

Eco-Compatible Continuous Halogenation of Aromatics

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Materials and supplementary experimental information

Chemicals, TCCA (Aldrich, 97%), iodobenzene (Alfa Aesar, 98%), dichloroethane (Aldrich, > 99.8%), acetic acid (Aldrich, > 99.8%), and all other organic compounds were purchased commercially and used without further purification.

As a comparison, several zeolites were purchased from Aldrich, UOP, Zeochem, Zeolyst. Besides, Cs₂PW₁₂O₄₀ heteropolyacid was synthesised according to the procedure reported elsewhereⁱ

Synthesis of *BEA-type zeolite micro-crystals (MC). The preparation of the MC sample was done in fluoride medium according to the procedure described by Cambor *et al.*ⁱⁱ The synthesis mixture was prepared by hydrolysing tetraethylorthosilicate (TEOS) (98 wt. %, Aldrich) in an aqueous solution of tetraethylammonium hydroxide (TEAOH) (35 wt.% in aqueous solution, Aldrich). Then a solution made by dissolving metal aluminum (99.95%, Aldrich) in aqueous TEAOH was added and the mixture kept under stirring until complete evaporation of ethanol formed upon hydrolysis of TEOS. Finally, hydrofluoric acid (40 wt. % in H₂O) was added. The obtained gel of the following molecular composition 0.573HF:0.226(TEA)₂O:0.016Al₂O₃:1SiO₂:7.03H₂O was hydrothermally treated at 170 °C for 14 days in a Teflon® lined stainless steel autoclave. After the required crystallisation time, the autoclave was cooled down to room temperature. The pH of the mother liquor was in the range 8–9.5. The product was filtered and extensively washed with distilled water. Finally, the sample was calcined under air at 550 °C during 5 h with a temperature ramp of 1°/min to remove the organic template.

Synthesis of *BEA-type zeolite nano-crystals (NC). The preparation of the NC sample was described in our previous paper.ⁱⁱⁱ A precursor solution of molecular composition 0.014Na₂O:0.18(TEA)₂O:0.020Al₂O₃:1SiO₂:11.80H₂O was hydrothermally treated at 95 °C for 9 days in a polypropylene bottle. The chemical reagents used were aluminum isopropoxide (98 wt. %, Aldrich), tetraethylammonium hydroxide (TEAOH, 35 wt. % in aqueous solution, Aldrich), sodium hydroxide

(99.99 wt. %, Riedel de Haën) and silica powder resulting from the lyophilisation of colloidal silica (Ludox AS-40, Aldrich). The resulting milky solution of *BEA zeolite was purified by several centrifugation-dispersion cycles in distilled water (at 20000 rpm for 30 min). The *BEA colloidal suspension was then dried by lyophilisation. In order to remove the template occluded in the porosity (tetraethylammonium cation), the solid was calcined under air at 550 °C during 5 h with a temperature ramp of 1°/min.

Synthesis of *BEA-type zeolite nano-sponges (NS). The NS sample was synthesised using a poly-quaternary ammonium surfactant (Scheme 1) denoted N_{4-phe} which was prepared according to Ryoo's studies.^{iv} In a typical synthesis of *BEA nano-sponge, ethanol (99.9%), sodium hydroxide (99.99 wt %, Riedel de Haën), sodium aluminate (56.7 wt. % Al₂O₃, 39.5 wt. % Na₂O) and TEOS (98 wt. %, Aldrich) were mixed to obtain a gel composition of 0.22Na₂O:0.05N_{4-phe}:0.025Al₂O₃:1SiO₂:4(ET)₂O:71H₂O. The resulting gel mixture was maintained under magnetic stirring at 60 °C for 6 h. The final gel was transferred to a Teflon®-lined stainless-steel autoclave and heated at 140 °C for 4 days under tumbling conditions at 60 rpm. After crystallisation, the zeolite product was filtered, washed with distilled water and dried at 120 °C. The products were calcined at 600 °C for 4 h under air to remove the surfactant.

