

WO₃/CeO₂/TiO₂ Catalysts for Selective Catalytic Reduction of NO_x by NH₃: Effect of the Synthesis Method

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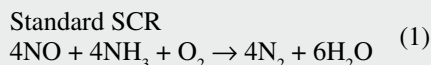
[§]SCS-DSM Award for best poster presentation

Abstract: WO₃/CeO₂/TiO₂, CeO₂/TiO₂ and WO₃/TiO₂ catalysts were prepared by wet impregnation. CeO₂/TiO₂ and WO₃/TiO₂ showed activity towards the selective catalytic reduction (SCR) of NO_x by NH₃, which was significantly improved by subsequent impregnation of CeO₂/TiO₂ with WO₃. Catalytic performance, NH₃ oxidation and NH₃ temperature programmed desorption of wet-impregnated WO₃/CeO₂/TiO₂ were compared to those of a flame-made counterpart. The flame-made catalyst exhibits a peculiar arrangement of W-Ce-Ti-oxides that makes it very active for NH₃-SCR. Catalysts prepared by wet impregnation with the aim to mimic the structure of the flame-made catalyst were not able to fully reproduce its activity. The differences in the catalytic performance between the investigated catalysts were related to their structural properties and the different interaction of the catalyst components.

Keywords: Flame spray synthesis · NH₃ · NO_x reduction · SCR · Wet impregnation

Introduction

The major source of nitrogen oxides (NO_x) emissions is the combustion of fossil fuels in vehicle engines and power plants. NO_x are formed thermally in the combustion process from N₂ and O₂ present in the supplied air. They are a major source of air pollution causing the formation of ozone, photochemical smog and acid rain.^[1] NO_x emissions from lean burn diesel engines are efficiently treated by the selective catalytic reduction using ammonia (NH₃-SCR) (Eqn. (1)).^[2,3]



Catalysts based on V₂O₅–WO₃/TiO₂ are most widely used in automotive and stationary applications. However, this very efficient catalytic system suffers from several drawbacks. Low thermal and hydrothermal stability with the resulting catalyst deactivation and simultaneous release of tungsten and vanadium species to the environment are the most detrimental. Therefore, there is an urgent demand to develop new thermally stable catalysts, which should also be cost-effective. In recent years, CeO₂ has received considerable attention in three-way catalysis due to its oxygen storage capacity and the high redox ability of the Ce⁴⁺/Ce³⁺ pair, which make it attractive also for use in SCR catalysts.^[4] CeO₂ possesses some intrinsic SCR activity,^[5] but its performance improves significantly when it is functionalized by another transition metal oxide. CeO₂-TiO₂ and CeO₂-WO₃-TiO₂ catalysts synthesized by various techniques, *e.g.* wet impregnation (WI),^[6] sol-gel (SG),^[7] co-precipitation (CP)^[8] or flame spray synthesis (FSS),^[9] displayed remarkable SCR activity. Recently, we have shown that understanding of the catalyst structure and the interaction of the catalyst components is crucial for the optimization of its performance.^[9b] Flame-made WO₃/CeO₂/TiO₂ nanomaterials demonstrated excellent activity for the selective catalytic reduction of NO_x by NH₃. The highest activity was observed for 10 wt% WO₃/10 mol% CeO₂-90 mol% TiO₂, which was comparable to a benchmark V-W/Ti catalyst. This

exceptional catalytic performance was related to its peculiar structure (Fig. 1) where CeO₂ protrusions on TiO₂ particles are homogeneously covered by amorphous WO₃. The arrangement of the metal oxide phases on TiO₂ is opposite to that commonly applied in conventional synthesis procedures. Moreover, we have shown that TiO₂ is not only a support material but its close interaction with CeO₂ is crucial to induce high surface concentration of Ce³⁺, which is considered an SCR active site. The presence of a layer of amorphous WO₃ on the surface of the entire catalyst provided an appropriate surface acidity for NH₃ adsorption and significantly improved N₂ selectivity. Therefore, the arrangement and

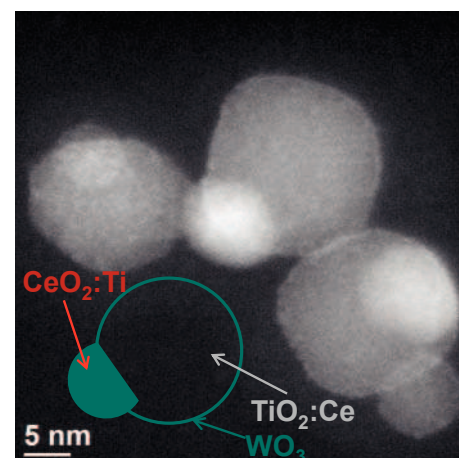


Fig. 1. STEM image of FSS-W/Ce/Ti with schematic illustration of the material composition.

