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**ARTICLE**

**Well-Defined Surface Tungstenocarbyne complex through the Reaction of \([W(=CtBu)(CH_2tBu)_3]\) with CeO\(_2\) : a highly and stable precatalyst for NO\(_x\) reduction with NH\(_3\)**

Cherif Larabi, a Cuirong Chen, a Nicolas Merle,a,b Marc Charlin,a Kai C. Szeto,a Aimery de Mallmann,a Anas Benayad,c Karima B. Meziane,a Akim Kaddouri,a Hai P. Nguyen**,a and Mostafa Taoufik**a

A novel well-defined precatalyst for ammonia selective catalytic reduction of NO\(_x\) (NH\(_3\)-SCR), \([W(=CtBu)(CH_2tBu)_3]/\text{CeO}_2\), was prepared by surface organometallic chemistry and characterized. Due to the high dispersion of the active phase, this catalyst showed an excellent activity, after calcination at 500 °C, up to 99 % conversion of NO\(_x\), a high N\(_2\) selectivity, a broad operation temperature window (225 - 500 °C) and an extremely high durability for the selective catalytic reduction of NO\(_x\) with NH\(_3\).

**Introduction**

Significant worldwide increase of stationary thermal power plants and mobile combustion engines culminate with the production of large quantity of carbon dioxide and nitrogen oxides (NO\(_x\)). NO\(_x\) contributes to ecosystem damage, serious health issues and worsens the climate changes, through the greenhouse effect, acid rains and ozone destruction.1 Therefore, the emission level legislation of this pollutant has been drastically going down.2,3 The NO\(_x\) emissions have been minimized through improvements such as exhaust gas recirculation, homogeneous charge compression ignition technologies and optimized injection systems as well as improved air control.4 These reducing measures will lower the emission of NO\(_x\) albeit with the net increase of the participate matter (PM) amount and unburned hydrocarbons. As the PM and NO\(_x\) emission are totally dependent, the declining of the former trigger the rising of the latter and vice-versa. Thus, to improve the combustion engine efficiency and minimize fuel consumption, it is desirable to operate at a lean fuel mixture, this is typically the case, for diesel engine.5 Under these conditions, in addition to a complete combustion product (CO\(_2\) and H\(_2\)O), a significant amount of NO\(_x\) is produced. Therefore, exhaust gas after-treatment systems are necessary in order to meet the stringent harmful emission limits. Catalysis has made impressive development in the field of NO\(_x\) reduction, since the beginning of the eighties, by the implementation of the three way catalyst systems. However, the diesel exhaust composition brings new challenges that mobilized industries, researchers and authorities to meet many improvement and innovative measures. A most effective and useful method for NO\(_x\) removal without compromising the engine performances is the selective catalytic reduction (SCR) assisted with reducing agents (NH\(_3\) or hydrocarbon).6,7 The most efficient approach is SCR using ammonia (NH\(_3\)-SCR). This process leads to high NO\(_x\) conversions at fairly low temperatures and in large temperature ranges.8

Initially, this technology is set up in power plants and industrial installations for many years ago, but currently, the are extensively adopted to heavy-duty and light-duty trucks as well as to locomotives and ships. A wide range of SCR catalysts have been developed. The most commercially viable and utilized catalysts are TiO\(_2\) supported V\(_2\)O\(_5\) with WO\(_3\) or MoO\(_3\) as promoters.9,10 Though the catalytic activity of this class of materials is acceptable, they suffer from lots of weaknesses such as low selectivity, narrow operation temperature range, poor deNO\(_x\) activity at low temperature and beyond all, another central environmental issue due to the releasing of deleterious and toxic VO\(_x\) species.11 Hence, alternative catalysts based on transition (W, Nb, Mo, Zr, Ta)12 and rare earth metals (Ce, Y) have further been developed.13 In particular, relevant studies on new catalytic systems as WO\(_3\)-CeO\(_2\), NbO\(_2\)-CeO\(_2\), MnO\(_x\)-WO\(_3\)-CeO\(_2\), Cu-Zeolite and Fe-zeolite have brought important improvements in the field of NO\(_x\) reduction.13-15 Due to the oxygen buffering capacity and redox properties of the ceria, it is widely used in these processes.16 The major drawbacks of pure ceria are related to low thermal resistance and weak acidity. Hence, in order to improve these
properties, new ceria based catalysts have been developed by introducing other rare-earth or transition metal oxides such as ZrO$_2$, TiO$_2$ and their modification with WO$_3$, resulting in improved redox properties, thermal stability as well as surface acidity.$^{13,16}$

