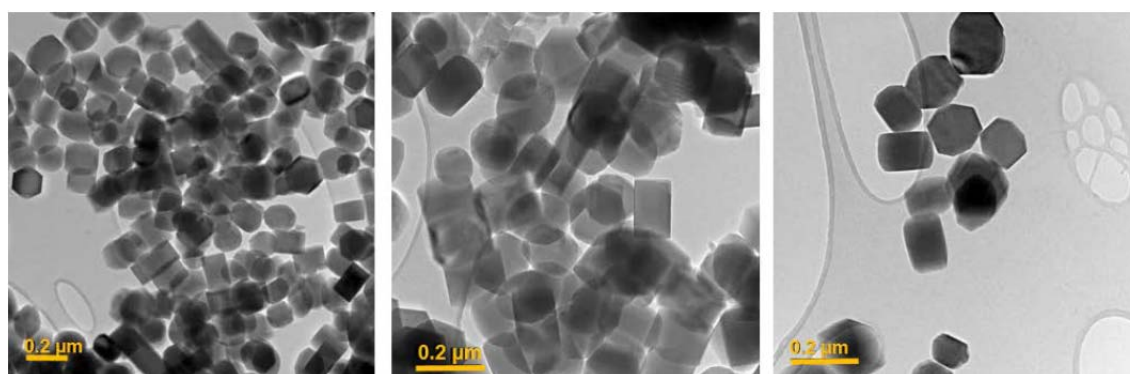


Figure S 1 - TEM images of PlainS-1.

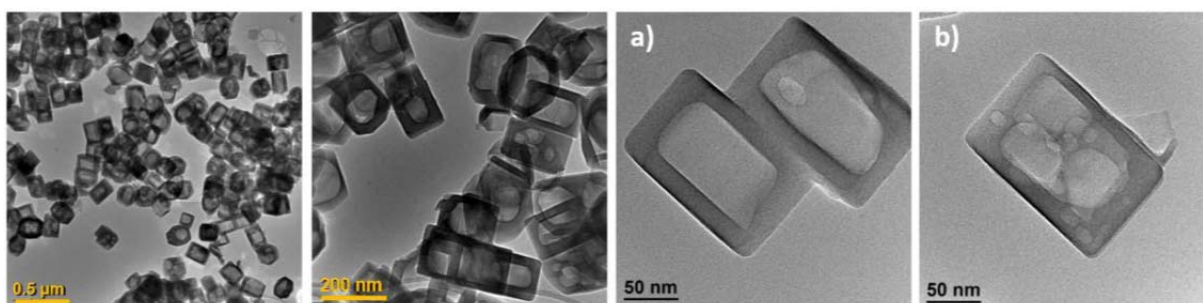


Figure S 2 - TEM images of HollowSil1.

Nitrogen adsorption/desorption isotherms of the considered samples are shown in Figure S 3. PlainS-1 presents a type I adsorption branch at low pressure, which is typical of a microporous material. HollowS-1 also present a Type I adsorption branch, confirming the microporous nature of the zeolite walls and it presents a desorption branch with a hysteresis, which has been associated with condensation phenomena in the inner cavity. Adsorption data of the samples are summarized in Table S 2, showing that both samples present very similar textural properties, with high microporous volume and BET surface, and small mesoporous volume.

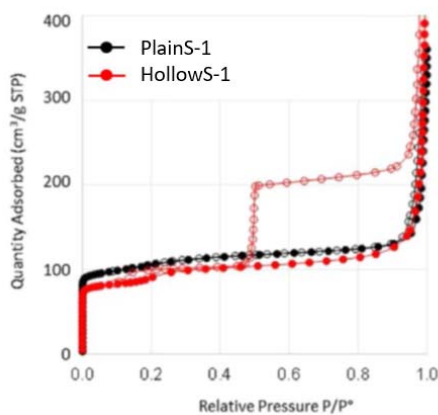


Figure S 3 - N2 adsorption isotherms of PlainS-1 and HollowS-1, according to Laprune et al.<sup>1</sup>

Table S 2 - Textural properties of the samples BulkSil1 and HollowSil1, according to Laprune et al.<sup>1</sup>

Sample name	PlainS-1	HollowS-1
Isotherms type according to IUPAC	Type I	Type I + hysteresis
BET [m <sup>2</sup> /g]	390	328
Vmicro [cm <sup>3</sup> /g]	0.13	0.12
Vmeso [cm <sup>3</sup> /g]	0.07	0.08

### 3. Characterization of Beta samples

XRD patterns of the Beta samples are presented in Figure S 4.

