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# Well-Defined Surface Tungstenocarbyne complex through the Reaction of $[W(\equiv C\textit{t}Bu)(CH_2\textit{t}Bu)_3]$ with $CeO_2$ : a highly and stable precatalyst for $NO_x$ reduction with $NH_3$

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## Supporting Information

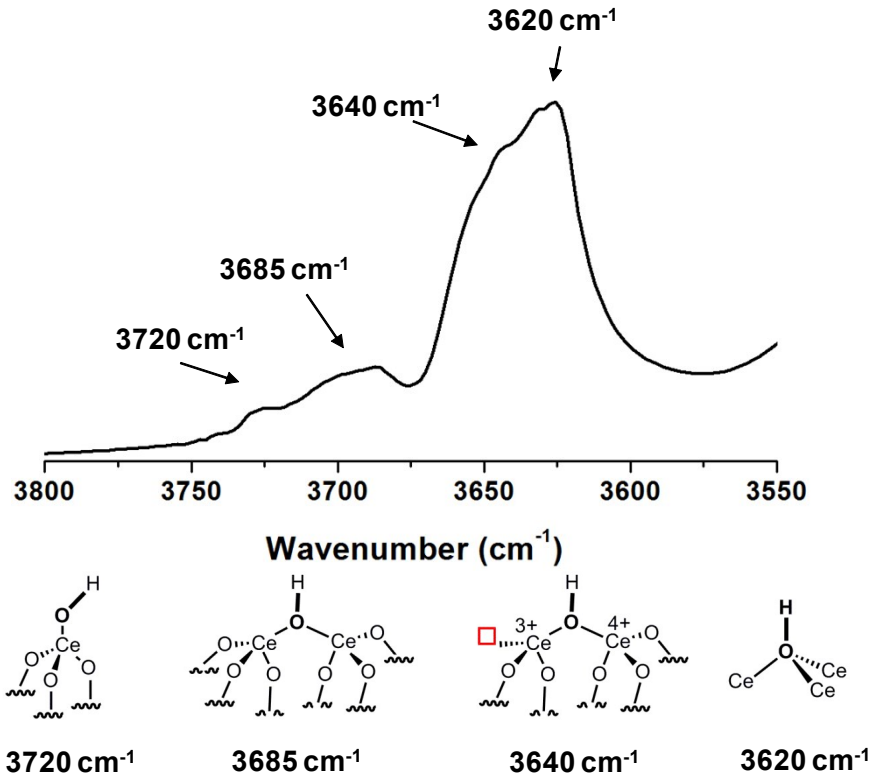


**Fig S1:** Attribution of (CeO-H) Stretching vibration according to literature.[1,2]

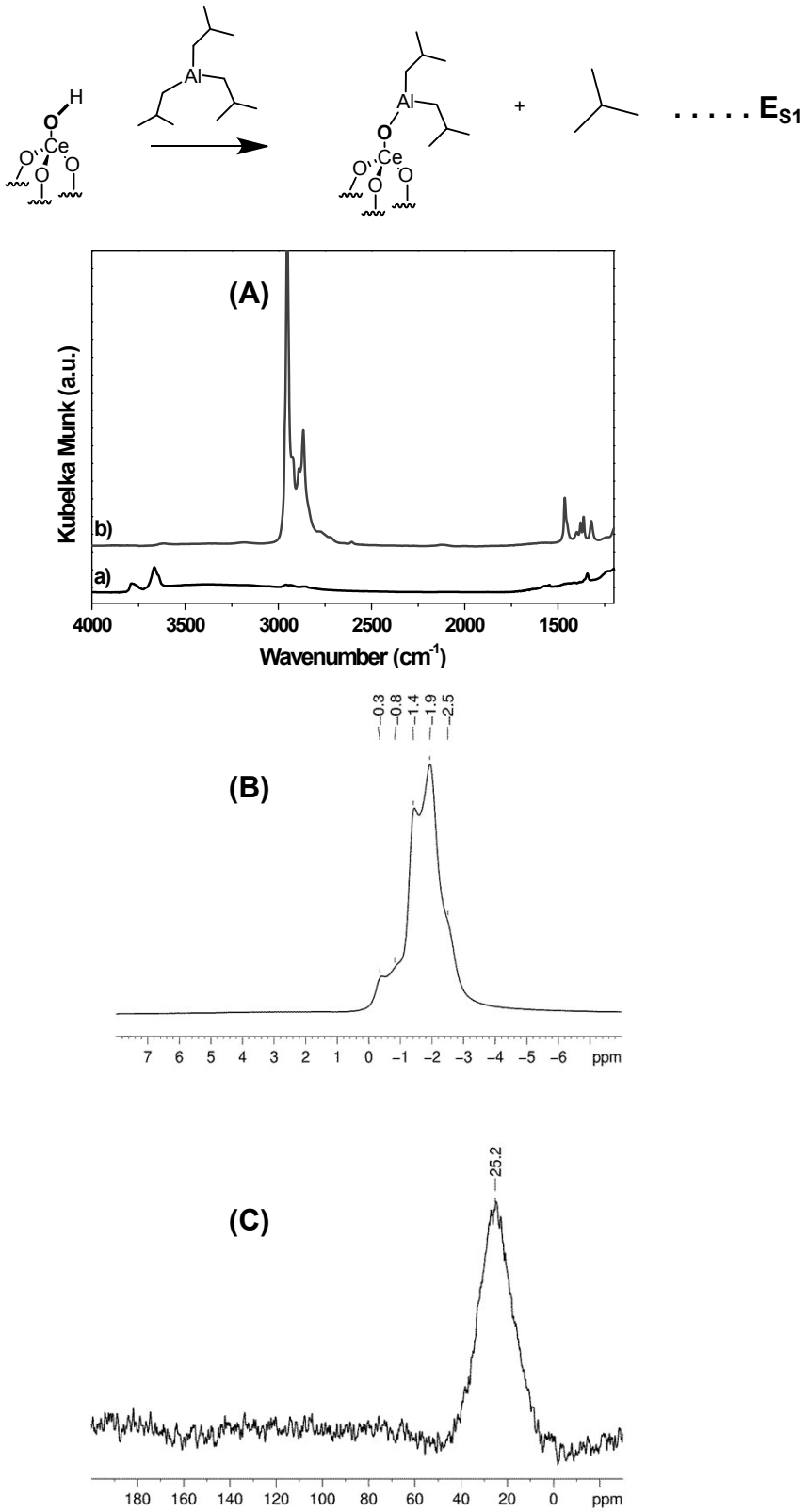


**Fig S2:** Titration of surface OH of the ceria partially dehydroxylated at 200 °C with $Al(iBu)_3$ ($E_{S1}$), DRIFT spectrum of a) $CeO_2$ dehydroxylated at 200 °C. b) after grafting of $Al(iBu)_3$ (A). This confirms that all types of the surface OH groups have reacted. Hence the quantification of surface OH groups with Al(iBu)3 gives 0.7 mmol OH/g. $^{1}H$ MAS (B) and $^{13}C$ (C), NMR spectra of $Al(iBu)_3/CeO_2$. The solid state NMR also shows the presence of isobutyl group.

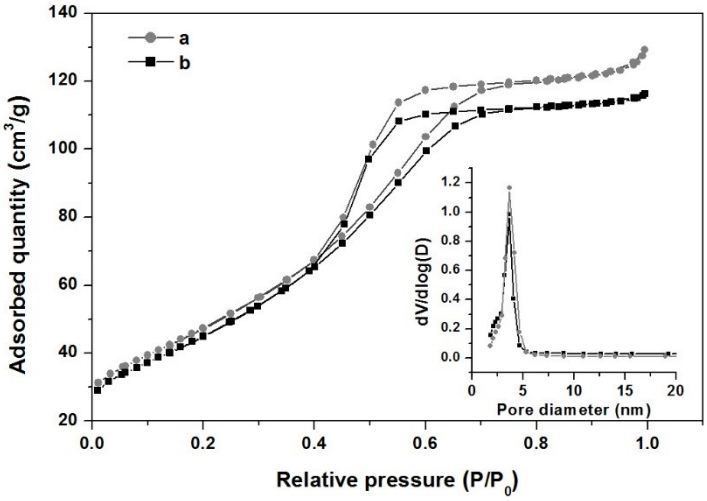


**Fig S3:** Nitrogen physisorption isotherms and corresponding pore size distribution (inset) of $CeO_{2\text{-}200}$ (a) and $W(\equiv C^tBu)(CH_2{}^tBu)_3/CeO_{2\text{-}200}$ (b).