Recently, through several mechanistic studies, it has been found that the catalytic activity depends not only on the acidic and redox properties of the material.$^{10,17}$ but also on the metal-support interactions.$^{18}$ In particular, the nature of the supported tungsten species is a determining factor. The reported conventional catalysts are normally prepared by uncontrolled impregnation, resulting in different species, including isolated surface tungsten sites, WxOy clusters, amorphous WO$_3$ and Ce$_2$(WO$_4$)$_3$. Indeed, those phases are all observed by any characterization technique and this will thereby complicate the surface species identification and the drawing of structure-activity relationships.

It has been proposed that single-site heterogeneous catalysts with a controlled coordination sphere of the metal are highly effective for the selective reduction of NOx.$^{20}$ The key step is the formation of isolated supported metal species which improves the metal dispersion and increases the metal-support interactions. Therefore, a powerful approach known as surface organometallic chemistry (SOMC) can be applied in order to prepare such single-site species. This methodology involves controlled grafting of a suitable organometallic precursor onto a support, creating a firmly bonded surface organometallic fragment. Previous studies have shown that catalytic materials prepared through this approach can lead to an enhanced activity and facilitate further mechanistic studies.$^{21}$ Moreover, great efforts have been undertaken to achieve a high-performance catalysts via chemical design. It is believed that the missing link for automotive application catalysts is related to increasing the amount of nano-sized and atomic scale catalysts without impinging their size, structure, shape and interactions. This can be carefully monitored by surface organometallic chemistry.$^{22}$

However, commercial SCR catalysts are loaded with high amounts of WO$_3$, in order to ensure a higher stability and a sufficient acidity, thus increasing the NH$_3$ adsorption strength which improves the activity and also the selectivity by inhibiting the oxidation of NH$_3$. This phenomenon is also found in the case of industrial metathesis catalysts, where a high amount of metal such as tungsten, ca. 10 wt%, is required to reach high catalytic activities, despite only a low fraction of metal sites is active.$^{25}$ Based on studies that unravelled the structure of the active species,$^{26-28}$ surface organometallic chemistry has led to the development of well-defined highly active catalysts that contain only a low amount of metal.$^{29-31}$ On the other hand, surface organometallic chemistry on oxidizing support and for deNOx applications is rare. We hereby report the first example of a highly active deNOx catalyst with low loading prepared by the grafting a Schrock type tungsten complex on ceria along with its characterization.

**Results and discussion**
The grafting reaction was monitored by DRIFT spectroscopy (Figure 1). After surface functionalization of ceria by W(≡CtBu)(CH\textsubscript{3}Bu), the isolated ν(Ce-O-H) band at 3712 cm\textsuperscript{-1} disappeared. The new bands appearing in the 3100-2850 cm\textsuperscript{-1} and 1620-1400 cm\textsuperscript{-1} ranges are characteristic of aliphatic ν(C-H), and δ(C-H) vibrations of the perhydrocarbyl ligands coordinated to surface tungsten. Noteworthy, a band at 2120 cm\textsuperscript{-1}, which is absent in the neat ceria sample (Figure 1a) is observed (Figure 1b). This signal has already been found and ascribed to the forbidden 2F\textsubscript{7/2}\textrightarrow2F\textsubscript{5/2} electronic transition of the subsurface Ce\textsuperscript{3+} (due to the partial reduction of ceria).\textsuperscript{38} Moreover, the DRIFT spectrum of the resulting material (Figure 1b) shows a partial consumption of the other OH vibration bands, located between 3700 and 3600 cm\textsuperscript{-1}, while a new broad band appears, resulting from the interaction of some OH groups with tungsten alkyl ligands. The evolution of the signals in this spectral region with the grafting has already been described for the reaction of W(≡CtBu)(CH\textsubscript{3}Bu)\textsubscript{2} with alumina dehydroxylated at 500 °C, where only terminal tetrahedral Al sites react completely.\textsuperscript{39}

The X-ray diffraction analyses, depicted in Figure S4, revealed that the samples exhibit the same diffraction peaks at 28.5°, 33.1°, 47.5°, 56.4°, 59.1°, 69.7° and 79.1° characteristic of the cubic fluorite structure of CeO\textsubscript{2}.\textsuperscript{40} From the diffraction pattern, the mean size of the average crystal sizes thus estimated, summarized in Table S1, indicated that the ceria particles have the tendency to agglomerate during the grafting of the tungsten complex, which corroborates the slight lowering in the surface area.

