

Les Zéolithes:

De la superacidité ... à la chimie fine



Benoît Louis



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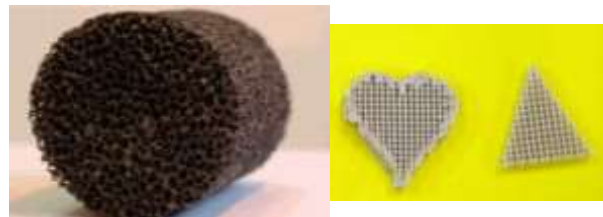
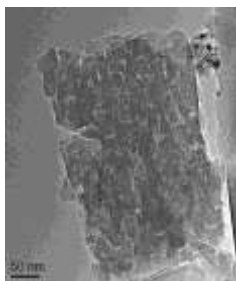
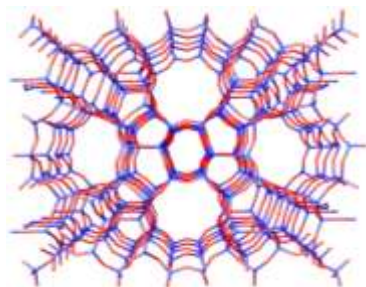
Laboratoire de Synthèse Réactivité Organiques et Catalyse (LASYROC)
1, rue Blaise Pascal
67000 Strasbourg Cedex

De bons collègues...



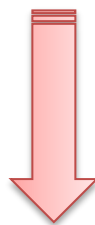
du site actif ... via the cristal ... au réacteur

- 1. Préparer une zéolithe ayant les propriétés “requisés” / “escomptées” pour une application visée**
- 2. Améliorer ces propriétés (acidité, dopage métallique) par processus itératif:**
préparation – caractérisation – test – modification – caractérisation – test ...
(cinétique, modélisation, marquage isotopique)
- 3. Design à l'échelle du cristal:** taille, porosité adaptée (micro / meso).
- 4. Développer un réacteur catalytique structuré**

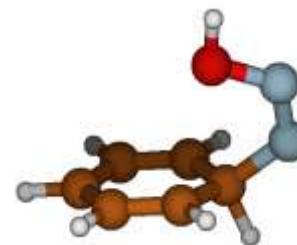
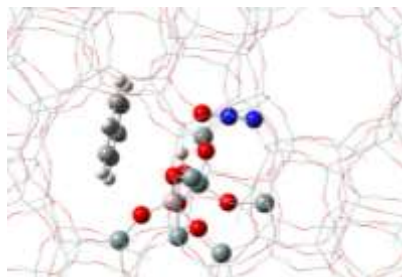
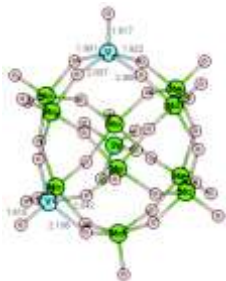


“ Rational Design ” de Zéolithes

- Connaissance du (des) site(s) actif(s)
- Taille / Morphologie / Assemblage des cristaux

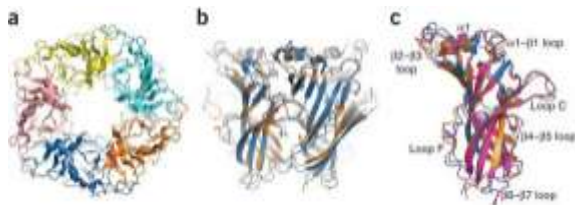


- **Pour la catalyse** : (superacide), confinement, bifonctionnelle



The chimaera paradox

- ❖ a fire-breathing female monster with a lion's head, a goat's body, and a serpent's tail. Any mythical animal formed from parts of various animals.
- ❖ a thing which is hoped but is illusory or impossible to achieve.



Nature Neuroscience 14 (2011) 1253



Pursue chimaera

Confinement effect

Porosity

Acidity

Metallic functions



Superacidity ?

Crystal size effects

Extra-Framework Al

Inside or *outside* ?

Zeolites as chimaera

The chimaera paradox

Confinement effect

Porosity

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Metallic functions



Superacidity ?

Crystal size effects

Extra-Framework Al

Inside or *outside* ?

The chimaera paradox

Confinement effect

Porosity

Acidity

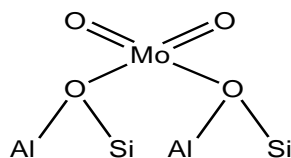
Metallic functions

Superacidity ?

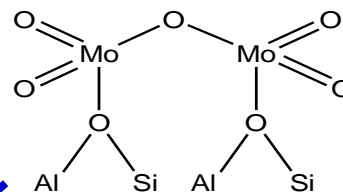
Crystal size effects

Extra-Framework Al

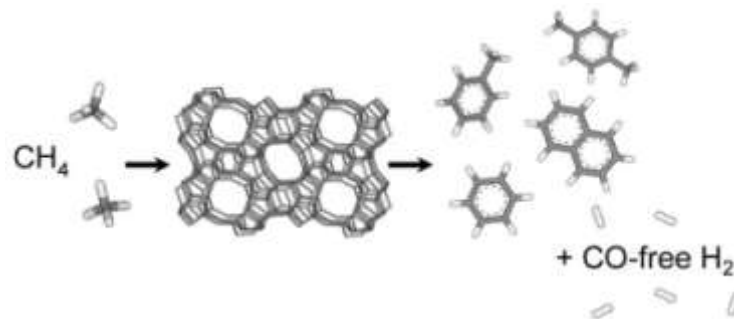
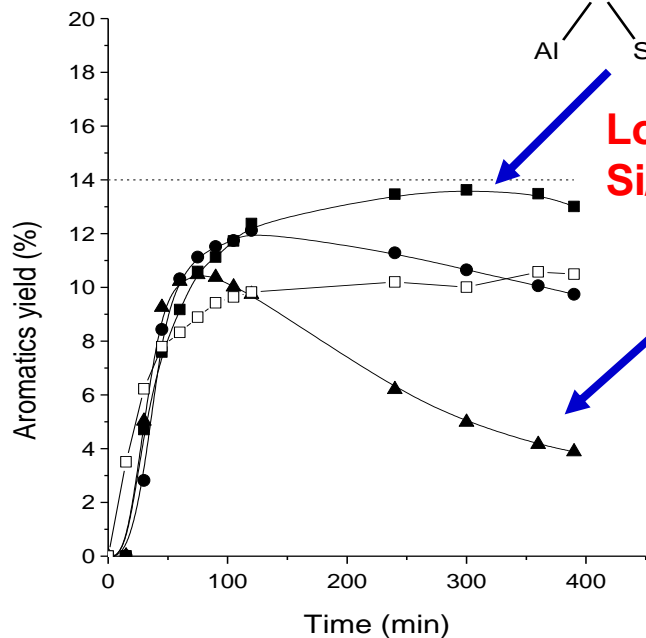
Inside or outside ?