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the interaction between each component in the catalyst are essential for its activity.

In this work, we tried to mimic the peculiar composite-like structure of the catalyst obtained by flame spray synthesis using conventional wet impregnation, which is cheaper and widely used. For this purpose we replicated the flame-spray catalyst by depositing CeO₂ on TiO₂ followed by impregnation with the tungsten precursor. The main purpose of this study was to unravel the effect of the arrangement of WO₃ on the catalyst activity.

Experimental

Synthesis

The SCR catalysts, with the compositions listed in Table 1, were prepared by wet impregnation (WI) and flame spray synthesis (FSS). Commercially available TiO₂ (DT51, Crystal Global) was suspended in water by ultrasonication; then, an aqueous solution of cerium (III) nitrate (Ce(NO₃)₃·6H₂O, assay ≥ 99%, Fluka) or ammonium metatungstate ((NH₄)₁₀(H₂W₁₂O₄₂·4H₂O, assay 85%, Aldrich) was added to obtain 10 mol% Ce/90 mol% TiO₂ and 10 wt% WO₃/TiO₂, respectively. After 10 min of ultrasonication, mixing in the rotavapor for 1 h and drying in vacuum at 70 °C, the powders were further dried in the oven at 120 °C for 12 h and calcined at 550 °C for 5 h. The 10 mol% Ce/90 mol% TiO₂ powder was ball milled (600 rpm, 2 min) with the addition of water and further impregnated with ammonium metatungstate ((NH₄)₁₀(H₂W₁₂O₄₂·4H₂O, assay 85%, Aldrich) to obtain 10 wt% WO₃/10 mol% Ce/90 mol% TiO₂.

In the case of flame-spray synthesis, titanium diisopropoxide bis(acetylac-

tonate) (TiC₁₆H₂₈O, 75% in isopropanol, ABCR), cerium (III) ethylhexanoate (Ce[OOCCH(C₂H₅)C₄H₉]₃, Ce content: 11.8–12.2%, Shepherd) and tungsten carbonyl (W(CO)₆, Sigma-Aldrich) precursors were dissolved in tetrahydrofuran (Sigma-Aldrich). Details of the flame spray setup are reported elsewhere.^[10] The required composition of the produced particles was obtained by adjusting the ratios of the different precursors in the precursor mixture. The total precursor concentration in the flame was kept constant at 0.5 mol·kg⁻¹. The precursor solution was fed by a syringe pump and was atomized by oxygen in a gas-assisted external mixing nozzle. The combustible aerosol was ignited by six acetylene-oxygen flamelets (C₂H₂, 217 cm³·s⁻¹; O₂, 283 cm³·s⁻¹) and the produced particles were collected on glass fiber filters (GF/A 150, Whatman) using vacuum pumps.

Structural Characterization

The specific surface area (SSA) was determined using a Quantachrome Autosorb 1C instrument from the N₂ adsorption/desorption isotherm using the Brunauer-Emmett-Teller (BET) method. Prior to analysis, powder samples were dried for 120 min at 180 °C in N₂.

X-ray diffraction (XRD) patterns were collected in the range of 5° < 2θ < 80° using a Bruker D8 Advance diffractometer equipped with a Ni-filtered Cu-Kβ radiation and a LinxEye detector. The phase identification was based on inorganic crystal structure database (ICSD) data files.