Results and Analyses

Detailed textural properties of synthesised *BEA-zeolites. The porous properties of the samples drawn from N₂ adsorption/desorption isotherms are reported in Table 2. According to the IUPAC classification,^v the MC sample shows a typical type-I isotherm characteristic of a solely microporous material. Due to its large crystal size, the external surface of this material is low and no mesopores could be observed. However, the microporous volume is similar to that of MC sample (~0.23 cm³ g⁻¹) and corresponds to the generally reported micropore volume for a beta zeolite. Thanks to its small crystallite size, the NC sample exhibits a high external surface that contributed to a higher BET surface area, i.e. 726 m² g⁻¹. As reported in our recent work, the isotherms of NS sample are representative of type IV with a triangular hysteresis loop of H2 type characteristic for mesoporous materials with ink-pore and pore network connectivity like SBA-16.^{vi} For this sample the micropore volume, determined from the *t*-plot method, is higher than those of the two others materials and larger than the one expected for a *BEA-type zeolite (0.30 instead of 0.23 cm³/g). Part of this micropore volume probably arises from supermicropores (pore diameter close to 0.15 nm). The mesopores correspond to an interparticular porosity (porosity between 4 nm thickness zeolite units).

For the three materials, the global Si/Al molar ratios, measured by XRF and reported in Table 3, are higher than those of the starting synthesis gel. However, these ratios are lower than the Si/Al framework ratio determined from IR spectroscopy (Table 3). This difference suggests the presence of

extra-framework aluminum species (EFAL); their number, estimated per zeolite unit cell, ranges between 0.6 to 1 (Table 3).

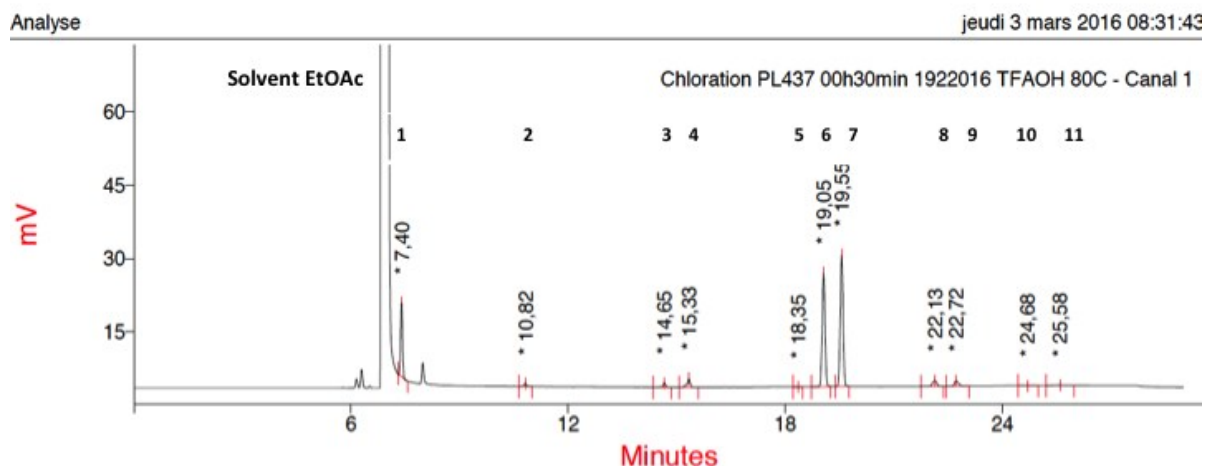


Figure S1. Typical chromatogram corresponding to entry 11 in Table 5.