Low
Si/Al



High
Si/Al

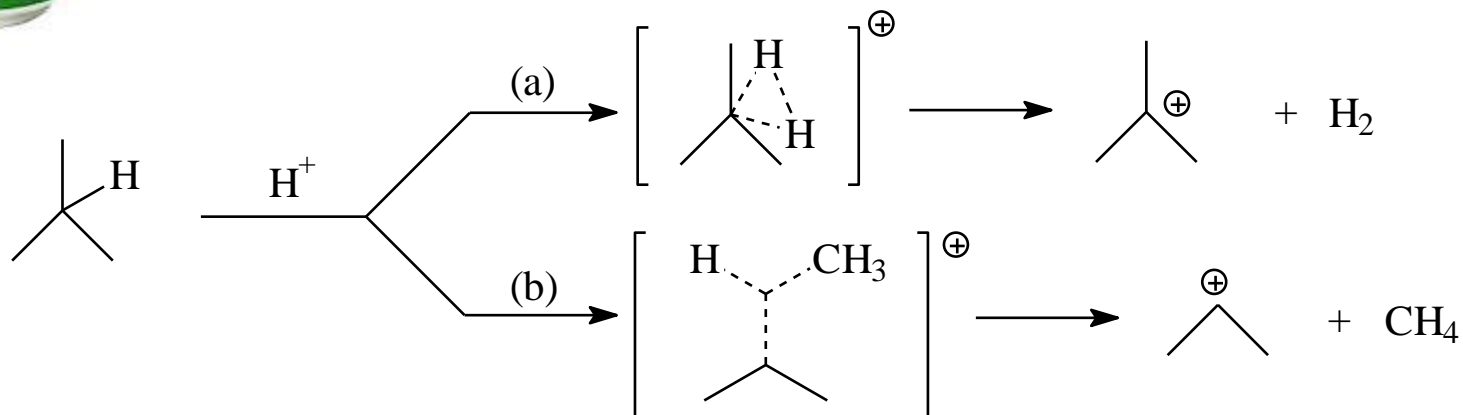


1. Zéolithes: “Canada Dry” de la superacidité



What is the first step in alkane activation ? at low temperature ?

Hypothesis: superacid-like protolytic activation even at low temperature

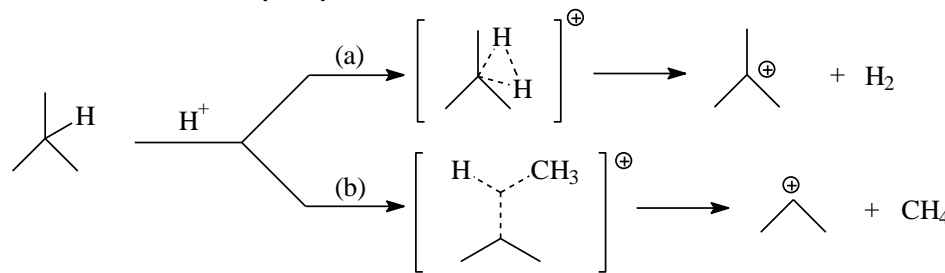
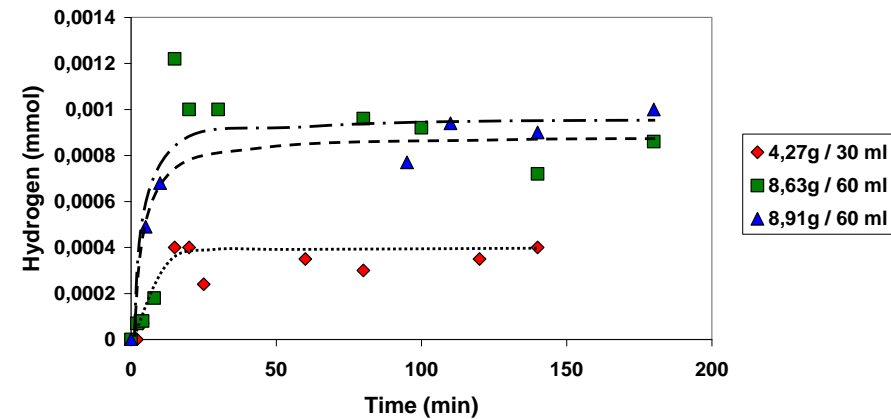
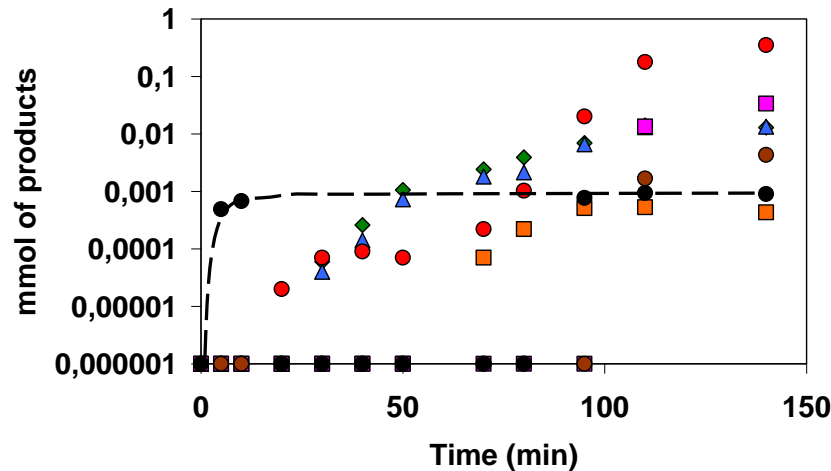


Interest for petrochemistry: FCC technology, isomerization

1. Zéolithes: "Canada Dry" de la superacidité

Craquage de l'isobutane sur H-ZSM-5 à 473 K

Conversion : 1-2%



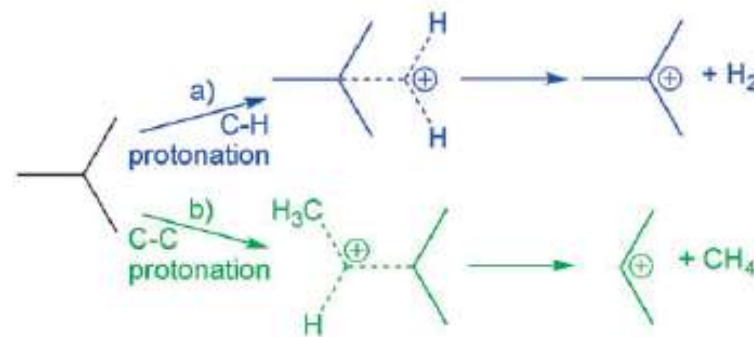
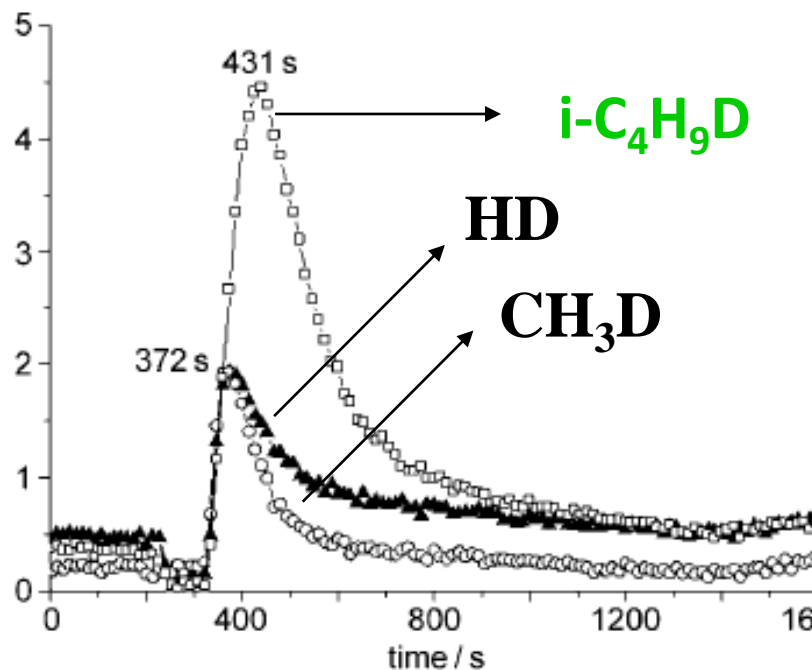
Proportionnalité entre le nombre de protons et H_2 formée !