Catalytic Activity

NH₃-SCR experiments were conducted in a quartz tube plug flow reactor. The catalyst (50 mg) was mixed with 0.5 g of

100–160 μm cordierite and firmly fixed between two quartz wool plugs. A thermocouple was inserted at the front end of the catalyst bed. The sample was pre-treated with 10 vol% O₂ in N₂ supplied at 450 °C for 45 min. The model gas feed for the activity test was composed of 10 vol% O₂, 5 vol% H₂O, 1000 ppm NO, 1200 ppm NH₃ (N₂ bal.). For NH₃ oxidation experiments, the feed gas consisted of 1000 ppm NH₃, 10 vol% O₂, 5 vol% H₂O (N₂ bal.). For all experiments, the gas flow rate was 100 mL·min⁻¹ (GHSV = 120 L·g⁻¹·h⁻¹). The reactor effluent was monitored online by FTIR spectroscopy (Thermo Scientific Antaris). The NO_x conversion expressed as DeNO_x was calculated as follows:

$$DeNO_x = \frac{NO_{x,in} - NO_{x,out}}{NO_{x,in}} \quad (2)$$

with

$$NO_x = C_{NO_+} + C_{NO} + 2 \cdot C_{N_2O} \quad (3)$$

Temperature Programmed Desorption

NH₃ temperature programmed desorption (NH₃-TPD) was applied to assess the surface acidity of the catalysts and their NH₃ uptake (normalized by mass and specific surface area of the material). NH₃-TPD was performed in the same quartz tube plug flow reactor used for the catalytic tests. Prior to TPD, the sample was pre-treated with 10 vol% O₂ in N₂ at 500 °C for 1 h and then cooled to 50 °C in N₂. NH₃ (1000 ppm in N₂) was supplied for adsorption for 1 h at 50 °C. The physisorbed species were removed by flowing N₂ at 50 °C for 1 h. The NH₃-TPD were carried out under N₂ flow from 50 to 500 °C at 10 °C·min⁻¹. The gas composition was monitored online by FTIR spectroscopy (Thermo Scientific Antaris). Deconvolution of the TPD profiles was carried out with the Fityk program for data processing and nonlinear curve fitting.^[11]

Results and Discussion

WO₃/CeO₂/TiO₂ SCR catalysts were prepared by two different synthesis methods: wet impregnation and flame spray synthesis. Binary CeO₂/TiO₂ and WO₃/TiO₂ were also prepared in order to rationalize the effect of each component on the catalytic performance. The composition of all catalysts is listed in Table 1.

The comparison of the X-ray diffraction patterns of the catalysts (Fig. 2) shows clear structural dissimilarities that can be associated with the synthesis methods. The commercial TiO₂ support for wet-impreg-

Table 1. Composition, specific surface area (SSA), WO₃ coverage and NH₃ uptake of all catalysts.

Sample name	Composition	SSA / m ² ·g ⁻¹	WO ₃ coverage ^a / –	NH ₃ uptake / ppm m ⁻²
V-W/Ti	2.4 wt% V ₂ O ₅ -10 wt% WO ₃ / TiO ₂	60.5	0.95	6771
FSS_Ti	TiO ₂	93.3	–	6820
FSS_W/Ti	10 wt% WO ₃ / TiO ₂	89.9	0.64	7047
FSS_Ce/Ti	10 mol% CeO ₂ /90 mol% TiO ₂	95.6	–	4708
FSS_W/Ce/Ti	10 wt% WO ₃ / 10 mol% CeO ₂ /90 mol% TiO ₂	94.0	0.64	5540
WI_Ti	TiO ₂ (DT51) untreated	93.1	–	21929
WI_Ti-550	TiO ₂ (DT51) after 550 °C heat treatment	74.3	–	–
WI_W/Ti	10 wt% WO ₃ / TiO ₂	61.0	0.95	9092
WI_Ce/Ti	10 mol% CeO ₂ /90 mol% TiO ₂	65.1	–	5737
WI_W/Ce/Ti	10 wt% WO ₃ / 10 mol% CeO ₂ /90 mol% TiO ₂	53.2	1.09	6436