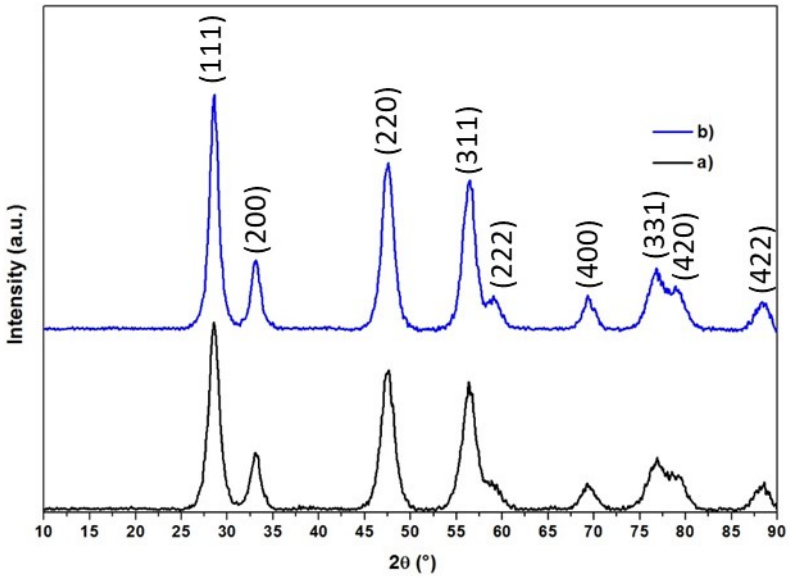


**Fig S4:** Powder X-Ray diffraction of the $CeO_{2\text{-}200}$ (a) and $W(\equiv CtBu)(CH_2tBu)_3/CeO_{2\text{-}200}$ (b). These data fit well with $CeO_2$ exhibiting a fluorite structure (JCPDS 34-0394).

**Table S1** average particle size of ceria samples calcined at various temperatures, estimated measured using Scherrer's equation

| **Sample** | **Average crystallite size** [a)] | **Surface area** [b)] | **BET** |
|---|---|---|---|
| $CeO_{2\text{-}200}$ | 45 (Å) | 173 $m^2.g^{-1}$ | 205 $m^2.g^{-1}$ |
| $W(\equiv C^tBu)(CH_2{}^tBu)_3/CeO_{2\text{-}200}$ | 52 (Å) | 155 $m^2.g^{-1}$ | 190 $m^2.g^{-1}$ |

[a)]The average size of the crystallites was calculated using the following equation (Scherrer's equation):

$$T = \frac{0.9 \times \lambda}{\cos\theta \times \sqrt{H^2 - H'^2}}$$ , where:

T - size of the particles (Å)
λ - X-Ray wavelength (Å).
θ - Bragg angle.
H - full width at half maximum (FWHM) of the measured line.
H' - full width at half maximum (FWHM) of the instrument's response.

[b)]The surface area is calculated assuming that the particles have a perfect spherical shape, S = 60000/ρ×d where:
ρ- Specific gravity of ceria (7.215 $g.cm^{-3}$)
d- Particle diameter (A°).