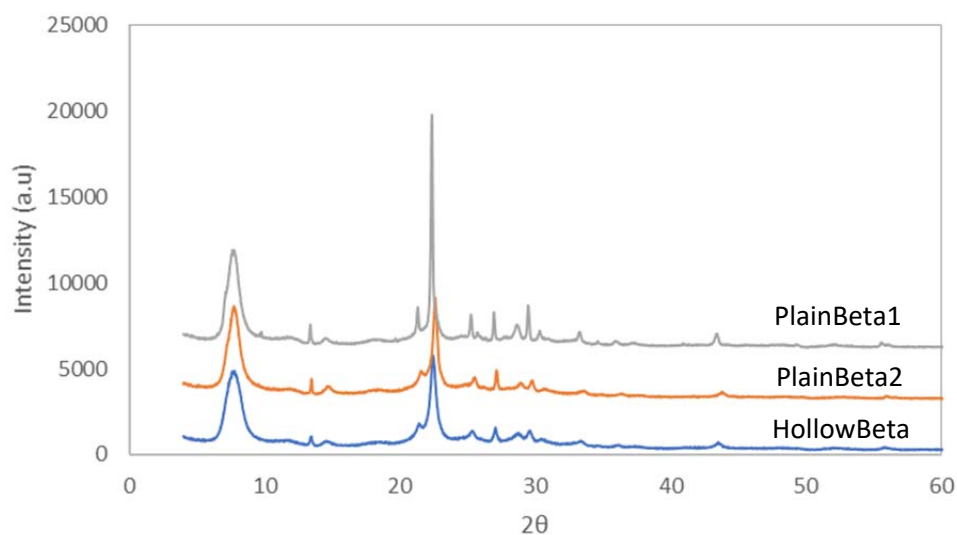


Figure S 4 – XRD patterns of PlainBeta1, PlainBeta2 and HollowBeta samples.

TEM and SEM images of the three samples are shown in Figure S 5. We consider that PlainBeta1 has an ellipsoid, which dimensions R1 and R2 were measured from microscopy images, see Figure S 6.

