Supporting Information for “Catalytic Mechanism of Interfacial Water in the Cycloaddition Reaction of Quadricyclane and Diethyl Azodicarboxylate”

Duy Nguyen,1 Sarah Casillas,1 Hnubci Vang,1 Anthony Garcia,1,† Hikaru Mizuno,2,3 Erika J. Riffe,2 Richard J. Saykally,2,3,* and Son C. Nguyen1,*

1Department of Chemistry and Biochemistry, University of California, Merced, CA 95343, United States.
2Department of Chemistry, University of California, Berkeley, CA 94720, United States.
3Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, United States.

Corresponding authors: saykally@berkeley.edu and son@ucmerced.edu

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1. Experimental section

1.1. Chemicals

All chemicals were purchased and used without further purification. Quadracyclane (C$_7$H$_8$, 97%) was purchased from Exciton. Diethyl azodicarboxylate (DEAD, >97%) 40% in toluene, tetraethyl orthosilicate (TEOS, 98%), tetramethyl orthosilicate (TMOS, 98%), sodium hydroxyl (NaOH, ≥98%), and 2-propanol (C$_3$H$_8$O, 99.8%) were purchased from Sigma-Aldrich. Hexadecyltrimethylammonium chloride (CTAC, >95.0%) was purchased from Tokyo Chemical Industry Co., LTD. Methanol (MeOH, 99.8%) and ammonia 28-30% solution in water (NH$_4$OH, ≥95%) were purchased from Fisher Scientific. MiliQ water was used for the synthesis of silica nanoparticles.

1.2. Characterizations

TEM and SEM images were collected by the FEI Talos F200C G2 with 200 kV acceleration and Zeiss Gemini SEM 500 with 3-5kV acceleration. Particle sizes were analyzed using ImageJ. The water adsorbed in silica nanoparticles was characterized by the Nicolet iS50R Research FTIR Spectrometer. Concentration of DEAD was monitored at $\lambda_{max} = 405$ nm by the Ocean Optics-USB 4000 UV-Vis spectrometer and the 1-cm pathlength quartz cuvette from Spectrocell (R-3010-T). Crude reaction mixture was characterized by $^1$H NMR (CDCl$_3$, Varian-INOVA 400 MHz and 500 MHz) in order to determine the reaction conversion. The conversion of quadracyclane to the product was calculated based on the peak area of the product (6.06 ppm) and the peak area of the remaining quadracyclane (2.02 ppm). No side product was detected. Data for the product: $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 6.06$ (t, 2H), 4.25 (q, J = 7.1 Hz, 4H), 4.19 (s, 2H), 1.89 (d, J = 10.1 Hz, 1H), 1.71 (d, J = 10.1 Hz, 1H), 1.30 (t, J = 7.1 Hz, 6H). Data for quadracyclane: $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 2.02$ (t, J = 1.2 Hz, 2H), 1.49 (d, J = 4.3 Hz, 4H), 1.39 – 1.33 (m, 2H).

1.3. Preparation of dry silica nanoparticles

Preparation of nonporous silica nanoparticles. Nonporous silica nanoparticles were synthesized by Stöber method. Tetraethyl orthosilicate (TEOS, 10 mL) was quickly injected into a mixture of H$_2$O (44 mL), 2-propanol (196 mL), and ammonia solution 28 – 30 % (20 mL) at room temperature and under stirring. After 3 hours of reaction, the particles were collected by centrifugation (16,639 g-force, 10 min), washed 3 times with water, and then heated overnight at 120 °C. The dry particles were then stored in vials sealed with Parafilm.

Preparation of mesoporous silica nanoparticles. Mesoporous silica nanoparticles with highly ordered hexagonal pore array were synthesized using modified Stöber method with the addition of hexadecyltrimethylammonium chloride (CTAC) as a structure-directing agent. This method produces porous particles with good size distribution, uniform spherical shape and less surface defects as compared other porous silica particles, such as SBA-15 or MCM-41. This condition is important for determining precisely the silica surface and adsorbed water for kinetic
study. Particle sizes can be tuned by increasing the methanol/water ratio for larger sizes. For a typical procedure of preparing particles of 542 nm diameter, 3.44 g of CTAC was dissolved in a mixture of water (400 g) and methanol (400 g). Then, 2.30 mL of NaOH 1.0 M was added to the solution under stirring. Then, 1.30 mL of tetramethyl orthosilicate (TMOS) was quickly injected under vigorous stirring. The mixture was stirred for another 8 hours, and then aged overnight at room temperature. The obtained particles were collected by centrifugation (16,639 g-force, 15 min), washed with methanol and water for 3 times, and subsequently dried at 50 °C for a day. Afterward, the CTAC was removed by calcinating the particles at 550 °C for 6 hrs. The particles were then stored in vials sealed with Parafilm.

