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Published in:
Reaction Chemistry and Engineering

Link to article, DOI:
[10.1039/d0re00033g](https://doi.org/10.1039/d0re00033g)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Bukowski, A., Schill, L., Nielsen, D., Mossin, S., Riisager, A., & Albert, J. (2020). NH₃-SCR of NO with novel active, supported vanadium-containing Keggin-type heteropolyacid catalysts. *Reaction Chemistry and Engineering*, 5, 935-948. <https://doi.org/10.1039/d0re00033g>

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NH₃-SCR of NO with novel active, supported vanadium-containing Keggin-type heteropolyacid catalysts

Anna Bukowski^a, Leonhard Schill^b, David Nielsen^b, Susanne Mossin^b, Anders Riisager^b and Jakob Albert^{a*}

^a Lehrstuhl für Chemische Reaktionstechnik, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany;

^b Technical University of Denmark, Department of Chemistry, Centre for Catalysis and Sustainable Chemistry, Kemitorvet, Building 207, 2800 Kgs. Lyngby, Denmark

*E-Mail: jakob.albert@fau.de

Contact details of the corresponding author:

Phone: (+49)-(0)9131-85-67417 Fax: (+49)-(0)9131-85-27421; e-mail: jakob.albert@fau.de

Abstract: Supported vanadium-substituted Keggin polyoxometalates (POMs) were applied as catalysts for the selective catalytic reduction of NO using NH₃ as reductant (NH₃-SCR). Interestingly, HPA-3 (H₆PV₃Mo₉O₄₀) was found to be the most active catalytic species, and TiO₂ (anatase) the most promoting support for the SCR reaction in the temperature range 200-350 °C. Moreover, 10 wt.% HPA-3 loading was found to be optimum resulting in nearly complete NO conversion at 350 °C. Characterization by several techniques, including N₂-physisorption, NH₃-TPD, FTIR, XPS and TEM showed distinctive structural HPA-3 support interactions explaining the beneficial interplay between both parts for the SCR reaction. Furthermore, different catalytically active surface species were identified at various reaction temperatures and SCR conditions by *in-situ* EPR spectroscopy. The study introduces a novel type of heterogeneous supported vanadium-based NH₃-SCR catalysts comprising redox-active POMs, which so far mainly have been applied for homogeneously catalyzed reactions.

Keywords: DeNO_x, selective catalytic reduction, polyoxometalates, EPR spectroscopy

Introduction

View Article Online
DOI: 10.1039/D0RE00033G

Thermal power plants are big emitters of harmful NO_x gases, which cause formation of acid rain (HNO₃), ground level ozone and photochemical smog that negatively affect ecosystems and human life. Despite the ever increasing cost competitiveness of fluctuating, renewable electricity sources like wind and solar ¹, some thermal power plant capacity is probably still needed due to insufficient storage capacity. ² Firing or co-firing of biomass can help to secure grid stability while causing little net-CO₂ emissions ³⁻⁷ and is on the rise in Europe ⁸ and elsewhere. ^{3, 9}

Selective catalytic reduction with ammonia (NH₃-SCR) has been implemented successfully at stationary power plants since the 1980s, and is considered a mature technology with catalyst lifetimes typically between three to five years. ¹⁰ The most widely used catalyst is V₂O₅-WO₃/TiO₂ (anatase) with V₂O₅ and WO₃ loadings in the ranges of 1-5 and 5-10 wt.%, respectively (WO₃ can be substituted by MoO₃). Unlike in coal-fired plants, rapid catalyst deactivation is experienced in biomass-fired power plants. ¹¹⁻¹⁴ The increased rate of deactivation is caused by the high content of alkali metals, especially potassium, in biomass. ¹⁵⁻¹⁶ Potassium-containing aerosols such as K₂SO₄ and KCl can penetrate the catalyst and react with its acid sites hampering adsorption of NH₃ on the surface of the catalyst. This lowers the activity since this adsorption is a vital step in NH₃-SCR. ¹⁷

Industrially proven method of cleaning NO_x from flue gases at biomass-fired plants are injection of fly ash rich in aluminosilicates ¹⁸ and tail-end placement of the deNO_x unit. ¹⁹ In the former case, potassium is removed from the flue gas by chemically binding to the aluminosilicates and in the latter case by the dust- and SO₂ removal units. Both strategies reduce catalyst deactivation by lowering the concentration of potassium in the flue gas duct.

Strategies to make NH₃-SCR catalysts inherently more potassium resistant have so far only been reported at the laboratory and pilot plant level and include coating with a basic, potassium repellent layer ²⁰⁻²² and increasing the number of acid sites on catalysts. Replacing WO₃ or MoO₃ with their respective Keggin-type heteropolyacids, H₃PW₁₂O₄₀ or H₃PMo₁₂O₄₀ has been reported to increase the number of acid sites and thereby the potassium tolerance at moderate loadings of 100 μmol K g⁻¹_{catalyst} ²³⁻²⁴ Those Keggin-type heteropolyacids belong to the class of polyoxometalates (POMs), which are well-defined metal-oxyanions linked with oxygen bridges of early transition metals at their highest oxidation state (e.g. Mo^{VI}, W^{VI} or V^V). The anions can also contain a multitude of heteroatoms to improve their chemical and thermal stability. ²⁵ POMs have attracted considerable attention due to their architectures and attractive physico-chemical properties including strong Brønsted acidity, high proton mobility, fast multi-electron transfer, high solubility and resistance to hydrolytic and oxidative degradations. This multifunctionality has especially also prompted their use in various homogeneous and heterogeneous catalysis applications. ²⁶⁻²⁷ For example, as highly selective homogeneous catalysts in lignocellulosic biomass oxidation to formic acid and as sustainable heterogeneous catalysts for esterification reactions between glycerol and acetic acid or methanol with oleic acid for biodiesel production. ²⁸⁻³¹

The above-mentioned Keggin-type heteropolyanions typically consist of a W- or Mo-based Keggin framework [XMo₁₂O₄₀]ⁿ⁻ or [XW₁₂O₄₀]ⁿ⁻ where vanadium polyoxoanions can be easily incorporated. ³² Keggin-type molybdophosphoric acid allows the incorporation of up to six vanadium atoms resulting in structures described by "H_{3+n}PV_nMo_{12-n}O₄₀" with n being the degree of substitution, which are easy to prepare. ³³ According to their stoichiometry, they add

more acid sites to the catalyst than the parent molybdophosphoric acid and further potassium tolerance improvements in NH₃-SCR might accordingly been expected. Furthermore, incorporation of V species into the Keggin structure might change their SCR activity compared to the V species present in the traditional V₂O₅-WO₃/TiO₂ catalyst. To the best of our knowledge, catalysts containing H_{3+n}PV_nMo_{12-n}O₄₀ (with n>0) have so far not been reported for the NH₃-SCR reaction.