The XPS measurements (Figure S5a,b and 1c) show that the samples exhibit the same diffraction peaks at 28.5°, 33.1°, 47.5°, 56.4°, 59.1°, 69.7° and 79.1° characteristic of the cubic fluorite structure of CeO\textsubscript{2}.\textsuperscript{40} Moreover, from a 30\% \textsuperscript{13}C labelled molecular complex, \textsuperscript{13}CP MAS NMR data highlighted in Figure S5b shows an intense and broad signal centered at 26 ppm assigned to the methyl of the t-Bu fragments and a broad, albeit weak signal at 80 ppm which can be assigned to the methylene carbons of the neopentyl fragment (CH\textsubscript{3}Bu). A weak signal at 287 ppm can be ambitiously attributed to the quaternary carbons of carbonyl ligands. The broadening of the resonances and their shift to higher field is presumably due to paramagnetic Ce\textsuperscript{3+} ions in trigonal and cubic sites present in the ceria support as already identified.\textsuperscript{41,42}

X-ray photoelectron spectroscopy analyses is carried out in order to provide more information on the oxidation state of the elements composing the sample (W, Ce, O). Figure 5b shows the representative XPS spectra for the Ce 3d, O 1s and W 4f area. Generally, ten features are found in the Ce 3d region due to the electronic transitions of different bonding states of Ce.\textsuperscript{43} Moreover, the DRIFT spectrum of a) ceria dehydroxylated at 200 °C. b) After the grafting of W(≡CtBu)(CH\textsubscript{3}Bu).
analysis was also used to investigate the oxidation state of tungsten loaded on the support. The W4f signal is depicted in Figure S6 e, it shows the presence of two signals attributed to W 4f7/2 and 4f5/2 at 37.5 and 35.3 eV respectively, after deconvolution. These values are characteristic of W (+VI) for the grafted complex. The W4f peaks overlap with the Ce 5s peaks, as shown in Figure S6 f, making discrepancies for the curve deconvolution. Nevertheless, these results are consistent with the presence of only W(+VI) but maybe with some light structure heterogeneities. Electron paramagnetic resonance (EPR) spectroscopy of the W(≡CtBu)(CH₂tBu)/CeO₂ material (Figure S7) did not show any signal of isolated W(V) ions expected with g factor between 1.39 and 1.85. This suggests that all tungsten atoms are present in oxide state of W(VI).

The sample with 3.3 wt% W was studied by X-ray absorption spectroscopy (Table 1 and Figure 2), in order to shed light on the structure of the supported species.

For the first peak of the Fourier transform (right in Figure 2), two levels of coordinated light atoms back-scatters could be evidenced at ca. 1.78 Å and 2.25 Å. Considering the level at 1.78 Å, two types of atoms, O and Ce were considered, oxygen coming from the ceria surface and carbon from a carbyne ligand. The parameters thus extracted from the fit of the EXAFS signal are in agreement with a bi-podal structure, (-O)₂W(≡CtBu)(CH₂tBu), with ca. two oxygen atoms at 1.78(1) Å, ca. one carbon atom at 1.78(1) Å and another one at 2.25(3) Å, attributed most probably to carbon atoms of a neopentylidyne and a neopentyl ligands respectively. The W-O distance seems lightly short but tungsten has been found to be surrounded by ca. six oxygen atoms at 1.787(1) Å in a W(C≡CtBu)(CH₂tBu) molecular complex (1.785(8) Å for W=tBu and 2.258(9) Å for WtBu).52 Similar parameters were obtained when fitting the kχ²(k) spectrum. The fit could be also improved by adding further layers of back-scatters, with in particular two types of oxygen atoms at 2.69(2) Å and 2.94(2) Å and only ca. one cerium atom at 3.57(3) Å. The inclusion of tungsten as a second neighbor was not statistically validated. Therefore, this EXAFS study suggests a single-site structure ([O]₂-W(≡CtBu)(CH₂tBu)), as the one represented in Figure 3, where the tungsten atom is in a pseudo-octahedral environment. The Ce-O bond distance is ca. 2.34 Å and the shortest Ce--Ce distance is ca. 3.83 Å.

