



Direct Evidence for Single Molybdenum Atoms Incorporated in the Framework of MFI Zeolite Nanocrystals

Florent Dubray, Simona Moldovan, Cassandre Kouvatas, Julien Grand, Cindy Aquino, Nicolas Barrier, Jean-Pierre Gilson, Nikolai Nesterenko, Delphine Minoux, Svetlana Mintova

► To cite this version:

Florent Dubray, Simona Moldovan, Cassandre Kouvatas, Julien Grand, Cindy Aquino, et al.. Direct Evidence for Single Molybdenum Atoms Incorporated in the Framework of MFI Zeolite Nanocrystals. Journal of the American Chemical Society, 2019, 141 (22), pp.8689-8693. 10.1021/jacs.9b02589 . hal-03027961

HAL Id: hal-03027961

<https://normandie-univ.hal.science/hal-03027961>

Submitted on 27 Nov 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Direct Evidences for Single Molybdenum Atoms Incorporated in the Framework of MFI Zeolite Nanocrystals

Florent Dubray[†], Simona Moldovan[‡], Cassandre Kouvat[†], Julien Grand^{†,||}, Cindy Aquino^{||}, Nicolas Barrier[†], Jean-Pierre Gilson[†], Nikolai Nesterenko^{||}, Delphine Minoux^{||}, Svetlana Mintova^{†,*}

[†]Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire Catalyse et Spectrochimie (LCS), 14000 Caen, France

[‡]Institut des Sciences Appliquées de Rouen, Rouen University, Groupe de Physique des Matériaux (GPM), 76801 Rouen, France

^{||}Total Research and Technologies, Feluy, B-7181 Seneffe, Belgium

^{*}Normandie Université, ENSICAEN, UNICAEN, CNRS, Laboratoire de Cristallographie et Science des Matériaux (CRISMAT), Caen, France

This article is dedicated to the 60st Birthday of Dr. Valentin Valtchev as an eminent researcher and mentor in the field of zeolites.

Supporting Information

ABSTRACT: Direct evidence of the successful incorporation of atomically dispersed molybdenum (Mo) atoms into the framework of nanosized highly crystalline MFI zeolite is demonstrated for the first time. Homogeneous distribution with a size of 0.05 nm is observed by STEM-HAADF. ³¹P MAS NMR and FTIR spectroscopy, using trimethylphosphine oxide (TMPO) and deuterated acetonitrile as probe molecules, reveal a homogeneous distribution of Mo in the framework of MFI nanozeolites, and the presence of Lewis acidity. ³¹P MAS NMR of TMPO shows probe molecules interacting with isolated Mo atoms in the framework, and physisorbed probe molecules in the zeolite channels. Moreover, 2D ³¹P-³¹P MAS radio frequency-driven recoupling (RFDR) NMR indicates the presence of one type of Mo species in different crystallographic positions in the MFI framework. The substitution of framework Si by Mo significantly reduces the silanol defect content, making the resulting zeolite highly hydrophobic. In addition, the insertion of Mo into the MFI structure induces a symmetry lowering, from orthorhombic (*Pnma*), typical of high silica MFI, to monoclinic (*P21/n*), as well as an expansion of unit cell volume. The novel material opens many opportunities of catalysts design for application in mature and emerging fields.

The introduction of metal ions into zeolites is known to modify their acid and/or redox properties, and can be achieved by different routes as recently reviewed.¹ One such route is framework isomorphous substitution where framework silicon ions are replaced by transition metal ions. The classic zeolite literature states that elements such as Ga, Ce, Be, B, Fe, Cr, P, and Mg can isomorphously substitute Si and Al in zeolite framework.^{2,3} In the 80s the introduction of Ti in the MFI zeolites was reported by ENI researchers.⁴ Two years ago the introduction of W into the framework of MFI zeolite was reported by our group.⁵ In general, this substitution greatly influences the physicochemical properties of the materials and opens many opportunities for new application in catalysis and adsorption.⁶⁻¹⁰ Ti-containing materials (TS-1) are very active and selective in partial catalytic oxidation of fine chemicals, in

particular in the presence of H₂O₂. The best known examples of such transformations are propylene epoxidation (Hydrox. Process, HPPO), hydroxylation of phenol, and cyclohexanone ammoximation.⁹

Properties of the metal-containing zeolites, such as Lewis acidity and higher resilience to water, are very valuable for future application in biomass upgrading.⁴ Our group described the preparation of a nanosized MFI zeolite containing atomically dispersed tungsten.⁵ The resulting W-containing MFI zeolite possessed exceptional stability, high hydrophobicity, and no silanol defects. These properties give them a great potential in catalysis as silanols (often referred to as framework and external defects) display unwanted hydrophilic properties related to water adsorption on silanol sites.^{11,12}