1.4. Preparation of water-adsorbed silica nanoparticles

*Preparation of water-adsorbed silica nanoparticles for kinetic studies and SHS experiments:* Dry silica nanoparticles were let to adsorb water vapor in a home-built box at room temperature. The box was sealed to build up a saturated water vapor at room temperature and the dry nanoparticles adsorbed vaporized water for a certain amount of time. The box was placed in a low power ultrasonic bath to promote mechanical agitation that ensured the adsorbed water was dispersed evenly inside the particles. The amount of adsorbed water was controlled by the period of the particles staying in the box and determined by FTIR spectroscopy (See section 1.5). The adsorbed water reached a plateau under 1 hour sonication, and there were about 4 water molecules per 1 nm² of silica surface in the porous particles.

![Scheme S1. The home-built humidity-controlled box for controlling water adsorbed on porous and non-prorous silica nanoparticles.](image)

*Preparation of water-adsorbed silica nanoparticles for studying kinetic isotope effects:* We first tried the above method to load D₂O on silica nanoparticles; however, there was a significant amount of pre-existed H₂O in the air that co-adsorbed on the particles. To mitigate this problem, we placed the box in an oven at 35 °C for 6 hours to promote the evaporation of D₂O (Scheme 2). To ensure that D₂O adsorbed evenly onto silica, the sample was stirred at the middle of the adsorption process. Eventually, the majority of adsorbed water is D₂O. FTIR spectroscopy confirmed that 85% of adsorbed water on silica nanoparticles was D₂O (Figure S4). A reference sample was prepared with H₂O under the same adsorption process for comparing the kinetic isotope effect.
Scheme S2. The home-built enclosed box for controlling D$_2$O (or H$_2$O) adsorbed on porous silica nanoparticles for studying kinetic isotope effects.

1.5. Determination of surface water molecules adsorbed in mesoporous silica nanoparticles via FTIR spectroscopy

Spectroscopic characterization of surface water adsorbed in silica pores: An amount of 2 mg mesoporous silica particles was mixed with 40 mg spectroscopic grade KBr, then pressed into a pellet (diameter of 7 mm and thickness of ~ 1 mm) for FTIR measurement. The result was reported in Figure S1.

Quantification of water adsorbed in silica pores: The total amount of adsorbed water was quantified by the peak area of the HOH bending mode at 1627 cm$^{-1}$. In order to use the absorption coefficient value of the HOH bending mode from a previous experiment,$^4$ we avoided using KBr matrix. In fact, the dry mesoporous silica nanoparticles were used as a matrix to achieve the same experimental condition as reported in the previous study. In our experiment, each water adsorbed-silica nanoparticle sample was mixed with the dried version (5.0 mg, served as a matrix) and pressed into a pellet for FTIR measurement. The following formula was used to calculate the amount of adsorbed water since the IR beam covers the entire base area $S$ of the pellet.

$$A_{H_2O} = \varepsilon_{H_2O}.l.C_{H_2O}$$

$$A_{H_2O} = \varepsilon_{H_2O}.l.n_{H_2O}/\pi r^2 l$$

$$A_{H_2O} = \varepsilon_{H_2O}.n_{H_2O}/S$$

where:

$A_{H_2O}$(cm$^{-1}$): peak area of the HOH bending mode.

$\varepsilon_{H_2O}$ (cm.$\mu$mol$^{-1}$) = 1.53 ± 0.03, which is the integrated molar absorption coefficient from a previous study.$^4$

$n_{H_2O}$(µmol): mole of water

$S$(cm$^2$) = $\pi r^2 = \pi \times (0.35)^2$, which is the base area of the pellet.
According to the original work on preparing these mesoporous silica nanoparticles, the particles have specific surface area of 1155 m².g⁻¹ and pore volume of 0.68 cm³.g⁻¹. These values were used to calculate the average percentage mass of water in silica nanoparticles, the average percentage volume of water occupied the particle pore and the average water molecules per nm² of silica surface. The results were reported in Figure 2b and Table S1.