In the present study, we have investigated the catalytic performance of vanadium-containing Keggin-type polyoxometalates supported on anatase (HPA-n/TiO₂) for NH₃-SCR in simulated flue gas, and characterized the prepared catalysts using analytical methods like TEM, XPS and *in-situ* EPR to obtain a detailed understanding of the SCR performance. Since only NO (and no NO₂) was used as reactant the standard SCR reaction (eq. 1) was expected to take place during the experiments.

Results and Discussion

Catalytic activity of HPA-n/TiO₂ catalysts

Initially, the catalytic activity of various vanadium-substituted Keggin-POMs with the general composition H_{3+x}PV_nMo_{12-n}O₄₀ (HPA-n with n = 0-6) supported on anatase (TiO₂) was investigated. All catalysts were prepared with a POM-loading of 15 wt.%. Anatase was applied as a state-of-the-art support already well known for many SCR applications including diesel engines, diesel locomotives and automobiles.³⁴⁻³⁷ The supported POM catalysts were prepared by wet impregnation, dried and the elemental composition determined by ICP-OES (for details see Table S1 in the ESI).

Figure 1 shows the temperature-dependent NO conversion for the different supported HPA-n catalysts, and as expected NO conversion increased with higher reaction temperature for all the catalysts. The unsubstituted and the lowest vanadium-substituted supported POMs (HPA-0/TiO₂ and HPA-1/TiO₂) showed the lowest activity in the performed SCR experiments, while the highest NO conversion, and thus SCR activity, was achieved with HPA-3/TiO₂. Two competing effects can possibly explain this behaviour: On the one hand, a higher vanadium content in the POM structure leads to increased SCR activity, due to an increased redox activity provided by the vanadium centres. On the other hand, the thermal stability of the HPA-n structures decreases with increasing vanadium content.³⁸ Moreover, it is reported that up to 180°C the crystal water free compounds are present. On raising the temperature up to 380°C, the constitutional water is totally removed without destroying the Keggin structure for low-substituted HPA-n with n = 1-3. The influence of the latter effect on catalytic activity was evident for the six-fold substituted POM (HPA-6/TiO₂) which possessed the highest activity up to 280 °C, but was less active at higher temperatures due to thermal instability of the structure.³⁹

The three-fold vanadium-substituted POM (HPA-3/TiO₂) catalyst had a good compromise regarding vanadium-content (and thus catalytic activity) and structural stability, resulting in nearly full NO conversion at 350°C and was selected for further studies. These results are well in line with previous findings showing comparable SCR performance of V₂O₅-WO₃/TiO₂ with higher vanadium contents.⁴⁰

Figure 1: NO conversion versus temperature for different HPA-*n*/TiO₂ (15 wt.% HPA-*n* with *n* = 0-6) catalysts in NH₃-SCR. Reaction conditions: 50 mg catalyst (180-300 μm), 300 mg diluting agent (SiO₂), 1000 ppm NO, 1100 ppm NH₃, 4.5 vol% O₂, 2.3 vol% H₂O, *F*_{tot} = 512 ml min⁻¹, *T* = 200-350 °C.

Optimization of the POM loading on HPA-3/TiO₂

In the next set of experiments, the SCR activity of the preferred HPA-3/TiO₂ catalyst was examined with different HPA-3 loadings of 7.5, 10, 15 and 20 wt.%, and Figure 2 shows the activity profiles for the different catalysts. The catalyst with 7.5 wt.% HPA-3 loading showed the lowest NO conversion up to 290 °C, where after its activity significantly increased in the temperature range from 290-350 °C reaching the performance of the 15 wt.% loaded catalyst at 350 °C. Furthermore, the catalyst with 20 wt.% HPA-3 loading showed the second lowest NO conversion up to 290 °C, and the lowest activity at higher temperatures of all tested catalysts. Interestingly, the 10 and 15 wt.% loaded catalysts performed very similar yielding the highest NO conversion and thus activity in the whole temperature range, suggesting that this loading range was optimum to reach monolayer coverage of HPA-3 on the TiO₂ support and thereby full utilization of the catalytically active POM. Theoretical calculations based on the surface area of the used TiO₂ support (82.9 m² g⁻¹, see ESI, Table S3) and an average POM-diameter of 13-14 Å⁴¹ confirm monolayer coverage at a POM-loading around 12-14 wt.%. However, further analysis is required to explain why 290 °C was a critical temperature for the 7.5 wt.% loaded HPA-3/TiO₂ catalyst, as addressed below.

Figure 2: Comparison of NO conversion over temperature for 7.5, 10, 15 and 20 wt.% HPA-3/TiO₂ catalyst in NH₃-SCR. Reaction conditions: 50 mg catalyst (180-300 μm), 300 mg diluting agent (SiO₂), 1000 ppm NO, 1100 ppm NH₃, 4.5 vol% O₂, 2.3 vol% H₂O, F_{tot} = 512 ml min⁻¹, T = 200-350 °C.