MAIS ne pourrait on pas imaginer une autre voie? **déshydrogénation ?**

Craquage de l'isobutane sur D-USY à 473 K



Pierre Mothé-Esteves
 Marcelo M. Pereira



HD et CH₃D comme produits primaires

➔ Première étape: Activation via protonation de liaisons

σ C-H et σ C-C

1. Zeolites are not superacids !



Alkane Activation over Acidic Zeolites: The First Step

Benoit Louis,^[a] M. Maciel Pereira,^[b] Fabiana M. Santos,^[b] Pierre M. Esteves,^[b] and Jean Sommer*^[c]

Abstract: The heterogeneous acid-catalyzed activation step of alkanes leading to the reaction intermediates (carbocationic or alkoxy species) was up to now the matter of a longstanding controversy. Gas chromatography and online mass spectroscopy measurements show that H₂ and methane are

formed over H-zeolites, whereas HD and CH₃D are formed over D-zeolites as the primary products in the reaction with isobutane. These results indicate

Keywords: alkanes • heterogeneous catalysis • hydrocarbons • zeolites

that σ -bond protolysis by strong acid sites is the first step for hydrocarbon activation on these catalysts at mild temperatures (473 K), in analogy to the activation path occurring in liquid superacid media.

1. Zeolites are not superacids ?



Alkane Activation over Acidic Zeolites: The First Step

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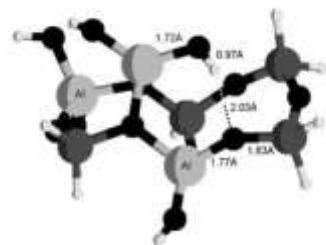
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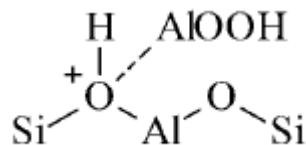
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Extra-framework aluminum species: "anti-chimaera"



C.J.A. Mota

Angew. Chem. Int. Ed. 43 (2004) 3050



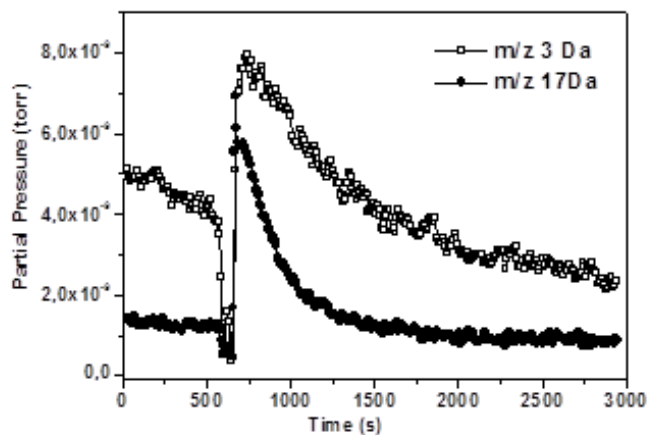
J.H. Lunsford

J. Catal. 118 (1989) 85



M.M. Pereira

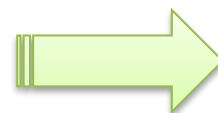
MMM 100 (2007) 276



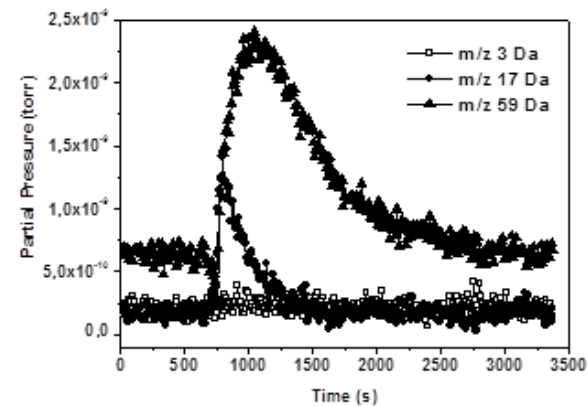
D-USY

J.A. van Bokhoven

Appl. Catal. A
333 (2007) 245



Na₂H₂-EDTA

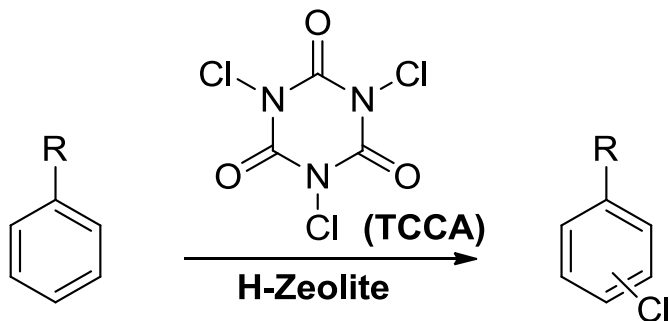


D-USY without EFAI

Extra-framework aluminum species: “anti-chimera”

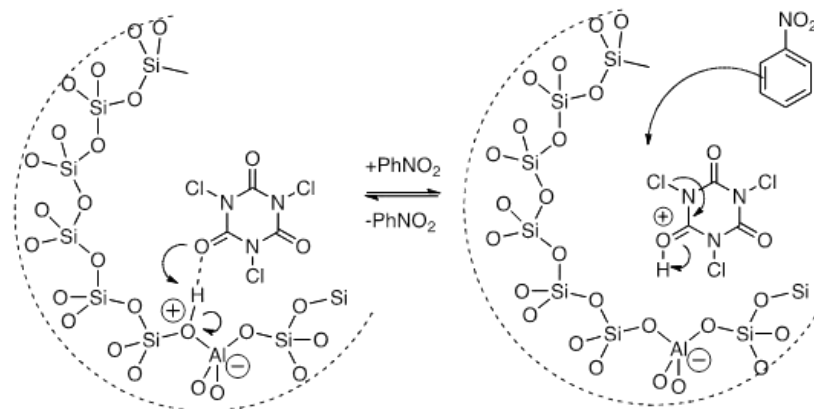


P. Mothé-Esteves, M.C.S. de Mattos



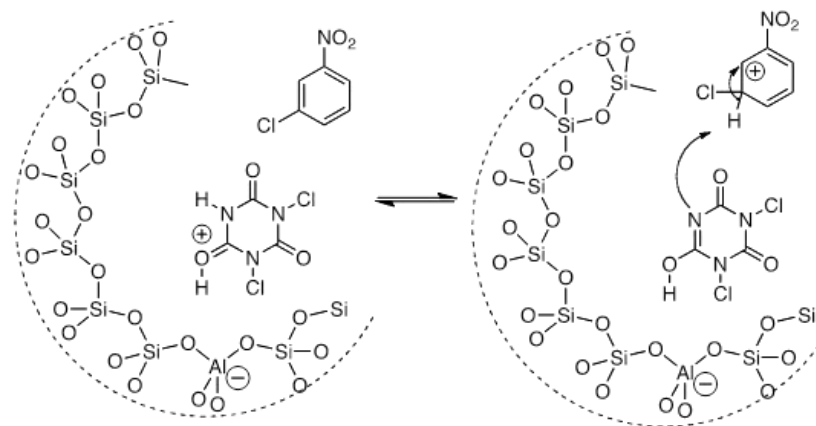
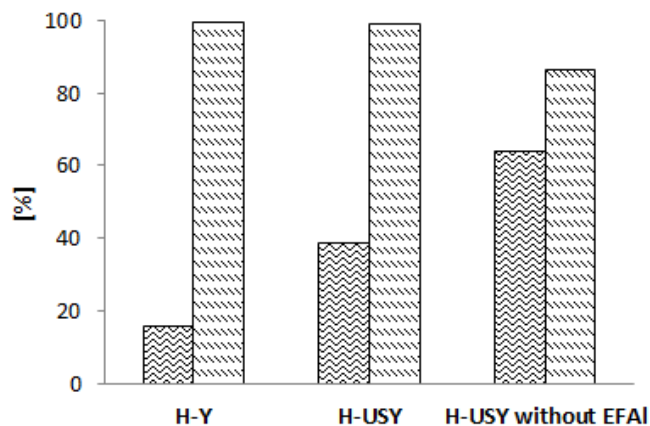
Aromatic