Finally, W(≡CtBu)(CH₂tBu)/CeO₂ has been submitted for HRTEM study. The distribution of atomic tungsten on the surface of ceria was confirmed through indirect manner by HRTEM and STEM analyses (Figure S8). Indeed the combination of HRTEM and STEM with EDX analyses showed the homogeneity of the sample. No observable cluster or nanoparticles even when extensive magnification (ca 1 nm) was applied, but at the same time the EDX examination confirmed the presence of tungsten has been investigated. The grafting occurs on Ce-OH groups by protonolysis, affording bipodal species, as suggested by quantification of released neopentane and elemental analysis. Further characterizations by DRIFT and solid state NMR confirm the presence of neopentyl fragments on the

![Figure 2. W L3-edge k²-weighted EXAFS (left) and its Fourier transform (right) for W(≡CtBu)(CH₂tBu)/CeO₂ material. Solid lines: experimental and dashed lines: spherical wave theory.](image)

The reactivity of W(≡CtBu)(CH₂tBu) with CeO₂ dehydroxylated at 200 °C has been investigated. The grafting occurs on Ce-OH groups by protonolysis, affording bipodal surface species, as suggested by quantification of released neopentane and elemental analysis. Further characterizations by DRIFT and solid state NMR confirm the presence of neopentyl fragments on the surface of ceria was confirmed through indirect manner by HRTEM and STEM analyses (Figure S8). Indeed the combination of HRTEM and STEM with EDX analyses showed the homogeneity of the sample. No observable cluster or nanoparticles even when extensive magnification (ca 1 nm) was applied, but at the same time the EDX examination confirmed the presence of tungsten.

![Figure 3. Proposed structure for the species resulting from the grafting of W(≡CtBu)(CH₂tBu) onto CeO₂](image)

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material. Tungsten, mainly at oxidation state VI has been revealed by XPS and EXAFS. XPS further provides quantitative information about the Ce⁴⁺/Ce⁴⁺ ratio on the surface upon grafting. A more representative environment around tungsten on the surface is proposed by EXAFS data. Surprisingly, there is only one cerium atom being close to the tungsten center. The proposed model (Figure 3) fits well with the data and comprises isolated bipodal tungsten surface species, as also indicated by elemental analysis and HRTEM.

Catalytic activity tests
The precatalyst \( W(=C\text{Bu})(\text{CH}_2\text{Bu})_3/\text{CeO}_2-200 \) has been calcined under dry air at 500 °C for 16 h, allowing removal of organic ligands (Figure 59) and affording catalyst 1 prior the evaluation for the selective reduction of \( \text{NO}_x \) in a continuous flow reactor. The temperature dependencies of the \( \text{NO}_x \) reduction are depicted in Figure 4. 1 shows more than 95 % conversion of \( \text{NO}_x \) between 280 and 400 °C (Figure 4, 1st cycle). Indeed, a high activity at low temperature (200-250 °C) with a sharp increase of the conversion with temperature is observed. The selectivity for \( \text{N}_2 \) is outstandingly high until 400 °C (Figure 4). The fresh catalyst starts to oxidize \( \text{NH}_3 \) from ca. 400 °C, resulting in a fast drop in the \( \text{NO} \) conversion and \( \text{N}_2 \) selectivity. However, upon repeating SCR cycles, it can be observed that the same catalyst becomes more stable, selective and temperature resistant. Full \( \text{NO} \) conversion is kept until 550 °C. Such evolution indicates that the surface sites responsible for \( \text{NH}_3 \) oxidation have gradually been inhibited. After five catalytic recycle tests, the catalyst seems to be stable and converts more than 99% \( \text{NO}_x \) between 250 and 500 °C. This suggest that the surface species occur under the catalytic conditions (\( \text{O}_2 \), \( \text{NH}_3 \), \( \text{NO} \) and high temperatures) to reach stable and more active species.