Variation of vanadium-species on TiO₂ support

To corroborate if incorporation of vanadium into the Keggin structure of the supported HPA-3/TiO₂ catalyst was associated with its observed NH₃-SCR activity, two reference catalyst systems were further examined based on physically mixed HPA-3 and TiO₂ as well as V₂O₅-HPA-0/TiO₂ prepared by impregnation. For comparison reasons, both catalysts had the same vanadium content and V/Mo ratio as the HPA-3/TiO₂ catalyst. As shown in Figure 3, the SCR activity for the catalyst with mixed components (HPA-3 and TiO₂) was very low resulting in NO conversions up to only 15 % in the temperature range 200-350 °C. Furthermore, the supported V₂O₅-HPA-0/TiO₂ catalyst gave around 78 % NO conversion at the highest reaction temperature of 350 °C. In comparison, the HPA-3/TiO₂ catalyst was significantly more active possessing a NO conversion of around 90 % at 350 °C confirming that interaction between the POM structure and support as well as vanadium incorporation into the POM structure both increased the NH₃-SCR activity.

Figure 3: Comparison of NO conversion versus temperature for 10 wt.% HPA-3/TiO₂, 10 wt.% V₂O₅-HPA-0/TiO₂ and physically mixed 10 wt.% HPA-3 and TiO₂ catalysts. Reaction conditions: 50 mg catalyst (180–300 μm), 300 mg diluting agent (SiO₂), 1000 ppm NO, 1100 ppm NH₃, 4.5 vol% O₂, 2.3 vol% H₂O, F_{tot} = 512 ml min⁻¹, T = 200–350 °C.

Activity comparison of HPA-3/support catalysts

The catalytic activity of supported vanadium catalysts in NO-SCR are known to be effected by several factors, including redox properties, acid sites, nature of promoters and the support itself.^{42–43} In order to investigate the effect of the support for the supported vanadium-substituted POMs, catalysts based on the most active POM, HPA-3, were prepared by impregnation using different traditional supports. ICP-OES was used to determine the metal content of the different supported catalysts, resulting in Mo contents between 5.8 (supported on C) and 7.5 wt. % (supported on Al₂O₃) and V contents between 0.9 (supported on C) and 2.1 wt. % (supported on ZrO₂, for more details see ESI Table S2). The results in Figure 4 clearly demonstrate that HPA-3/TiO₂ had the highest SCR activity of the tested catalysts at temperatures above 200 °C yielding a NO conversion of 94 % at 350 °C. In comparison, HPA-3/ZrO₂ gave a NO conversion of 38 % at the highest temperature applied, whereas the NO conversion using HPA-3/C, HPA-3/SiO₂ and HPA-3/Al₂O₃ was negligible under the applied reaction conditions. Therefore, HPA-3/TiO₂ was selected for all further investigations.

Figure 4: Comparison of NO conversion versus temperature for HPA-3 (15 wt.%) based catalysts with SiO₂, Al₂O₃, C, ZrO₂ and TiO₂ supports. Reaction conditions: 50 mg catalyst (180–300 μm), 300 mg diluting agent (SiO₂), 1000 ppm NO, 1100 ppm NH₃, 4.5 vol% O₂, 2.3 vol% H₂O, F_{tot} = 512 ml min⁻¹, T = 200–350 °C.

Characterization of HPA-3/support catalysts

In order to try to explain the observed difference in performance of the various supported HPA-3 catalysts, the specific surface area, pore volume and average pore diameter of all catalysts were determined by N₂-physisorption. Moreover, temperature-programmed desorption (TPD) of NH₃ were performed to elucidate the influence of the surface acidity on the SCR-activity. In Table 1 the physicochemical properties of the HPA-3/support catalysts are compiled.

Table 1 Textural properties and NH₃-TPD results of the various 15 wt.% HPA-3/support catalysts.

Catalyst	BET surface area [m ² /g]	Pore vol. [cm ³ /g]	Av. pore diameter [Å]	Ads. NH ₃ [mmol/g]	T _{max} [°C]
HPA-3/ZrO ₂	125.4	0.11	36.16	0.74	180.2
HPA-3/TiO ₂	71.5	0.20	110.34	0.36	175.6
HPA-3/SiO ₂	393.2	0.58	59.14	0.63	176.6
HPA-3/Al ₂ O ₃	235.4	0.54	91.10	0.56	183.3
HPA-3/C	598.4	0.84	56.08	0.69	186.5

Interestingly, the most active catalyst HPA-3/TiO₂ possessed the lowest specific surface area (71.5 m²/g) and the largest average pore diameter (110 Å), while the second most active catalyst, HPA-3/ZrO₂ had the second lowest BET area of around 125 m²/g and the smallest pore diameter (36 Å). Therefore, we conclude that no direct relationship between the textural properties and the SCR activity can be given.

The NH_3 -SCR reaction requires NH_3 to adsorb on the catalyst surface, and the number of surface acid sites and their strength influence the adsorption capacity and desorption patterns as a function of temperature.⁴⁴⁻⁴⁵ It is well described in the literature, that ammonia adsorption takes place on both the Brønsted and the Lewis sites on the catalyst surface. Nevertheless, the adsorption on Brønsted sites is energetically more favourable.⁴⁵ Thus, the Brønsted and the Lewis sites of the POM as well as the acidic sites of the support are crucial for the ammonia adsorption. The physicochemical properties of the pure supports are compiled in the ESI, Table S3). Thus, the ZrO_2 and the Al_2O_3 showed the highest NH_3 adsorption (0.51 mmol/g ZrO_2 and 0.48 mmol/g Al_2O_3) of the tested support materials. Besides the adsorption on the Brønsted acidic sites of the supported heteropolyacid, NH_3 can therefore also adsorb on the Lewis acidic sites that are for example provided by the Al_2O_3 support.

To examine if the acidity of the supported HPA played an important role regarding the SCR catalyst activity, the acidity of the prepared HPA-3/support catalysts was measured using NH_3 -TPD and the results are included in Table 1. Here, HPA-3/ ZrO_2 showed the highest (0.74 mmol/g) and HPA-3/ TiO_2 the lowest (0.36 mmol/g) number of acid sites, and the latter gave the lowest desorption temperature (i.e. weakest acid sites). Thus, no clear trend between the NH_3 -TPD measurements of the supported POM-catalysts, the acidity of the pure supports and the SCR performance was observed suggesting that active POM surface species were linked to the observed catalytic activity.