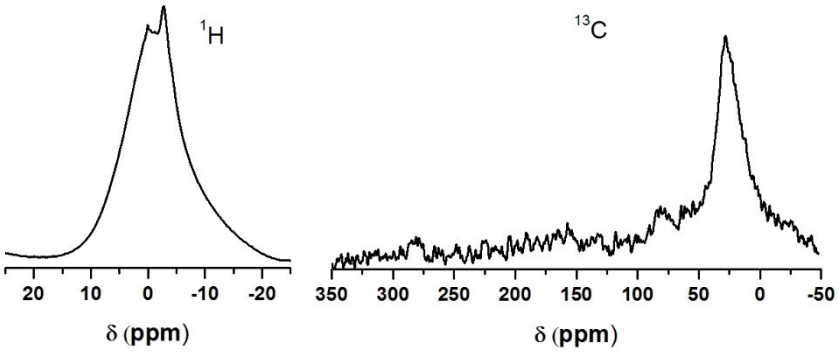


**Fig S5:** $^{1}$H MAS (left) and $^{13}$C (right), NMR spectra of W(≡CtBu)($CH_2$tBu)$_3$/$CeO_{2\text{-}200}$

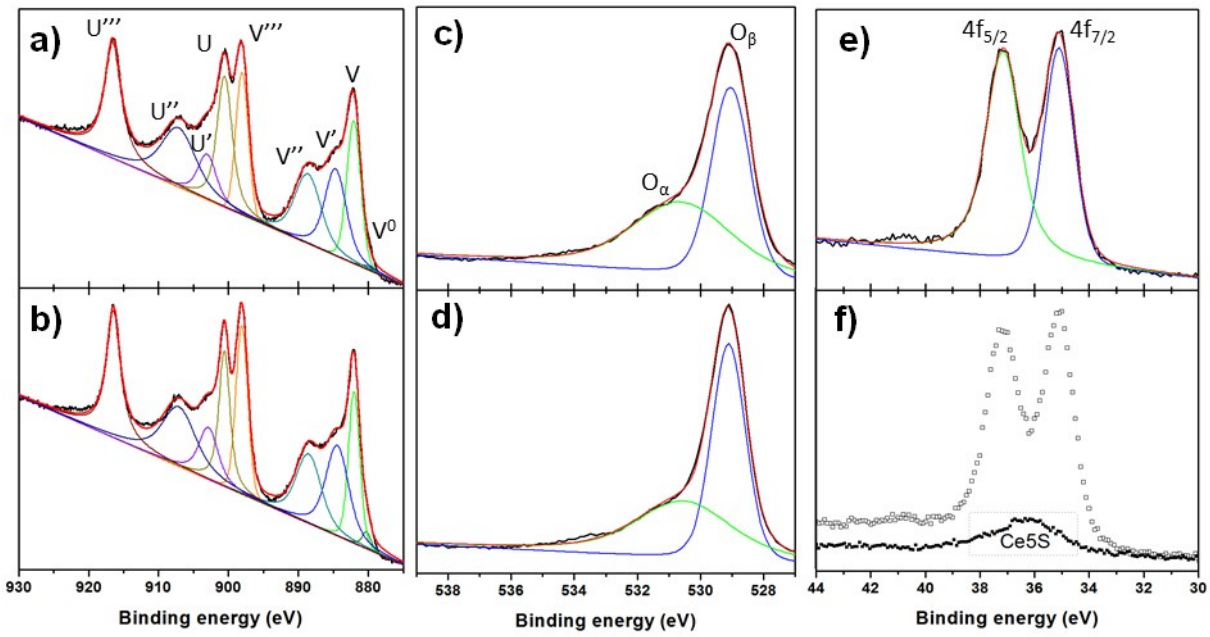


**Fig S6 :** XPS spectra of $CeO_{2\text{-}200}$; Ce3d (a), O1S (c) and W(≡CtBu)($CH_2$tBu)$_3$/$CeO_2$ catalyst; Ce3d (b), O1S (d), W4f (e). f) Shows the overlap of Ce5S signal of neat ceria and W4f of the catalyst.