Moreover, long terms stability of the catalyst at 300 °C was also studied. The results depicted in Figure S10 indicated that the activity of the catalysts remains stable for more than 50 h, with a conversion of about 99%. To extend the behavior of this catalysts for \( \text{deNOx} \) related reactions, two experiments with a separate (\( \text{NO} + \text{O}_2 \)) and (\( \text{NH}_3 + \text{O}_2 \)) feed were performed. The results of \( \text{NO} \) and \( \text{NH}_3 \) oxidation versus temperature, presented in Figure S11, show that the oxidation of \( \text{NO} \) into \( \text{NO}_2 \) occurs at low temperature, ca. 150 °C and increase linearly with the temperature to reach a pseudo-plateau between 280 and 380 °C before increasing gradually again. The first part of the curve can be explained by role of the surface oxygen available that can promote the oxidation of the \( \text{NO} \) into \( \text{NO}_2 \) to reach a plateau when the oxygen are consumed. Then, thermal oxidation can follow. In contrast, the oxidation of \( \text{NH}_3 \) did not take place before the reaction temperature reaches 300 °C, where a sharp increase was observed for temperatures higher than 300 °C. This can explain the high activity observed for this SOMC catalysts (1) where the oxidation of \( \text{NO} \) into \( \text{NO}_2 \) is favored over \( \text{NH}_3 \) oxidation, the \( \text{NO}_2 \) can promote the fast SCR.

Additional catalysis cycles have been investigated in the presence of 5% water (Figures 5), reflecting a more realistic conditions in combustion engines. Although the activity in the first cycle is far lower, that can be explained by strong adsorption of water on the surface, the same tendency upon multiple recycling tests remains the same. After each catalytic run, the activity improves.

This better activity is due to a better W dispersion on the ceria where only isolated sites are obtained in the case of the catalyst prepared through SOMC approach, contrary to catalysts prepared by classical methods (2) composed of a statistical distribution of surface species (Figure S12). Thus, the catalytic behavior is highly dependent on the preparation method. The well-controlled distribution of the W species on the surface of ceria prepared through the advanced surface organometallic functionalization could result in a higher concentration and strength of the Brønsted acids sites in or in the formation of \( W_9\text{Ce}_{14}\text{O}_{38} \) alloy clusters on the surface, being highly active and more accessible to the reactants.

Conclusions

Figure 4. \( \text{NO} \) conversion. \( \text{N}_2 \) selectivity over 1 in function of temperature during 7 cycles. Feed composition: 300 ppm \( \text{NO} \), 350 ppm \( \text{NH}_3 \) and 10 vol. % \( \text{O}_2 \) in He.

Figure 5. \( \text{NO} \) conversion. \( \text{N}_2 \) selectivity over 1 in function of temperature during 5 cycles. Feed composition: 300 ppm \( \text{NO} \), 350 ppm \( \text{NH}_3 \), 5 vol. % \( \text{H}_2\text{O} \) and 10 vol. % \( \text{O}_2 \) in He.
Present work describes the first example of deNOx catalyst prepared by surface organometallic chemistry. Grafting of W(≡C\text{tBu})(\text{CH}_3\text{Bu})_3 on CeO$_2$ dehydroxylated at 200 °C affords isolated bipodal species, as revealed by DRIFT, solid state NMR, elemental analysis, TEM, XPS and EXAFS. The catalyst transforms NO and NH$_3$ to N$_2$ in a typical exhaust gas composition after calcination at 500°C, with almost full conversion between 280 – 400 °C. Importantly, when multiple SCR cycles were studied, the catalytic performance increased, leading to a full conversion of NO in the 220 – 500 °C temperature range including in the presence of 5 vol.% water. Such an evolution is surprising, and is presumably due to an inhibition of NH$_3$ oxidation by flawed sites of ceria. The good dispersion of tungsten may also increase the acidity and the oxygen buffering capacity of the material and thereby result in a more active SCR catalyst. Ongoing experiments using in-operando techniques (EXAFS and DRIFT) during the recycling process should provide information on the evolution of the catalyst when increasing the number of SCR cycles and explain the higher activity by identification of different sites on the surface.

**Experimental**

All syntheses were performed under pure and dry argon, using a standard Schlenk techniques and a glove box. Solvents were purified and dried according to standard procedures. C$_6$D$_6$ (Aldrich, 99.8%) was distilled over Na/benzophenone and stored on NaK.