However, the proven incorporation of the molybdenum atoms in the MFI was not described in literature so far. Attempts were reported by Raghavan et al.¹³ who prepared a molybdenum containing silicalite-2 (MEL structure) by hydrothermal synthesis in aluminum-free alkaline mixtures that was active for the oxidative dehydrogenation of ethanol to acetaldehyde. Then, the synthetic effort to introduce Mo in silicalite-1 (MFI structure) was also reported by the same group.¹⁴ Interestingly, the samples were more hydrophilic than silicalite-1 (more defects) and thermally stable; they displayed a high activity in the catalytic oxidation of thioethers to the corresponding sulfoxides. A non-linear unit cell volume expansion with the introduction of molybdenum was observed, indicating a significant co-formation of non-framework metallic species. The partial incorporation of molybdenum in the silicalite-1 framework synthesized in fluoride media was reported by Tavalaro.¹⁵ The framework insertion of a portion of the molybdenum was claimed to occur based on the thermal decomposition behavior of TPA⁺ cations blocked in the zeolite micropores without any further evidences.

Here we present for the first time direct evidence for the hydrothermal synthesis of a nanosized MFI zeolite containing atomically dispersed Mo in the zeolite framework, hereinafter referred to as Mo-MFI-D. A reference sample, prepared by molybdenum wet-impregnation of silicalite-1, hereinafter referred to as Mo-

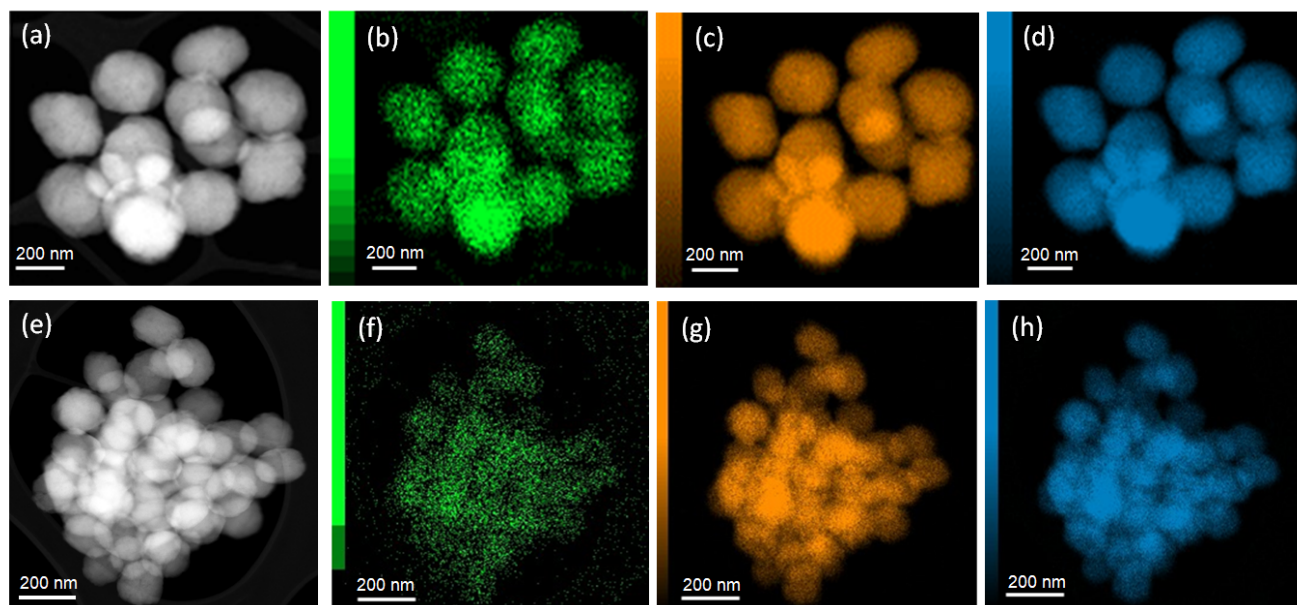


Figure 1. STEM-EDS elemental maps of (a,b,c,d) Mo-MFI-D and (e,f,g,h) Mo-MFI-P: Si (orange), O (blue), and Mo (green)