**Table S2** Surface atom concentration of different elements estimated by XPS of $CeO_{2\text{-}200}$ and W(≡CtBu)($CH_2$tBu)$_3$/$CeO_2$ catalyst.

| Samples | Oα/(Oα + Oβ) % | $Ce^{3+}/(Ce^{4+} + Ce^{3+})$% |
|---|---|---|
| Ceria ($CeO_{2\text{-}200}$) | 45 | 32 |
| W(≡C*t*Bu)($CH_2$*t*Bu)$_3$/$CeO_2$ | 37 | 34 |

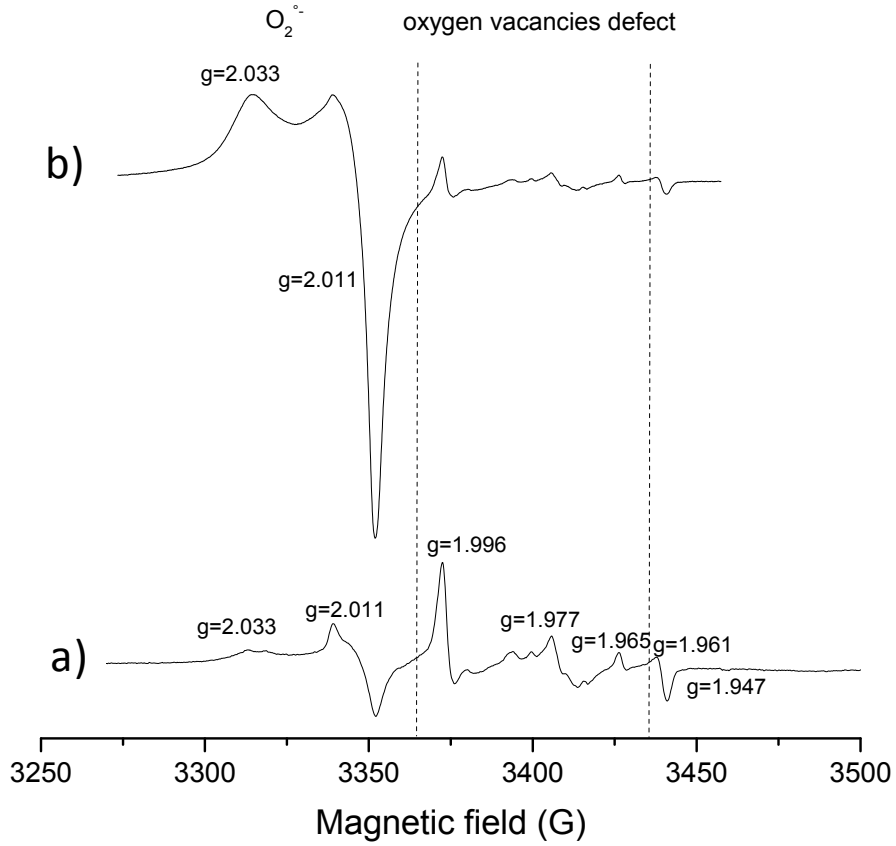


**Fig S7:** CW EPR spectra of $W(\equiv CtBu)(CH_2tBu)_3/CeO_{2\text{-}200}$ recorded at room temperature with microwave power of 1.6mW (a) and 0.6mW (b)