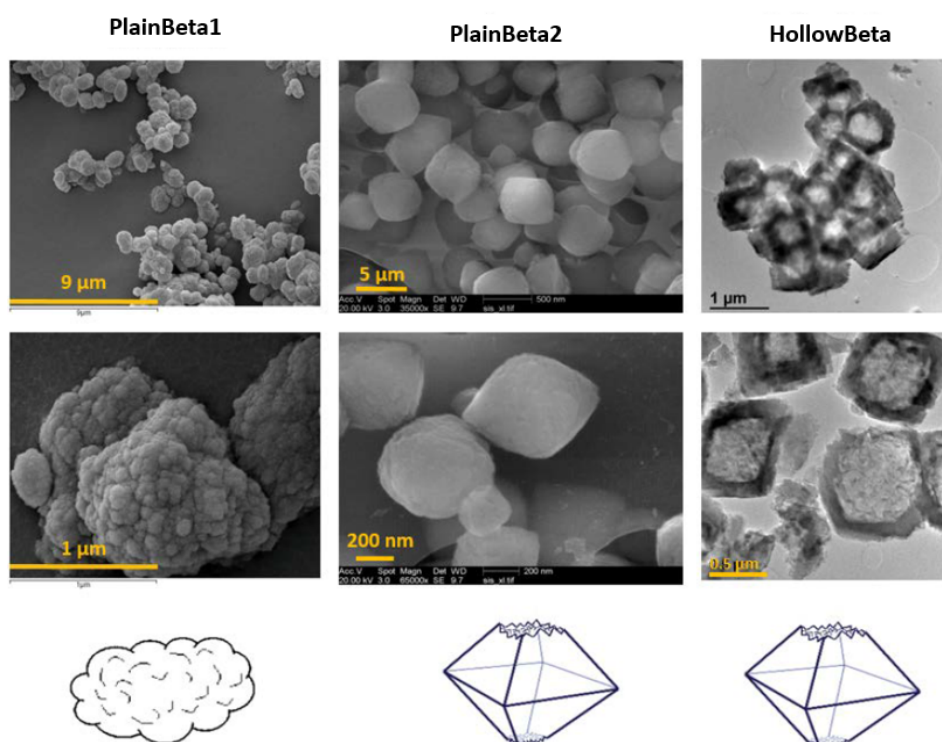


Figure S 5 - Electronic microscopic images of the three Beta samples, PlainBeta1, PlainBeta2 and HollowBeta, and the respective external morphology representations below.

## Ellipse Shape

R1 0.443  $\mu\text{m}$

R2 0.606  $\mu\text{m}$

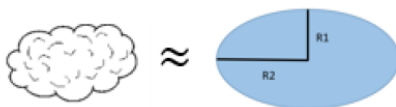


Figure S 6 – External morphology and dimensions for PlainBeta1.

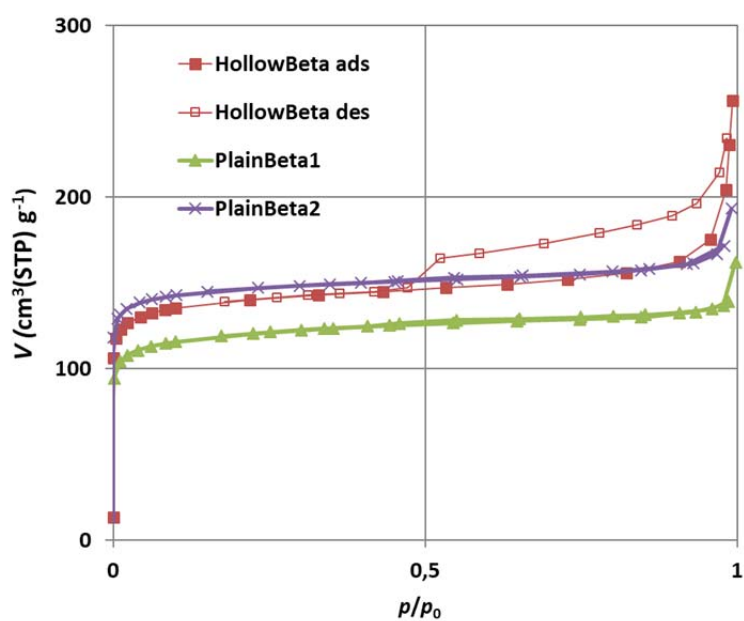


Figure S 7 - N2 adsorption isotherms of PlainBeta1, PlainBeta2 and HollowBeta.

Table S 3 - Textural properties of the samples PlainBeta1, PlainBeta2 and HollowBeta.

Sample	Isotherm type	BET [ $\text{m}^2/\text{g}$ ]	Vmicro [ $\text{cm}^3/\text{g}$ ]	Vmeso [ $\text{cm}^3/\text{g}$ ]
PlainBeta1	Type I	500	0.15	0.06
PlainBeta2	Type I	564	0.18	0.06
HollowBeta	Type I + hysteresis	542	0.16	0.09

## 4. ZLC Model

Data were analyzed considering the ZLC analysis of desorption curves developed by Eic and Ruthven<sup>2</sup>. The model considers a very thin layer of adsorbent uniformly equilibrated with a gas phase, and a certain adsorbate concentration  $c_0$ . It is assumed that external film mass transfer is fast enough to ensure that, under purging conditions, the sorbate concentration is very low not only in the bulk gas but also at the crystal surface. When neglecting hold-up in the gas phase, and assuming an adsorbent with a spherical shape of radius  $R$ , the transient mass balance for diffusion can be expressed in terms of effluent concentration  $c$  such as:

$$\frac{c(t)}{c_0} = 2L \sum_{n=1}^{\infty} \frac{\exp\left(-\frac{\beta_n^2 D_{eff} t}{L^2}\right)}{\beta_n^2 + L_{ZLC}(L_{ZLC} - 1)}$$

