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Supplementary information

Title: **Silica-Supported Aminoxyls as Reactive Materials for NO_x Removal**

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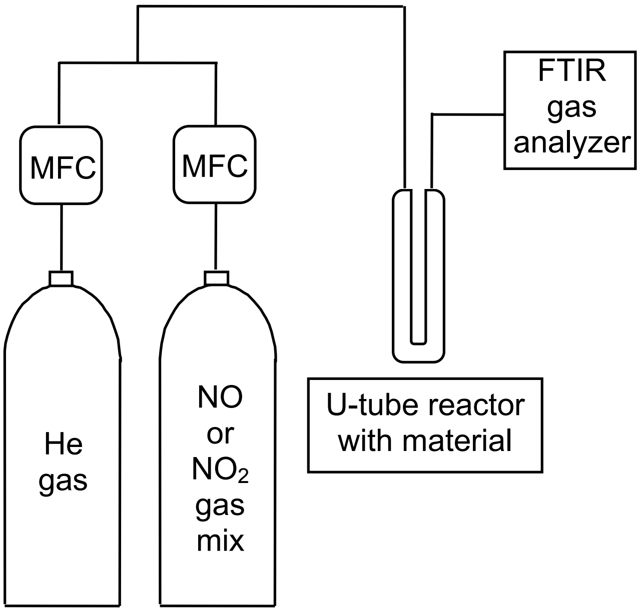


Scheme S1. Schematic illustration of flow apparatus used for NO_x storage studies.