^aWO₃ monolayer = 4.5 W atoms·nm⁻²^[14]

nation (WI_Ti) consists of the metastable anatase polymorph (ICSD 01-084-1285), which retained its structure after calcination at 550 °C (Fig. 2a) despite the loss of *ca.* 20% of specific surface area (SSA, Table 1). Anatase was the only TiO₂ phase present in the WI samples. Wet impregnation of TiO₂ by WO₃, CeO₂ and by both of them followed by calcination gradually decreased the SSA but did not affect the primary structure of the support. XRD indicates that both WO₃ and CeO₂ are present in crystalline form in WI_W/Ti, WI_Ce/Ti and WI_W/Ce/Ti catalysts suggesting the clear separation of each oxide component at least at XRD level. Given the low contribution of cubic WO₃ (ICSD 00-046-1096) to the XRD of WI_W/Ti, we can assume that this phase coexists with a fraction of amorphous WO₃. On the contrary, the XRD patterns of FSS_W/Ti and FSS_W/Ce/Ti catalysts did not show any indication of crystalline WO₃ (Fig. 2b) supporting the evidence that WO₃ formed only an amorphous layer on TiO₂ and on CeO₂/TiO₂ (Fig. 1). A significant difference can also be seen between diffraction patterns of WI_Ce/Ti and FSS_Ce/Ti catalysts. In the former catalyst, cerium is present as crystalline cubic CeO₂ (ICSD 00-004-0593) and does not form phases with tungsten or titanium. The diffraction pattern of FSS_Ce/Ti is more complicated. Beside cubic CeO₂, the brannerite CeTi₂O₆ (ICSD 01-084-0496) structure was detected which is indicative of a defined Ce-Ti interaction. Moreover, the fraction of rutile TiO₂ (ICSD 01-087-0920), the thermally stable TiO₂ polymorph, significantly increases at the expense of anatase. The phase transformation was associated with the presence of a large fraction of Ce³⁺ observed by XPS and by its incorporation in the TiO₂ lattice.^[9b] Oxygen vacancies allow structural rearrangement and promote an anatase to rutile transformation.^[12] Diffraction patterns of WI_W/Ce/Ti and FSS_W/Ce/Ti appear as the simple combination of the patterns of the corresponding binary systems.

The structural differences between wet-impregnated and flame-made materials caused the observed changes of NH₃-SCR activity. Addition of WO₃ (WI_W/Ti) improved significantly the performance of bare TiO₂ (Fig. 3) with full NO_x conversion (DeNO_x) at 400 °C, which rapidly dropped to 13% at 300 °C. The DeNO_x curve of WI_W/Ti was shifted to lower temperature compared to that of the same composition prepared by flame-spray synthesis (FSS_W/Ti). This difference could be attributed to the high coverage of mixed crystalline and amorphous WO₃ in WI_W/Ti.^[13] The difference in the catalytic activity is even more pronounced for the Ce/Ti samples. The operating temperature win-

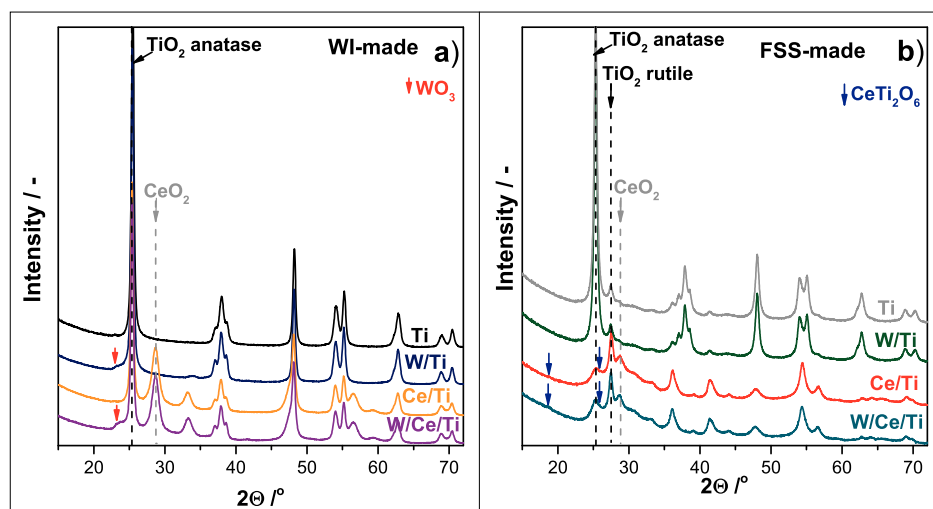


Fig. 2. X-ray powder diffraction patterns of wet-impregnated (a) and flame-made (b) catalysts.