1.6. Typical reaction condition for “on-water” catalysis

Generally, the 2 mL-vial containing DEAD 40% in toluene (546 µL, 1.87 M) and silica nanoparticle catalyst (11 % w/w) was sonicated for 1 min to disperse the particles. Then, quadricyclane (94 µL, 1.57 M) was added. The reaction mixture was stirred at room temperature for 24 hours and the particles dispersed well during the reaction. After reaction completion, the catalyst was removed by centrifugation (14,100 g-force, 5 min) and the supernatant was used as the crude reaction mixture for ¹H NMR analysis. All experiments were repeated multiple times to get experimental uncertainties which are reported as one standard deviation of the means.

1.7. Determination of initial reaction rate

The initial reaction rates were determined by observing the DEAD concentration within less than 10 % reaction conversion via UV-Vis spectroscopy. The absorbance of DEAD (at λₘₚₐₓ = 405 nm) is well separated from those of quadricyclane, reaction product and toluene solvent. During the reaction, a certain amount of reaction mixture was extracted at a particular time, then diluted by cold toluene (10 °C) to quench the reaction (Table S3). The solution was then centrifuged (14,100 g-force, 5 min) to remove silica particles, and the concentration of DEAD was determined by UV-Vis spectroscopy and scaled by the above dilution. The extinction coefficient of DEAD is 51.89 L.mol⁻¹.cm⁻¹, which was obtained from our standard curve. The initial reaction rate was determined from the slope of a linear regression of DEAD concentration versus reaction time. As mentioned in the main text, the initial rate of the catalyzed reaction was corrected by subtracting the initial rate of non-catalyzed reaction within similar experimental condition.

1.8. The Gibbs free energy of adsorption of DEAD on the water adsorbed mesoporous silica nanoparticles

Second harmonic scattering (SHS) spectroscopy: The angle-resolved second harmonic spectroscopy was described elsewhere. The 800 nm laser pulses with an average 100 fs duration are directed through an 800-nm bandpass filter and an 800-nm λ/2 plate to obtain the desired input polarization. The laser beam is then focused through an objective lens into the sample vial. The output second harmonic light is collected at the desired angle and polarization, spectrally filtered, then directed into a spectrograph with a PMT operated in photon counting mode. The data collection was performed in LabVIEW and data analysis were performed in Python. The raw SHS intensities were subtracted by the scattering of the optics and normalized to the scattering of toluene solvent.
Scheme 4. The second harmonic scattering optical setup.

**Experimental condition:** Samples contained ~0.01 % w/w water-adsorbed or dry mesoporous silica nanoparticles (size of 430 nm) and DEAD (concentration range of 0 - 40µM) in toluene. Due to the low dispersion of the particles in the solution, the samples were sonicated for at least 10 minutes prior to SHS measurements. Each sample was collected for 3 minutes under XX-polarization (X-in, X-out) condition.

**Data analysis:** The SHS data were fit to a modified Langmuir adsorption isotherm model:

\[
I_{SHS} = B + \left[ b + a \times \theta_D \times e^{i\phi} \right]^2
\]

Where \(B\) is the constant corresponded to non-resonant background scattering, \(b\) is the bulk contribution from the sample, \(a\) is a fit constant describing the signal from DEAD molecules at the interface of toluene and water, \(\theta_D\) is the fractional coverage of DEAD, and \(\phi\) is a phase factor corresponding to the interference between the particle signal and the DEAD signal. All constants in the above equation are unitless because the SHS intensity is normalized and unitless. This modified Langmuir adsorption isotherm is a typical first-order model, adjusted to account for the decrease in bulk DEAD concentration due to adsorption to the surface.

The fractional coverage is given by

\[
\theta_D = \frac{\left( c_D + N_m^D + \frac{9.44}{K_D} \right) - \sqrt{\left( c_D + N_m^D + \frac{9.44}{K_D} \right)^2 - 4c_D N_m^D}}{2N_m^D}
\]

Where \(c_D\) is the total concentration of DEAD molecule in mol.L\(^{-1}\), \(N_m^D\) is the maximum surface density of DEAD molecule in mol.L\(^{-1}\), 9.44 M is the concentration of neat toluene, and \(K_D\) is the equilibrium constant for adsorption of DEAD on the surface water on the silica pores, given by the equilibrium:

\[
\text{DEAD(in toluene solution)} + \text{toluene} \cdot \text{surface water} \rightleftharpoons \text{toluene} + \text{DEAD} \cdot \text{surface water}
\]

To calculate the Gibbs free energy of the adsorption, \(\Delta G_{\text{ads}}^{\circ}\), we use the following equation for a temperature of 25°C.

\[
\Delta G^{\circ} = -RT\ln K^{\circ} = -RT\ln (9.44 K_D)
\]
2. Supplementary figures