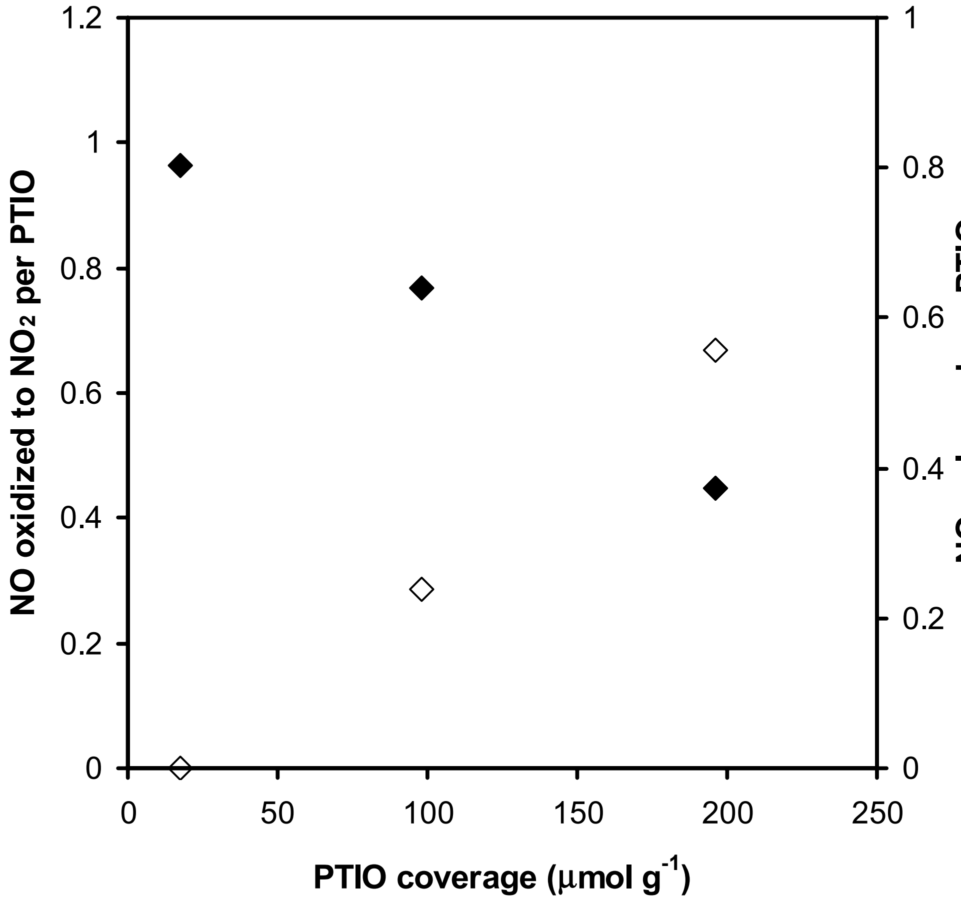


Figure S1. NO oxidized to NO_2 per PTIO within the regime of fast NO consumption (♦) and total amount of NO_2 released per PTIO (◊) during treatment of silica-1073-supported PTIO materials at different coverages with NO.

Section S1: The analysis of the products of NO/NO_2 interaction with PTIO

Interaction of PTIO with both NO and NO_2 in gas phase and the absence of N-oxides elution upon complete conversion of NO suggest that two products are formed upon silica-1073-supported PTIO exposure to NO (PTI and oxoammonium PTIO salt):

1) $\text{PTIO} + \text{NO} \rightarrow \text{PTI} + NO_2$

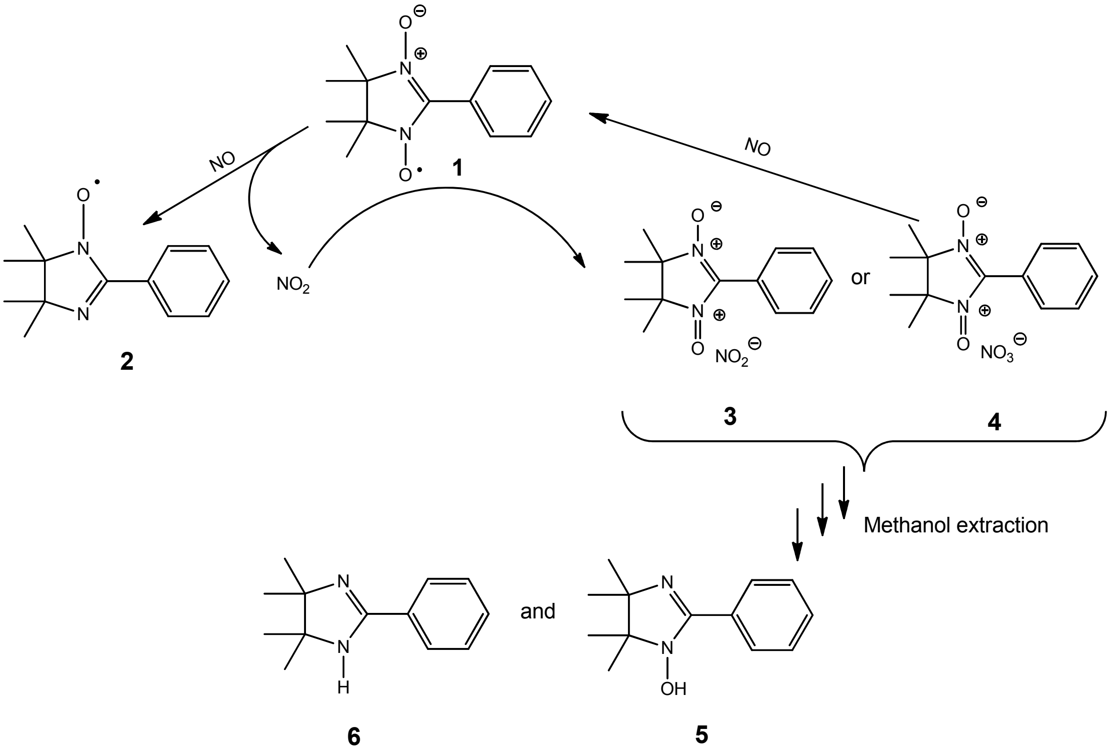
2) $\text{PTIO} + 2\,NO_2 \rightarrow \text{PTIO}^+NO_3^- + \text{NO}$