dow of FSS_Ce/Ti was extended towards low temperature, showing more than 30% DeNO_x at 200 °C and nearly full conversion at 300 °C. In contrast, the DeNO_x curve of WI_Ce/Ti presented a maximum of conversion of only 49% at 300 °C, the overall performance of this material being inferior to that of the flame-made counterpart. WI_Ce/Ti was also less selective and produced a significant amount of undesired N₂O, 88 ppm at 300 °C. Under the same SCR experimental conditions, FSS_Ce/Ti produced only 17 ppm of N₂O slip at 450 °C. The better dispersion of Ce-containing phases (Fig. 2) and the presence of Ce³⁺^[9b] in FSS_Ce/Ti are probably responsible for the superior performance of this material. Deposition of WO₃ on CeO₂/TiO₂ caused in both cases an enhancement of DeNO_x activity and improved product selectivity. No N₂O slip was detected in WI_W/Ce/Ti and FSS_W/Ce/Ti catalysts. The promoting role of WO₃ of both WI- and FSS-made catalysts is in agreement with the literature.^[4] FSS_W/Ce/Ti clearly outperformed the equivalent catalyst pre-

pared by wet impregnation and its activity was comparable to that of 2.4 wt% V₂O₅-10 wt% WO₃/TiO₂ (V-W/Ti). Therefore, the choice of the synthesis method greatly affected the catalytic performance.

During NH₃-SCR several reactions influence the overall catalyst performance. NH₃ oxidation is an undesired reaction that decreases the efficiency of the SCR process. The propensity of all catalysts to oxidize NH₃ was tested independently from the NH₃-SCR tests (Fig. 4). The NH₃ oxidation activity of WI_Ce/Ti was remarkable over all the temperature range investigated. Contrary to FSS_Ce/Ti, WI_Ce/Ti produced larger amounts of NO₂, NO and N₂O, which we consider a consequence of the presence of well-crystallized cubic ceria (Fig. 2a). This NH₃ oxidation activity of WI_Ce/Ti explains the drop of DeNO_x activity above 300 °C observed in Fig. 3. NH₃ oxidation was suppressed once WO₃ was deposited on the Ce/Ti catalyst.

The presence of WO₃ on the surface of CeO₂/TiO₂ blocked some of the oxidation active sites of CeO₂ and improved

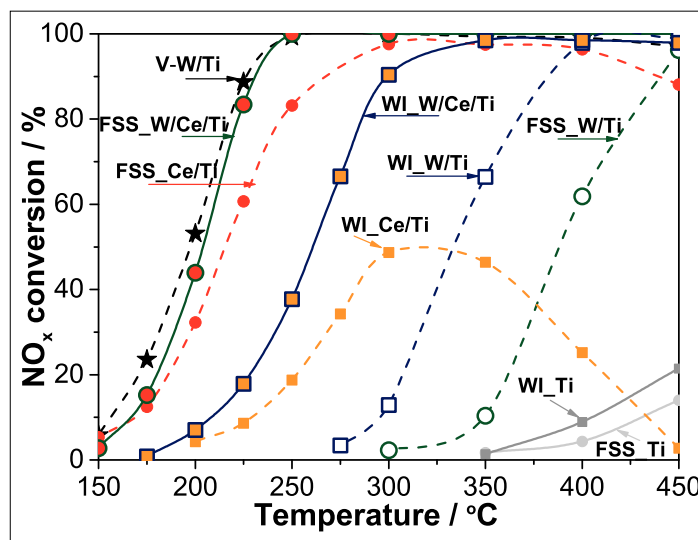


Fig. 3. NO_x conversion of all catalysts.

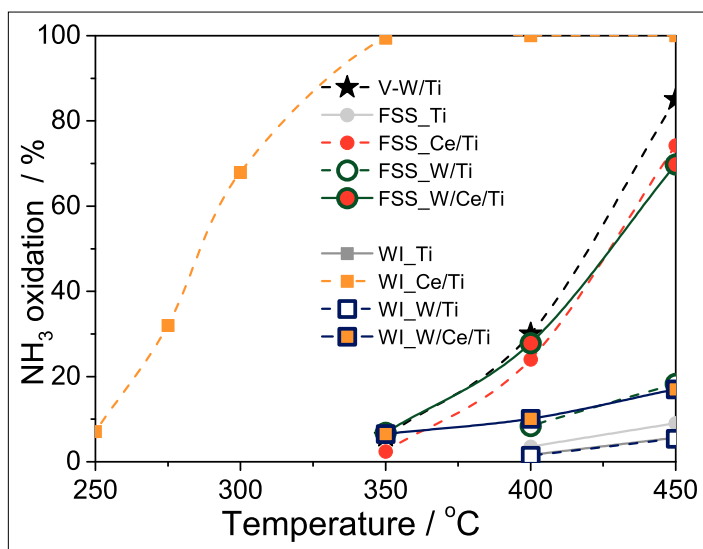


Fig. 4 NH_3 oxidation activity of all catalysts.