Analyse : Chloration PL437 00h30min 1922016 TFAOH 80C

Informations sur l'acquisition

Date d'acquisition : 19/02/2016 16:27:42 (+01:00) (WiniLab III 5.0.10.0)
 Source de l'acquisition :
 Durée : 29,00 Minutes Nb de points : 1741
 Vitesse d'acquisition : 1,00 points/seconde

Informations sur l'échantillon

Nom : Chloration PL437 00h30min 19220 Type d'échantillon : Echantillon
 N° Flacon : 1
 Quantité : 0,000000 mg Volume d'injection : 1,00 µl
 Dilution : 1 Diviseur : 1
 (* = valeur initiale modifiée)

Informations :

Prog : 110°C 7 min 15°C/min 270°C x 10 min
 Flux : He 17 PSI
 Inj : 300°C
 Det : 270°C

Résultats d'intégration

#	Nom du pic	Tr.	Aire	% Aire
1	Internal Standard DCE	7.40	55,61	15,07
2	Chlorobenzene	10.82	2,74	0,74
3	Impurity	14.65	3,96	1,07
4	Iodobenzene	15.33	9,88	2,68
5	m-chloroiodobenzene	18.35	0,13	0,04
6	p-chloroiodobenzene	19.05	127,39	34,53
7	o-chloroiodobenzene	19.55	149,96	40,65
8	dichloroiodobenzene	22.13	9,66	2,62
9	dichloroiodobenzene	22.72	8,65	2,34
10	trichloroiodobenzene	24.68	0,15	0,04
11	trichloroiodobenzene	25.58	0,77	0,21
SOMME			368,90	100,00

Figure S2. Analysis of the typical chromatogram corresponding to entry 11 in Table 5. Integration areas of these chromatogram-peaks are used to calculate the reactions conversion and respective selectivities.

