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Catalytically Active Silicon Oxide Nanoclusters Stabilized in a Metal–Organic Framework

Martino Rimoldi,^[a] Leighanne C. Gallington,^[b] Karena W. Chapman,^[b] Keith MacRenaris,^[a] Joseph T. Hupp,^[a] and Omar K. Farha^{*[a,c]}

Abstract: Post-synthetic modification of the zirconium-based metalorganic framework NU-1000 by atomic layer deposition (ALD) using tetramethoxysilane (Si(OMe)₄) as a precursor led to the incorporation and stabilization of silicon oxide clusters composed of only a few silicon atoms in the framework's pores. The resulting SiO_x functionalized material (Si-NU-1000) was found to be catalytically active despite the inactivity of related bulk silicon dioxide (SiO₂), thus demonstrating the positive effects of having nanosized clusters of SiO_x. Moreover, Si-NU-1000 showed activity greater than that found for aluminum oxide based catalysts - oxides known for their high acidity - such as an aluminum oxide functionalized MOF (AI-NU-1000) and bulk y-Al₂O₃. X-ray photoelectron spectroscopy and infrared spectroscopy measurements unmasked the electron donating nature of Si-NU-1000 explaining the unusual electronic properties of the nanosized SiO_x clusters and supporting their high catalytic activity.

Introduction

Well-known heterogeneous acid catalysts such as amorphous silica-aluminas and aluminas or crystalline aluminosilicate zeolites can perform a variety of transformations, and currently find a wide range of applications from laboratory scale syntheses to industrial uses.^[1]

Recently, zirconium-based metal–organic frameworks (Zr-MOFs), an exceptionally robust sub-class of MOFs that has proven promising both as catalysts and catalyst supports,^[2] have been introduced as high surface area and high porosity acid catalysts.^[3] They have been used successfully in a number of acid catalyzed reactions, mostly taking advantage of the acidity and ease of functionalization of the zirconium oxide node.^[4]

The use of atomic layer deposition (ALD) $^{[5]}$ – a self-limiting deposition technique conducted in the vapor-phase that is able to achieve surface modification with atomic precision – has been recently applied to hybrid and porous, high-surface-area materials, $^{[6]}$ in order to achieve selective and controlled functionalization.

[a] M. Rimoldi, K. MacRenaris, J. T. Hupp, and O. K. Farha Department of Chemistry, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, United States. E-mail: o-farha@northwestern.edu

[b] L. C. Gallington, K. W. Chapman X-ray Science Division, Advanced Photon Source Argonne National

Laboratory, 9700 S. Cass Avenue, Argonne, Illinois 60439, United States. [c] O. K. Farha

Department of Chemistry, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia.

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NU-1000, a high surface area Zr-MOF composed of 1,3,6,8-tetrakis(p-benzoic acid)pyrene linkers and zirconium oxide cluster nodes (Zr₆O₈) (Figure 1),^[7] has been shown to be a promising ALD platform, principally due to its high chemical stability, mesoporosity, and the availability of hydroxyl groups on the Zr-oxide node of the framework which can serve as reactive deposition sites.^[7-8]

Given the tunability and the stability of NU-1000 as well as the versatility of the atomic layer deposition technique, we targeted MOF modification – more specifically, zirconium-oxide node modification – to tune its properties such as acidity.

Herein, we report the use of ALD to post-synthetically install low nuclearity SiO_x clusters at the zirconium oxide nodes of NU-1000 and demonstrate how confinement of the clusters within the small apertures (about 8–10 Å in size) of the framework preserves their nanoscale nature, conferring unusual electronic properties as well as unexpected catalytic activity.



Figure 1. View of NU-1000 (a) perpendicular to and (b) parallel to the *c*-axis. showing the small apertures in the NU-1000 framework where the oxide clusters are found after atomic layer deposition.

