UCCS
UNITÉ DE CATALYSE ET CHIMIE DU SOLIDE

Matériaux pour la catalyse : Veille et prospective

Eric Marceau

CARMEN EVOLUTION – 21.06.22

Université de Lille · cnrs · UNIVERSITÉ D'ARTOIS · centralelille · institut Chevreul

“Matériaux pour la catalyse: veille”

Veille sur… des matériaux innovants?

… des matériaux pour des procédés innovants?

…des synthèses innovantes?

“Matériaux pour la catalyse: veille”

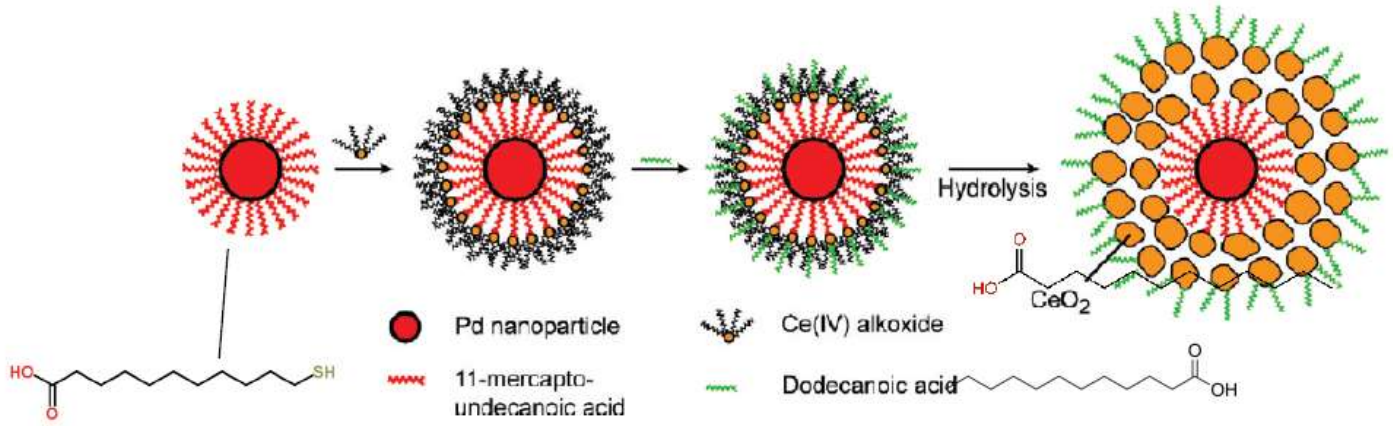
X. Carrier

CAT PREP Summer School 2019

Synthesis of $Pd@CeO_2$ core-shell nanostructures

M. Cargnello, N.L. Wieder, T. Montini, R.J. Gorte, P. Fornasiero *J. Am. Chem. Soc.* 2010
M. Cargnello, J.J. Delgado Jaén, J.C. Hernandez-Garrido, K. Bakhmutsky, T. Montini, J.J. Calvino Gamez, R.J. Gorte, P. Fornasiero *Science* 2012

4 steps synthesis : (1) Synthesis of thiolate-protected Pd nanoparticles
(2) Self-assembly of Ce(IV) alkoxide on protected Pd NPs
(3) Hydrolysis of the Ce alkoxide → $Pd@CeO_2$ nansotructures



“Matériaux pour la catalyse: veille”

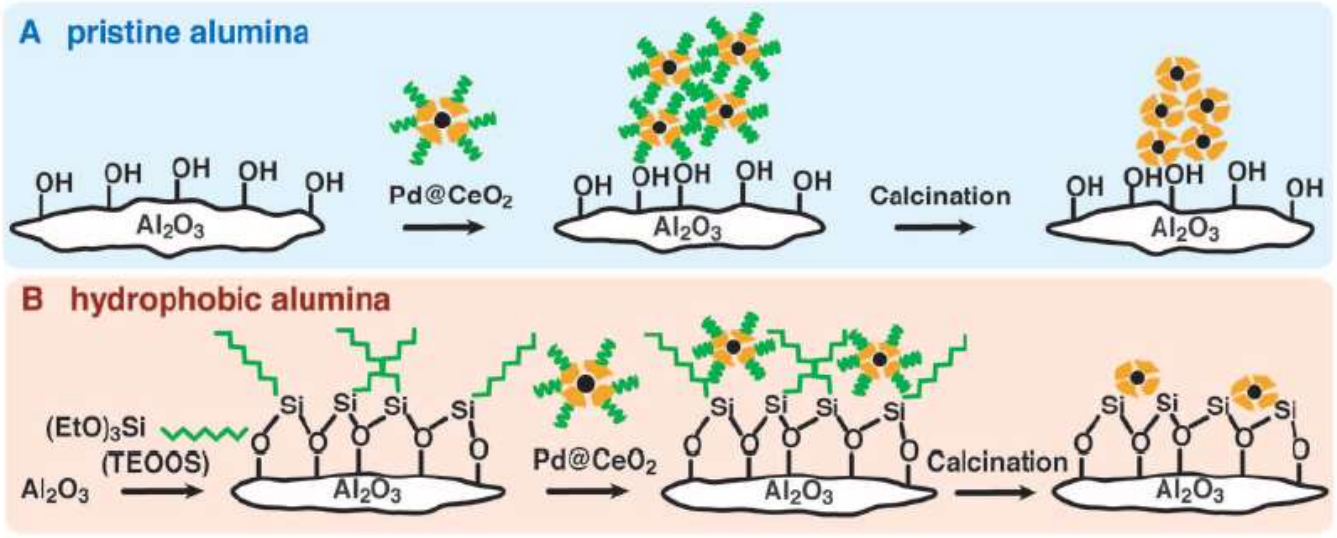
X. Carrier

CAT PREP Summer School 2019

Deposition on alumina

Weak interaction between hydrophobic $Pd@CeO_2$ structures and hydrophilic alumina surface

→ Functionalisation of alumina with organosilane



“Matériaux pour la catalyse: veille”

X. Carrier

CAT PREP Summer School 2019

Versatile synthesis :
variation of Pd NPs size & thickness of CeO_2 shell

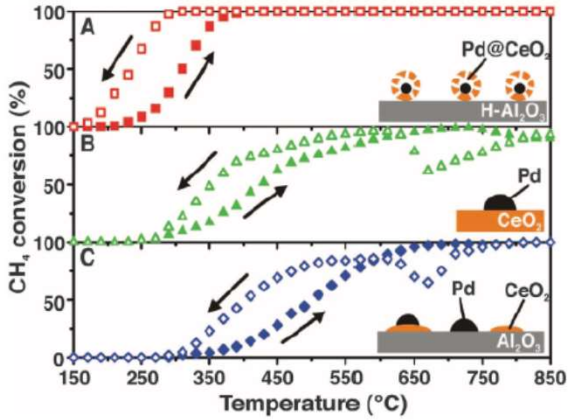
(1) Synthe
(2) Synthe
(3) Self-as
(4) Deposi

Coût?
Rendement?
Sécurité?

noparticles : 5 steps
le) : 8 steps
rotected Pd NPs and hydrolysis : 2 steps
more than 10 steps

Use of organic (potentially toxic) solvents : toluene, dichloromethane, methanol….

But highly active catalyst (methane combustion)



- ✓ Accessible Pd NPs (CO chemisorption)
- ✓ Complete conversion 300°C lower than other systems :
- High resistance of Pd toward sintering due to the oxide shell
- Enhanced CeO_2-Pd interaction improves the stabilization of the active PdO_x phase

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“Matériaux pour la catalyse: veille”

QUELS CRITERES DE CHOIX RETENIR?

Exhaustivité?
Virtuosité scientifique?
Applicabilité?

Objectif ou subjectif?

“Matériaux pour la catalyse: veille”

Choix : la subjectivité, du particulier au général

Fil rouge: le projet NobleFreeCat

Mise en exergue: tout ce que nous **N’AVONS PAS** su faire

Verrou 1

Economie de la synthèse:

Matières premières
Saut d'échelle
Recyclage

Economie de la synthèse

FCCAT 2022: “Mechanism investigation and support optimization for the **iridium**-catalyzed **hydrodeoxygenation of phenols**”

Matériau catalytique **« durable »**?

Economie de la synthèse

Métaux nobles : les disperser au maximum au moyen de synthèses supportant le changement d'échelle