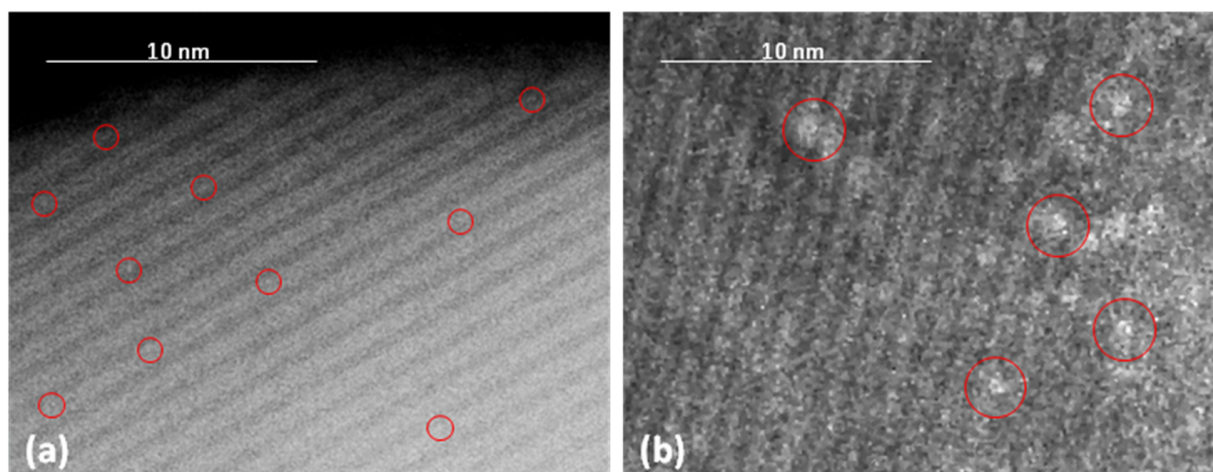


Figure 2. STEM-HAADF micrographs revealing the distribution of Mo species in (a) Mo-MFI-D and (b) Mo-MFI-P

MFI-P, was used for comparative purposes. Both samples are in H-form, obtained by ion exchange with ammonium chloride. The residual concentration of alkali metals was below 500 ppm in the samples after ion-exchange.

The distribution of molybdenum in the Mo-MFI-P and Mo-MFI-D samples was investigated by STEM-EDS (Figure 1). Both Mo-containing samples show a homogeneous distribution of Mo with a mean content of 0.8 to 1.2 wt. %. STEM-HAADF results reveal structural information of the materials by providing Z-contrast images. The white dot-like features identified by the high-resolution STEM-HAADF micrographs disclose the homogeneous distribution of Mo in Mo-MFI-D. The size of the white dots is 0.05 nm, which is approximately 10 times smaller than the crystalline fringes. This indicates that atomically dispersed Mo atoms are part of the MFI framework (Figure 2a). Similar dots that are of a larger size (1.5 nm) are observed in Mo-MFI-P (Figure 2b). For comparison, the STEM-HAADF micrograph of the pure siliceous calcined MFI zeolite used for the preparation of sample Mo-MFI-P prior

ion-exchange is presented in Figure S1. The larger white dots observed in sample Mo-MFI-P correspond to small molybdenum oxide clusters homogeneously distributed in the MFI sample as indicated by Raman spectroscopy (Figure S2). The bands at 247, 621, 890, and 980 cm^{-1} in the Raman spectrum of Mo-MFI-P are assigned to molybdenum oxide.¹⁶ These bands are not observed in Mo-MFI-D, indicating the absence of any oxide phases in this sample. A small peak at 980 cm^{-1} in Mo-MFI-D is not attributed to an oxide phase (narrow signal), but to a small amount of silanols (wide band). Furthermore, in Mo-MFI-D, two new bands (803 and 820 cm^{-1}) possibly originate from single Mo atoms in the MFI framework positions. Two shoulders (332 and 416 cm^{-1}) are attributed to the perturbation of Si-O-Si vibrations linked to the presence of neighboring Mo-O-Si species, or possibly Mo-O-Si vibrations.¹⁷ This result is further supported by the presence of a broad band at 1105 cm^{-1} in the FTIR spectrum of sample Mo-MFI-D, corresponding