**Characterization methods**

Elemental analyses were performed at Mikroanalytisches Labor Pascher (Remagen, Germany). Gas-phase analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector and a KCl/Al$_2$O$_3$ column (30 m × 0.32 mm). Diffuse reflectance infrared spectra were collected in a Nicolet 6700 FT-IR spectrophotometer in 4 cm$^{-1}$ resolution. An air-tight IR cell with CaF$_2$ windows was applied and the final spectra comprise 64 scans. Solution NMR spectra were recorded on an Avance-300 Bruker spectrometer. All chemical shifts were measured relative to residual $^{1}$H or $^{13}$C resonances in the deuterated solvent: C$_6$D$_6$, 6.715 ppm for $^{1}$H, 128 ppm for $^{13}$C. $^{1}$H and $^{13}$C solid-state NMR spectra were recorded on Bruker Avance-500 spectrometers with a conventional double-resonance 4 mm CP-MAS probe. The samples were introduced under argon in a zirconia rotor (4 mm), which was then tightly closed. In all experiments, the rotation frequency was set to 10 kHz. Chemical shifts were given with respect to tetramethylsilane (TMS) as external reference for $^{1}$H and $^{13}$C NMR. X-ray diffraction was performed on a Siemens D8 diffractometer at Bragg-Bretano geometry (ISA, Villerubanne). The instrument is equipped with Cu-tube ($\lambda = 1.5406$ Å). The Electron paramagnetic resonance (EPR) continuous-wave (CW) measurements were performed through sealed quartz tube on X-Band Bruker ELEXSYS E500 spectrometer operating at 9.8 GHz. Spectra were recorded with the same modulation frequency (100 kHz), the same modulation of amplitude and the same power level for each sample. In order to avoid the saturation effect, the measurements were made at different microwave power levels (0.1-4 mW). The modulation of amplitude (1-5 G) was adjusted for the same reason. The low-temperature measurements were made with cryogenic systems. Transmission electron microscopy was executed on an environmental tomographic transmission electron microscope by FEI TITAN (IRCE Lyon, Villeurbanne). TGA was performed on a Mettler Toledo TGA2 Star® system.

Extended X-ray absorption fine structure (EXAFS) spectra were acquired at ELETTRA, using XAFS beam-line (experiment code: 20145422) at room temperature at the tungsten L$_{3}$-edge. A pair of Si(111) crystals were used as monochromator and the harmonics were rejected by a detuning of the second crystal. The spectra were recorded in the transmission mode between 9.9 and 11.43 keV. Three scans were collected for each sample. Each data set was collected simultaneously with a W metal foil reference (11206.7 eV), and was later aligned according to that reference (maximum in the first derivative of the W foil first peak). The W supported sample was packaged within a nitrogen filled glovebox in a double air-tight sample holder equipped with kapton windows. The data analyses were carried out using the program “Athena” and the EXAFS fitting program “RoundMidnight”, from the “MAX” package, using spherical waves. The program FEFF8 was used to calculate theoretical files for phases and amplitudes based on model clusters of atoms. The scale factor, $S_0^2 = 0.94$, was evaluated from [W(≡C\text{tBu})N$_3$] molecular complex diluted in BN and conditioned as a pellet (one carbon at 1.76(1) Å, with three carbon atoms at 2.10(1) Å in the first coordination sphere and one carbon atom at 3.25(3) Å and three carbon atoms at 3.34(3) Å). The refinements were carried out by fitting the structural parameters Ni, Ri, $\theta$, and the energy shift, $\Delta E_0$ (the same for all shells).

**Materials**

Ceria (CeO$_2$) HAS-5 Actalys 922 from Solvay (“Rare Earth La Rochelle”) was calcined for 16 h at 500 °C under a flow of dry air, then evacuated under vacuum at high temperature. After a re-hydration under an inert atmosphere, the ceria was partially dehydroxylated at 200 °C under a high vacuum (10$^{-5}$ mbar) for 15 h to give a yellow solid, noted as CeO$_2$-$500$.

Tungsten complexes [W(≡C\text{tBu})(\text{CH}_3\text{Bu})$_5$]$_{56}$ as well as 30% labelled W(≡C\text{tBu})(\text{CH}_3\text{Bu})$_3$ were prepared according to the described procedures.