Results and Discussion

Amongst other available molecular compounds,^[9] tetramethoxysilane (Si(OMe)₄) has been found to be the most suitable precursor for silicon oxide ALD in NU-1000, in combination with water as a second reactant to displace the unreacted methoxy groups after Si(OMe)₄ deposition (the parameters of the process are reported in the Supporting Information).

The integrity of the framework after ALD has been preserved. In fact, Si-NU-1000 maintained its high surface area and mesoporosity as demonstrated by nitrogen physisorption isotherms and pore size distribution analyses (Figures S1 and S2). Si-NU-1000 was also found to retain crystallinity as demonstrated by its powder X-ray diffraction pattern (Figure S3). Additionally, scanning electron microscopy-energy dispersive

FULL PAPER

10.1002/chem.201701902

spectroscopy (SEM-EDS) showed retention of crystal morphology and a homogeneous distribution of the silicon incorporated through the NU-1000 crystallite (Figure S4). Diffuse reflectance infrared Fourier transform (DRIFT) spectra showed, after dehydration, the appearance of broad peaks at 3712 cm⁻¹ and 3733 cm⁻¹, attributed to silanol features (Figures S5 and S6). The ²⁹Si MAS NMR spectrum of Si-NU-1000 (Figure S7) reveals the absence of Q⁴ sites (*Si*-(OSi)₄ sites, commonly at δ – 110 ^[10]) suggesting the occurrence of small, bulk-free SiO_x units.

Additionally, difference envelope density (DED) analyses of the powder diffraction data reveals an increase in electron density between Zr_6 nodes aligned along the *c*-axis following silicon oxide deposition, as similarly observed with other examples of ALD in NU-1000.^[8b-d] The distribution of new species from ALD throughout the framework is shown in Figure 2.



Figure 2. View of the lattice of NU-1000 (left) perpendicular to and (right) parallel to its c-axis. A difference envelope indicating extra electron density present in Si-NU-1000 is represented in purple. Zr_6O_8 clusters are represented in cyan.

Overall, the spectroscopic and crystallographic information suggests that the SiO_x introduced to NU-1000 via ALD is present as SiO_x nanoclusters – more precisely consisting of only a few silicon atoms and below one nanometer in size – with the clusters localized in the small cavities of the MOF network rather than homogeneously distributed over the zirconium node. The confinement in the small apertures (Figure 2) is pivotal to their stabilization in preventing aggregation phenomena.

Given the unusual (nanosized) nature of the clusters embedded in the framework, we decided to further investigate Si-NU-1000, and in particular with respect to its use as an acid catalyst. Reactions such as dehydration, isomerization, or cracking are commonly used to benchmark the acidity of solid catalysts. We opted to evaluate the performance of Si-NU-1000 in isopropanol dehydration (Scheme 1). Besides being a way to benchmark the catalyst, isopropanol dehydration also represents a practicable route to produce propene – one of the most important feedstocks in the chemical industry – whose interest is confirmed by a number of recent patents.^[11]



Scheme 1. Acid catalyzed dehydration reaction of 2-propanol.

Catalytic tests were conducted in a vertical tubular gas flow reactor and the reaction temperature was set to 250 °C.^[12] To evaluate the catalyst, we determined turn-over frequencies (TOFs) of the catalytic dehydration reaction.

We obtained a TOF of $5.18 \pm 0.05 \text{ h}^{-1}$ for Si-NU-1000, whereas SiO₂ (bulk silicon dioxide), which was run for comparison purpose, was found to be inactive in isopropanol dehydration. Under the adopted experimental conditions, bare NU-1000 showed only minimal activity with a TOF, obtained from a single point determination, of 0.05 h⁻¹. This value falls within the conversion experimental error and therefore it can be reasonably considered as a negligible background reaction. Therefore we can exclude any contribution from the zirconium oxide node when evaluating the activity of the ALD-modified NU-1000.