Figure S1. a) FTIR spectra of bulk water, water-adsorbed mesoporous silica nanoparticles (diameter of 542 ± 23 nm), and dry mesoporous silica nanoparticles (diameter of 542 ± 23 nm). b) Normalized absorbance of HOH bending peak from (a). (see experimental details in Section 1.5)

Figure S2. Comparison of catalytic activity of pure water droplets and water-adsorbed mesoporous silica nanoparticles. The diameter of the silica particles is 360 ± 56 nm. Reaction conditions: quadricyclane (100 μL), DEAD 40% in toluene (490 μL), and the catalyst under stirring. The sizes of the water droplets are unknown.
Figure S3. Measured SHS signal versus bulk DEAD concentration. a) when using dry porous silica nanoparticles (size of 430 nm); b) when using water-adsorbed porous silica nanoparticles (size of 430 nm). The experimental data were fitted to a modified Langmuir adsorption model described in Section 1.8. The extracted equilibrium constant (K_D) for adsorption of DEAD on surface water (or toluene-water interface) in the silica pores is 30.9 with the percentage error of 182%, the estimated ΔG^o_ads is -3.4 kcal/mol with the propagated error of 32%. Due to the limitation of experimental points and the simplicity of the fitting model, the ΔG^o_ads has a larger error and was not used in our mechanistic interpretation. However, the isotherm follows a Langmuir model, and this information was used in the main text.

Figure S4. FTIR spectra of dry mesoporous silica nanoparticles (size of 568 ± 25 nm), the 100% pure H_2O adsorbed version of the same particles, and the 85% D_2O/15% H_2O version. All spectra are normalized to Si-O stretching vibration of silica at 1049 cm^{-1}. See sample preparation in Section 1.4.
Figure S5. Representative TEM images show the perfect spherical shape of 597 nm mesoporous silica nanoparticles as an example for the high uniformity of the studied catalysts.

Figure S6. SEM image and the size distribution with a Gaussian distribution fitting of 463 nm non-porous silica nanoparticles.

Figure S7. SEM image and the size distribution with a Gaussian distribution fitting of 360 nm mesoporous silica nanoparticles.
Figure S8. SEM image and the size distribution with a Gaussian distribution fitting of 425 nm mesoporous silica nanoparticles.

Figure S9. SEM image and the size distribution with a Gaussian distribution fitting of 456 nm mesoporous silica nanoparticles.

Figure S10. SEM image and the size distribution with a Gaussian distribution fitting of 506 nm mesoporous silica nanoparticles.
Figure S11. SEM image and the size distribution with a Gaussian distribution fitting of 542 nm mesoporous silica nanoparticles.

Figure S12. SEM image and the size distribution with a Gaussian distribution fitting of 568 nm mesoporous silica nanoparticles.

Figure S13. SEM image and the size distribution with a Gaussian distribution fitting of 597 nm mesoporous silica particles.
3. Supplementary tables

Table S1. Quantification of surface water molecules per nm$^2$ surface silica in mesoporous silica nanoparticles (see experimental details in Section 1.4 and 1.5)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Particle diameter (nm)</th>
<th>$\frac{m_{H_2O}}{m_{\text{particle}}}$ (%)</th>
<th>$\frac{\nu_{H_2O}}{\nu_{\text{particle pore}}}$ (%)</th>
<th>#H$_2$O/nm$^2$ (molecules)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>542 ± 23</td>
<td>11.8 ± 1.2</td>
<td>20.1 ± 2.3</td>
<td>4.0 ± 0.5</td>
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<td>2</td>
<td>506 ± 25</td>
<td>12.5 ± 1.6</td>
<td>21.4 ± 3.1</td>
<td>4.2 ± 0.6</td>
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<tr>
<td>3</td>
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<td>11.7 ± 1.1</td>
<td>19.0 ± 2.1</td>
<td>4.0 ± 0.4</td>
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<tr>
<td>4</td>
<td>425 ± 23</td>
<td>1.2 ± 0.1</td>
<td>1.8 ± 0.1</td>
<td>0.4 ± 0.02</td>
</tr>
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<td>5</td>
<td>425 ± 23</td>
<td>3.5 ± 0.6</td>
<td>5.4 ± 1.0</td>
<td>1.1 ± 0.2</td>
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<td>425 ± 23</td>
<td>6.1 ± 1.5</td>
<td>9.7 ± 2.7</td>
<td>1.9 ± 0.5</td>
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<td>8.7 ± 0.3</td>
<td>14.0 ± 0.5</td>
<td>2.8 ± 0.1</td>
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<tr>
<td>8</td>
<td>425 ± 23</td>
<td>12.2 ± 1.1</td>
<td>20.6 ± 2.2</td>
<td>4.1 ± 0.4</td>
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</tbody>
</table>