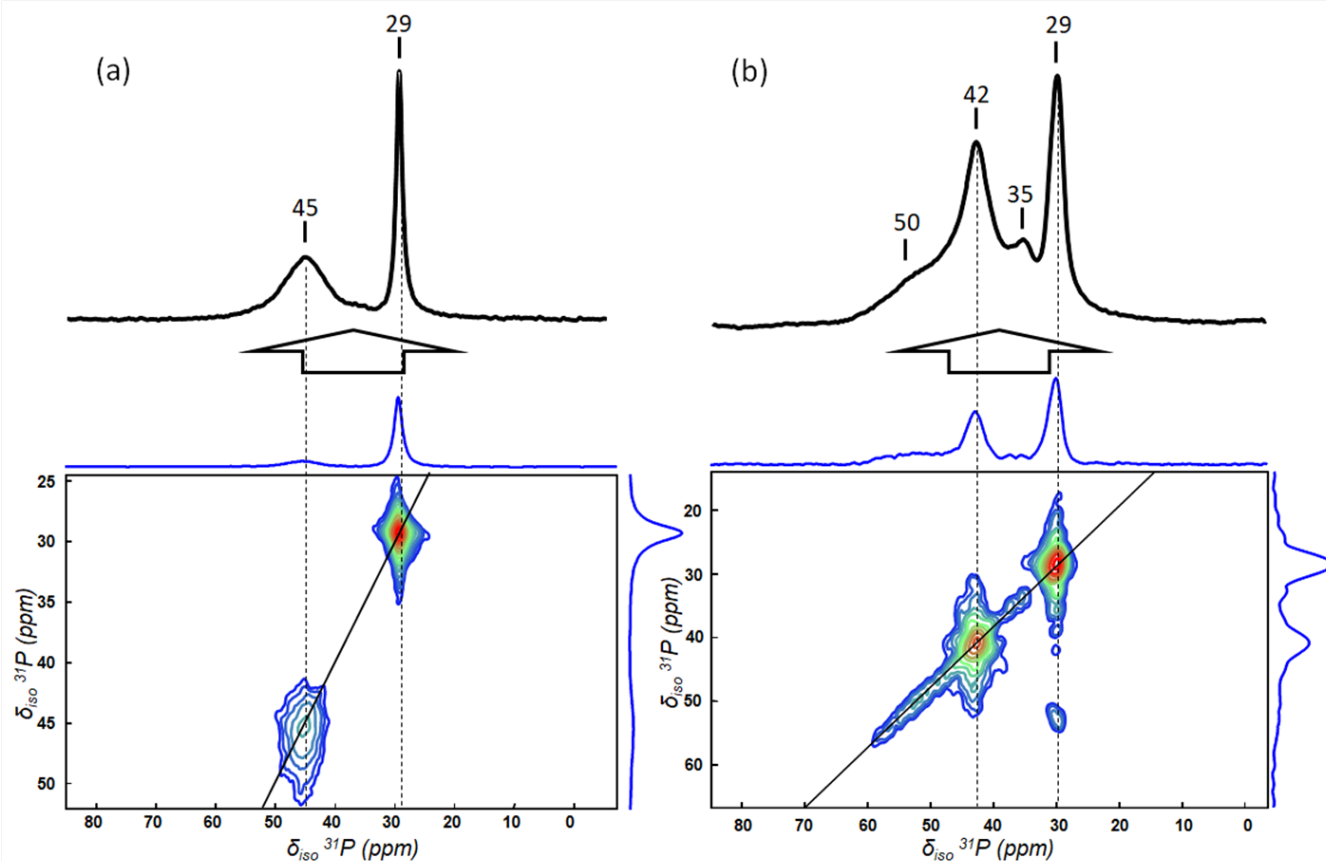


Figure 3. ^{31}P - ^{31}P MAS RFDR NMR spectra (top: 1D ^{31}P MAS NMR spectra) of (a) Mo-MFI-P and (b) Mo-MFI-D under ^1H spin-164 decoupling (magnetic field of 500 MHz, MAS at 12 kHz and 14 kHz for 1D and RFDR spectra, respectively)

to Si-O-Mo framework vibration (Figure S3). The two samples differ substantially: (i) sample Mo-MFI-D contains Mo atoms in the MFI framework and no oxide phase, with a negligible amount of isolated silanols (3745 cm^{-1}), and (ii) sample Mo-MFI-P contains molybdenum oxide and silanols as shown by FTIR (Figure S4).