It is remarkable that the SiO_x-functionalized MOF is catalytically active despite the inactivity of the related bulk oxide (silicon dioxide). We speculate that the unusual catalytic performance of Si-NU-1000 can be ascribed to the nanosized nature of the SiO_x units, whose electronic properties and local structure possibly differs from those of bulk silica.

To further support and understand the origin of the unexpected high activity of Si-NU-1000 we performed Si2p X-ray photoelectron spectroscopy (XPS). Si2p binding energies (BEs) of SiO₂ have commonly been reported between 103.5 eV and 103.3 eV.^[13] Accordingly we obtained a BE of 103.3 eV for SiO₂, but on the other hand we found the Si2p binding energy of Si-NU-1000 at 102.5 eV, significantly shifted with respect to bulk SiO₂ (Figure 3).



Figure 3. Si2p XPS measurements of (right) Si-NU-1000 and (left) SiO_2 Binding energies (eV) are referenced to C1s = 284.8 eV.

It is known that the Si2p BEs of aluminum silicates and zeolites –oxides of well-proven acidity – are shifted to lower values when compared to silicon dioxide. For instance, Si2p BE values of zeolites have been reported between 100.0 eV and 102.9 eV and this feature, although its interpretation is not straightforward, is commonly ascribed to the higher acidity of the oxide material.^[14] XPS data demonstrates a tangible difference between the electronic properties of the SiO_x nanoclusters incorporated in NU-1000 and bulk silica, suggesting a significantly higher acidity and thus supporting the unexpected remarkable activity of Si-NU-1000 in an acid catalyzed reaction. Given that aluminas and aluminates are common acid catalysts, for a fair and thorough evaluation of the catalytic activity, we compared the performance of Si-NU-1000 with Al-NU-1000 ^[8d] –

FULL PAPER

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a structurally related catalyst obtained by aluminum oxide ALD – and $\gamma\text{-Al}_2\text{O}_3.$

In our catalytic tests we obtained TOFs of $0.73 \pm 0.07 \text{ h}^{-1}$ for Al-NU-1000 (Figure 4 shows a representative residence time vs conversion plot used to determine the TOFs of Si-NU-1000 and Al-NU-1000) and of 2.6 \pm 0.2 h⁻¹ for γ -Al₂O₃, values significantly lower than those obtained with Si-NU-1000. This comparison additionally proves the uniqueness of Si-NU-1000 not only with respect to the related bulk oxide (SiO₂) but also an analogous aluminum oxide-modified MOF and bulk γ -Al₂O₃.



Figure 4. Representative Conversion vs W/F (h) (Residence Time) plots of isopropanol dehydration catalysed by Si-NU-1000 (blue circles) and Al-NU-1000 (red squares).

To further support the activities trend amongst the MOF-based catalysts and examine the properties of small oxide clusters within the framework, we turned to investigating the electron donor properties of the ALD-modified catalysts *vs* bare NU-1000 (whose activity is exclusively associated with the acidity of the zirconium-oxide node) by using the iridium(I) complex [Ir(CO)₂(acac)] (acac is acetylacetonate – Scheme 2) as probe molecule.



Scheme 2. [Ir(CO)₂(acac)] (left) and schematic representation of the grafted fragment [Ir(CO)₂] (right).

The IR carbonyl stretching of the $[Ir(CO)_2]$ fragment grafted onto a solid support via displacement of the acetylacetonate ligand upon reaction with the –OH groups (Scheme 2) is indicative of the electron density on the iridium metal center (in formal oxidation state +1) which, in turn, probes the electron-donor ability of the support. This method was proven effective with materials such as HY zeolite, ZrO_2 , MgO, and more recently with zirconium-based MOFs, including NU-1000.^[15] To compare the acidity of Si- and Al-NU-1000, as well as NU-1000, we grafted the Ir(I) carbonyl complex onto the Zr-MOFs and measured their v_{CO} stretching frequencies. Since the Si- and Al-oxide functionalities were found to be installed only at certain faces of the zirconium node (Figure 2) we expected the iridium complex to react with Zr-OH on the node of NU-1000, in addition to the Si-OH and Al-OH species introduced into the MOF by ALD. The IR spectra revealed – besides a peak at 1991 cm⁻¹ (asymmetric v_{CO}) typical of [Ir(CO)₂] grafted onto the zirconium node of bare NU-1000 – the appearance of new peaks at 2009 cm⁻¹ (and 2001 cm⁻¹) on Si-NU-1000 and at 2003 cm⁻¹ on Al-NU-1000 (see Supporting Information for more details).