To investigate the promoting effect of TiO_2 on the SCR performance FTIR ATR analysis was further carried out on the various supported HPA-3 catalysts as well as the bulk HPA-3 as a reference. Additionally, reference measurements of the blank supports were also performed (for details see ESI, Figure S10). Figure 5 shows the obtained FTIR spectra for the HPA-3 catalysts based on the different supports (Al_2O_3 , C, SiO_2 , ZrO_2 , and TiO_2) and bulk HPA-3. The characteristic stretching vibrations of the Keggin-oxoanion were in all samples observed at 1045 cm^{-1} ($\nu_{\text{as}}\text{ P-O}_a$), 948 cm^{-1} ($\nu_{\text{as}}\text{ Mo-O}_d$), 869 cm^{-1} ($\nu_{\text{as}}\text{ Mo-O}_b\text{-Mo}$) and 739 cm^{-1} ($\nu_{\text{as}}\text{ M-O}_b\text{-Mo}$), which were at slightly lower wavenumbers compared to the non-substituted HPA-0 as also previously reported elsewhere⁴⁴ (O_a refers to the oxygen atom common to PO_4 tetrahedron and one trimetallic group Mo_3O_{13} ; O_b connects two trimetallic groups; O_c binds two octahedral MoO_6 inside a trimetallic group, and O_d is the terminal oxygen atom). The presence of the characteristic vibrations indicated that the POM structure prevailed in the supported samples, however the intensity of the bands strongly depended on the nature of the support and were most pronounced with SiO_2 and C. Hence, also here no clear trend between the FTIR ATR analysis and the SCR performance was evident.

Figure 5: FTIR spectra of HPA-3/support catalysts with the different supports TiO_2 , ZrO_2 , SiO_2 , C and Al_2O_3 .

Characterization of HPA-3/ TiO_2 catalyst before/after SCR reaction

Post-reaction characterization of the superior HPA-3/ TiO_2 catalyst was performed to investigate structural transformations and possible instabilities of the POM structure on the support surface during reaction, which potentially limit long-term application. Figure 6 shows representative TEM images of both the fresh HPA-3/ TiO_2 catalyst (top) and the catalyst after being used for the SCR reaction (bottom). In both catalysts, the POM particles (small white dots) were well dispersed and uniformly distributed on the support surface without cluster formation, suggesting a good access of substrate to the active centres and good thermal stability.

Figure 6: TEM images of fresh HPA-3/TiO₂ (top) and HPA-3/TiO₂ after SCR use (bottom).

XPS spectra of the as-prepared HPA-3/TiO₂ catalyst (top) and the analogous catalyst after SCR use (bottom) are shown in Figure 7. For both samples, the molybdenum spectra (left) revealed binding energies around 232.5 and 236.3 eV corresponding to Mo⁶⁺ species, while no lower binding energies corresponding to reduced Mo species were observed.⁴⁶ The vanadium spectra (right) of the samples showed also similar binding energies around 516.2 and 517.0 eV corresponding to V⁴⁺ and V⁵⁺, respectively.⁴⁷ Via integration of the corresponding peak area the ratios of V⁴⁺ to V⁵⁺ in the fresh and used HPA-3/TiO₂ catalyst was determined to be 53 to 47 % and 58 to 42 %, respectively, thus revealing no significant changes in the oxidation states of molybdenum and vanadium in the catalysts.

Figure 7: XPS spectra of fresh HPA-3/TiO₂ (top) and HPA-3/TiO₂ after SCR use (bottom) with molybdenum (left) and vanadium (right) binding energies.

The presence of the POM structure in the HPA-3/TiO₂ catalyst used for the SCR reaction was recognized by FTIR analysis as shown by the spectra in Figure 8. Here, the characteristic stretching vibrations of the Keggin-oxoanion were identified at 1065 cm⁻¹ (ν_{as} P-O_a), 959 cm⁻¹ (ν_{as} Mo-O_d), 865 cm⁻¹ (ν_{as} Mo-O_b-Mo) and 771 cm⁻¹ (ν_{as} M-O_b-Mo), respectively, demonstrating that no critical structural transformations or instabilities of the POM structure occurred during catalysis. Notably, the intensity of the signals in the spent catalyst were weaker than the signals for the HPA-3/TiO₂ catalyst, because the sample was diluted with SiO₂ (diluting agent in NH₃-SCR).

Figure 8: FTIR spectra of fresh HPA-3/TiO₂ (top) and HPA-3/TiO₂ after SCR use (bottom) with wavenumbers ranges of the stretching vibrations of the Keggin-oxoanion highlighted.

In-situ EPR spectroscopy of the-supported HPA catalysts

In order to explain the catalytic behavior and to get a deeper understanding of the POM-support interactions, *in-situ* EPR studies were performed on HPA-3/TiO₂, HPA-3/Al₂O₃, HPA-0 and V₂O₅/TiO₂ under different gas exposures relevant for SCR, i.e. NH₃, NH₃/NO, O₂/NO and NH₃/NO/O₂, at temperatures of 25-290 °C. As described below all observed spectra can be assigned to V⁴⁺ species. No signal for reduced Mo⁵⁺ was observed.

The EPR spectra of the fresh catalyst samples before gas exposure are shown in Figure 9 (top). The TiO₂ supported samples HPA-3/TiO₂ and V₂O₅-HPA-0/TiO₂ provided similar spectra, whereas HPA-3/Al₂O₃ showed an EPR signal with low intensity. The spectra were typical for the solid state of V⁴⁺ as vanadyl ([VO]²⁺) species in a tetragonal coordination environment.⁴⁸⁻⁴⁹ A small signal at $g = 4.3$ was observed in HPA-3/Al₂O₃ originating from impurities in the alumina support, likely a small amount of iron oxides (see Figure S3). A broad and temperature dependent signal from the same impurity was centered at $g = 2.0$, making quantification of the signal difficult, especially when the intensity of the vanadium signal was low.