The uncertainty is one standard deviation of the mean.
Table S2. Calculated total surface areas of various silica nanoparticle catalyst in this study. (See the reaction condition on Section 1.6)

<table>
<thead>
<tr>
<th>Entry</th>
<th>10 mg of silica nanoparticle samples</th>
<th>Total external surface area (cm$^2$)</th>
<th>Total internal surface area (cm$^2$)</th>
<th>Ratio of total internal surface area over total external surface area</th>
<th>Conversion $^{[a]}$ (%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>nonporous 463 nm</td>
<td>563</td>
<td>N/A</td>
<td>N/A</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>porous 360 nm</td>
<td>1858</td>
<td>113642</td>
<td>61</td>
<td>15</td>
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<td>3</td>
<td>porous 456 nm</td>
<td>1467</td>
<td>114033</td>
<td>78</td>
<td>14</td>
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<td>4</td>
<td>porous 597 nm</td>
<td>1120</td>
<td>114379</td>
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<tr>
<td>5</td>
<td>nonporous 463 nm</td>
<td>563</td>
<td>N/A</td>
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<td>99869</td>
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<td>1398</td>
<td>100241</td>
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<tr>
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<td>1068</td>
<td>100572</td>
<td>94</td>
<td>41</td>
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</tbody>
</table>

$^{[a]}$ after subtracting the conversion of the background reaction.

The total external surface areas were calculated from the total numbers of particles in the reaction solution and the assumption that each particle has a full surface area of a sphere. The total internal surface areas were calculated by subtracting the total external surface areas from the total surface areas. The total surface areas of the porous samples were calculated from the mass of porous silica nanoparticles and the specific surface area (about 1155m$^2$/g) from a previous study.$^2$
Table S3. Reaction condition of kinetic studies using water-adsorbed mesoporous silica nanoparticle catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Experiment</th>
<th>Quadricyclane concentration in toluene (M)</th>
<th>DEAD concentration in toluene (M)</th>
<th>Porous silica nanoparticle catalyst Mass (mg)</th>
<th>Diameter (nm)</th>
<th>Temp. (°C)</th>
<th>Extracted volume (µL)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Activation energy</td>
<td>1.57</td>
<td>1.87</td>
<td>20.0</td>
<td>542 ± 23</td>
<td>24</td>
<td>50</td>
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<tr>
<td>2</td>
<td></td>
<td>1.57</td>
<td>1.87</td>
<td>20.0</td>
<td>39</td>
<td>50</td>
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<td>3</td>
<td></td>
<td>1.57</td>
<td>1.87</td>
<td>20.0</td>
<td>50</td>
<td>50</td>
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<td>4</td>
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<td>1.57</td>
<td>1.87</td>
<td>20.0</td>
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<td>50</td>
<td></td>
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<tr>
<td>5</td>
<td>Reaction order in quadricyclane</td>
<td>0.84</td>
<td>1.00</td>
<td>20.0</td>
<td>506 ± 25</td>
<td>24</td>
<td>100</td>
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<td>1.67</td>
<td>1.00</td>
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</tr>
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<td>9</td>
<td>Reaction order in DEAD</td>
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<td>0.24</td>
<td>15.0</td>
<td>542 ± 23</td>
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<td>0.48</td>
<td>15.0</td>
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<td>200</td>
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<td>11</td>
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<td>0.72</td>
<td>15.0</td>
<td>24</td>
<td>150</td>
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<td>12</td>
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<td>1.20</td>
<td>0.96</td>
<td>15.0</td>
<td>24</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Reaction order in catalyst sites</td>
<td>1.57</td>
<td>1.87</td>
<td>5.0</td>
<td>597 ± 22</td>
<td>24</td>
<td>50</td>
</tr>
<tr>
<td>14</td>
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<td>1.57</td>
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<td>1.87</td>
<td>20.0</td>
<td>24</td>
<td>50</td>
<td></td>
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</tbody>
</table>

Since a large amount of mesoporous silica nanoparticles was used in our experiment, it was impossible to prepare one particle size by one large batch for all kinetic studies. Instead, particles with a bit variation in size were conveniently used for each set of experiment as showed in the table. As we proved in the main text, particles size has no effect on the catalytic activity, thus the above size variation does not affect the mechanistic interpretation.

References