A chromatographic separation of the extracted product mixture after NO treatment of a large batch silica-1073-supported PTIO (130 µmol PTIO g^{-1}) and analysis using proton nuclear magnetic resonance (^{1}H NMR), elemental analysis and electrospray ionization mass spectrometry (ESI MS) showed two thirds of the total mass to be mostly PTI (Table

S1). All other products belong to polar fraction extracted with methanol. These products were difficult for identification, presumably, because of secondary processes associated with highly oxidative properties of oxoammonium salts previously reported to oxidize alcohols (Scheme S1).[1]

Table S1. Analysis of extracted fractions after NO adsorption by silica-1073-supported PTIO (130 μmol PTIO g^{-1}) at 5 ks of residence time. Note: for ESI MS results the numbers represent molecular peak with relative abundance in parentheses.

	At point of NO breakthrough		At complete reaction with NO	
Eluent	Benzene/ether	Methanol	Benzene/ether	Methanol
Yield of extraction (wt.%)	70	30	66	42
^{1}H NMR	Inactive	Active	Inactive	Active
ESI MS (relative abundance, %)	***2*** (100)	***5*** (100) ***6*** (42)	***2*** (100)	***5*** (82) ***6*** (100)



Scheme S2. The schematic mechanism of proposed reactions taking place upon NO treatment of silica-supported PTIO. This scheme does not include the possible NO_2 adsorption onto the silica support.

Extraction of NO-treated material

All solvents used for extraction were purchased from Fisher Scientific as HPLC grade and were used without further purification. An identical extraction procedure was carried out for all studied systems. Chromatographic column was filled with silica gel (Selecto Scientific, 32-63 μm) as a lower layer in the amount equal to material mass. An upper layer was filled with NO-treated material. The column was run with effluent amount calculated as triple column volume. First effluent was benzene/ether mixture (1:1 by volume) and the second was methanol. The extracted fractions were collected and solvent was removed under reduced pressure using rotary evaporator.

Analytical methods

^{1}H-NMR: NMR spectra were recorded on Bruker Avance 400 console with a Bruker 9.39 T magnet (400 MHz) using deuterated chloroform for non-polar and deuterated acetone for polar compounds as a solvent and referenced to tetramethylsilane. Non-polar fraction showed NMR silence, while polar products were a mixture of the products, difficult for interpretation.

ESI MS: Electrospray ionization analysis was performed with acetonitrile solution of non-polar compounds and methanol solution for polar ones.

CHN microanalysis: CHN analysis of PTI was performed on Perkin Elmer 2400 Series II combustion analyzer: found 71.64% C, 7.91% H, 12.97% N; calculated 71.89% C, 7.83% H, 12.90% N.

Section S2: In-site FTIR analysis of surface species formed upon reaction of NO_2 with silica-supported TEMPO

In-situ IR analysis

Infrared spectra of the surface upon NO_x treatment were recorded using a Nicolet 8700 infrared spectrometer. A self-supporting wafer (2-5 mg) was held within a stainless steal cell with a well-mixed geometry and CaF_2 windows. Spectra were acquired in the region 4000 - 1200 cm^{-1}. Each spectrum was obtained by averaging 64 scans collected at 2 cm^{-1} resolution. The sample was pretreated in flowing He (0.5 cm^3 s^{-1}) at ambient temperature for 15 h before measuring spectra.