R= NO₂ or Cl



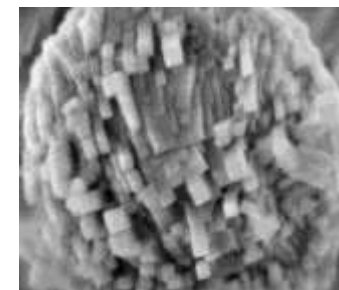
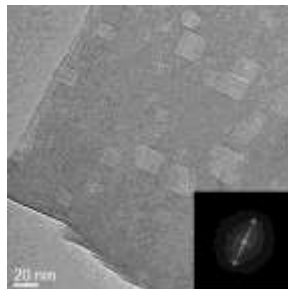
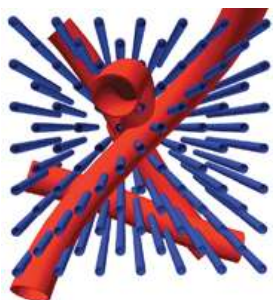
Conditions: TCCA/Aromatic/H⁺ = 1/1/0,8, T=150°C, t_R= 5 h

▣ Nitrobenzene conversion □ Selectivity toward monochlorinated products

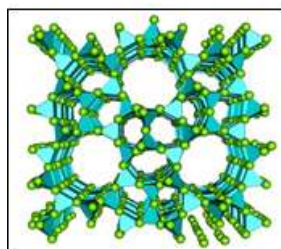


EFAl has a negative impact (... in this case)

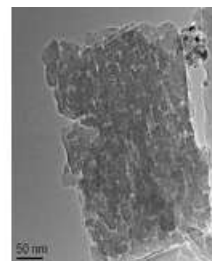
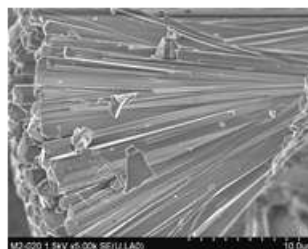
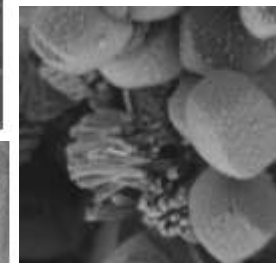
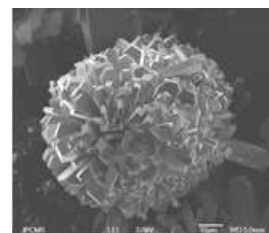
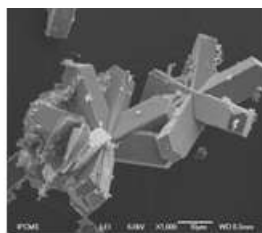
2. Porosité hiérarchisée et assemblage de cristaux



Chem. Eng. J. 161 (2010) 397; *Cryst. Growth & Des.* 9 (2009) 3721; *Appl. Catal. A* 390 (2010) 102



ZSM-5



ChemCatChem 3 (2011) 1263

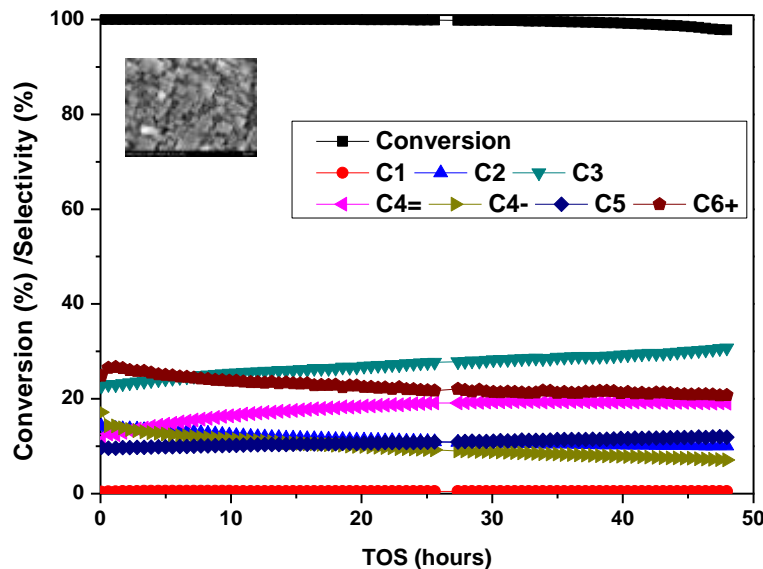
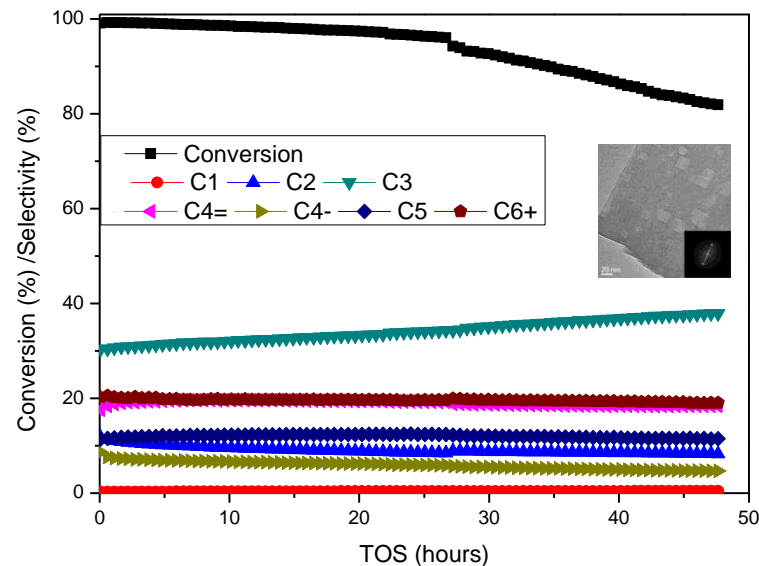
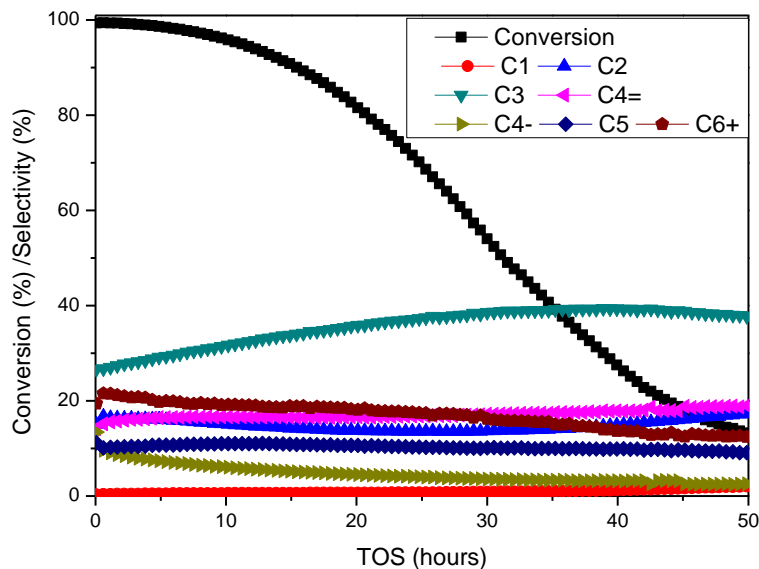