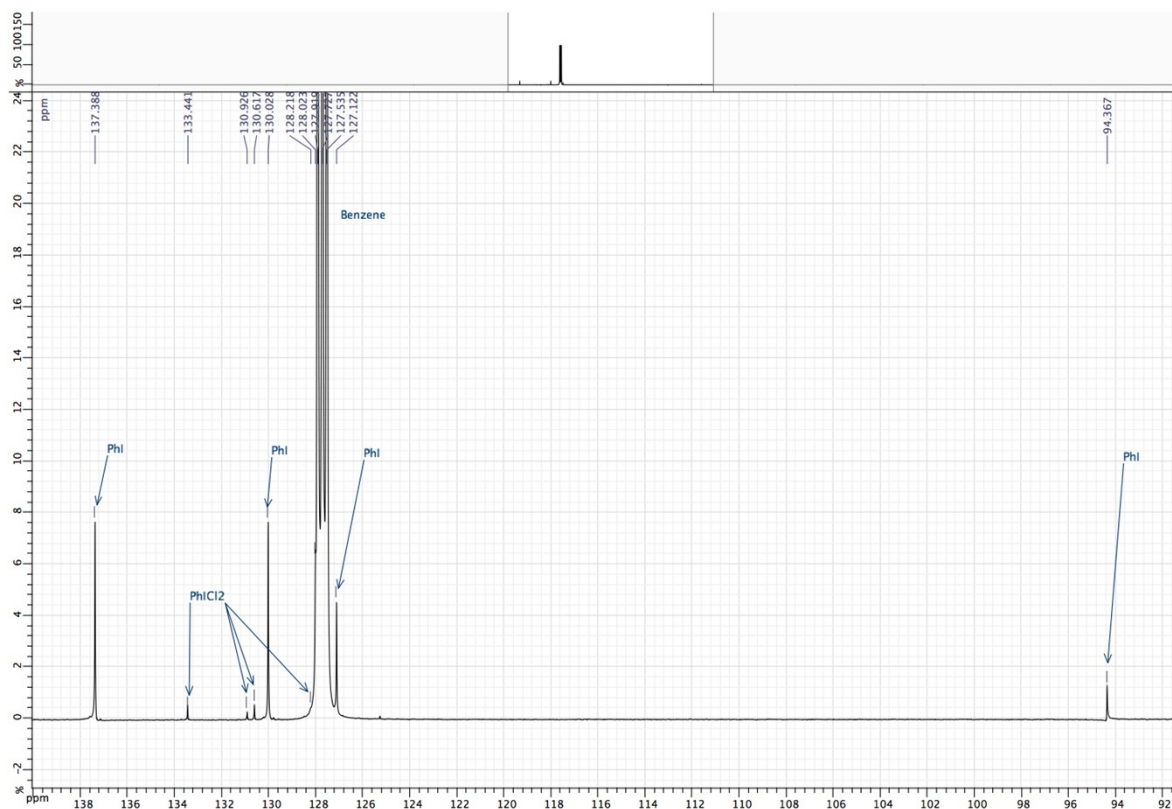


Figure S3. ^{13}C -NMR spectrum of PhICl_2 in PhI in d_6 -benzene.

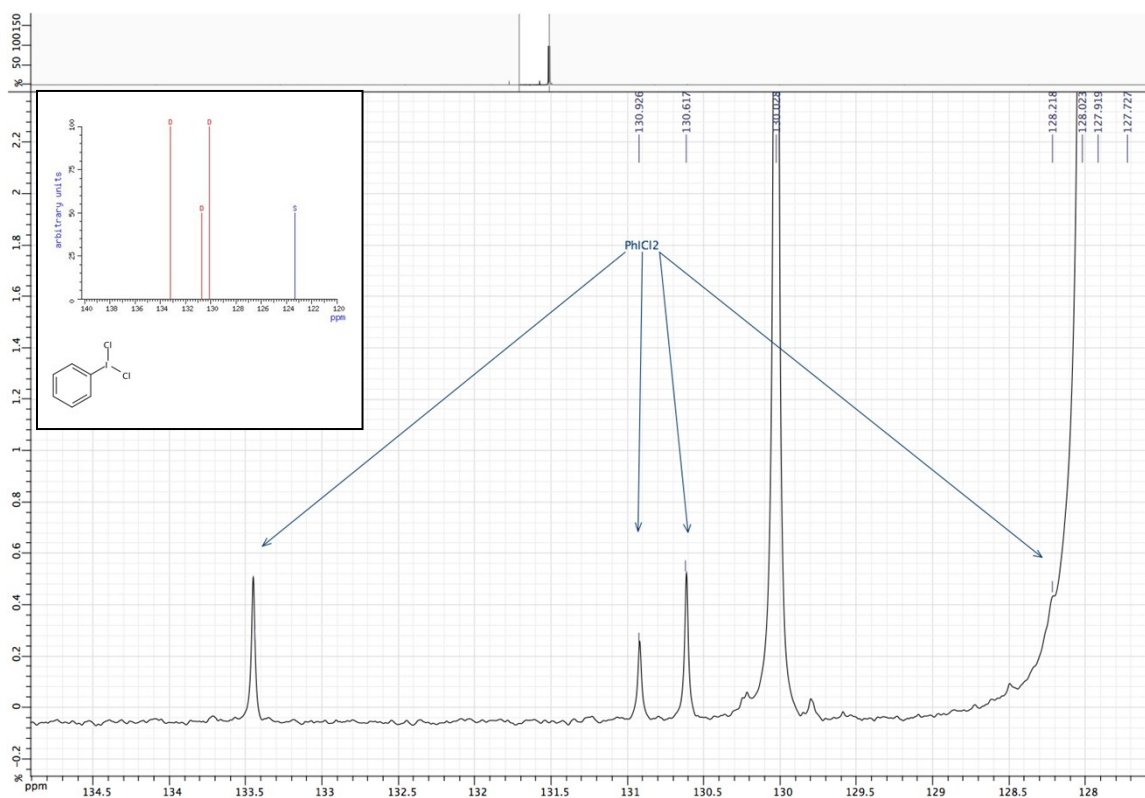


Figure S4. ^{13}C -NMR spectrum of PhICl_2 in PhI in d_6 -benzene. Zoom for the characteristic PhICl_2 peaks. With the inset corresponding to reported ^{13}C -NMR for PhICl_2 .^{vii}