The shifting of the CO stretching to higher frequencies indicates a lower electron density on the metal center of the supported dicarbonyl species $[Ir(CO)_2]$, tentatively associated to an increase in the acidity of both Si- and Al-NU-1000 with respect to bare NU-1000. In addition, Si-NU-1000 causes a shift to a higher frequency with respect to Al-NU-1000, indicative of a lower electron donor ability of Si-NU-1000. Although unexpected for a silicon oxide-based material, this outcome is in line with and supports the catalytic results.

The spectroscopic data, along with the catalytic data, are summarized in Table 1 and Figure 5 ^[16] shows the TOF (h⁻¹) values vs v_{CO} frequency (cm⁻¹) which underlines the enhanced performance of Si-NU-1000. Overall, the electron donor ability extrapolated from the carbonyl stretching frequency highlights a trend that agrees with the catalytic results, and in particular confirms the superiority of Si-NU-1000.

Table 1. Carbonyl stretching frequencies (v_{CO}) and TOF values in isopropanol dehydration of bare NU-1000 and ALD-modified NU-1000.

	$\nu_{CO} \ [lr(CO)_2] \ (cm^{-1})^{\ [a]}$	TOF (h ⁻¹) (\pm STD Error) ^[d]
Si-NU-1000	2009 ^[b]	5.18 (± 0.05)
AI-NU-1000	2004	0.73 (± 0.07)
NU-1000	1990 ^[c]	0.05 ^[e]

[a] Asymmetric carbonyl stretching of the grafted $[Ir(CO)_2]$ organometallic fragment onto Si-NU-1000, Al-NU-1000, and NU-1000 (see ESI for more details). [b] Peak at higher frequency. [c] Previously reported value (Ref. 15). [d] Turn-over frequency values in isopropanol dehydration (\pm standard error). [e] Value obtained from a single point determination.



Figure 5. TOF (h^{-1}) in isopropanol dehydration vs v_{CO} of $[Ir(CO)_2]$ (cm^{-1}) fragment grafted on the Zr-oxide node of NU-1000, on Al-NU-1000, and on Si-NU-1000.

Conclusion

Atomic layer deposition, a vapor-phase deposition method, has been used to post-synthetically incorporate SiO_x units into a Zrbased MOF. This approach combines the advantages of solvent-free reaction conditions with precise atomic control of the incorporation of desired functional sites. In the present system, the confinement of the SiO_x units in the small windows of the framework (less than 1 nm in size) is pivotal in preserving their nanometer structure, a feature we believe plays a relevant role in conferring their unusual properties. Despite the catalytic inactivity of bulk silicon oxide, Si-NU-1000 surpasses the activity in an acid catalyzed reaction of an analogous aluminum-based MOF and γ -alumina. The unexpected activity of Si-NU-1000 is corroborated by X-ray photoelectron spectroscopy data and determining its electron donating properties. These results also demonstrate that silicon oxide atomic layer deposition into a Zr-MOF can be efficiently used to post-synthetically modify a MOF to enhance its acidity.

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FULL PAPER

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- [16] The correlation between TOFs and IR stretching of the grafted [Ir(CO)₂] fragment has been previously found to fit an exponential curve,^[15]

however in Figure 5 we report the data on a linear scale (see Figure S9 for more details).

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

FULL PAPER