**Catalysts preparation - SOMC catalyst**

A mixture of W(≡C\text{tBu})(\text{CH}_3\text{Bu})$_3$ (1.6 g, 1.2 mmol) and CeO$_2$-$500$ (7 g) was stirred in pentane (Carlo Erba, 99%) for 4 h, at room temperature. The W(≡C\text{tBu})(\text{CH}_3\text{Bu})$_3$/CeO$_2$-$500$ material was washed three times with pentane via filtration-condensation cycles. Then, all volatiles were condensed into a 6 L vessel in order to quantify neopentane evolved during the grafting reaction. After evaporation of the solvent, the resulting grey powder was dried under vacuum (10$^{-5}$ mbar). The material was calcined under dry air at 500 °C for 16 h prior the catalytic tests.
Catalysts preparation - Conventional catalyst

For comparison, the impregnated catalyst based on tungsten (W) supported on ceria was prepared by a conventional wet impregnation. In a typical reaction, at room temperature a water solution of ammonium metatungstate (Aldrich, 99.99%), (NH₄)₆H₃W₁₈O₆₆, 100 mg in 5 mL of water) was added to 2 g of ceria. The suspension was stirred overnight at room temperature and then water was evaporated in a rotary evaporator at 50 °C. The material obtained was then calcined under dry air at 500 °C for 16 h. The elemental analysis indicated the presence of ca. 3.5 wt% W.

NH₃-SCR Catalytic performance tests

The NH₃-SCR catalytic evaluations were performed in a quartz fixed-bed reactor. A total gas flow rate of 300 mL·min⁻¹ (hourly space velocity: 30000 h⁻¹) at atmospheric pressure, typically composed of 300 ppm NO (Air Liquid, Crystal grade), 350 ppm NH₃ (Air Liquid, Crystal grade), 10 vol. % O₂ (Air Liquid, Crystal grade) and 5% H₂O (when used), was sent through 30 mg of the presented catalyst diluted with 500 mg of silicon carbide, in order to ensure a volume of 1 cm³. The reactor equipped with an internal thermometer, was heated from room temperature to 600 °C with a heating rate of 10 °C·min⁻¹. The system was kept at 600 °C for 10 min before cooling down. Analyses of the gas temperature and then water was evacuated in a rotary evaporator at 50 °C. The material obtained was then calcined evaporator at 50 °C. The material obtained was then calcined in order to ensure a volume of 1 cm³. The reactor equipped with an internal thermometer, was heated from room temperature to 600 °C with a heating rate of 10 °C·min⁻¹. The system was kept at 600 °C for 10 min before cooling down. Analyses of the gas concentrations of NO, NO₂, N₂O and NH₃ were carried out using Antaris IGS FTIR (Thermo-Fischer) equipped with a gas cell of 200 mL. N₂ selectivity was evaluated assuming that the outlet gas contains no other N-compounds than NO, NO₂, N₂O and NH₃ (Scheme 2).

\[
\begin{align*}
6\text{NO} + 4\text{NH}_3 & \rightarrow 5\text{N}_2 + 6\text{H}_2\text{O} \\
4\text{NO} + 4\text{NH}_3 + \text{O}_2 & \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \\
6\text{NO}_2 + 8\text{NH}_3 & \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O} \\
2\text{NO}_2 + 4\text{NH}_3 + \text{O}_2 & \rightarrow 3\text{N}_2 + 6\text{H}_2\text{O} \\
\text{NO} + \text{NO}_2 + 2\text{NH}_3 & \rightarrow 2\text{N}_2 + 3\text{H}_2\text{O}
\end{align*}
\]

Scheme 2. Reactions occurring during the SCR of NO, with NH₃.

The catalytic activity and N₂ selectivity were calculated by the following equations:\(^{19}\)

\[
\text{NO conversion} (%) = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}} - [\text{N}_2O]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100
\]

\[
\text{N}_2 \text{ selectivity} (%) = \frac{[\text{N}_2]_{\text{out}} + [\text{N}_2O]_{\text{out}} - 2[\text{N}_2]_{\text{out}} - [\text{N}_2H]_{\text{out}}}{[\text{N}_2]_{\text{in}} + [\text{NO}]_{\text{in}}} \times 100
\]

Conflicts of interest

There are no conflicts to declare.

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