2. ZSM-5 crystals in the MTO reaction



Influence of mesoporosity type

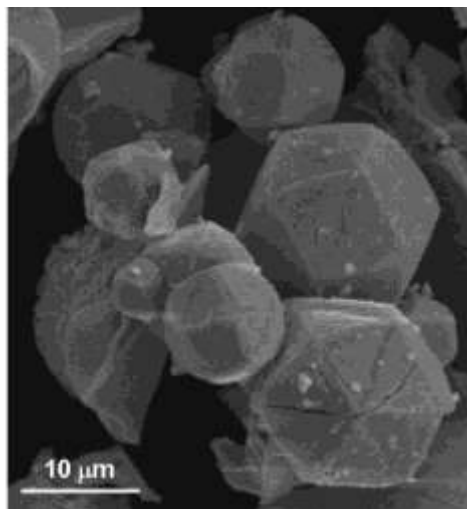
Intra-crystalline versus Inter-crystalline



WHSV = 1.8 g methanol / g_{zeolite} / h ; T_R = 350 °C

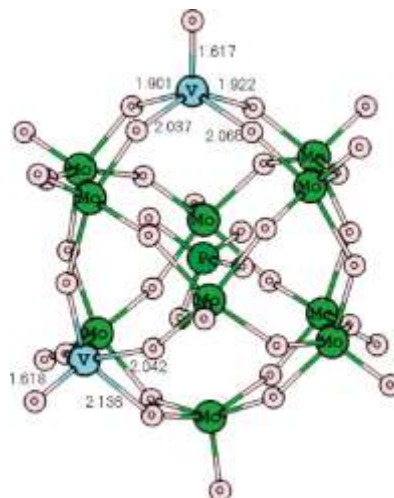
3. Assemblage de Polyoxométallates

DFT, PM6, XANES, ^{51}V MAS NMR



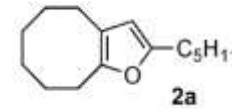
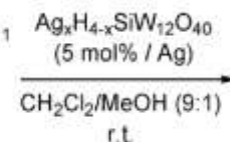
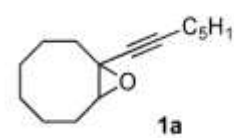
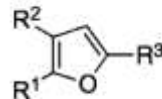
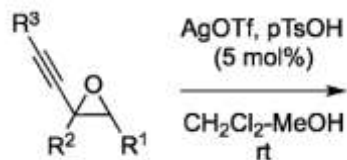
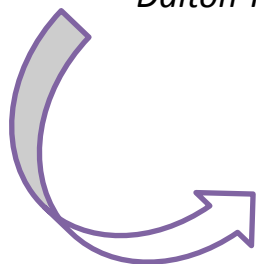
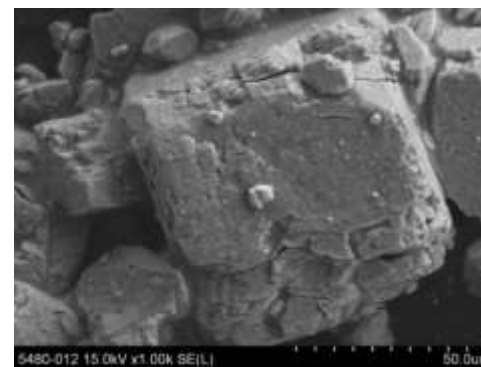
$\text{Ag}_4\text{SiW}_{12}\text{O}_{40}$

Dalton Trans. 40 (2011) 1220



$\text{H}_5\text{V}_2\text{PW}_{12}\text{O}_{40}$

Cryst. Growth & Des. 10 (2010) 371

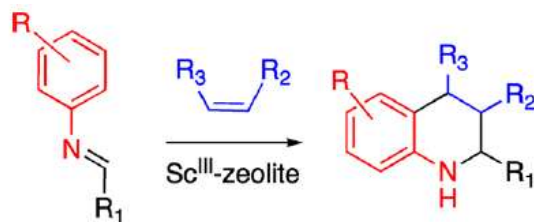


Rdt: 96-100% (5h) pour x = 1, 2 ou 3

Catalysis Science & Technology 1 (2011) 981–986

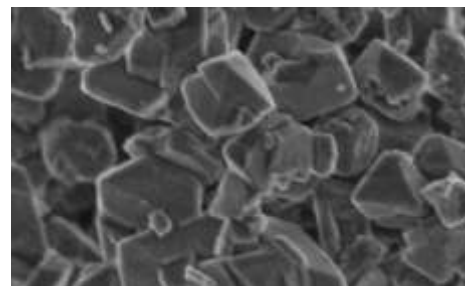
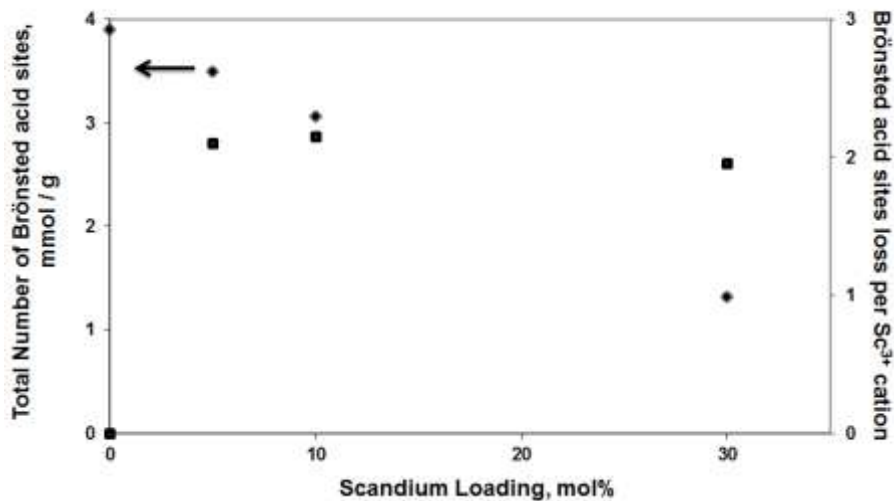
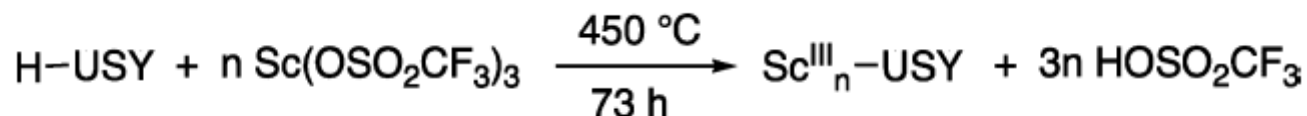
4. Catalyse bifonctionnelle