Upon exposing the supported samples to a flow of 4.5 vol% O₂ and 2.3 vol.% H₂O in balance He at room temperature the spectra changed as shown in Figure 9 (left). The EPR spectra can be modeled with the spin Hamiltonian

$$H = g_x S_x B_x + g_y S_y B_y + g_z S_z B_z + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z$$

where g_i and A_i are the electronic g-values and hyperfine coupling constants along the molecular axes ($i = x, y, z$), respectively (see ESI for details on the modeling). The spectra of water exposed samples were isotropic (i.e. the observed g- and A tensors were independent of molecular axes and can each be represented by a single value) with $g_{iso} = 1.96$ and $A_{iso} = 318$ MHz. This species have previously been assigned to [VO(H₂O)₅]²⁺.³¹ Isotropic spectra indicated that the EPR active [VO]²⁺ either changes the anisotropy axis or rotates fast on the EPR time scale. This species became even more dominant when the TiO₂ supported catalysts were exposed to a moist gas flow, whereas the Al₂O₃ supported sample was not responsive.

When heating the samples in the same gas flow, the relative humidity decreased below 100% and the spectrum rapidly changed to reveal EPR active $[\text{VO}]^{2+}$ species with a more complicated and anisotropic (axial) EPR spectra ($g_x = g_y \neq g_z$), see Figure 9 (right). When subsequently cooling the samples to room temperature, the isotropic signal did not reoccur right away indicating that the change was quite slow or irreversible. Exposing a fresh catalyst to a dry flow (4.5 vol% O_2 in He) at room temperature resulted in a similar axial spectrum.

Figure 9: EPR spectra of fresh HPA-3/TiO₂, V₂O₅-HPA-0/TiO₂ and HPA-3/Al₂O₃ catalysts at room temperature measured as the first spectrum of the *in-situ* measurement without gas exposure (top) and after exposure to 2.3 vol% H₂O (saturated) and 4.5 vol% O₂ in He at room temperature (left). Change in EPR spectra of HPA-3/TiO₂ as the gas flow was kept constant at 2.3 vol% H₂O + 4.5% O₂ in He and the temperature was raised by 5 °C/min.

The catalysts were exposed to cycles of reducing (NH₃/NO gas) and oxidizing (NO/O₂ gas) conditions at 250 °C in order to quantify the amount of $[\text{VO}]^{2+}$ and to follow the reduction of vanadium under SCR conditions. The development in the EPR intensity and the individual spectra during such gas exposures are shown in Figure 10 left and right, respectively. The

results showed that exposure to NO/O₂ caused a rapid decrease of the EPR signal intensity for all the samples with paramagnetic [VO]²⁺ likely being oxidized into (EPR inactive) diamagnetic V⁵⁺ (a small amount of vanadium remained as [VO]²⁺). Analogously, exposure to NO/NH₃ caused an increase in signal intensity as V⁵⁺ was reduced to [VO]²⁺. The reduction proceeded slower than the oxidation for all samples. Moreover, the TiO₂ supported samples responded faster and more efficiently to the NH₃ and NO gases than the Al₂O₃ supported sample. The EPR signal intensity in Figure 10 was calculated by double integration of individual background-corrected spectra for all samples. The analysis of the EPR signal of the HPA-3/Al₂O₃ sample was complicated by a contribution from a non-vanadium paramagnetic impurity. The quantification for this sample are less reliable than for the other samples. A more careful analysis of the spectrum suggests that the amount of EPR active vanadium may be as low as 0.05 wt.% for this sample. About 11 % of the V in the fresh HPA-3/TiO₂ was observed as EPR active V⁴⁺, see ESI, Figure S2-S7 and a maximum amount of 25 % could be detected under reaction conditions.

The EPR spectra of the three samples exposed to different gas mixtures revealed that HPA-3/Al₂O₃ only contained V⁴⁺ species of type B, see Figure 10. The amount changes with exposure to the different gases, but no other EPR active species appeared. In contrast, the two TiO₂ supported catalysts showed overlapping EPR signals from at least three different species: Two distinct species with well-resolved hyperfine coupling patterns (type A and B) and one species with unresolved features, which can be modeled as being isotropic (type C). The distribution of sites changes when the sample is exposed to the different gas mixtures. The results of the analysis using simulations of the spectra in Figure 10 (right) are given in Table 2. Simulated spectra can be seen in Figure S4. The maximum amount of EPR active vanadium is found under reducing conditions. It is given in Table 2, rightmost column as the percentage of the total amount of vanadium present. The values obtained when combining A, B and C are comparable for HPA-3 on TiO₂ and for V₂O₅/HPA-0 on TiO₂ at 19% and 24%, respectively.

Figure 10: EPR active vanadium in wt.% of sample during *in-situ* experiments with HPA-3/ TiO_2 , V_2O_5 -HPA-0/ TiO_2 and HPA-3/ Al_2O_3 catalysts at 250 °C. White columns represent exposure to 550 ppm NH_3 /500 ppm NO in 2.3 vol% H_2O and balance He. Grey columns represent exposure to 500 ppm NO /4.5 vol% O_2 in 2.3 vol% H_2O and balance He. The colored dots show which spectra were selected for plotting to the right with same color.