ARTICLES
https://doi.org/10.1038/s41565-021-01022-y

nature nanotechnology

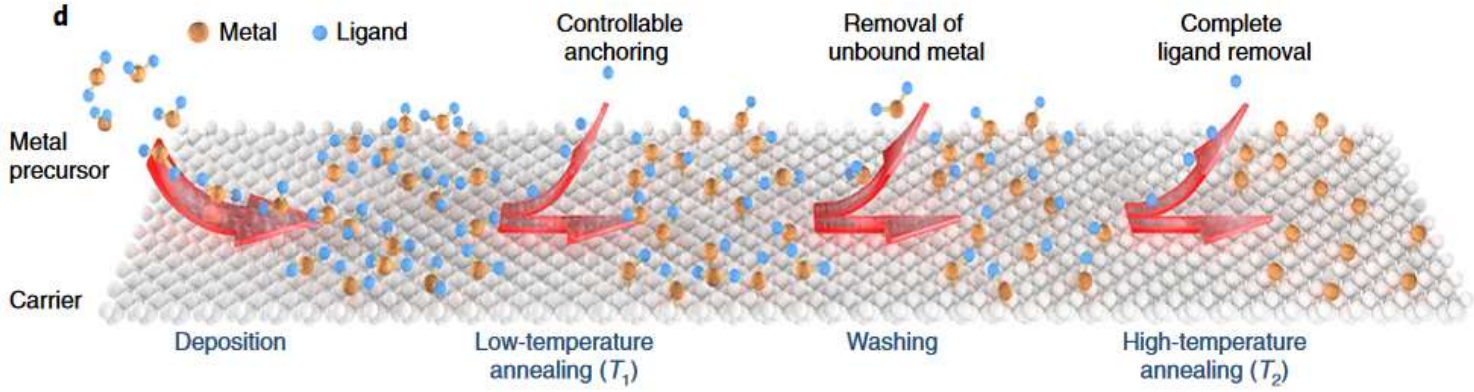
Check for updates

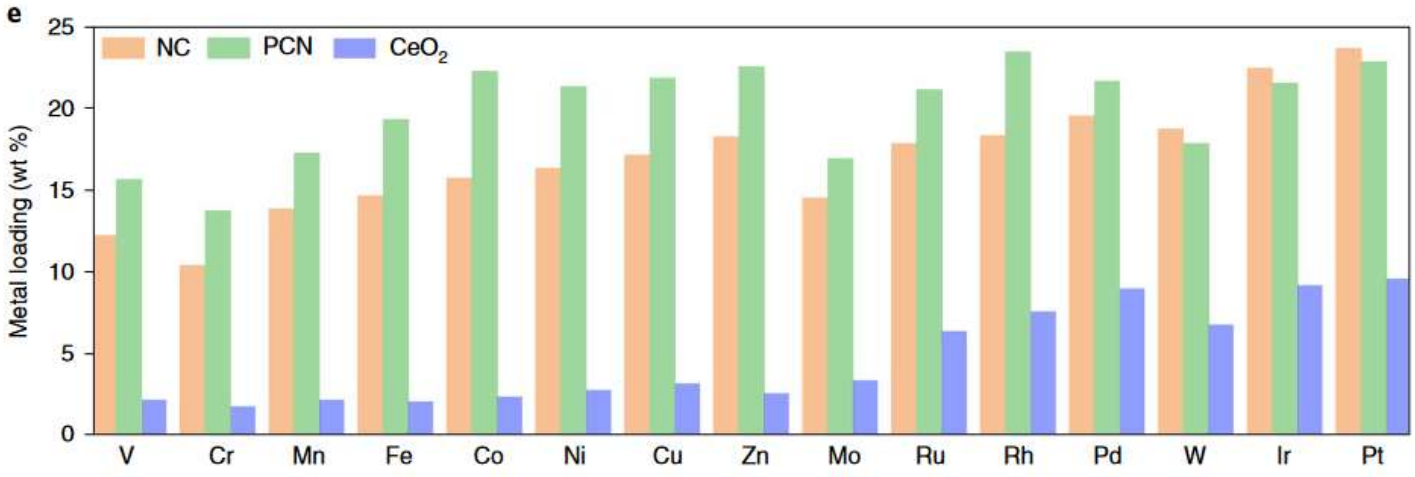
Scalable two-step annealing method for preparing ultra-high-density single-atom catalyst libraries

Xiao Hai[1,11], Shibo Xi[2,11], Sharon Mitchell[3,11], Karim Harrath[4,5,11], Haomin Xu[1], Dario Faust Akl[3], Debin Kong[6], Jing Li[1], Zejun Li[1], Tao Sun[1], Huimin Yang[1], Yige Cui[1], Chenliang Su[7], Xiaoxu Zhao[8]✉, Jun Li[4,5]✉, Javier Pérez-Ramírez[3]✉ and Jiong Lu[1,9,10]✉

NATURE NANOTECHNOLOGY | VOL 17 | FEBRUARY 2022 | 174–181 | www.nature.com/naturenanotechnology

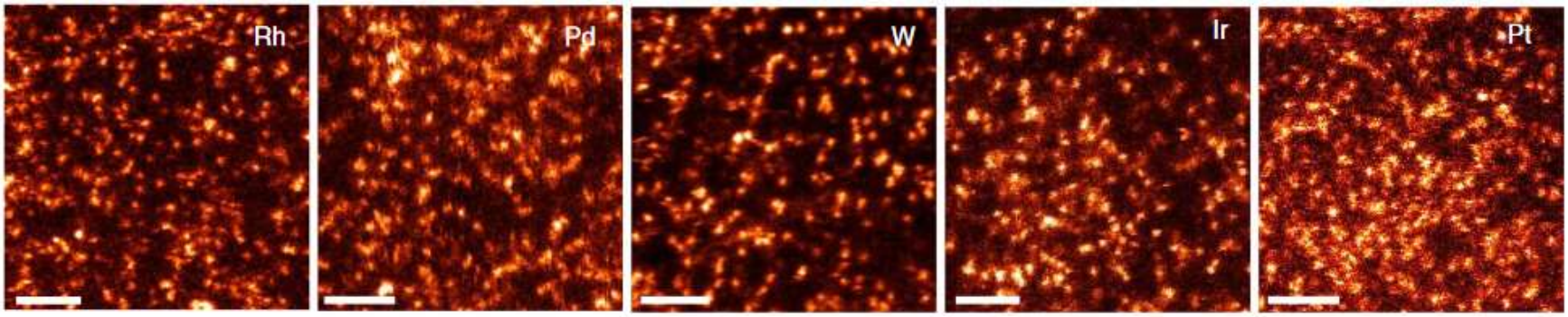
Economie de la synthèse



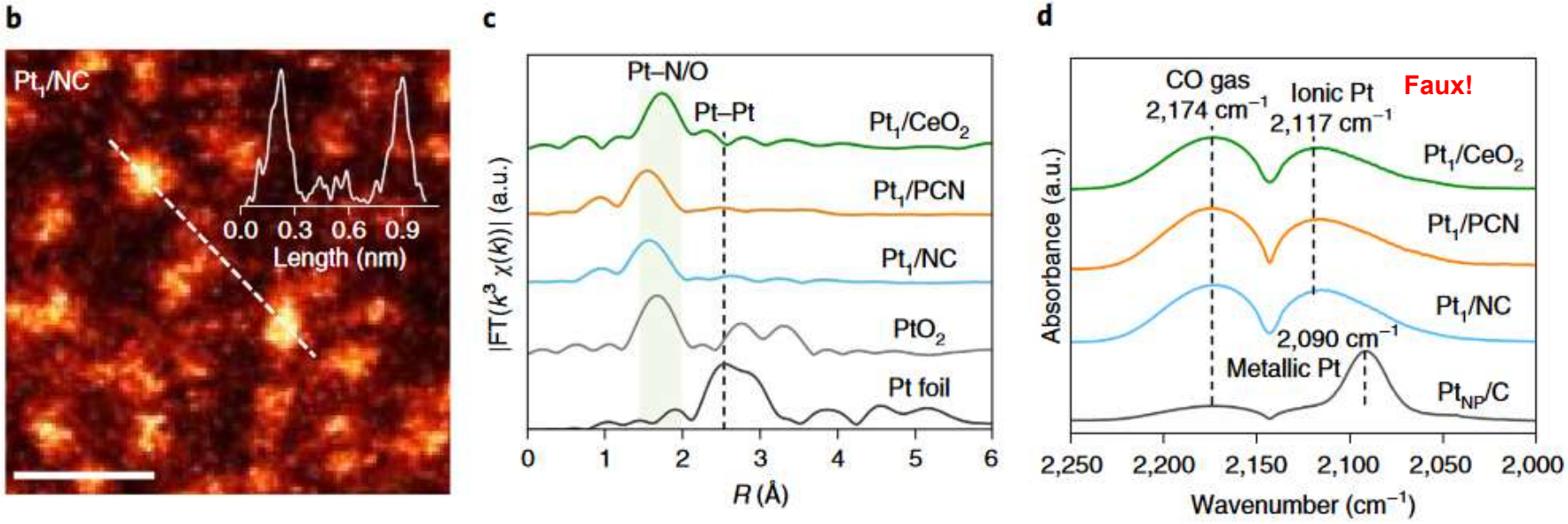


NC: carbone dopé à N; PCN: nitrure de carbone polymérique

Economie de la synthèse



0,5 nm



Economie de la synthèse

Quelques dizaines de pages plus haut…

SINGLE-ATOM CATALYSIS

All the lonely atoms, where do they all belong?

A spectacular advance in catalyst synthesis is demonstrated by a two-step process that yields high loadings of single atoms at a kilogram scale suitable for industrial deployment.