Where  $\beta_n$  and  $L_{ZLC}$  are some parameters defined as:

$$\beta_n \cot \beta_n + L_{ZLC} - 1 = 0$$

$$L_{ZLC} = \frac{FL^2}{3V_{cat}K_H D_{eff}}$$

$L_{ZLC}$  represents the ratio of purge flow rate and the diffusional time constant, where  $F$  is the volumetric flow rate,  $L$  is the radius of the spherical particle,  $V_{cat}$  is the adsorbent volume,  $K_H$  is the Henry's constant if adsorption takes place within Henry's region and  $D_{eff}$  is the effective diffusion coefficient. The  $L_{ZLC}$  value expressed how far the system is for equilibrium.<sup>3</sup>

When the purge **flow rate (F) is high**, the system is in the kinetically controlled regime,  $L_{ZLC}$  is large and  $\beta_n = n\pi$ ; so the equation is simplified to:

$$\frac{c(t)}{c_0} = 2L \sum_{n=1}^{\infty} \frac{\exp\left(-\frac{n^2 \pi^2 D_{eff} t}{L^2}\right)}{(n\pi)^2 + L_{ZLC}(L_{ZLC} - 1)}$$

On the **long time region** of the desorption curve, only the first term of the summation ( $n=1$ ) is significant, and the summation becomes an asymptote:

$$\ln\left(\frac{c(t)}{c_0}\right) = \ln\left[\frac{2L_{ZLC}}{\beta_1^2 + L_{ZLC}(L_{ZLC} - 1)}\right] - \frac{\beta_1^2 D_{eff}}{L^2} t$$

Under those conditions, we can determine the **characteristic diffusion time  $\tau = L^2/D_{eff}$**  directly from the slope of the asymptote.

In order to obtain reliable diffusivity data, we must ensure that the run is made under kinetic transport regime. In our study, we have used the value of the parameter  $L_{ZLC}$  as an indicator of the regime, where  $L_{ZLC}$  should be greater than 10 for assuring kinetic regime<sup>4</sup>.

## 5. ZLC Set-up

Figure S 8 - Zero Length Column (ZLC) experimental set-up. Figure S 8 shows a simplified schematic diagram of the ZLC set-up. The **adsorption line** carries a low concentration of sorbate diluted in He. This is prepared by dilution of a low flow saturated stream with a relatively large flow He bypass. The low flow saturated stream was prepared by passing a small He flow through a bubbler, maintained at low temperature by a Julabo ED (V.2) low temperature thermostat. The **desorption line** is a high flow He line. Both adsorption and desorption streams are feed by a mass flow controller. The "Switch valve" controls which of the two streams (adsorption or desorption) are delivered to the ZLC cell, that is placed

in a gas chromatograph oven (Agilent, 6850 Series GC system). Two pressure indicators are placed before the switching valve, one on the adsorption line – PI Ads – and the other on the desorption line – PI Des. These continuously control the pressure of each stream, and pressure drops during each run.

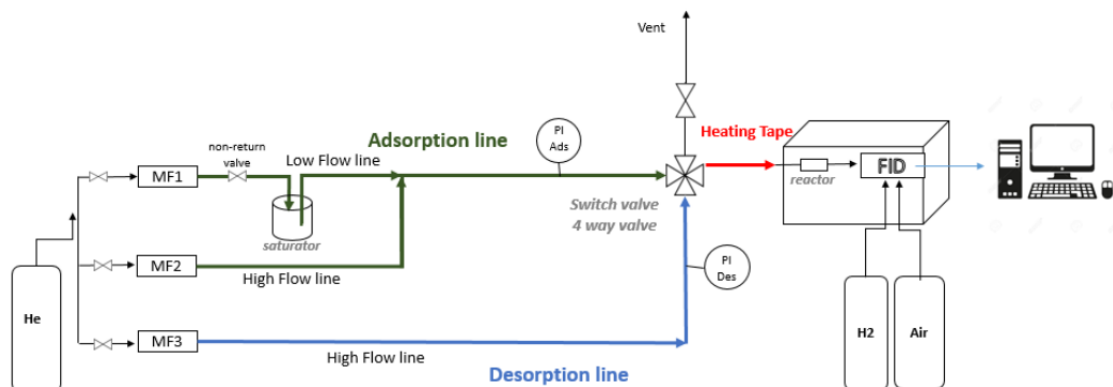


Figure S 8 - Zero Length Column (ZLC) experimental set-up.