Upon direct introduction of molybdenum in the MFI framework (Mo-MFI-D), the diffraction peaks at 23.30 , 23.75 , and 24.50° 2θ split (Figure S5). This is a direct consequence of the symmetry lowering from orthorhombic ($Pnma$) to monoclinic ($P21/n11$), confirmed by Le Bail profile refinements of the respective diffraction patterns (see Table S1 and Figure S5). The unit cell volume of Mo-MFI-D expands also from 5337.4 to $5360.6\text{ \AA}^3$ compared to Mo-MFI-P. Such a polymorphic transition is observed in MFI zeolite, and its transition temperature depends on the incorporation of T-elements such as aluminum and titanium into the MFI framework.¹⁸⁻²⁰ The Mo-MFI-D sample exhibits monoclinic symmetry, although the incorporation of Mo in the MFI framework is expected to lower the transition temperature of the monoclinic-orthorhombic phase transition instead.²¹ This result is probably a consequence of the hydrophobic and silanol defect-free properties of the Mo-MFI-D material. An increase in the unit cell volume proportional to the amount of metals introduced into the zeolite framework has been previously reported.^{22,23} The unit cell volume expansion and symmetry change of the MFI type zeolite are due to distortion of the framework to accommodate Mo atoms with an ionic radius larger than Si.²⁴ The space group transition and volume expansion observed for Mo-MFI-D provide additional evidence for the incorporation of molybdenum atoms into the framework of the MFI type zeolite. In contrast, Mo-MFI-P does not show any evidence for the presence of framework Mo. This is based on its orthorhombic symmetry and its unit cell volume that are both similar to purely

siliceous MFI type zeolite (orthorhombic symmetry, measured volume = $5333.1\text{ \AA}^3$).

The nature of the silicon environment in the MFI type zeolite framework was investigated by ^{29}Si magic-angle spinning (MAS) NMR and [^1H] cross-polarization (CP) ^{29}Si MAS NMR spectroscopy (Figure S6). The absence of Q3 species in Mo-MFI-D is highlighted by a one-pulse experiment (absence of a -104 ppm peak). Few silanols are observed by ^{29}Si CP MAS NMR for Mo-MFI-D, while for Mo-MFI-P a higher concentration of Q3 species is detected. Moreover, well resolved Q4 species in Mo-MFI-D are attributed to the local homogeneity of the sample. Mo-MFI-D can be described as a silanol-free material with a high degree of local homogeneity.

The nature of the Mo and the acidity of the zeolites is studied using trimethylphosphine oxide (TMPO) adsorption monitored by ^{31}P MAS NMR spectroscopy (Figure 3). The spectra of Mo-MFI-D exhibits contributions from TMPO interacting with framework Mo atoms (45 ppm) as well as physisorbed TMPO (29 ppm).²⁵ The absence of a peak at 50 ppm indicates that no or few silanols are present on Mo-MFI-D. This is further supported by 2D ^{31}P - ^{31}P MAS RFDR NMR (Figure 3). The symmetry and shape of the 45 ppm peak related to framework molybdenum Lewis acid sites indicates the presence of a single chemical species, with some small variations in its environment. This is potentially indicative of Mo atoms in different crystalline positions of the framework. In contrast, the spectra of Mo-MFI-P exhibits contributions from silanols (50 ppm), crystalline TMPO (42 ppm), and physisorbed TMPO (29 ppm). The 50 ppm peak in Mo-MFI-P is attributed to the presence of different species such as Q2, Q3, silanol nests, and isolated silanols. The absence of correlation in the 2D experiment indicates that the amount of TMPO is too low to observe interactions

between probe molecules and high enough to observe physisorbed species. Moreover, the peak at 29 ppm attributed to physisorbed TMPO is narrower on Mo-MFI-D than on Mo-MFI-P. This indicates that the local geometry for the physisorbed TMPO is different in the two samples, possibly due to a lower anisotropy of the local environment in Mo-MFI-D compared to Mo-MFI-P. The higher anisotropy of the TMPO would then be attributed to the presence of different species in the zeolite pores, such as Mo oxides and silanols in Mo-MFI-P. In Mo-MFI-D, the narrow peak at 29 ppm may be attributed to the local homogeneity in the micropores, i.e., a single type of Lewis acid site as discussed above. Additionally, the peak corresponding to physisorbed TMPO on Mo-MFI-D is shifted by -0.5 ppm compared to Mo-MFI-P. A slightly lower chemical shift in Mo-MFI-D is linked to the absence of silanol groups and thus to a higher hydrophobicity compared to Mo-MFI-P. It was reported that the higher the chemical shift of TMPO, the stronger the acidity of the zeolite.²⁵ The presence of a significant number of silanol groups in Mo-MFI-P, compared to Mo-MFI-D, makes the material more acidic, as observed by a shifting of the peak attributed to physisorbed TMPO to higher ppm values compared to Mo-MFI-D.