John R. Regalbuto and Abhaya K. Datye

NATURE NANOTECHNOLOGY | VOL 17 | FEBRUARY 2022 | 109–111 | www.nature.com/naturenanotechnology

Economie de la synthèse

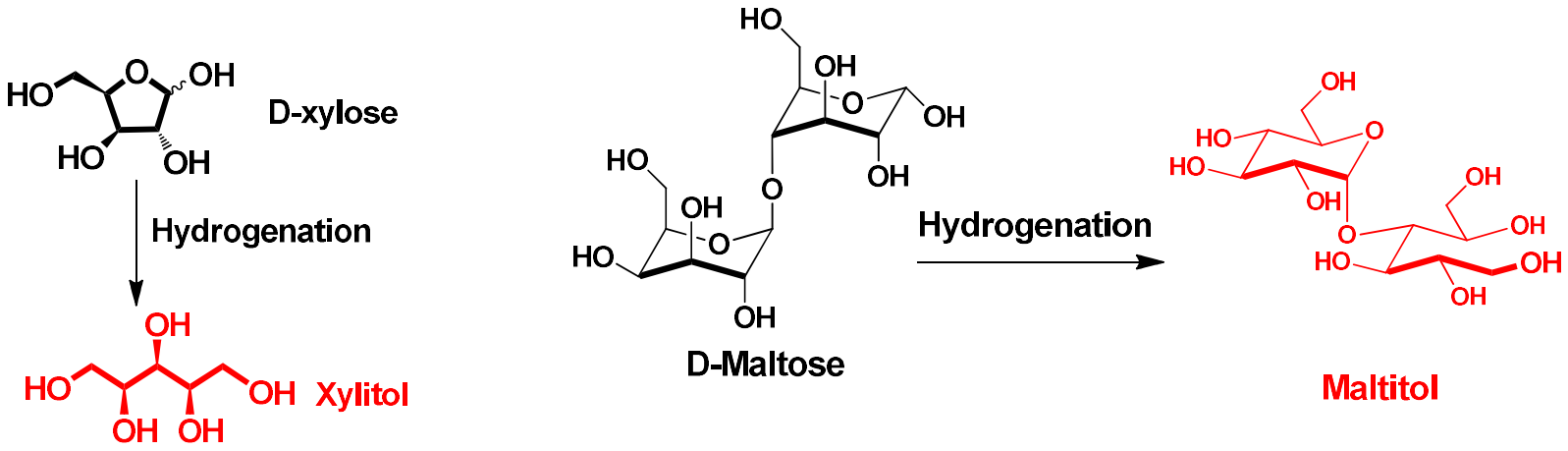
More work is needed to validate some of the critical steps in Hai et al.'s approach. For example, improved CO infrared spectroscopy characterization, in which the CO gas-phase background is subtracted, could more clearly reveal the adsorbed species, as has been shown with single-atom platinum catalysts of much lower weight loading[4,9]. The high metal loading achieved here should make this characterization much easier. Post-reaction characterization of additional metals will further confirm the general stability of atoms synthesized by this method. While the authors demonstrate scale up to kilogram-sized batches, the washing step might create a waste stream of dilute catalyst precursors, which should be minimized or eliminated.

The ability to stabilize high densities of single atoms is a holy grail of catalyst synthesis, from which point many other controllable syntheses become possible. A great palette of fundamental study of atom engineering now awaits: can the density of atoms and the degree of interaction between single sites or multiple metals be controlled by the degree of nitrogen doping in a carbon surface or oxygen defect formation? Are there better anchoring sites? Can the distance between anchored atoms be tuned to change reactivity, and how might this be done? What about engineering interwoven, dense patterns of different metals to achieve bifunctionality? What are the limits of stability? On the practical side, the commercial potential for single-atom catalysts has already been recognized[10]. Higher densities of catalyst sites make their potential all the more relevant.

Economie de la synthèse

Du côté des métaux non nobles :

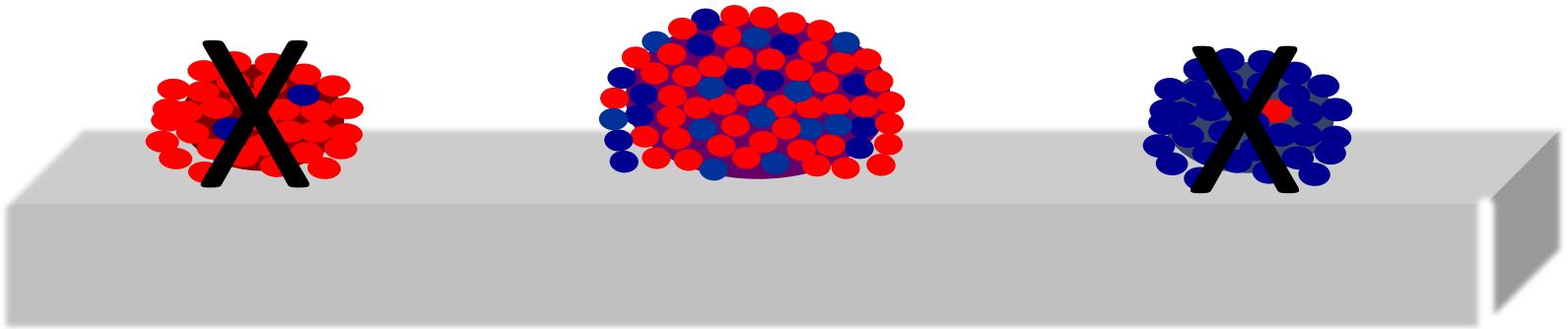
- Catalyse d'hydroconversion sélective de molécules biosourcées

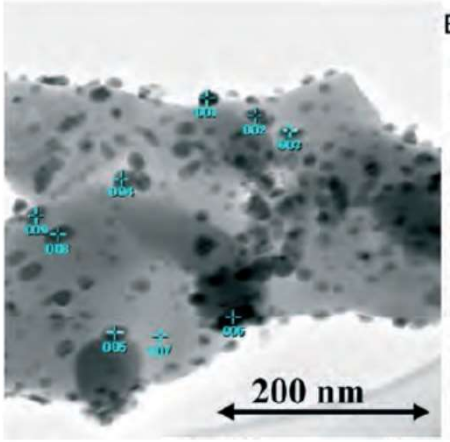


- Remplacement des métaux nobles ou du nickel de Raney par des combinaisons **Ni-Fe** à base de deux métaux abondants

Economie de la synthèse

➢Verrou: **contrôle de la taille, de la composition ET de l'ordre chimique** des nanoparticules Ni-Fe





EDX analysis

Pos.	Fe/Ni
001	48/52
002	14/86
003	6/94
004	17/83
005	68/32
006	61/39
007	0/0
008	68/32
009	72/28

Co-imprégnation de $Ni(NO_3)_2$ et $Fe(NO_3)_3$ sur α-Al_2O_3

Wang at al., Appl. Catal. A 392 (2011) 248

Economie de la synthèse

Ar

SiO_2

H_2SO_4

$NiSO_4 \cdot 6H_2O$

$CO(NH_2)_2$

$FeSO_4 \cdot 7H_2O$

Dépôt-précipitation à l'urée

$$CO(NH_2)_2 + 3H_2O \longrightarrow 2NH_4^+ + HCO_3^- + OH^-$$

Formation d'un phyllosilicate mixte réduit par H_2 en Ni-Fe/SiO_2

Shi at al., Catal. Today 334 (2019) 162

Economie de la synthèse

Ar

SiO_2

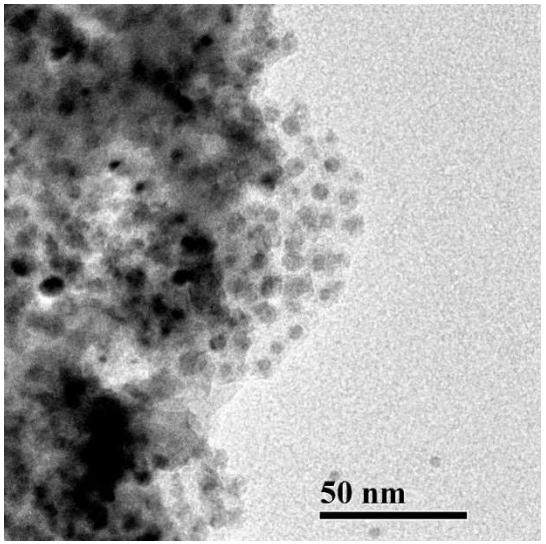
H_2SO_4

$NiSO_4 \cdot 6H_2O$

$CO(NH_2)_2$

$FeSO_4 \cdot 7H_2O$

Fonctionne…



Ni-Fe/SiO_2 après réduction

Shi at al., Catal. Today 334 (2019) 162

Economie de la synthèse

Ar

SiO_2

H_2SO_4

$NiSO_4 \cdot 6H_2O$

$CO(NH_2)_2$

$FeSO_4 \cdot 7H_2O$

Fonctionne…

mais

30% du Ni
et 60% du Fe
restent en solution
en fin de synthèse !

Shi at al., Catal. Today 334 (2019) 162

Economie de la synthèse

Une synthèse de matériau catalytique doit-elle être jugée comme pertinente en fonction de son **rendement en métal utile**

et de la **stabilité de ce rendement après utilisation**

… et ce d'autant plus que le métal est coûteux?

Economie de la synthèse

Une synthèse de matériau catalytique doit-elle être pensée avec sa **stratégie de recyclage ou de régénération**?