Table 2: Simulated spin Hamiltonian values as well as fitted linewidth (given as full width at half maximum) for the HPA-3/TiO₂, V₂O₅-HPA-0/TiO₂ and HPA-3/Al₂O₃ catalysts under different conditions (see Figures S5-S7).^a

Catalyst	Gas ^a	Type	g_x	g_y	g_z	g_{iso}	A_x, A_y [MHz]	A_z [MHz]	A_{iso} [MHz]	FWHM [mT]	% of signal	V_{EPR}/V_{ICP}^b [%]
HPA-3/TiO ₂	Ox.	A	1.97	1.93	1.96	155	490	267	3.1	19	1	
		C	-	-	1.96	-	-	-	38	81	3	
	Red.	A	1.97	1.93	1.96	155	460	257	3.2	4	1	
		B	1.98	1.92	1.96	195	510	300	3.8	11	2	
		C	-	-	1.96	-	-	-	38	85	16	
V ₂ O ₅ -HPA-0/ TiO ₂	Ox.	A	1.97	1.93	1.96	155	490	267	3.2	30	2	
		C	-	-	1.96	-	-	-	38	70	4	
	Red.	A	1.97	1.93	1.96	155	460	257	3.2	7	2	
		B	1.98	1.92	1.96	195	510	300	2.8	8	2	
		C	-	-	1.96	-	-	-	38	85	20	
HPA-3/Al ₂ O ₃	Ox.	B	1.98	1.93	1.96	190	510	297	3.5	100	<12	
	Red.	B	1.98	1.93	1.96	185	505	292	3.5	100	<17	

^a Ox. represents oxidizing condition with a gas flow of 200 mL/min containing 4.5 vol% O₂, 500 ppm NO and 2.3 vol% H₂O in balance He at 250 °C. Red. is reducing conditions in a gas flow of 200 mL/min containing 550 ppm NH₃, 500 ppm NO and 2.3 vol% H₂O at 250 °C. ^b V_{EPR}/V_{ICP} refers to the amount of vanadium that is EPR active based on the calculated intensity relative to the initial EPR spectrum and the amount of V as determined by ICP. The intensity of EPR spectra were Boltzmann corrected according the temperature of the relevant spectrum.

The HPA-3/TiO₂ catalyst was further examined by EPR under operando SCR conditions at temperatures from 175-290 °C, and spectra from selected temperatures are shown in Figure 11. No significant change in the EPR signal was observed (except a slight line broadening), when the temperature was increased. Furthermore, the sample was kept at 290 °C under SCR conditions for 30 minutes without any change in the EPR signal, indicating no further change in the distribution of EPR active species under these conditions.

Figure 11: EPR spectra of the HPA-3/TiO₂ catalyst during SCR operation with 550 ppm NH₃, 500 ppm NO, 4.5 vol% O₂ and 2.3 vol% H₂O in He, F_{tot} = 200 mL/min at increasing temperatures.

The g - and A -values averaged over the different axes (the isotropic values) can be plotted as g_{iso} vs. A_{iso} as shown in Figure 12. This empirical plot is often used in the literature,⁴⁹ since the different regions are indicative of different types of vanadium species. The alpha area corresponds to square pyramidal or axially distorted octahedral V⁴⁺ species. The beta area is characteristic of tetrahedral V⁴⁺ species and the gamma area corresponds to V⁴⁺ with biaxially distorted octahedral symmetry. All the vanadium species observed by EPR in the supported HPA catalysts correspond to tetragonally distorted octahedral [VO]²⁺-centers.⁴⁹ For such species it would be expected that $g_z < g_x = g_y$ and $A_z > A_x = A_y$. The A -values observed here were lower than otherwise observed for V₂O₅ species on different oxide supports.^{24, 50-52}

Figure 12: Isotropic spin Hamiltonian values for HPA-3/ Al_2O_3 (red symbols) and HPA-3/ TiO_2 (black symbols) plotted as in ⁴⁹. Square symbols represent the “reduced” samples and circles represent “oxidized” samples. The hollow circles are the TiO_2 supported samples when saturated by water at room temperature.

The species of type A has very similar EPR parameters to the ones previously reported for Keggin polyoxometallates with one V^{4+} site.⁵³ ($g_x = g_y = 1.98$, $g_z = 1.94$, $A_x = A_y = 156$ MHz, $A_z = 453$ MHz) The species of type B, on the other hand, have a different set of g - and A -values and do not compare well with the literature of EPR on V in Keggin POMs. It is only present in very low percentages and one suggestion is that it corresponds to a minor amount of vanadium on the surface of a POM or in a partially broken down POM on the support.⁵⁰ It seems not to have any significant activity in the SCR reaction since it is the only species present in the catalytically inactive HPA-3/ Al_2O_3 . The species of type C is dominant in the TiO_2 -supported samples and is much more interesting concerning catalytic activity since the observation of this species coincides with SCR activity and the total amount of this species changes with the identity of the reaction gases. The broad feature of the EPR signal of type C is caused by magnetically interacting V centers. The lack of features makes it impossible to identify structural details of these sites and the signal may be due to a combination of several types of sites. We can only comment that a strong interaction is compatible with several V^{4+} centers present in the same POM unit. It is very interesting that no species of either type A or C are observed on the Al_2O_3 support. We tentatively conclude that vanadium in POM units on the Al_2O_3 support are caught in oxidation state +5 and could not be reduced by $NO + NH_3$.

In the generally accepted mechanisms for the SCR reaction, vanadium is surrounded by oxygen atoms whereas NO and NH_3 are in the second coordination sphere which is generally not detected by EPR spectroscopy.^{44, 54} This is in accordance with our results since all observed spectra correspond to V coordinated to oxygen atoms. The lack of change in the EPR spectrum of the HPA-3/ Al_2O_3 catalyst during exposure to SCR gases suggested a difference in either the ability of vanadium in the POM to interact with the gases or a difference in the reduction potential due to the different POM-support interaction between TiO_2 and Al_2O_3 supported catalysts. The difference in the response during interaction with NH_3 further

corroborated this observation (see Figures S8-S9) since the small amount of EPR active vanadium of type B in the Al_2O_3 supported catalyst was shown to be more easily reduced by NH_3 than vanadium on TiO_2 supported catalysts.

The vanadium in TiO_2 supported catalysts, especially site C, were much more responsive to oxidation by NO/O_2 and reduction by NO/NH_3 than the vanadium in the Al_2O_3 supported catalyst and this coincided with a higher activity in the SCR reaction. For each material a redox-window can be calculated based upon the EPR results: The weight of vanadium, which has changed oxidation state between steady-state at oxidizing and at reducing SCR conditions, divided by the total weight of the catalyst. The redox-window can be observed directly in the left graphs in Figure 10 as the magnitude of the gap between the upper and lower plateaus. The values are much higher in the catalysts that are active for the SCR reaction.