catalysts selectivity by conveying surface acidity, which was studied by temperature programmed desorption of NH_3 (NH_3 -TPD, Fig. 5). The NH_3 uptake levels of all catalysts are reported in Table 1. Although the catalytic performance of FSS- and WI-made materials is different, they behave very similarly with respect to NH_3 desorption. Unmodified TiO_2 exhibited a broad NH_3 desorption profile ranging from 50–450 °C for FSS_Ti and 50–500 °C for WI_Ti. The NH_3 -TPD profile of WI_Ti is intentionally not shown to its full scale in Fig. 5a to give a clearer picture of the NH_3 -TPD profiles of the other materials and to better represent the effect of cerium and tungsten on NH_3 adsorption. The NH_3 uptake of WI_Ti was the largest among the investigated materials (Table 1), which produces the very intense and broad NH_3 -TPD profile of Fig. 5a. The high content of SO_3 (~1.25 wt%) in the sample increases significantly its surface acidity. The tem-

perature range 50–125 °C of the NH_3 -TPD profiles of Fig. 5 (zone I) can be assigned to desorption of physisorbed NH_3 . The temperature range 125–350 °C (zone II) is the most relevant for the SCR performance and is assigned to weak acid sites. NH_3 desorption above 350 °C (zone III) can be assigned to strong acid sites and strong surface bonding of NH_3 species that can be detrimental for the SCR performance. WO_3 suppressed the high temperature acid sites of WI_Ti that are responsible for strong NH_3 adsorption. In case of FSS, WO_3 increased the fraction of weak acid sites, thus increasing the NH_3 uptake. Ceria decreased the overall amount of weak and strong acid sites and suppressed the high temperature NH_3 desorption. As a result of the contrasting effect of WO_3 and CeO_2 , the NH_3 uptake of the ternary W/Ce/Ti catalysts was intermediate between that of the binary compositions irrespective of the synthesis method.

It should be noted in Table 1 that wet-impregnated samples possess higher WO_3 coverage per unit surface area than the flame-made counterparts. The observed differences of NH_3 uptake and desorption of wet-impregnated and flame-made catalysts could be explained based on WO_3 surface coverage. Though the content of WO_3 is equal to 10 wt% on all catalysts, the specific surface area of the wet-impregnated samples is nearly 40% lower than that of their flame-made counterparts (Table 1). Therefore, the WO_3 coverage is higher for the WI-made (around 1 monolayer) than for the FSS-made (0.65 of monolayer) catalysts. Tungsten coverages below the monolayer (3–4 W atoms·nm⁻²) are characterized by the presence of polytungstate species and mixed Lewis and Brønsted acidity.^[14] Such extent of WO_x surface coverage was reported to be optimal for the NO_x reduction efficiency^[15] and hydrothermal stability.^[16] The flame-made catalysts exhibit WO_3 coverage in this range and thus high De NO_x activity. On the contrary, the higher tungsten coverage of the wet-impregnated catalysts generates crystalline WO_3 nanoparticles on the amorphous tungstate layer^[9] and decreases the Lewis acidity.^[10a] Additionally, less redox active sites are available because they are covered by the WO_3 species. Hence, the De NO_x activity of WI_W/Ce/Ti is reduced compared to that of FSS_W/Ce/Ti (Fig. 3).