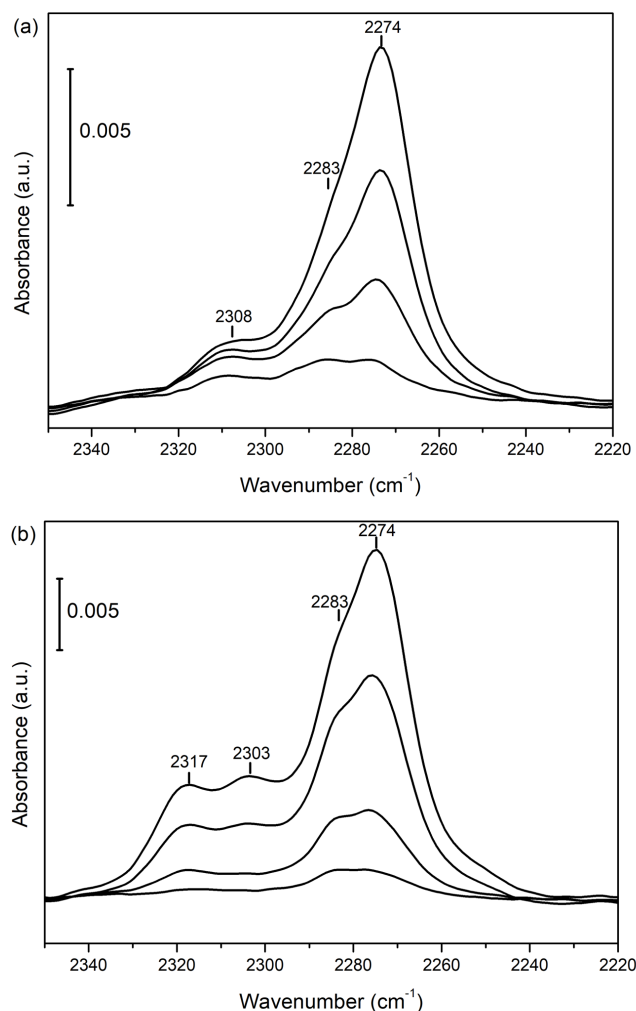


Figure 4. FTIR spectra of CD₃CN adsorbed on (a) Mo-MFI-D (3.7, 11.3, 26.2, 41.4 × 10⁻³ mmol/g), and (b) Mo-MFI-P (2.6, 7.8, 18.1, 28.0 × 10⁻³ mmol/g) at room temperature.

The acidity of these two molybdenum containing zeolites is also investigated by the adsorption of deuterated acetonitrile (CD₃CN) monitored by FTIR spectroscopy (Figure 4). The spectra of Mo-MFI-D exhibits one band at 2308 cm⁻¹ corresponding to CD₃CN adsorbed on the Lewis acid sites brought by the atomically dispersed framework molybdenum and low intensity bands at 2283

and 2274 cm⁻¹ indicative of trace amounts of alkali metal and silanols. The 2308 cm⁻¹ band is attributed to closed Lewis acid sites, i.e. non-hydrolysed framework Mo, that may also correspond to Mo^{VI} in the MFI framework (O=Mo(-OSi)₄), based on previous reports on Me-containing zeolites.²⁶⁻²⁸ In contrast, the spectra of Mo-MFI-P exhibits two bands at 2317 and 2303 cm⁻¹ indicating the presence of molybdenum oxide species. In addition, low intensity band at 2283 cm⁻¹ is due to trace amounts of alkali metals, and peak at 2274 cm⁻¹ corresponds to silanol groups. The bands at 2303 and 2317 cm⁻¹ highlight the presence in Mo-MFI-P of two different molybdenum oxide species with slightly different acidity.

In summary, a nanosized MFI type zeolite with atomically dispersed molybdenum in framework is prepared. Mo-MFI zeolite displays high local homogeneity of the atomically dispersed Mo atoms, low silanol content, and high hydrophobicity. These properties originate from the incorporation of Mo atoms into the MFI framework as closed Lewis acid sites (O=Mo(-OSi)₄). The insertion of Mo in the MFI structure induces a space group transition and increase of the unit cell volume. The uniform nature of the Mo incorporated into the MFI framework is confirmed by IR spectroscopy (deuterated acetonitrile probe) and ³¹P MAS NMR spectroscopy (trimethylphosphine oxide probe). The homogeneous distribution of the atomically distributed Mo in the MFI framework is proven by STEM-HAADF. The materials open many opportunities of catalysts and adsorbents design for applications in mature and emerging fields.

ASSOCIATED CONTENT

Supporting Information

Synthesis description, Characterization details, STEM-HAADF micrograph of pure siliceous MFI zeolite (Figure S1), Raman spectra (Figure S2), FTIR spectra using KBr (Figure S3), FTIR spectra using self-supported zeolite wafers (Figure S4), XRD patterns (Figure S5), ²⁹Si MAS NMR and CP{¹H}²⁹Si MAS NMR spectra (Figure S6), Le Bail profile refinements (Table S1).