Cycloaddition [4+2] catalysée par une zéolithe Sc-USY



aza Diels Alder

tétrahydroquinolines



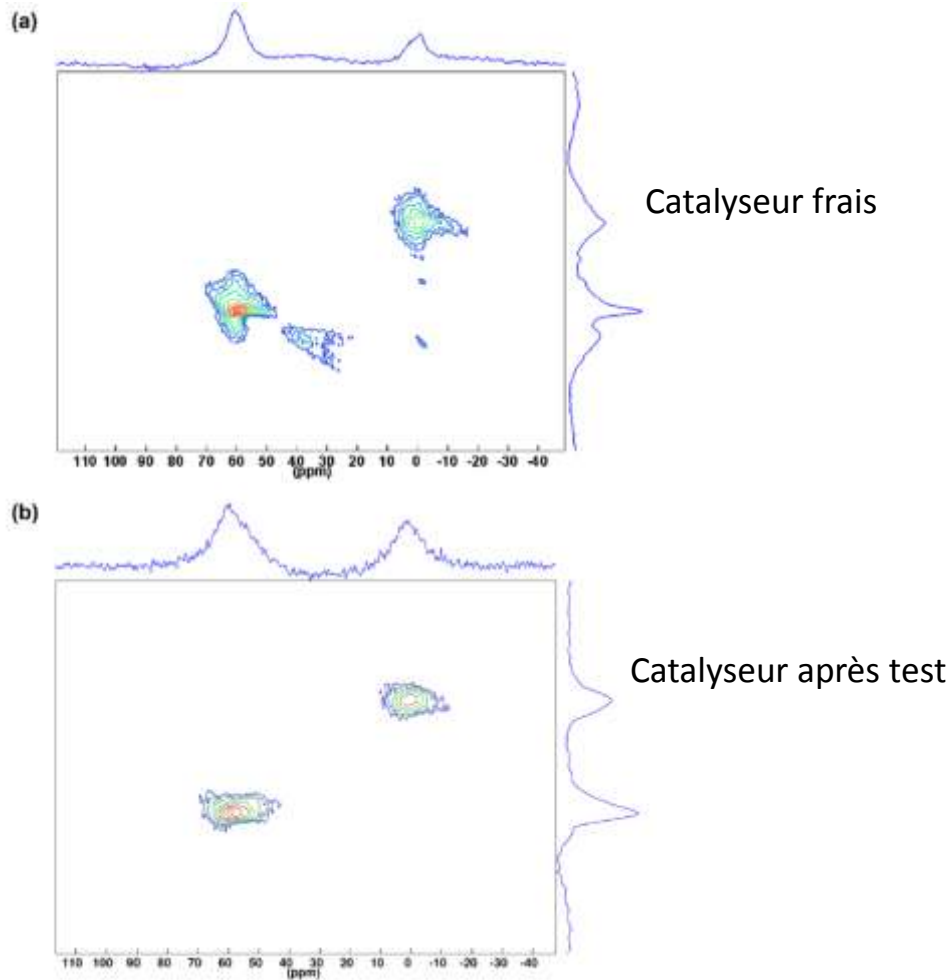
Cristallinité préservée pour Sc
 ≤ 10 % atomique
 EDX: **3F pour 1Sc**



1 Sc³⁺ substitue 2 sites de Brønsted

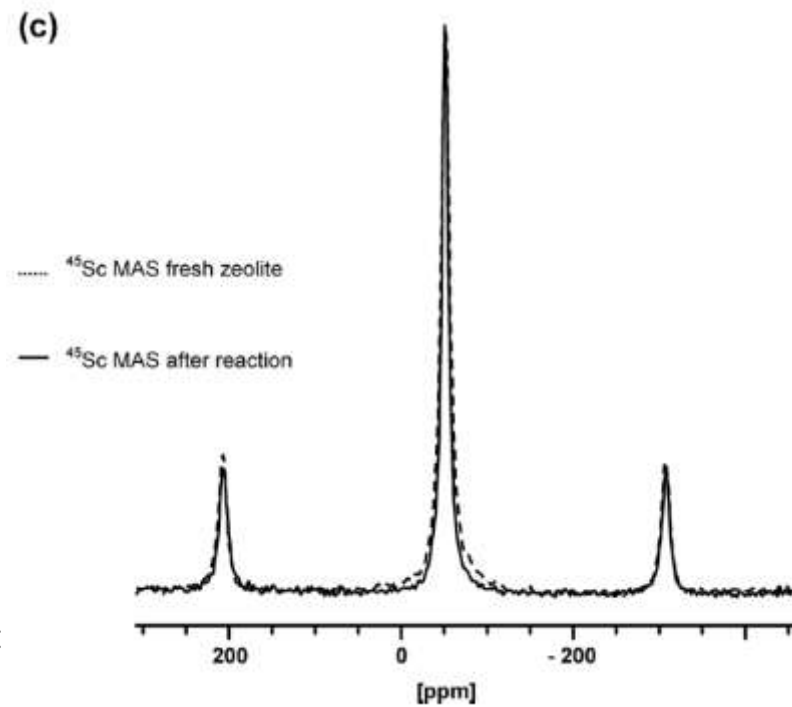
J. Phys. Chem. C 116 (2012) 13661

Cycloaddition [4+2] catalysée par une zéolithe Sc-USY



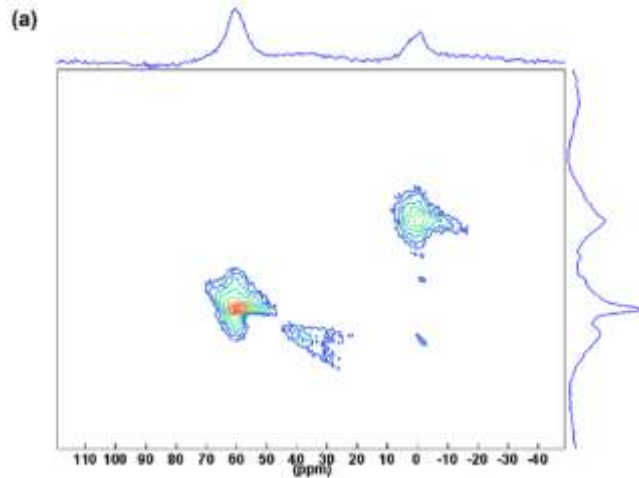
^{27}Al MQ-MAS

Disparition d'une contribution EFAl
 Structuration au voisinage de l'Al « healing effect »