Although the materials obtained by wet impregnation were produced with the aim to mimic the structure of the flame-made catalyst, clear structural and thus activity differences have been observed. The structural dissimilarities can be explained considering the different synthesis procedures. Wet impregnation is a stepwise process where TiO_2 was first impregnated with the cerium precursor and calcined, followed

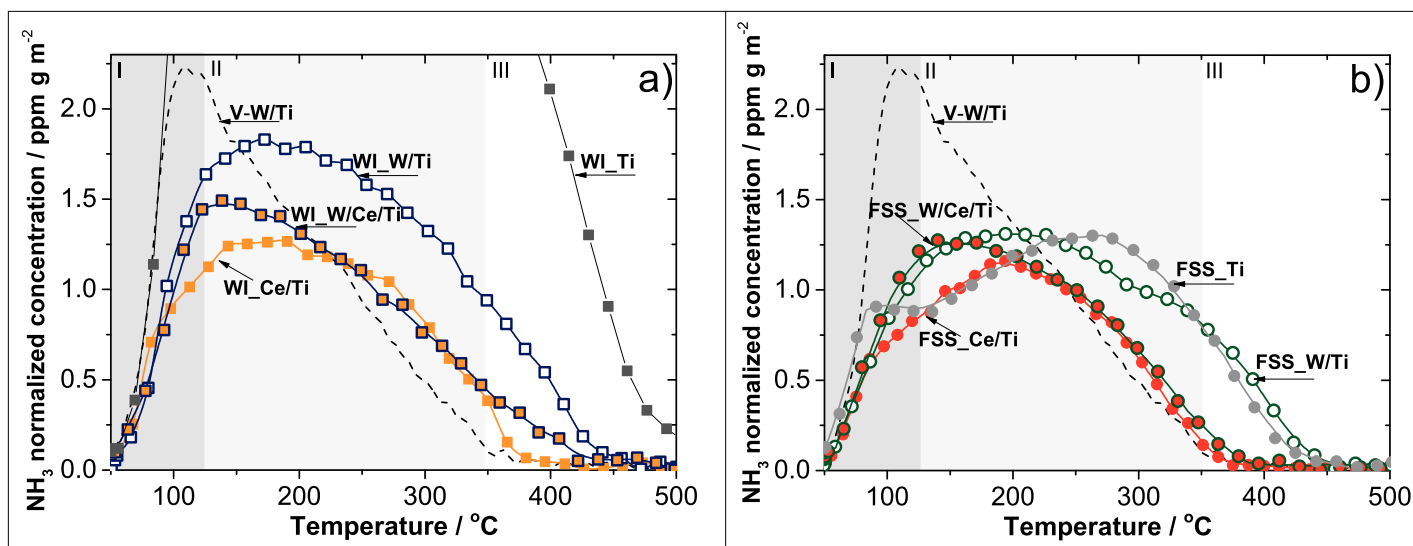


Fig. 5 NH_3 -TPD profiles of wet-impregnated (a) and flame-made (b) catalysts. The dash profile corresponds to NH_3 -TPD of the reference V-W/Ti catalyst. All profiles are normalized by the specific surface area of the catalyst.

by addition of the W precursor and calcination to generate supported WO_3 . In flame spray synthesis, the well-mixed precursor solution of all components was sprayed into the oxygen-acetylene flame and was instantly vaporized. During particle formation, CeO_2 - TiO_2 and TiO_2 particles nucleate first due to their high melting point followed by subsequent WO_3 condensation on their surface and fast quenching. The volatility of WO_3 in the high temperature zone of the flame is induced by the presence of H_2O , largely available in the flame itself as a combustion product.^[17] Therefore, contrary to the classic synthesis route of an active SCR catalyst resulting in the deposition of the redox active species on WO_3/TiO_2 , FSS produces a sort of ‘inverse catalyst’ that is characterized by strong interaction between its components that is not easily reproduced by wet impregnation. The lower DeNO_x activity of WI_W/Ce/Ti can be explained by the limited interaction between the oxide components, the higher WO_3 coverage, which could block $\text{Ce}^{3+/4+}$ -related redox active sites, the strong NH_3 adsorption and the lower SSA.

Conclusions

Ternary 10 wt% WO_3 /10 mol% CeO_2 /90 mol% TiO_2 was prepared by consecutive

wet impregnation of TiO_2 by the Ce and the W precursors and by one-pot flame spray synthesis. Flame-spray synthesis produces a superior active SCR catalyst whose peculiar structure cannot be mimicked using a conventional synthesis method such as wet impregnation. This is ascribed to the particular conditions of FSS. Wet impregnation is not able to reproduce the arrangement and the type of interaction between the various components that appear crucial to impart defined structural characteristics and high catalytic activity.

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