AUTHOR INFORMATION

Corresponding Author

*mintova@ensicaen.fr

Notes

The authors declare no competing financial interests.

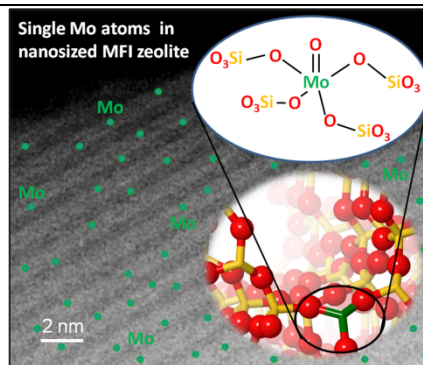
ACKNOWLEDGMENT

This research was supported by TOTAL and Industrial Chair ANR-TOTAL “Nanoclean Energy”. GENESIS is supported by the Région Haute-Normandie, the métropole Rouen Normandie, the CNRS via LABEX EMC and the French National Research Agency as a part of the program “Investissements d’avenir” with the reference ANR-11-EQPX-0020.

REFERENCES

- (1) Kosinov, N.; Liu, C.; Hensen, E.J.M.; Pidko, E.A. Engineering of Transition Metal Catalysts Confined in Zeolites. *Chem. Mater.* **2018**, 30 (10), 3177-3198.
- (2) Barrer, R.M. Hydrothermal Chemistry of Zeolites. *Academic Press*, London, 1982.
- (3) Jacobs, P.A.; Leuven K.U. Acid Zeolites: an Attempt to Develop Unifying Concepts. *Catal. Rev. Sci. Eng.* **1982**, 24 (3), 415-440.