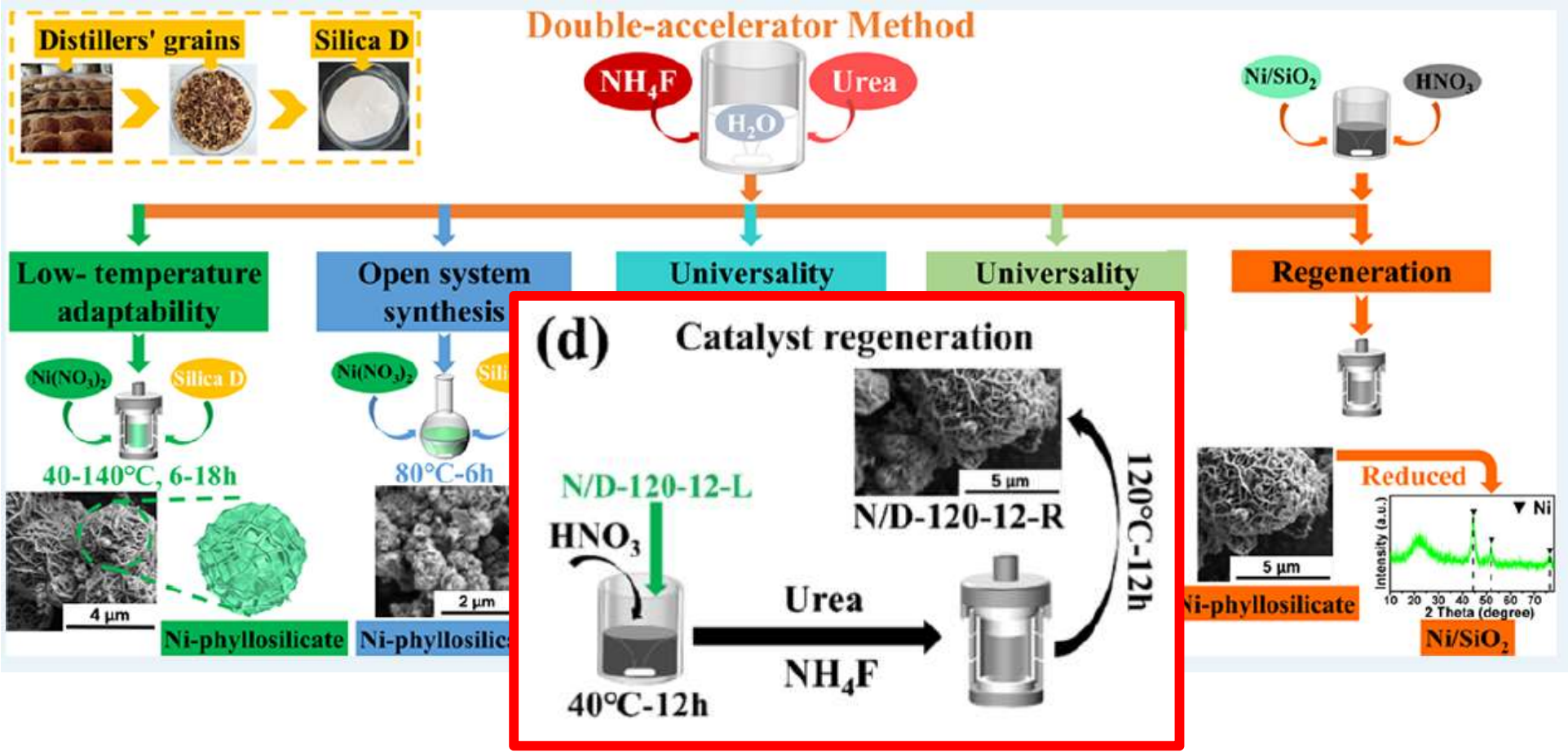
Synthesis and Regeneration of Ni-Phyllosilicate Catalysts Using a Versatile Double-Accelerator Method: A Comprehensive Study

Yaqi Chen and Qing Liu*

Cite This: *ACS Catal.* 2021, 11, 12570–12584

Read Online

Economie de la synthèse



Verrou 2

Analyses locales:

Echelle atomique
Hétérogénéité

Analyses locales

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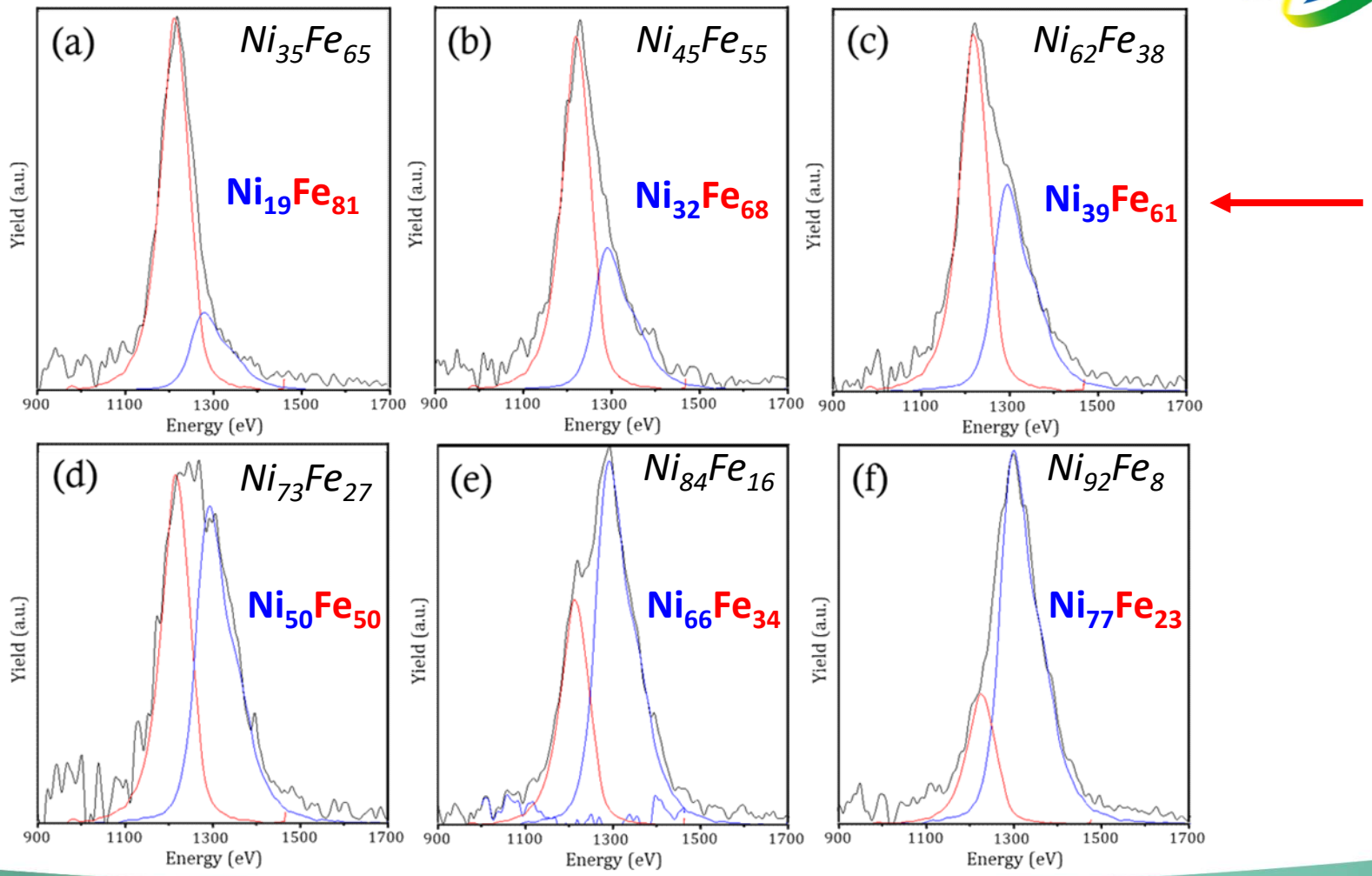
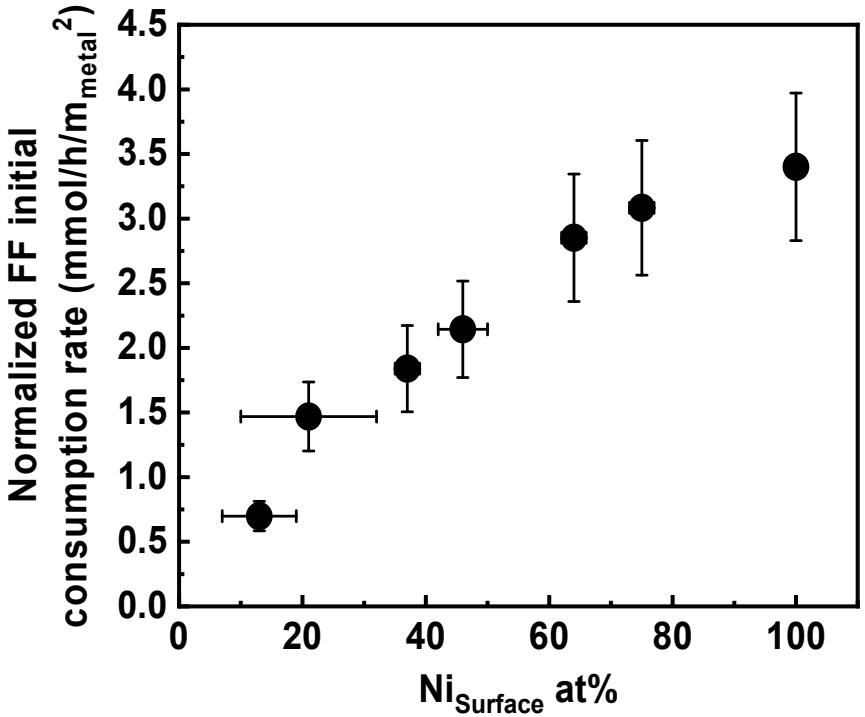
Analyses locales

Analyse de surface de Ni-Fe/SiO_2 par spectroscopie LEIS



Analyses locales

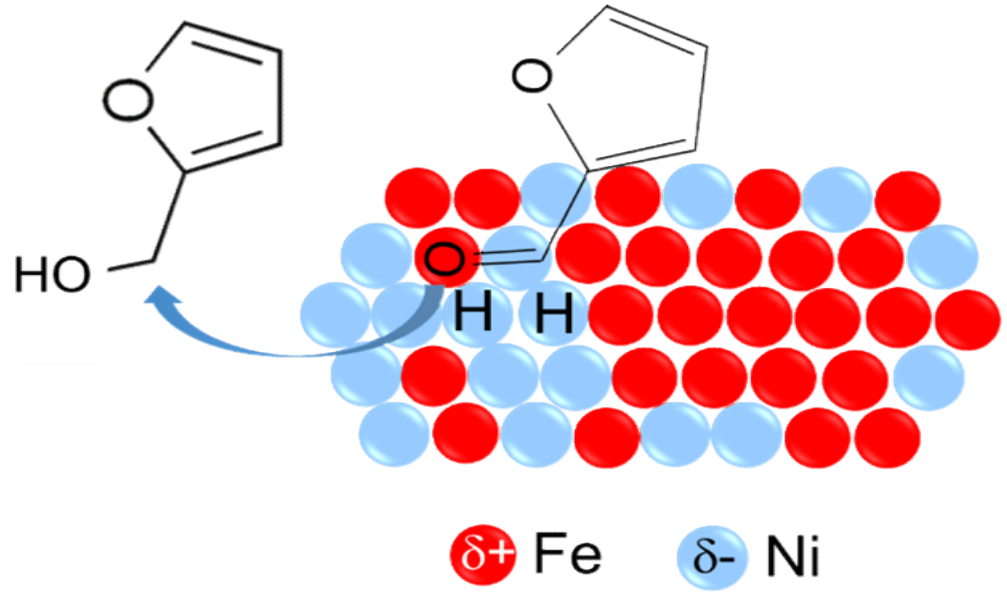
Catalyse: une répartition sans doute hétérogène de Ni



Vitesse initiale de consommation du furfural par hydroconversion à 150 ° C dans l'isopropanol = f (Ni surface at %)

Analyses locales

Des îlots de Ni dilués par Fe?