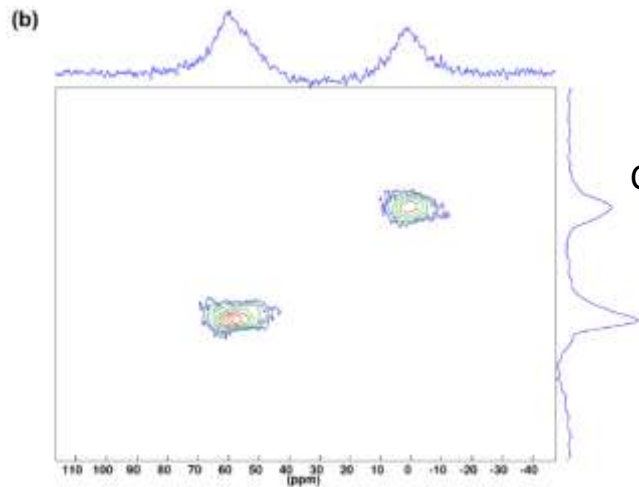


^{45}Sc MAS NMR

Cycloaddition [4+2] catalysée par une zéolithe Sc-USY



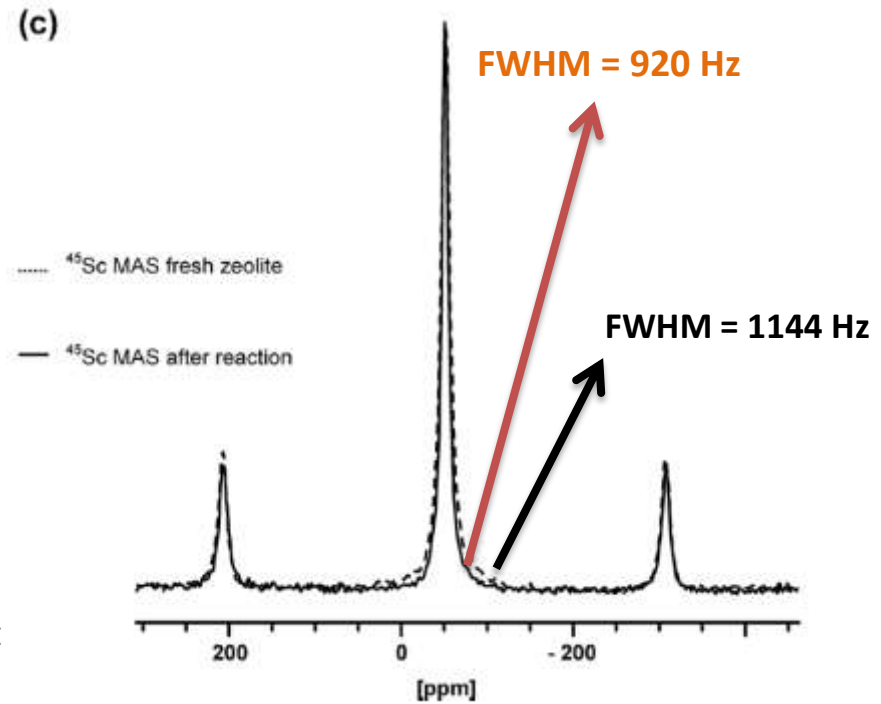
Catalyseur frais



Catalyseur après test

²⁷Al MQ-MAS

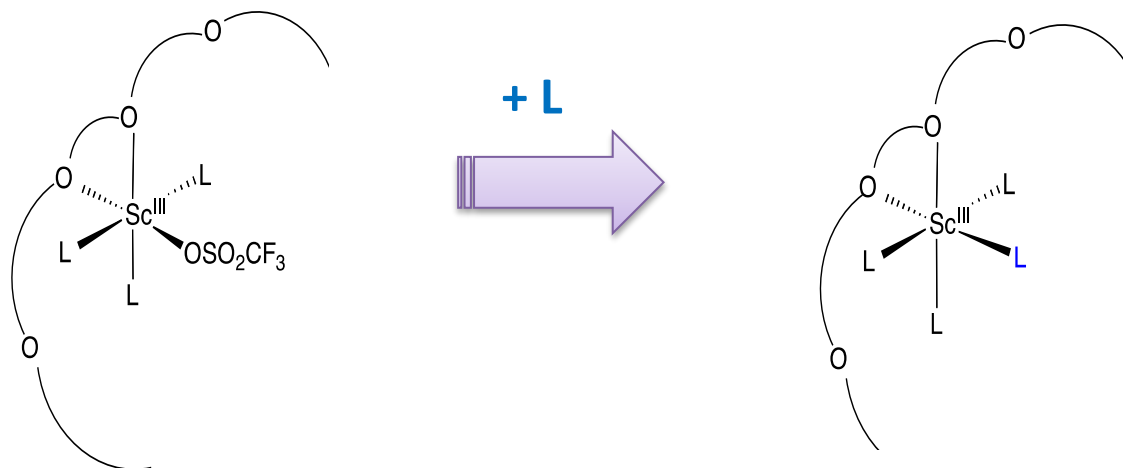
Disparition d'une contribution EFAl
 Structuration au voisinage de l'Al « healing effect »



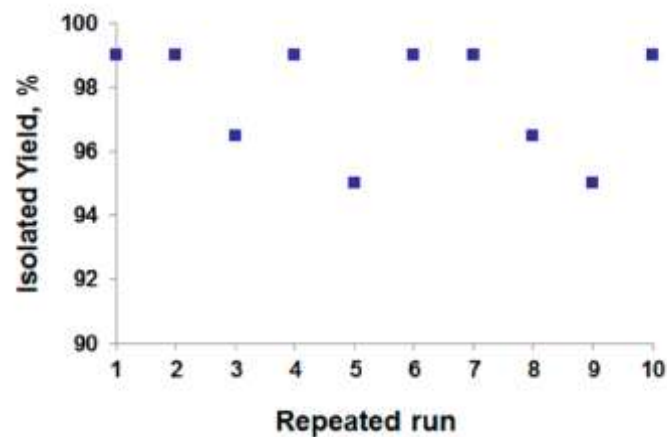
⁴⁵Sc MAS NMR

Structuration au voisinage du Sc

4. Catalyse bifonctionnelle

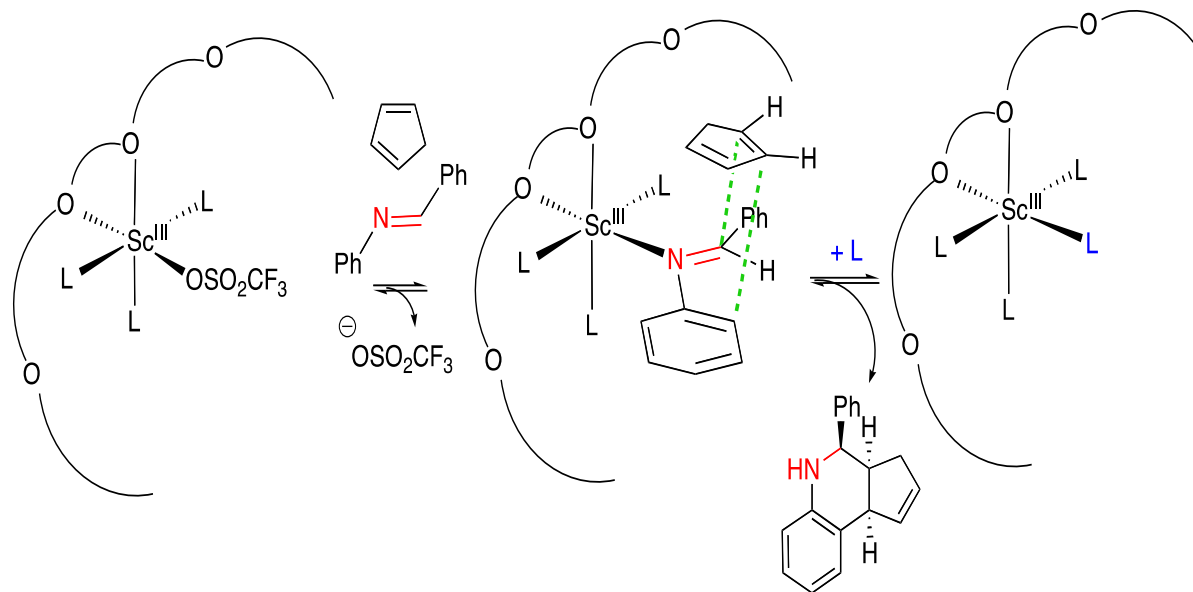


X-USY	time (h)	yield (%)
HUSY	24	traces
2ScUSY	2	99
5ScUSY	5	97
10ScUSY	22	78
30ScUSY	24	64