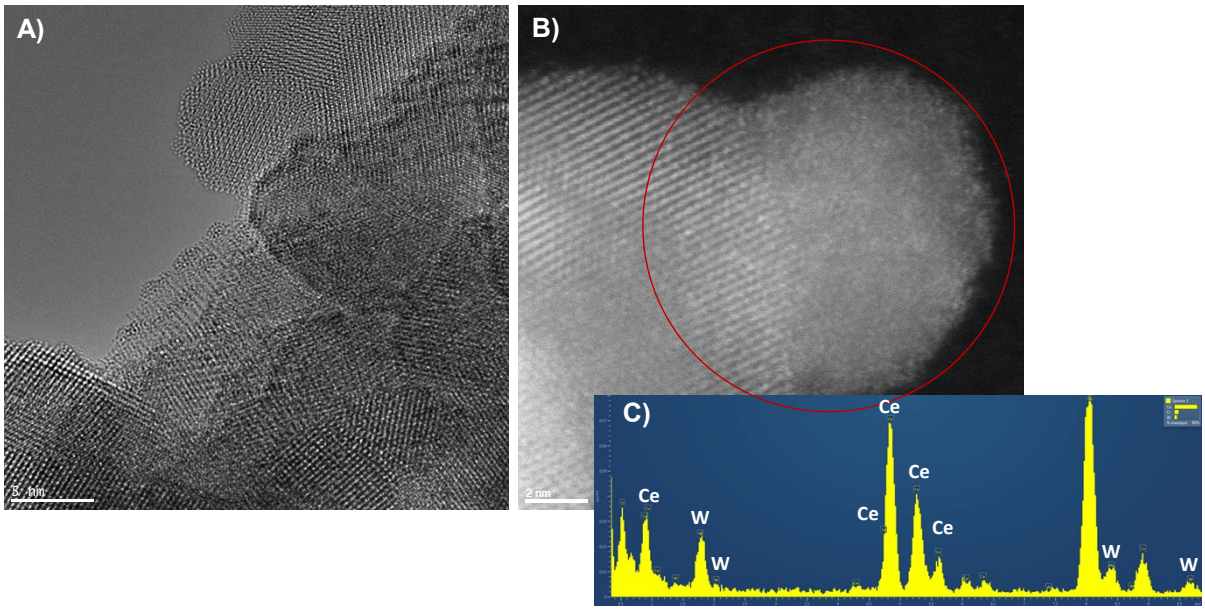


**Fig S8 :** HRTEM (a), STEM (b) and EDX analysis (c) of W(≡CtBu)($CH_2$tBu)$_3$/$CeO_2$.

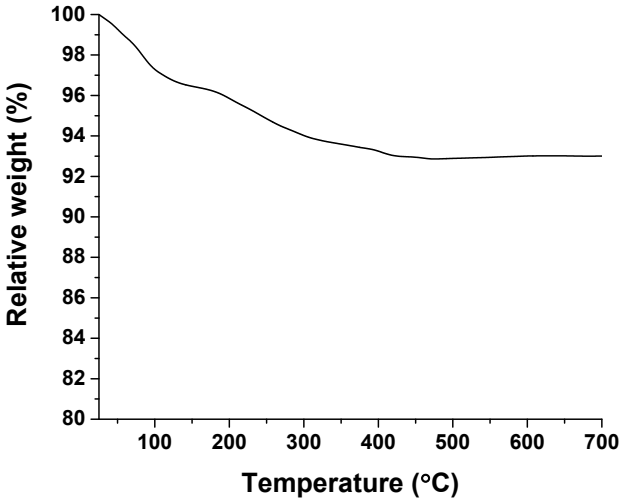


**Fig S9 :** TGA curve of W(≡CtBu)($CH_2$tBu)$_3$/$CeO_2$ under air (heating rate: 10 °C/min)

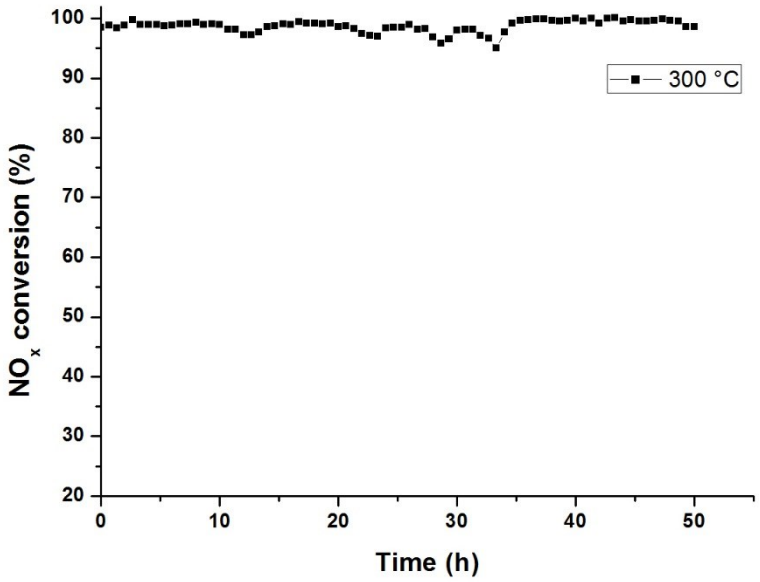