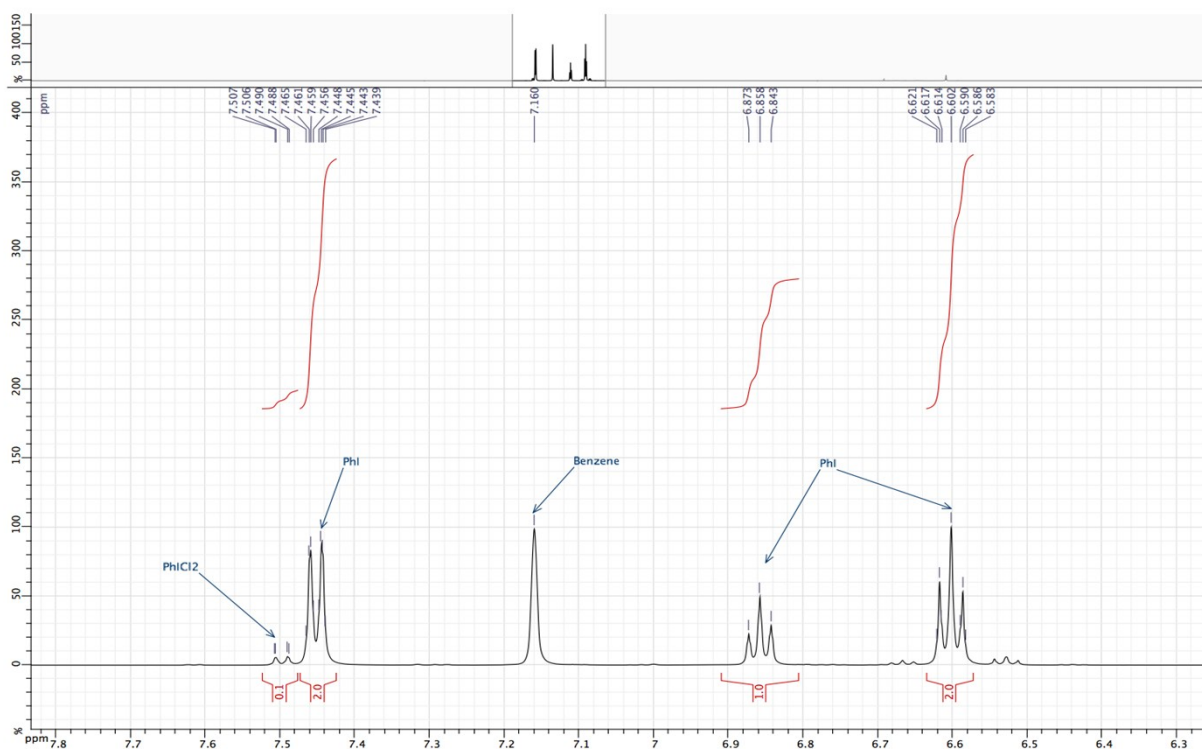


Figure S5. $^1\text{H-NMR}$ spectrum of PhICl_2 in PhI in d_6 -benzene. Integration of the peaks shows that less than 10 % of PhI are converted to PhICl_2 .