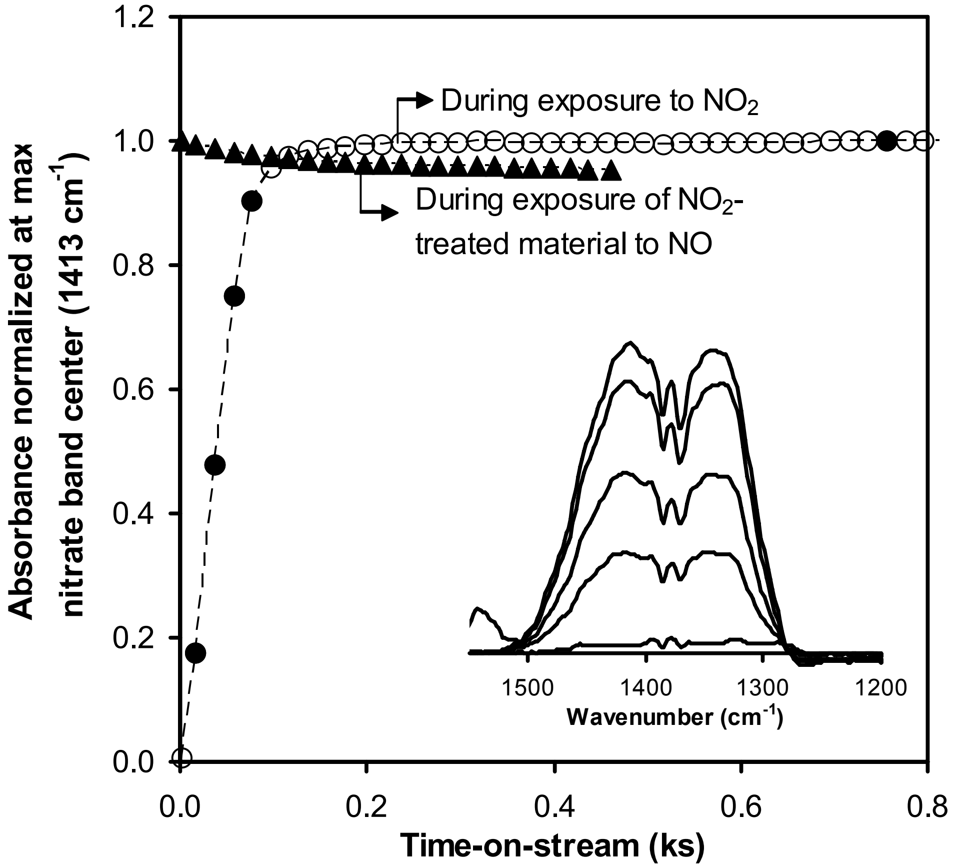


Figure S2. Absorbance of nitrate band during reaction of silica-473-supported TEMPO (140 μmol TEMPO g^{-1}) with NO_2 (0.07 kPa NO_2, flowing at 0.5 cm^3 s^{-1}) (○), where (●) represents time when shown spectra was taken; and NO treatment of NO_2-saturated material (0.04 kPa NO, flowing at 0.5 cm^3 s^{-1}) at ambient temperature (▲).

Section S3: Further insight into silica-supported PTIO treated with NO in the absence of NO_2 trap

Slow NO consumption during high density PTIO on silica reactions with NO must be attributed to side reactions occurring with the product of NO_2 interaction with PTIO. NO_2-treated silica-1073-supported PTIO (200 μmol PTIO g^{-1}) was studied for its reducibility by reaction with NO, after being purged in He. It was found that there is a slow adsorption of NO provided by release of NO_2 along this treatment (Figure S3). The total amount of NO consumed and NO_2 released per initial number of PTIO sites after 2.5 ks of this treatment corresponds to 1.2 and 0.8, respectively. This indicates that the product of NO_2 treatment of PTIO undergoes slow reduction by NO with a concurrent release of NO_2 that was found for high coverage PTIO materials during exposure to NO (Figure 2 in manuscript). This creates for a rather convoluted NO adsorption process in a bed consisting of PTIO immobilized on silica at high coverage. Such a bed when treated with NO forms NO_2 as a principal product that, due to lack of an available trap (such as silica or TEMPO shown in examples above) forms a product that itself appears to be reduced by NO. This latter process of a NO_2-degraded PTIO reduction by NO releases NO_2, and must be coupled with bed effects in order to understand ultimately the reactions occurring when high coverage silica-supported PTIO is treated with NO.