The other characterization methods applied in this work did not reveal a strong correlation between the respective responses and the SCR activity. We conclude that the changes in structural parameters within the POM units are relatively modest during reaction and that the acidity, porosity and surface area of the catalyst is not decisive here. On the other hand, the redox window observed during the *in-situ* EPR analysis was seen to be a very good descriptor for the SCR activity in these materials.

Conclusion

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Different supported vanadium-substituted HPA-n catalysts on TiO_2 (anatase) have been prepared and examined for catalytic performance in the NH_3 -SCR reaction. Two competing effects were deduced within the HPA-n catalyst series; On the one hand, higher vanadium content increased the amount of redox-active sites, while on the other hand it also led to a lower thermal stability of the resulting HPA-n species due to an increasing basicity. HPA-3/ TiO_2 showed the best compromise between these two effects, and 10 wt% HPA-3 loading was found to provide the highest SCR activity in the studied temperature range reaching nearly full NO conversion at 350 °C. HPA-support interaction as well as vanadium incorporation into the POM structure of the HPA increased the NH_3 -SCR activity when compared to reference catalysts with different combinations of vanadium-based catalysts on TiO_2 . Moreover, TiO_2 clearly demonstrated to provide catalysts with superior activity.

Post-reaction analysis of the catalyst by TEM and XPS confirmed that the POM particles remained uniformly distributed and the HPA structure stable after reaction with an unchanged V^{4+} and V^{5+} distribution of 58 and 42 %. Finally, *in-situ* EPR studies showed that the TiO_2 supported catalysts, including HPA-3/ TiO_2 , were more responsive to oxidation and reduction by NO/O_2 and NO/NH_3 gases than the Al_2O_3 supported samples, which corresponded well to the fact that these samples were more catalytically active. Thus, it is reasonable to suggest that the redox-window can be used as measure of the SCR activity of the novel HPA catalysts. Due to the promising results obtained, a potassium tolerance study will be completed in the near future with the most promising catalyst.

Experimental details

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Materials and methods

All chemicals were commercially available and used without further purification. V_2O_5 ($\geq 99.9\%$) was purchased from Alfa Aesar, MoO_3 ($\geq 99\%$) and H_3PO_4 (in water, $\geq 85\%$) from Acros organics, H_2O_2 (30% aqueous solution) from Supelco®, ammonium meta-vanadate ($\geq 99\%$) and oxalic acid (99.9%) from Sigma Aldrich. TiO_2 (anatase, DT51-D crystal) was purchased from Cristal Global, SiO_2 (Silica gel 60) from Fluka, Carbon Black (BlackPearl 1400) from Carbor, ZrO_2 (NorPro) and $\gamma-Al_2O_3$ from Saint Gobain.

Catalyst synthesis

Vanadium-substituted HPA-n POMs, $H_{3+n}PV_nMo_{12-n}O_{40} \cdot xH_2O$ with $n = 0-6$, were synthesized according to the literature using a two-step method with non-substituted phosphomolybdic acid $H_3PMo_{12}O_{40}$ precursor and the stable vanadium-precursor $H_9PV_{14}O_{42}$.⁵⁵ $H_3PMo_{12}O_{40}$ was obtained by heating MoO_3 (0.620 mol) in an aqueous solution of H_3PO_4 (0.051 mol) followed by water removal under vacuum to give a crystalline solid. $H_9PV_{14}O_{42}$ was synthesized by dissolving water-insoluble V_2O_5 (for HPA-5 synthesis exemplarily: 0.220 mol) in cooled aqueous H_2O_2 (300 ml of 30 wt.% in water) followed by adding H_3PO_4 (0.033 mol) to stabilize the precursor. Subsequently, the aqueous vanadate precursor solution was added to the molybdate precursor under boiling conditions to yield the final HPA-n solution, where the water was removed under vacuum to give a crystalline solid (Yields $> 95\%$). The prepared materials were characterized by FTIR and compositional analysis using ICP-OES. The characterization data are included in the ESI (Figure S1, Table S1).

Supported HPA-n catalysts were prepared by suspending a known amount of dried support (TiO_2 , SiO_2 , Carbon Black, ZrO_2 or $\gamma-Al_2O_3$) in aqueous solution of the corresponding HPA-n POM. Furthermore, a catalyst containing V_2O_5 and HPA-0 ($H_3PMo_{12}O_{40}$) on TiO_2 (V_2O_5 -HPA-0/ TiO_2) was prepared by wetness impregnation of HPA-0 and 2 M vanadium(IV) oxalate solution on TiO_2 , followed by calcination at $450\text{ }^\circ\text{C}$ prior to use. The vanadium oxalate solution for impregnation was prepared from ammonium meta-vanadate and oxalic acid in the molar ratio 1:2 at $70\text{ }^\circ\text{C}$.

The metal loadings of V and Mo on the different supports were determined using ICP-OES. The characterization data are included in the ESI (Table S2). The impregnated catalysts were dried at $120\text{ }^\circ\text{C}$ for 12 h in an oven prior to characterization. Unless otherwise stated, all the catalysts were prepared with a POM loading of 15 wt.%.

Catalyst characterization

Inductive coupled plasma (ICP-OES)

The compositional analysis of HPA-n materials and the weight percentage of Mo and V contained in the impregnated catalysts were determined by ICP-OES. The measurements were carried out using a Perkin Elmer Plasma 400 by dissolving ca. 20 mg of the HPA-n catalyst in 250 mL of double distilled water. For evaluation of the composition of the supported catalysts, sample preparation was done by carefully dissolving the catalysts in *aqua regia* (3:1 mixture of concentrated HNO_3 and HCl) in a microwave oven. For calibration, phosphorous, molybdenum and vanadium ICP-standard solutions ($1000\text{ }\mu\text{g mL}^{-1}$) were used.