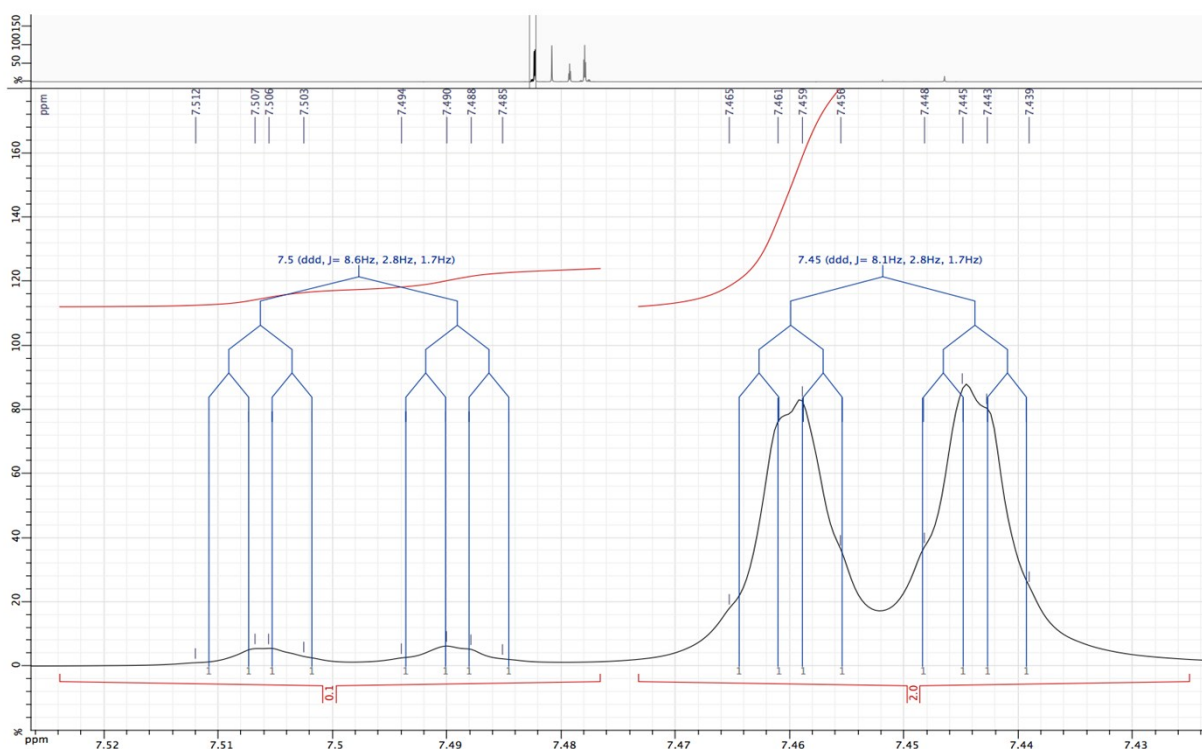


Figure S6. $^1\text{H-NMR}$ spectrum of PhICl_2 in PhI in d_6 -benzene. Zoom for the characteristic PhICl_2 peaks.

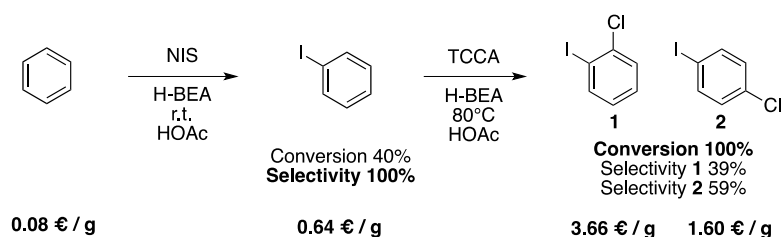


Figure S7. Possible set-up of stepwise heterogeneous continuous flow process (or batch 30 min each step) presented in this work allowing the selective production of monohalogenated highly value-added chemicals.