The effluent stream from the ZLC cell is continuously monitored by a flame ionization detector (FID). The effluent concentration response is recorded after the valve switch to desorption.

## 6. ZLC Results

Table S 4 present the diffusion parameters extracted from the theoretical fitting of the ZLC over the desorption curves. All  $L_{ZLC}$  values are greater than 10, showing that the processes are in the diffusion controlled regime<sup>4</sup>.

Table S 4 – Parameters  $\tau$  and  $L_{ZLC}$  extracted from ZLC desorption curves.

Sample	T(°C)	$L_{ZLC}$	$\tau$ (s)
PlainS-1	40	24	3236
	50	17	2703
	60	14	1712
HollowS-1	40	19	1645
	50	16	1445
	60	14	1134
PlainBeta1	80	427	10460
	100	365	5848
	120	158	2193
PlainBeta2	80	401	8197
	100	239	4167
	120	113	1613
HollowBeta	80	533	1822
	100	570	1495
	120	218	544

The Arrhenius plots for toluene and silicalite-1 sample and cyclohexane and Beta samples are presented Figure S 9.

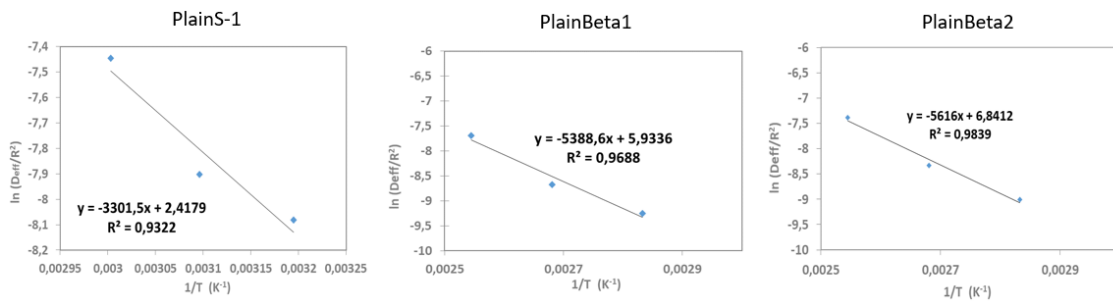


Figure S 9 - Arrhenius plots for toluene and PlainS-1 and for cyclohexane and Plain Beta samples.



- (1) Laprune, D.; Tuel, A.; Farrusseng, D.; Meunier, F. C. Highly Dispersed Nickel Particles Encapsulated in Multi-Hollow Silicalite-1 Single Crystal Nanoboxes: Effects of Siliceous Deposits and Phosphorous Species on the Catalytic Performances. *ChemCatChem* **2017**, *9* (12), 2297–2307. <https://doi.org/10.1002/cctc.201700233>.
- (2) Eic, M.; Ruthven, D. M. A New Experimental Technique for Measurement of Intracrystalline Diffusivity. *Zeolites* **1988**, *8* (1), 40–45. [https://doi.org/10.1016/S0144-2449\(88\)80028-9](https://doi.org/10.1016/S0144-2449(88)80028-9).
- (3) Mangano, E.; Brandani, S.; Ruthven, D. M. Analysis and Interpretation of Zero Length Column Response Curves. *Chem. Ing. Tech.* **2013**, *85* (11), 1714–1718. <https://doi.org/10.1002/cite.201300083>.
- (4) Teixeira, A.; Chang, C.-C.; Coogan, T.; Kendall, R.; Fan, W.; Dauenhauer, P. Dominance of Surface Barriers in Molecular Transport through Silicalite-1. *J. Phys. Chem. C* **2013**, *117*, 25545–25555. <https://doi.org/10.1021/jp4089595>.