Fourier-transformed infrared spectroscopy (FTIR)

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Both freshly synthesized HPA-n materials and supported HPA-n catalysts were analysed by IR at ambient conditions using a Jasco FT/IR-4100 spectrometer equipped with a PIKE GladiATR ATR-accessory with a resolution of 4 cm⁻¹. The FTIR spectra were recorded in the range between 4000 and 400 cm⁻¹.

Nitrogen physisorption

N₂ physisorption was carried out on a Quantachrome Autosorp iQ to determine specific surface area, pore volume and average pore diameter. The isotherms were measured at 77 K and 273 K, respectively, with samples that were degassed for 12 h at 250 °C in vacuum prior to the adsorption measurement. The total surface area was calculated by the Brunauer-Emmett-Teller (BET) method, the micro-pore volume and external surface area were calculated by the t-plot method and the total pore volume was determined from the isotherm adsorption branch by a single point at around $p/p^0 = 0.95$.

Ammonia temperature-programmed desorption (NH₃-TPD)

The NH₃-TPD measurements were carried out on a Micromeritics Autochem-II instrument. In a typical experiment, 100 mg of dried sample was placed in a u-shaped quartz tube and pretreated in flowing He at 300 °C. Afterwards, the temperature was lowered to 100 °C and the sample was treated with anhydrous NH₃ gas (Air Liquide, 5% NH₃ in He). Then, after NH₃ adsorption, the sample was flushed with He (50 ml/min) for 100 min at 100 °C and the NH₃-TPD was finally carried out by heating the sample from 100 to 300 °C (10 °C/min) in a flow of He (25 ml/min). The NH₃ concentration was measured using a TCD detector.

X-ray photoelectron spectroscopy (XPS)

XPS samples were measured on a ThermoScientific instrument using Al K α X-rays (150 W). A constant analyser energy (CAE) mode was used to measure the survey spectra at a pass energy of 160 eV. An electron flood gun was used to achieve charge compensation. The software used for the deconvolution was a commercial Advantage 4.87.

Transmission electron microscopy (TEM)

TEM analysis was performed with a FEI Tecnai microscope operated at 200 kV. All samples were directly dispersed on holey or lacey carbon grids.

Electron paramagnetic resonance (EPR) spectroscopy

All EPR measurements were performed using an ER 4102ST cavity in a CW X-band Bruker EMX spectrometer. The power was set to 6.6 mW, modulation amplitude was 5.2 G and the modulation frequency was 100 KHz. Quantitative measurements were performed *ex-situ* using a VOSO₄ standard diluted in KSO₄. Approximately 20 mg sample was transferred to a closed 4 mm suprasil quartz EPR tube and measured at ambient conditions. The measurement of each sample was done by addition of three scans in the range of 230-440 mT. *In-situ* measurements were performed by adding approximately 20 mg sample to an open-ended quartz tube immobilized by two pieces of quartz wool resulting in a plug-flow reactor setup. The tube was placed in the cavity connected to a Bruker EMX VT heater permitting measurements in a temperature interval from room temperature to 290 °C. The gas flows were controlled by MKS mass-flow controllers. Unless otherwise stated, the total flow was 200 mL/min in balance He and the concentrations of gases were 500 ppm for NO, 550 ppm NH₃, 2.3 vol% for H₂O and 4.5 vol% O₂, whenever the relevant gas was applied. Simulations and general data treatment was done in Matlab (2017R) using EasySpin 5.2.23.⁵⁶

EPR spectra of all fresh samples and five standard samples containing $\text{VOSO}_4 \cdot 3\text{H}_2\text{O}$ in K_2SO_4 were collected *ex-situ* at room temperature. The intensity (the double integral) of the EPR spectrum of each fresh sample was then compared to a calibration curve based on the reference samples in order to determine the percentage of EPR active vanadium by weight. The *in-situ* measurements all started from a fresh catalyst sample and the first spectrum was therefore used as a reference point to calculate the time resolved intensity of each spectrum using the results of the *ex-situ* experiments. To account for the effect of temperature, a Boltzmann correction of the intensity for each individual spectrum was performed. Using this procedure the wt.% of EPR active vanadium on each sample throughout an *in-situ* measurement was determined.

The *ex-situ* experiments of fresh samples showed that the HPA-3/ TiO_2 catalyst contained 0.18 ± 0.01 wt.% EPR active $[\text{VO}]^{2+}$, while V_2O_5 -HPA-0/ TiO_2 contained 0.13 ± 0.08 wt.% EPR active $[\text{VO}]^{2+}$. HPA-3/ Al_2O_3 only gave a weak signal but it was estimated that it contained less than 0.05 wt.% EPR active $[\text{VO}]^{2+}$. These amounts corresponded to 11, 8 and 4% of the total V measured by ICP being EPR active for the catalysts. The quantification results are collected in Table 2 and in the ESI (Figure S2).

Catalytic experiments

The SCR activity measurements were carried out in a fixed-bed reactor loaded with 50 mg of fractioned catalyst (180-300 μm) and SiO_2 as diluting agent (300 mg) at atmospheric pressure. The reactant gas composition was adjusted to 1000 ppm NO, 1100 ppm NH_3 , 4.5 vol% O_2 , 2.3 vol% H_2O using Bronkhorst EL-Flow F-201C/D mass-flow controllers. The total gas flow was maintained at 512 mL/min. NO and NH_3 concentrations were continuously monitored by a Thermo Electron Model 1C chemiluminescent NH_3 - NO_x gas analyzer. The temperature was increased stepwise from 200 to 350 $^\circ\text{C}$ during the activity measurements, and the SCR activity determined after steady-state was obtained at the desired temperature.

Acknowledgements

AB and JA thank the Erlangen Cluster of Excellence "Engineering of Advanced Materials" (www.eam.fau.de) for financial support. Additionally, we thank Simone Zacho (DTU) for performing TEM measurements.

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