- (4) Moliner, M. State of the Art of Lewis Acid-Containing Zeolites: Lessons from Fine Chemistry to New Biomass Transformation Processes. *Dalton Trans.* **2014**, 43, 4197-4208.
- (5) Grand, J.; Talapaneni, S.N.; Vicente, A.; Fernandez, C.; Dib, E.; Aleksandrov, H.A.; Vayssilov, G.N.; Retoux, R.; Boullay, P.; Gilson, J-P; Valtchev, V.; Mintova, S. One-Pot Synthesis of Silanol-Free Nanosized MFI Zeolite. *Nat. Mater.* **2017**, 16, 1010-1017.
- (6) Price, G.L.; Kanazirev, V. Ga₂O₃/HZSM-5 Propane Aromatization Catalysts: Formation of Active Centers via Solid-State Reaction. *J. Catal.* **1990**, 126 (1), 267-278.
- (7) Kharitonov, A.S.; Aleksandrova, T.N.; Vostrikova, L.A.; Sobolev, V.I.; Ione, K.G.; Panov, G.I. Selective Oxidation of Benzene to Phenol over FeAlPO Catalysts Using Nitrous Oxide as Oxidant *USSR Pat.* 1805127 June 22, 1988.
- (8) Panov, G.I.; Shevelena, G.A.; Kharitonov, A.S.; Romannikov, V.N.; Vostrikova, L.A. Oxidation of Benzene to Phenol by Nitrous Oxide over Fe-ZSM-5 Zeolites. *App. Catal. A* **1992**, 82 (1), 31-36.
- (9) Bellussi, G.; Millini, R.; Pollesel, P.; Perego, C. Zeolite Science and Technology at Eni. *New. J. Chem.* **2016**, 40, 4061-4077.
- (10) Taramasso, M.; Perego, G.; Notari, B. Preparation of Porous Crystalline Synthetic Material Comprised of Silicon and Titanium Oxides *US pat.* 4410501 June 29, 1982.
- (11) Mintova, S.; Jaber, M.; Valtchev, V. Nanosized Microporous Crystals: Emerging Applications. *Chem.Soc.Rev.* **2015**, 44, 7207-7233.
- (12) Chezeau, J.M.; Delmotte, L.; Guth, J.L. Influence of Synthesis Conditions and Postsynthesis Treatments on the Nature and Quantity of Structural Defects in Highly Siliceous MFI Zeolites: A High-Resolution Solid-State ²⁹Si n.m.r. Study. *Zeolites* **1991**, 11 (6), 598-606.
- (13) Raghavan, P.S.; Kannan, S.; Belhekar, A.A. Synthesis and Characterization of Molybdenum Containing Silicalite-2 (MoS-2) Molecular Sieve. *Indian J. Chem. Sec. A* **1997**, 36 (10), 905-907.
- (14) Raghavan, P.S.; Ramaswamy, V.; Upadhya, T.T.; Sudalai, A.; Ramaswamy, A.V.; Sivasanker, S. Selective Catalytic Oxidation of Thioethers to Sulfoxides over Mo-Silicalite-1 (MoS-1) Molecular Sieves. *J. Mol. Catal. A.* **1997**, 122 (1), 75-80.
- (15) Tavoraro, A. Thermal Characterization of the Metal-Silicalites Obtained from Aqueous Nonalkaline Fluoride Gels. *J. Therm. Anal.* **1996**, 47 (1), 171-179.
- (16) Dieterle, M.; Mestl, G. Raman Spectroscopy of Molybdenum Oxides – Part II. Resonance Raman Spectroscopic Characterization of the Molybdenum Oxides Mo₄O₁₁ and MoO₃. *Phys. Chem. Chem. Phys.* **2002**, 4, 822-826.
- (17) Xia, C.; Liu, Y.; Lin, M.; Peng, X.; Zhu, B.; Shu, X. Confirmation of the Isomorphous Substitution by Sn Atoms in the Framework Positions of MFI-Typed Zeolite. *Catal. Today* **2018**, 316, 193-198.
- (18) Wu, E.L.; Lawton, S.L.; Olson, D.H.; Rohrman, A.C.; Kokotailo, Jr.; Kokotailo, G.T. ZSM-5-Type Materials. Factors Affecting Crystal Symmetry. *J. Phys. Chem.* **1979**, 83 (21), 2777-2781.
- (19) Van Kningsveld, H.; Jansen, J.C.; Van Bekkum, H. The Monoclinic Framework Structure of Zeolite H-ZSM-5. Comparison with the Orthorhombic Framework of As-Synthesized ZSM-5. *Zeolites* **1990**, 10 (4), 235-242.
- (20) Marra, G.L.; Artioli, G.; Fitch, A.N.; Milanese, M.; Lamberti, C. Orthorhombic to Monoclinic Phase Transition in High-Ti-Loaded TS-1: an Attempt to Locate Ti in the MFI Framework by Low Temperature XRD. *Micropor. Mesopor. Mat.* **2000**, 40 (1-3), 85-94.
- (21) Ardit, M.; Martucci, A.; Cruciani, G. Monoclinic-Orthorhombic Phase Transition in ZSM-5 Zeolite : Spontaneous Strain Variation and Thermodynamic Properties. *J. Phys. Chem. C* **2015**, 119, 7351-7359.
- (22) Borin, M.F.; da Silva, T.; Felisbino, R.F.; Cardoso, D. Synthesis of TS-1 Molecular Sieves Using a New Ti Source. *J. Phys. Chem. B* **2006**, 110 (31), 15080-15084.
- (23) Tuel, A.; Taârit, Y.B. Influence of the Nature of Silicon and Titanium Alkoxides on the Incorporation of Titanium in TS-1 *App. Chem. A* **1994**, 110 (1), 137-151.
- (24) Ch. Deka, R.; Nasluzov, V.A.; Shor, E.A.I.; Shor, A.M.; Vayssilov, G.N.; Rösch, N. Comparison of All Sites for Ti Substitution in Zeolite TS-1 by an Accurate Embedded-Cluster Method. *J. Phys. Chem. B* **2005**, 109 (51), 24304-24310.
- (25) Zheng, A.; Liu, S.B.; Deng, F. ³¹P NMR Chemical Shifts of Phosphorous Probes as Reliable and Practical Acidity Scales for Solid and Liquid Catalysts. *Chem. Rev.* **2017**, 117 (19), 12475-12531.
- (26) Bermejo-Deval, R.; Orazov, M.; Gounder, R.; Hwang, S.-J.; Davis, M.E. Active Sites in Sn-Beta for Glucose Isomerization to Fructose and Epimerization to Mannose. *ACS Catal.* **2017**, 4 (7), 2288-2297.
- (27) Boronat, M.; Concepcion, P.; Corma, A.; Renz, M.; Valencia, S. Determination of the Catalytically Active Oxidation Lewis Sites in Sn-Beta Zeolites, and Their Optimisation by the Combination of Theoretical and Experimental Studies. *J. Catal.* **2005**, 234 (1), 111-118.
- (28) Otomo, R.; Kosugi, R.; Kamiya, Y.; Tatsumi, T.; Yokoi, T. Modification of Sn-Beta Zeolite: Characterization of Acidic/Basic Properties and Catalytic Performances in Baeyer-Villiger Oxidation. *Catal. Sci. Technol.* **2016**, 6, 2787-2795.



Insert Table of Contents artwork here