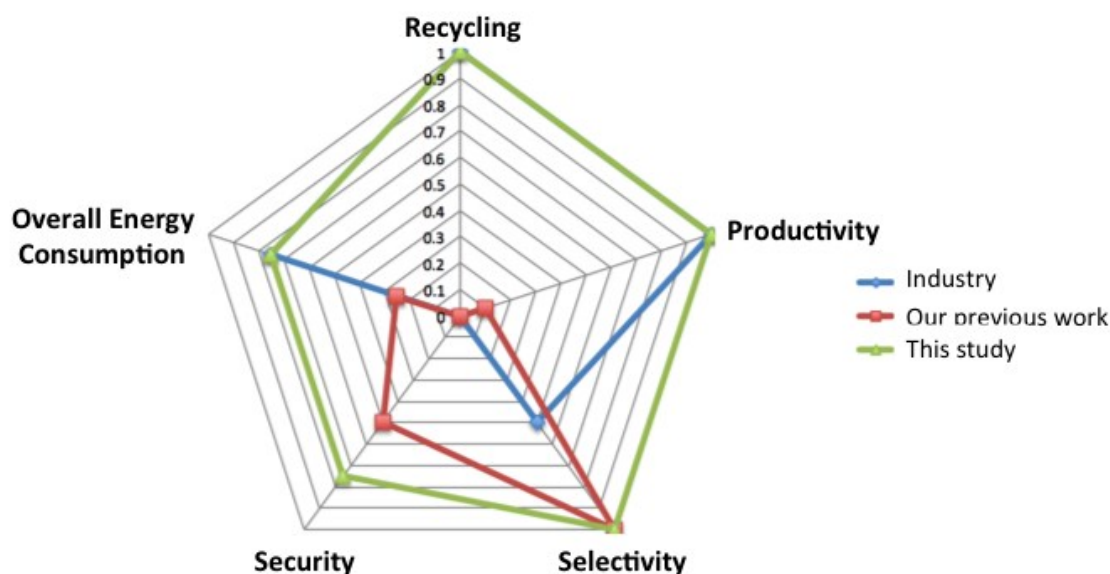


Figure S8. Simplified life cycle assessment (LCA) comparing the current industrial processes⁵ to our previous work¹⁶ and to the present study. Normalised relative values were estimated using our results and available data.

Table S1. Normalised prices for considered chemicals in this study.

Molecule	Price [€/g _{product}]	Role
Benzene	0.08	Starting material from petrochemistry
TCCA	0.08	Very cheap chlorinating agent: 1/3 eq. needed
Chlorobenzene	0.12	Value added chemical
1,4-dichlorobenzene	0.09	Undesired by-product
Bromobenzene	0.07	Very cheap
2-Chlorobromobenzene	1.04	High value added chemical
4-Chlorobromobenzene	0.40	Value added chemical
Iodobenzene	0.64	Value added chemical
2-Chloriodobenzene	3.66	High value added chemical
4-Chloriodobenzene	1.60	High value added chemical

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- ⁱ N. Essayem, G. Coudurier, J. C. Vedrine, D. Habermacher and J. Sommer, *J. Catal.*, 1999, **183**, 292–299.
- ⁱⁱ M. A. Cambor, A. Corma and S. Valencia, *J. Mater. Chem.*, 1998, **9**, 2137.
- ⁱⁱⁱ N. Lauridant, T. J. Daou, G. Arnold, J. Patarin and D. Faye, *Microporous Mesoporous Mater.*, 2013, **166**, 79.
- ^{iv} (a) K. Na, C. Jo, J. Kim, K. Cho, J. Jung, Y. Seo, R. J. Messinger, B. F. Chmelka and R. Ryoo, *Science*, 2011, **333**, 328; (b) M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki and R. Ryoo, *Nature*, 2009, **461**, 246; (c) K. Na, M. Choi, W. Park, Y. Sakamoto, O. Terasaki and R. Ryoo, *J. Am. Chem. Soc.*, 2010, **132**, 4169.
- ^v IUPAC, *Pure Appl. Chem.*, 1985, **57**, 4, 603.
- ^{vi} (a) D. Y. Zhao, Q. S. Huo, J. L. Feng, B. F. Chmelka and G. D. Stucky, *J. Am. Chem. Soc.*, 1998, **120-24**, 6024; (b) P. I. Ravikotich, A. V. Neimark, *Langmuir*, 2002, **18-25**, 9830.
- ^{vii} Wiley subscription services, Inc. (US).