**Fig S10 :** Long terms catalytic stability for $NH_3$-SCR test of **1**.

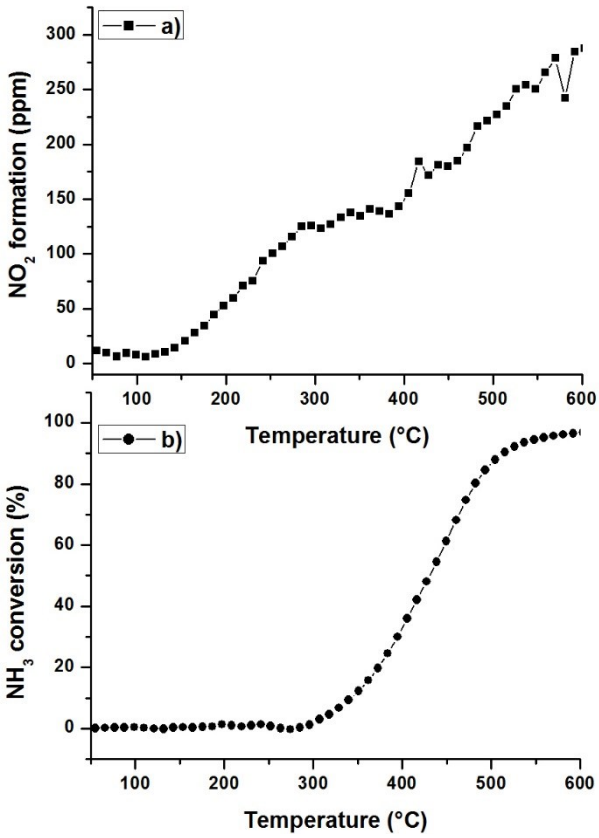


**Fig S11 :** Separate oxidation reaction of NO into $NO_2$ (a) and $NH_3$ (b) over **1**.

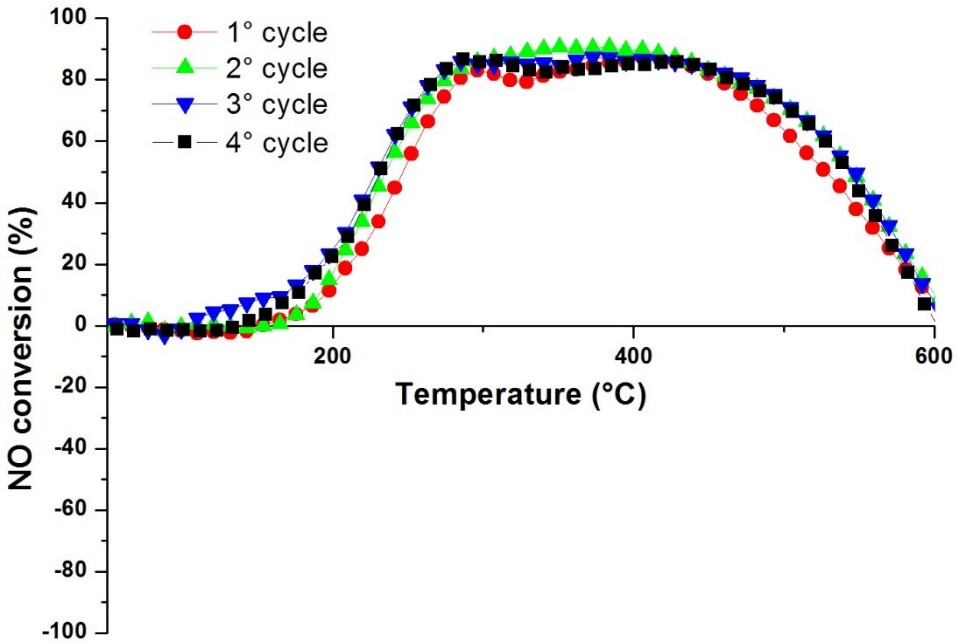


**Fig S12** : Recyclability of **2**, catalyst prepared by conventional method