Shi at al., Chem. Catal. 2 (2022), https://doi.org/10.1016/j.checat.2022.04.009
Shi et al., L'Actualité Chimique, 473-474 (2022) 62

Analyses locales

Commentaires de Jean-Luc Rousset (IRCELYON)

Entropie favorable au mélange Ni-Fe

Energie de surface favorable à Ni

?

Quelles perspectives pour la **modélisation de systèmes à plusieurs centaines d'atomes** en interaction partielle avec un **support**, sous **pression de réactifs**?

Analyses locales

Pour la compréhension des performances du matériau catalytique, sa synthèse peut-elle se concevoir **autour d'un élément de mesure interne**?

Operando Nanoscale Sensors in Catalysis: All Eyes on Catalyst Particles

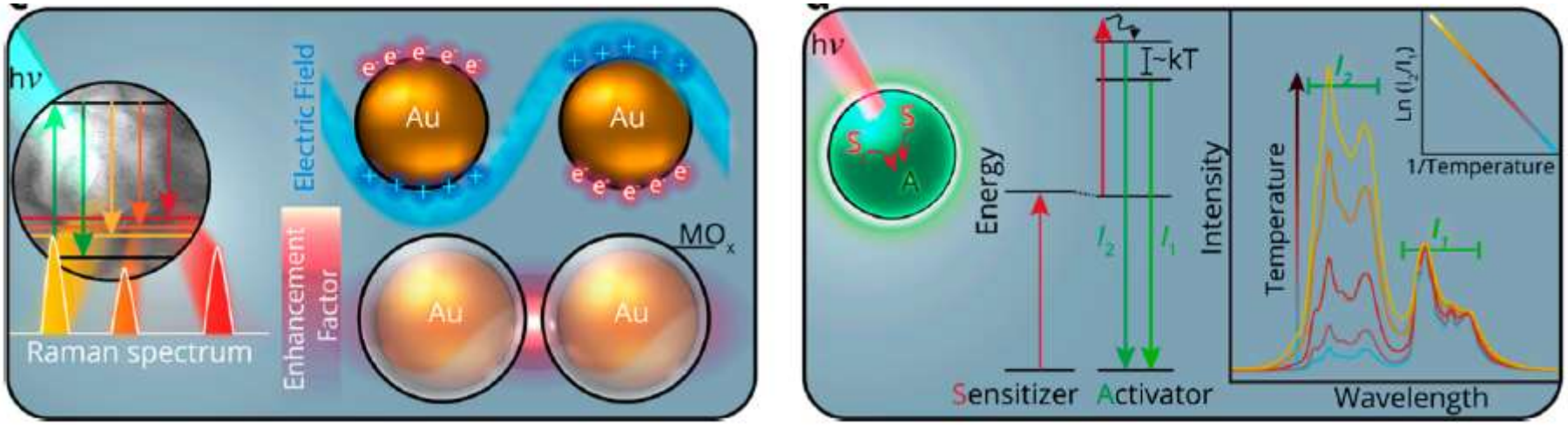
Thomas Hartman, Robin G. Geitenbeek, Caterina S. Wondergem, Ward van der Stam, and Bert M. Weckhuysen*

Cite This: *ACS Nano* 2020, 14, 3725–3735

Read Online

ABSTRACT: An era of circularity requires robust and flexible catalysts and reactors. We need profound knowledge of catalytic surface reactions on the local scale (*i.e.*, angstrom–nanometer), whereas the reaction conditions, such as reaction temperature and pressure, are set and controlled on the macroscale (*i.e.*, millimeter–meter). Nanosensors operating on all relevant length scales can supply this information in real time during *operando* working conditions. In this Perspective, we

Analyses locales



Schematic illustration of the working principles of plasmon-enhanced Raman spectroscopy (PERS). Raman spectroscopy probes the inelastic scattering of light after excitation of matter using monochromatic light to obtain molecular structures. The Raman scattering intensity and the incident light can be enhanced by plasmonic nanoparticles by exciting the dipolar localized surface plasmon resonance. This Raman enhancement can be strongly improved in hot spots between two or more shell-isolated nanoparticles. (d) Schematic illustration of the working principles of luminescence thermometry. Absorption of near-infrared light results in the emission of upconverted green light using lanthanide sensitizers and activators. Temperature-dependent luminescence is governed by Boltzmann statistics; the logarithm of the luminescence intensity ratio plotted *versus* $1/T$ yields a linear correlation; the steepness of the fitted line corresponds to the energy difference between the excited states.

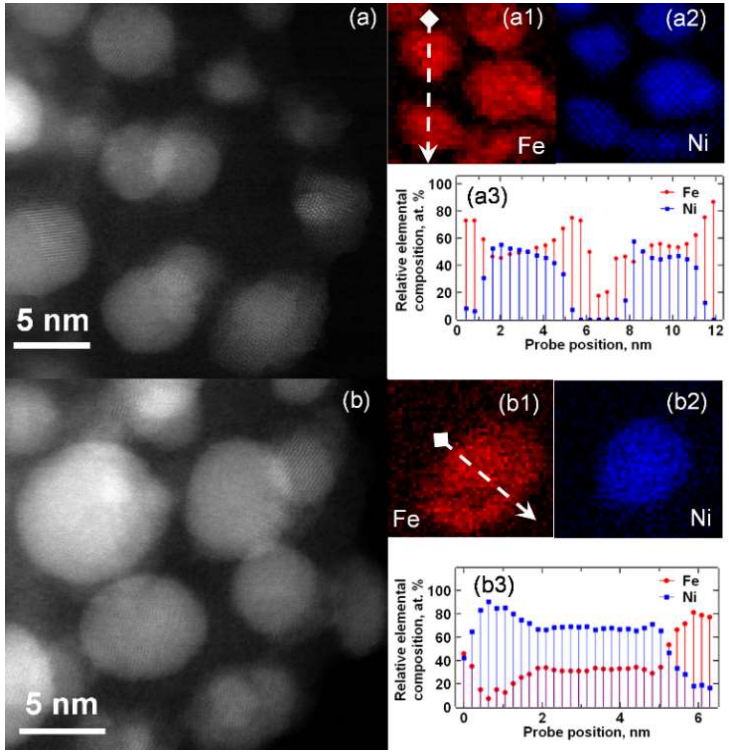
Verrou 3

Représentativité:

Echantillonnage
Statistiques
Analyse des données

Représentativité

Mise en évidence par STEM-HREELS de l'enrichissement en Fe en bord de nanoparticules



Ni_{55}-Fe_{45}/SiO_2

≈ 10 particules par catalyseur

Ni_{62}-Fe_{38}/SiO_2

Shi at al., Chem. Catal. 2 (2022), https://doi.org/10.1016/j.checat.2022.04.009

Représentativité

Commentaire d'un reviewer:

Etape 1: " In Table S4, significant variability exists in the composition of the nanoparticles measured… **How confident are the authors** that the particles are **sufficiently uniform** to make average catalytic correlations? "

Etape 2: " The authors… do not provide any additional characterization beyond citing their previous work. **I think it is essential to obtain more STEM-EDS *(sic)* measurements of individual nanoparticles for the three new samples studied in this paper "**

?

Représentativité

Beaucoup d'analyses sur différentes particules…

Mimicking industrial aging in fluid catalytic cracking: A correlative microscopy approach to unravel inter-particle heterogeneities

M. Gambino [a], A.E. Nieuwelink [a], F. Reints [a], M. Veselý [a], M. Filez [a], D. Ferreira Sanchez [b], D. Grolimund [b], N. Nesterenko [c], D. Minoux [c], F. Meirer [a,*], B.M. Weckhuysen [a,*]

[a] Inorganic Chemistry and Catalysis, Department of Chemistry, Utrecht University, Universiteitsweg 99, 3584 CG Utrecht, the Netherlands
[b] Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland
[c] Total Research and Technology Feluy, Seneffe, Belgium