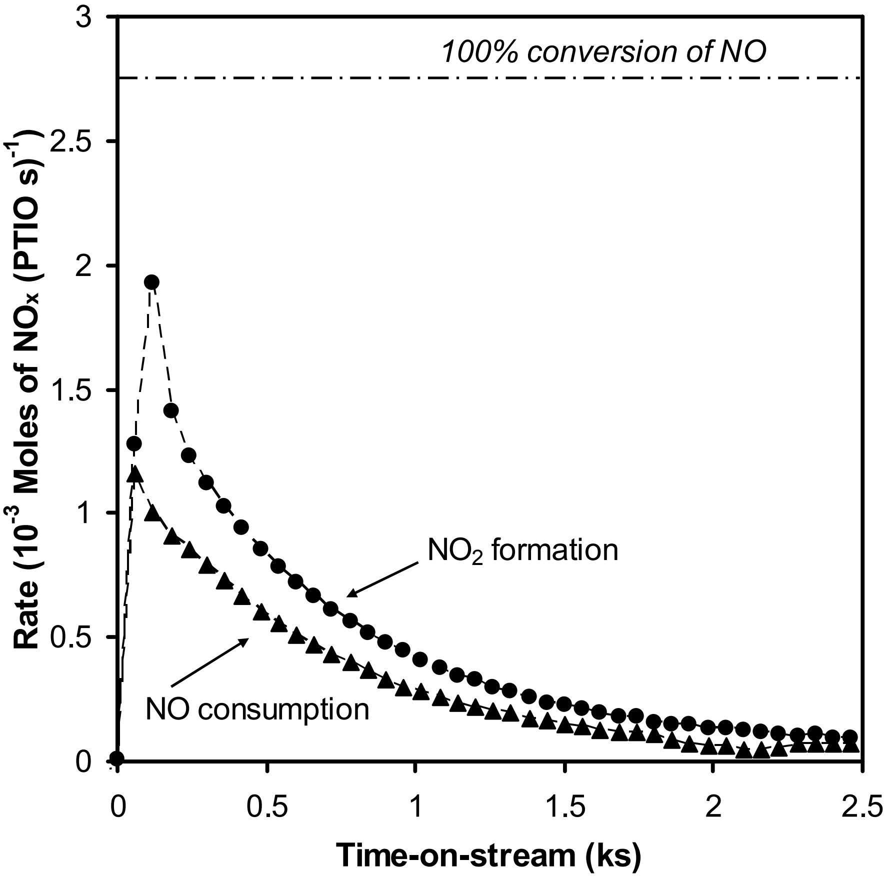


Figure S3. NO consumption and NO_2 formation rates for NO reaction with NO_2-treated silica-1073-supported PTIO (200 μmol PTIO g^{-1}) at $2.8*10^{-3}$ mol NO (PTIO $s)^{-1}$.

Section S4: Structural data of N_2O_4 interactions with $Si_4O_{11}H_6$ molecular cluster

Internal coordinates (Å) were calculated using B3LYP functional with a 6-311+G(d,p) basis set.

N	1.484	-6.118	-0.809
N	-0.213	-5.931	-1.353
O	-0.55	-1.196	-1.26
O	-1.065	1.269	-0.217
O	1.333	1.324	0.872
O	0.063	-2.857	0.838
O	1.061	0.825	-1.688
O	1.85	-1.148	-0.155
O	-0.921	1.17	2.423
Si	-0.235	1.826	1.099
Si	-0.552	0.437	-1.534
Si	2.012	0.485	-0.364
Si	0.59	-2.151	-0.525
H	-0.349	-3.725	0.808
H	-0.813	1.607	3.271
O	-0.285	3.456	1.265
H	0.242	4.012	0.686
O	1.041	-3.361	-1.561
H	1.308	-3.127	-2.454
O	3.569	0.92	-0.53
H	4.207	0.287	-0.864
O	-1.458	0.832	-2.823
H	-1.617	0.185	-3.512
O	2.211	-6.438	-1.689
O	1.614	-5.899	0.349
O	-0.944	-5.574	-0.481
O	-0.368	-6.195	-2.499

[1] E. F. Ullman, J. H. Siecki, D. G. B. Boocock, and R. Darcy, *J. Am. Chem. Soc.*, 1972, **94**, 7049.