**Sc-USY catalyseur très actif et recyclable
 pour la synthèse de tétrahydroquinolines**

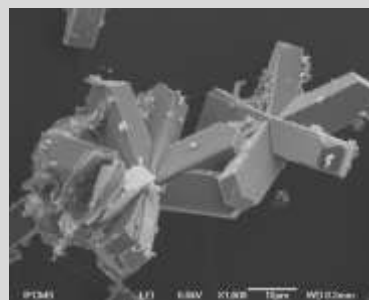
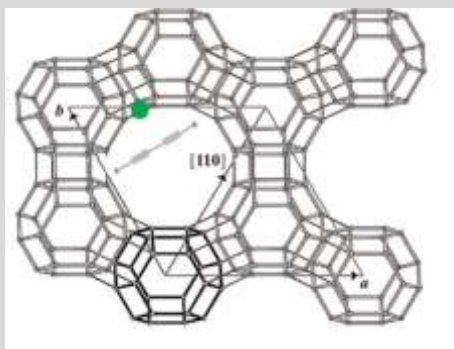
4. Catalyse bifonctionnelle



Rôle important de l'acidité de Brønsted et Lewis

Influence de la topologie de la zéolithe

Effet crucial de la méthode de dopage métallique



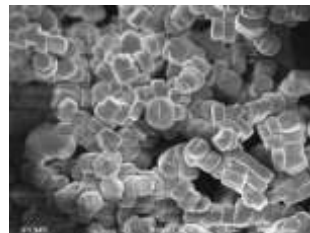
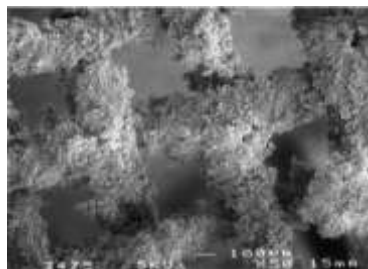
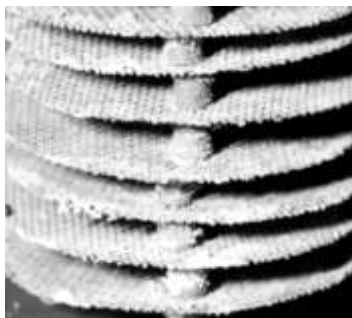
Du site actif ... au Réacteur

Les Zéolithes se comportent comme des superacides « doux »

Les espèces d'EFAl sont importantes pour la catalyse

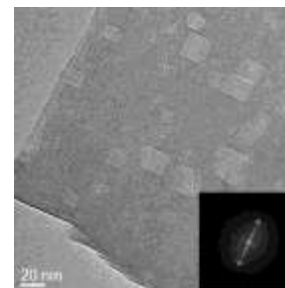
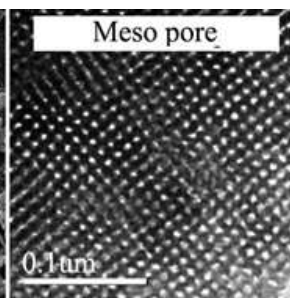
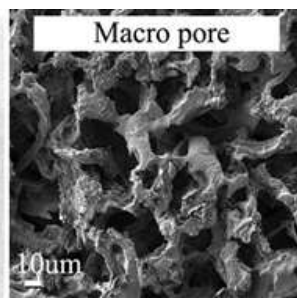
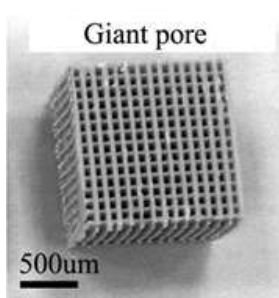
Lien structure ↔ activité nécessaire pour la compréhension

Structured reactors via zeolite coatings



Appl. Catal. A. 210 (2001) 103

Ind. Eng. Chem. Res. 40 (2001) 1454

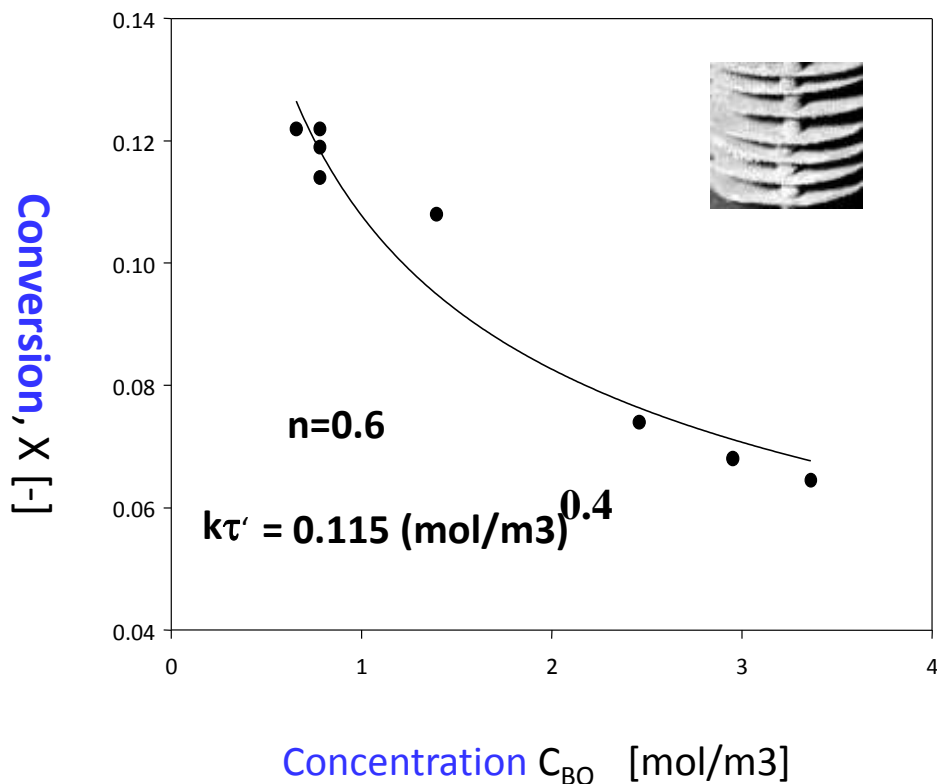
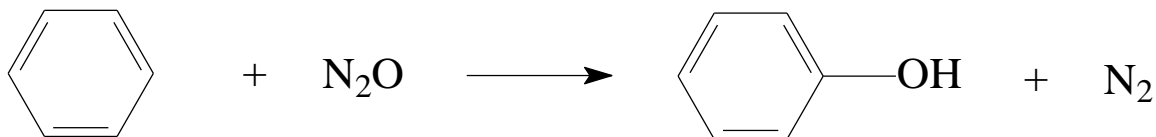


ChemCatChem 3 (2011) 1263

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Cryst. Growth & Des. 9 (2009) 3721

Structured reactors via zeolite coatings



$$X = 1 - \left(1 + (n-1) \cdot k\tau' \cdot C_{BO}^{n-1} \right)^{1/(1-n)}$$

τ' constant

$$k = 1.7 \cdot 10^{-4} \text{ mol}^{0.4} \cdot \text{m}^{1.8} \cdot \text{kg}^{-1} \cdot \text{s}^{-1}$$

$$k_{\text{powder}} = 1.0 \cdot 10^{-4}$$

$$k_{\text{extrudates (Süd-Chemie)}} = 1.2 \cdot 10^{-4}$$

Assistance technique : Thierry Roméro (ICPEES), Jean-Philippe Tessonier (Iowa State University), Marc Willinger (FHI Berlin)

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