Journal of Catalysis 404 (2021) 634–646

Représentativité

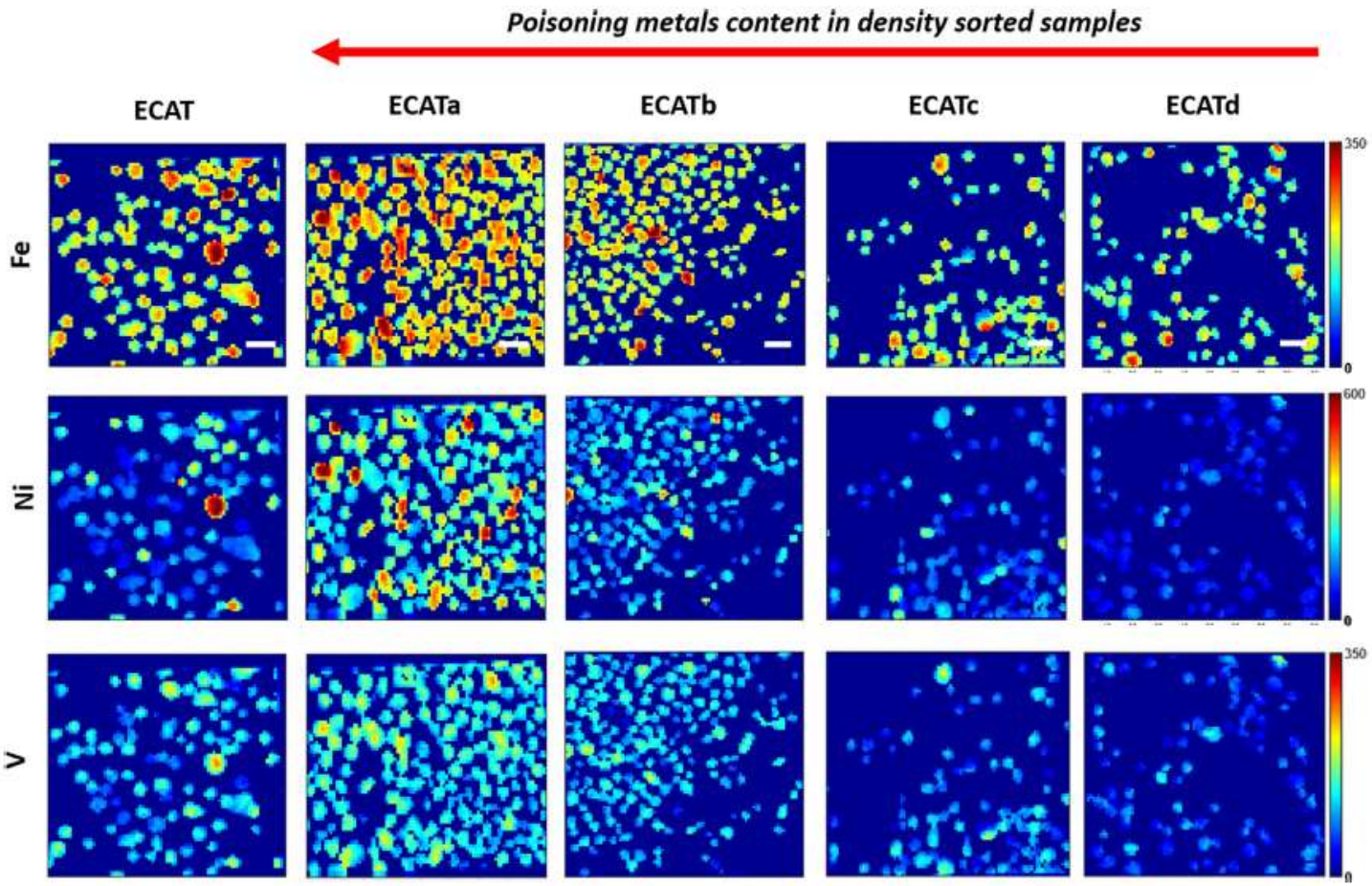


Fig. 3. Elemental distribution maps of Fe, Ni and V poisoning metals for the different ECATs samples, obtained after batch fitting analysis of the μXRF dataset. The scale bar indicates 150 μm.

… mesures à l'échelle de la **centaine de microns**

Représentativité

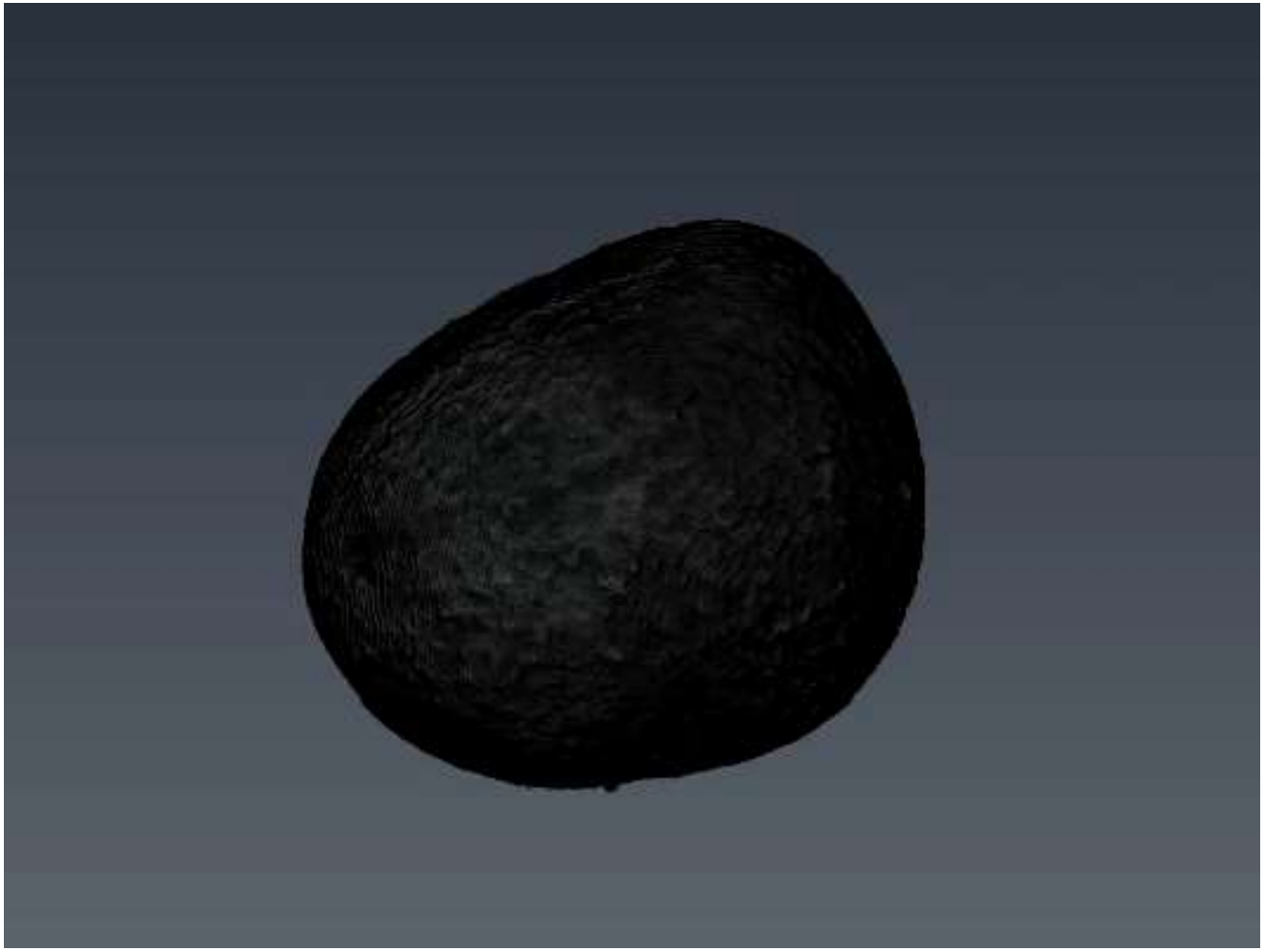
… ou une analyse très poussée d'une seule particule?

3-D X-ray Nanotomography Reveals Different Carbon Deposition Mechanisms in a Single Catalyst Particle

Martin Veselý,[a] Roozbeh Valadian,[a] Leon Merten Lohse,[b] Mareike Toepperwien,[b] Kathryn Spiers,[c] Jan Garrevoet,[c] Eelco T. C. Vogt,[a, d] Tim Salditt,[b] Bert M. Weckhuysen,*[a] and Florian Meirer*[a]

ChemCatChem **2021**, *13*, 2494–2507

Représentativité



Représentativité

Comment définir l'**équilibre entre le "coût appareil" (€, t) et une description jugée représentative du matériau** à l'echelle souhaitée?

Le futur chercheur / la future chercheuse sur les matériaux catalytiques doit-il/elle être également formé/formée **en codage et en traitement de données?**

Représentativité

Laboratoire interdisciplinaire

Formation interdisciplinaire
(master universitaire / écoles)

Pérennisation des compétences

Verrou 4

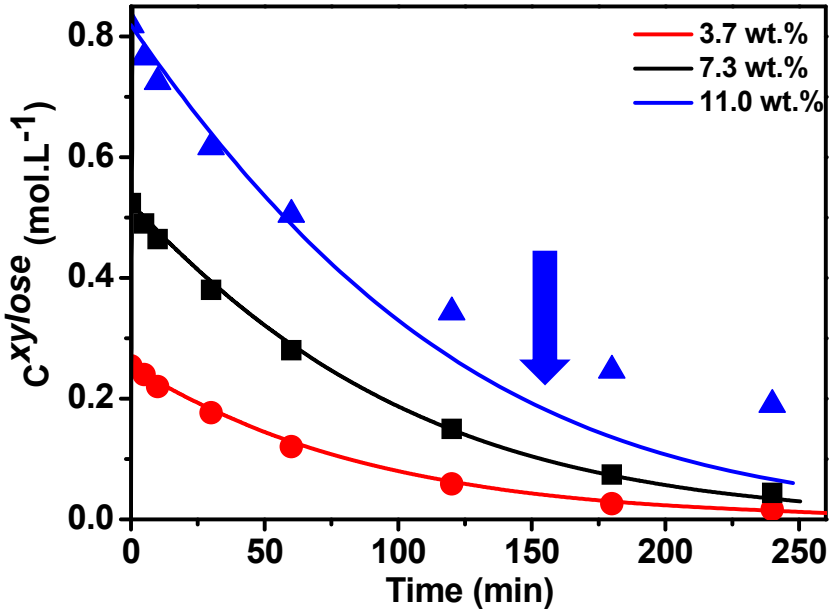
Stabilité:

Phase liquide
Analyse in situ

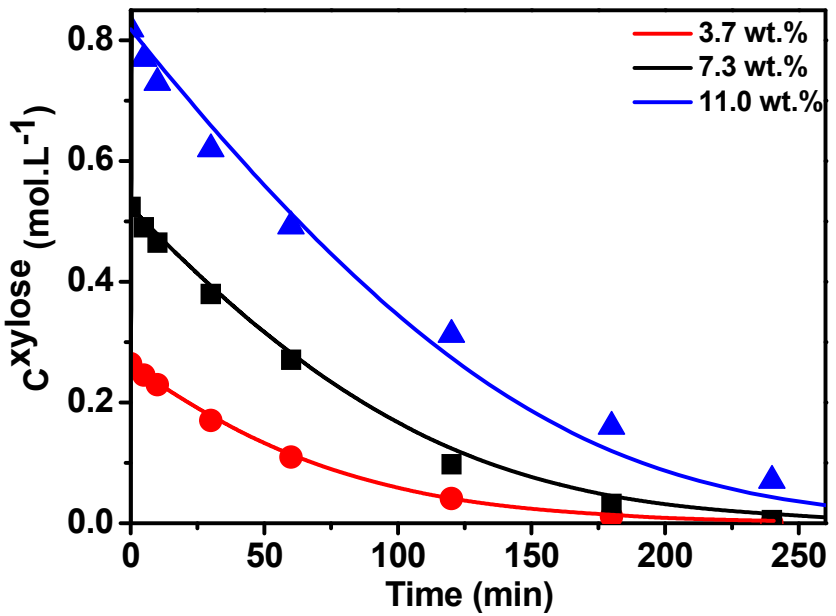
Stabilité

Performances en hydrogénation du xylose en xylitol dans l'eau

Ni_{100}/SiO_2



Ni_{62}-Fe_{38}/SiO_2

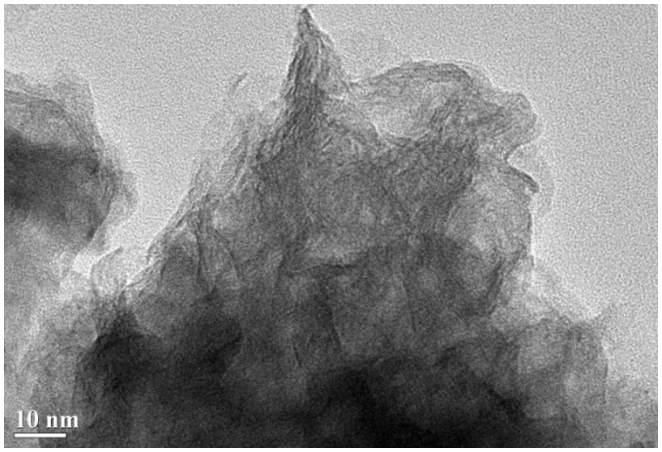


symboles: mesures expérimentales; courbes: modèle cinétique

Sadier et al., Appl. Catal. B, 298 (2021) 120564

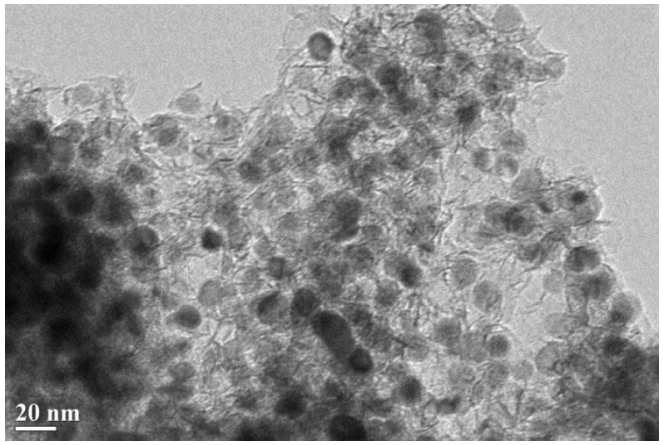
Stabilité

Ni_{100}/SiO_2



Retour à l'état phyllosilicate

Ni_{62}-Fe_{38}/SiO_2

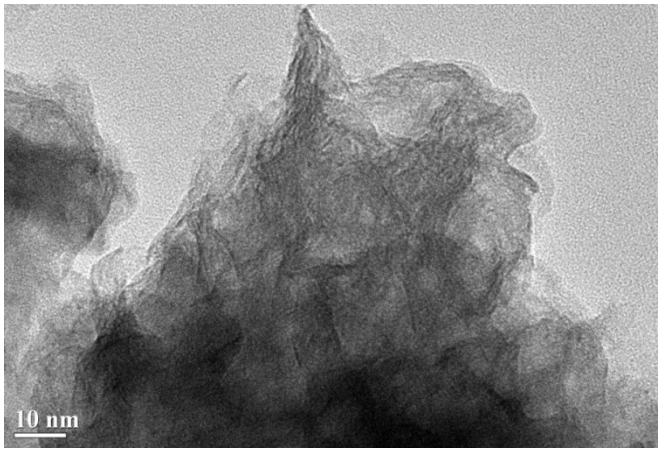


Stable en apparence…

Sadier et al., Appl. Catal. B, 298 (2021) 120564

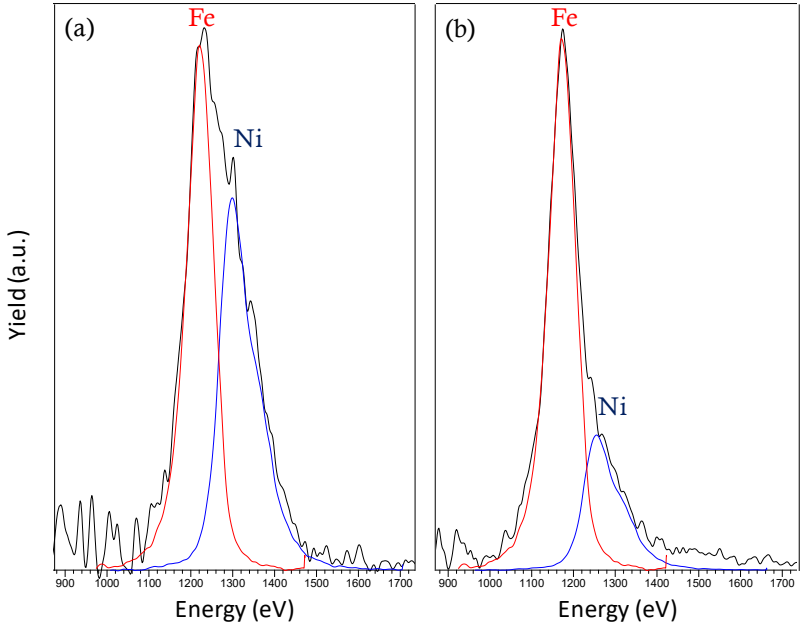
Stabilité

Ni_{100}/SiO_2



Retour à l'état phyllosilicate

Ni_{62}-Fe_{38}/SiO_2



LEIS, avant…. *…LEIS, après*

…mais enrichissement en Fe en surface

Sadier et al., Appl. Catal. B, 298 (2021) 120564

Stabilité

Le **suivi de l'évolution du matériau en conditions de réaction est indispensable** pour tirer des conclusions pertinentes…

… mais comment suivre la **cinétique d'évolution** d'un metal supporté :

au sein d'un système triphasique

dans lequel le solide est sous forme granulaire (≠ électrochimie)

sous pression

dans un réacteur à forte inertie thermique?

Ingénierie

Stabilité

In Situ Microfocus Chemical Computed Tomography of the Composition of a Single Catalyst Particle During Hydrogenation of Nitrobenzene in the Liquid Phase**

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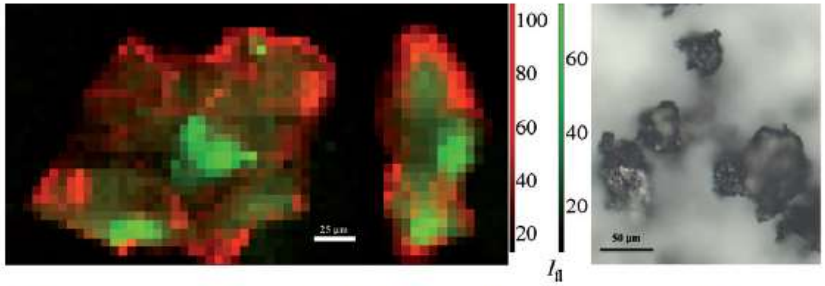

Figure 1. Left: Orthogonal XRF maps (at 20.3 keV) of a particle under operating conditions (ethanol, 22.3 mM nitrobenzene, and 1 bar H_2) after collection of µ-XRF-CT and µ-XRD-CT sinograms. Elemental distributions throughout the carbon support are shown in red (Pt) and green (Mo). Each pixel is 5×5 µm. Red and green scale bars at the side show fluorescent signal intensity (I_{fl}), white scale bar (in the image) = 25 µm. Right: Photo of typical catalyst particles (ex situ); scale bar = 50 µm.

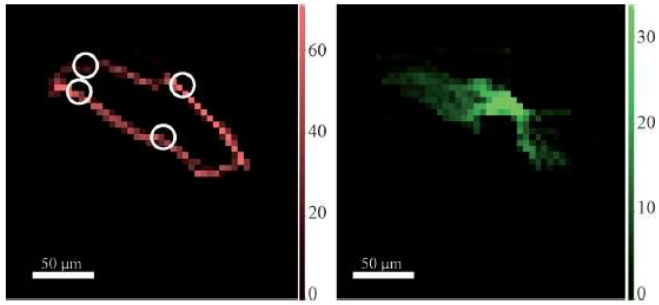

Figure 2. Cross-sections from µ-XRF-CT at 20.3 keV showing Pt (red, left) and Mo (green, right) distributions throughout the carbon support. Each pixel is 5×5 µm. Data collected under operating conditions (ethanol, 22.3 mM nitrobenzene, and 1 bar H_2). The slice corresponds to a horizontal cross-section 60 µm from the bottom of the particle (see Figure 1). The white circles correspond to the approximate locations of the Pt crystals (identified from the 111 reflection). Scale bars at the sides show fluorescent signal intensity (I_{fl}), white scale bars (within the images) = 50 µm.

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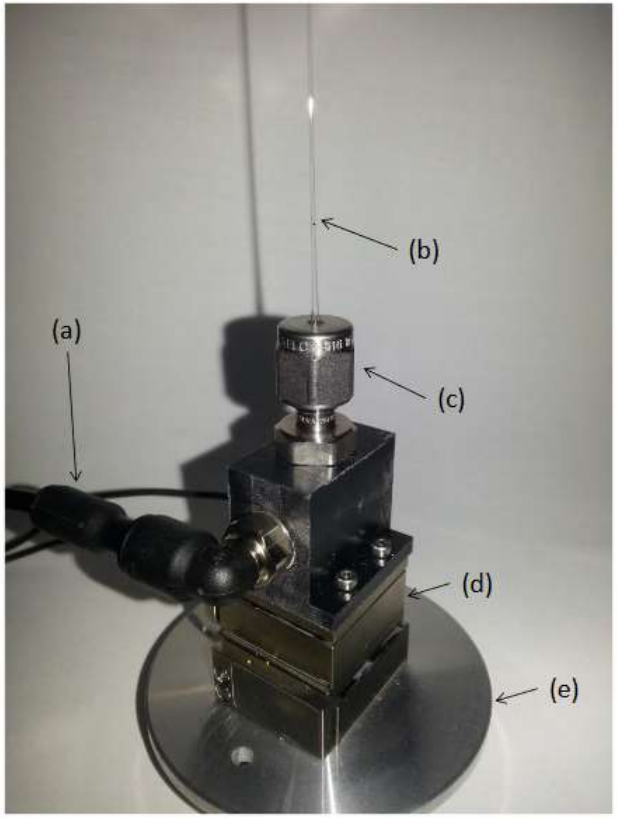

SI Figure 11: Microreactor for in situ tomography. (a) gas inlet, (b) single catalyst particle mounted in 0.4 mm diameter glass capillary, (c) capillary sealed with two o-rings, (d) nano-positioning motors for centring capillary, (e) base to connect to beamline rotation stage.

A single particle was mounted in 0.4 mm OD borosilicate glass capillary (0.01 mm wall thickness) using quartz wool and H_2 purged ethanol was injected into the capillary (circa 10 µL) then pressurized to 1 bar with H_2.

However, the activity was moderated (23°C and 1 bar H_2, with no stirring because of the capillary dimensions) to suit the conditions for performing tomography so as to allow for real-time imaging during steady-state catalytic turnover. In all particles chosen in this and in our previous study,[Ib] the elemental distribution is consistent, and does not appear to be influenced by particle size. It should be noted that with the lack of stirring, diffusion becomes the main mass-transport process of reactant/product and therefore may influence the activity of the catalyst, and also the ratio of products detected by Raman spectroscopy.

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Operando X-ray Absorption Spectroscopy Studies of Sintering for Supported Copper Catalysts during Liquid-phase Reaction

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For *operando* reactions, catalyst samples were diluted by half with silica to improve X-ray transmission and loaded into a glassy C tube reactor (10 mm x 4 mm x 200 mm OD x ID x L).[2] Next, the catalysts were reduced at 573 K at the beamline, cooled to room temperature, pressurized to 22 bar with He at 30 cm^3 (STP)/min and checked for leaks. Once the reactor was determined to be leak free, the reactor was depressurized, re-pressurized to 22 bar with H_2 at 30 cm^3 (STP)/min, and then heated to the reaction temperature of 403 K. Once the reaction temperature was reached, the flow of the liquid reaction feed (5 wt% furfural in 1-butanol) was started using a syringe pump (Teledyne-Isco). The X-ray beam was 0.5 x 0.3 mm^2, and data were collected in quick scan transmission mode. Each spectrum was obtained in about 30 sec and approximately 10 spectra were obtained at each reaction time. Gas bubbles from the H_2 co-feed in the liquid created irregularities in the spectrum which could not be removed during data processing. It was important to minimize these effects, so the gas flow was reduced (0-5 cm^3 (STP)/min) during XAS data acquisition. Only spectra free of these features were averaged,

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Continuous-flow reactor setup for *operando* x-ray absorption spectroscopy of high pressure heterogeneous liquid–solid catalytic processes

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Stabilité

saturation préalable du liquide avec le gaz

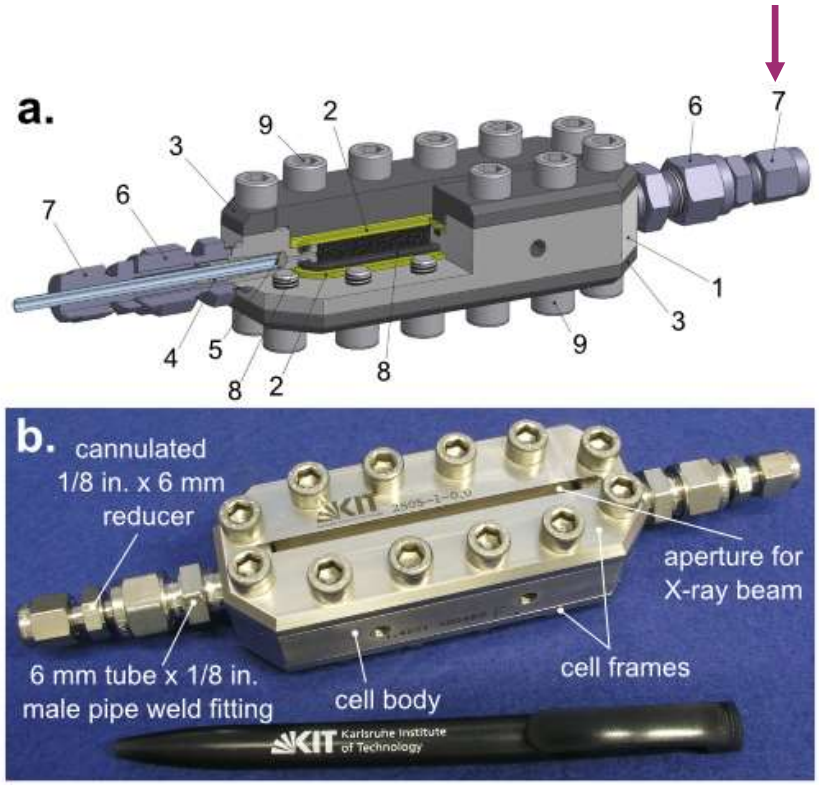

FIG. 1. (a) Drawing of the assembled *in situ* continuous-flow XAS cell. The numbers refer to list parts as described in Table S2. (b) Photograph of the manufactured cell.

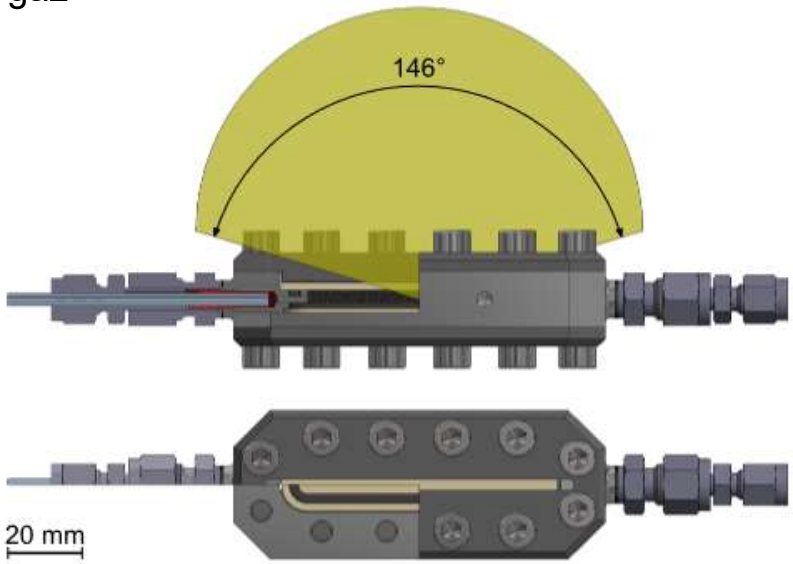

FIG. 3. Accessibility of the outgoing x-ray beam over a wide angular range, allowing transmission, fluorescence, and diffraction studies on the catalyst.

Provided the catalyst is supported on a light-atom material, our cell equipped with 2 mm PEEK windows allows XAS studies at the Pt L_3 (11.56 keV) and Au L_3 (11.92 keV) edges and—with thinner 1 mm windows—reaches as low as the Cu K edge (8.98 keV) (see Fig. 6).

Conclusions: verrous

Economie de la synthèse

Matériau catalytique

Analyse locale des hétérogénéités

Représentativité de l'analyse

Stabilité en milieu bi/triphasique "réaliste"

Conclusions: descripteurs, outils, pistes

Rendement en metal utile

Matériau catalytique

Modélisation / Eléments de mesure internes

Coût (€, t) / Formation

Ingénierie

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Thank you for your attention!