

# Novel catalysts for selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> prepared by atomic layer deposition of V and Ti oxides on SiO<sub>2</sub> powder

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## Problem formulation

According to the 2019 report of European Environment Agency about air quality in Europe, nitrogen oxides (NO<sub>x</sub>) are included to the most harmful air pollutants in terms of damage to ecosystems and impact on human health. Anthropogenic emissions of NO<sub>x</sub> are mainly generated by combustion of fossil fuels. Nitrogen oxides being emitted into the atmosphere cause such environmental problems as acid rains, acidification of soil, lakes and rivers, eutrophication and photochemical smog [1].

The most effective and widely used technology to purify flue gases from NO<sub>x</sub> is selective catalytic reduction with ammonia (NH<sub>3</sub>-SCR de-NO<sub>x</sub>). Nowadays, the important direction in the field of NH<sub>3</sub>-SCR de-NO<sub>x</sub> is preparation of new catalysts possessing high specific surface area (SSA), uniformity, dispersion of active sites, thermal and chemical stability (resistance to H<sub>2</sub>O and SO<sub>2</sub>), high activity and selectivity [2]. It is well-known that the higher is dispersion of catalytically active species on a carrier surface the higher NO<sub>x</sub> conversion efficiency can be achieved. However, preparation of supported catalysts using highly porous carriers with a large SSA by traditional catalyst preparation techniques (e.g. impregnation and deposition precipitation) is problematic due to aggregation of deposited materials which consequently results in clogging the pores and significantly reduces an SSA. Therefore, application of nonconventional methods for preparation of SCR de-NO<sub>x</sub> catalysts possessing large SSA and highly dispersed active species without aggregation and clogging the pores is of great importance.



## Solution

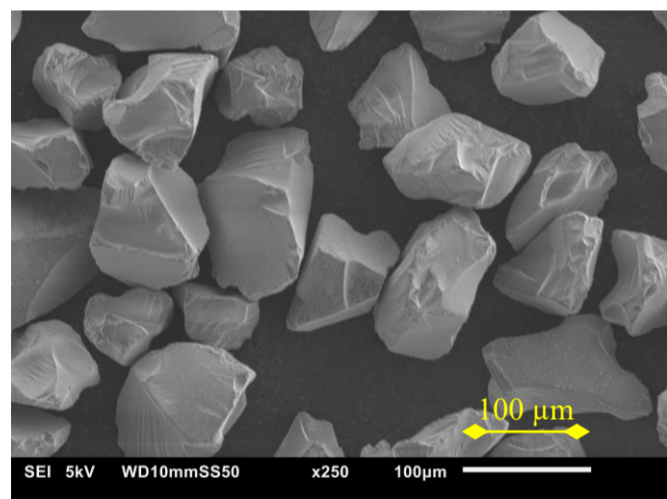
Atomic layer deposition (ALD) is an attractive technique for deposition of uniformly distributed active catalytic layers or nanoparticles on highly porous substrates being characterized by a complex structure and intricate morphology with a high surface area, where the application of conventional methods can be problematic [3]. The significant advantage of ALD application for preparation of supported catalysts is that the preparation process can be controlled on the atomic scale providing the required thickness of an active layer synthesized with a "sub-nm" accuracy. Moreover, ALD ensures the formation of catalysts in a gas phase instead of a liquid phase, which enhance the possibility of active species to be deposited inside pores which are very small in size. In this study ALD was applied for preparation of VO<sub>x</sub>-based NH<sub>3</sub>-SCR de-NO<sub>x</sub> catalysts (pure VO<sub>x</sub>/SiO<sub>2</sub> and Ti-incorporated VO<sub>x</sub>/SiO<sub>2</sub> catalysts). Highly porous silica gel powder (63-100 μm) with a specific surface area of up to 450 m<sup>2</sup>·g<sup>-1</sup> was used as a substrate for active layer deposition.

## Methodology

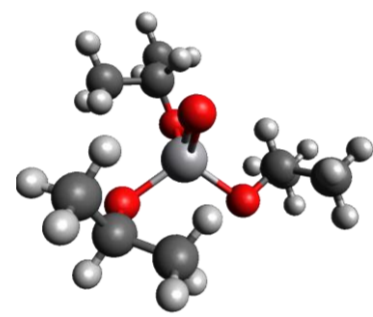
### Materials used for catalyst preparation

**Substrate used for deposition of V and Ti species:**

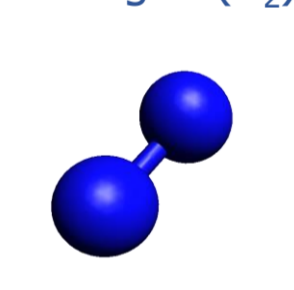
Highly porous SiO<sub>2</sub> powder



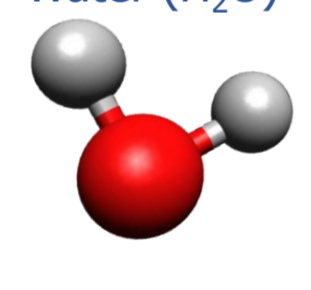
**Vanadium precursor:**  
vanadium (V) tri-*i*-propoxy oxide (VTIP)



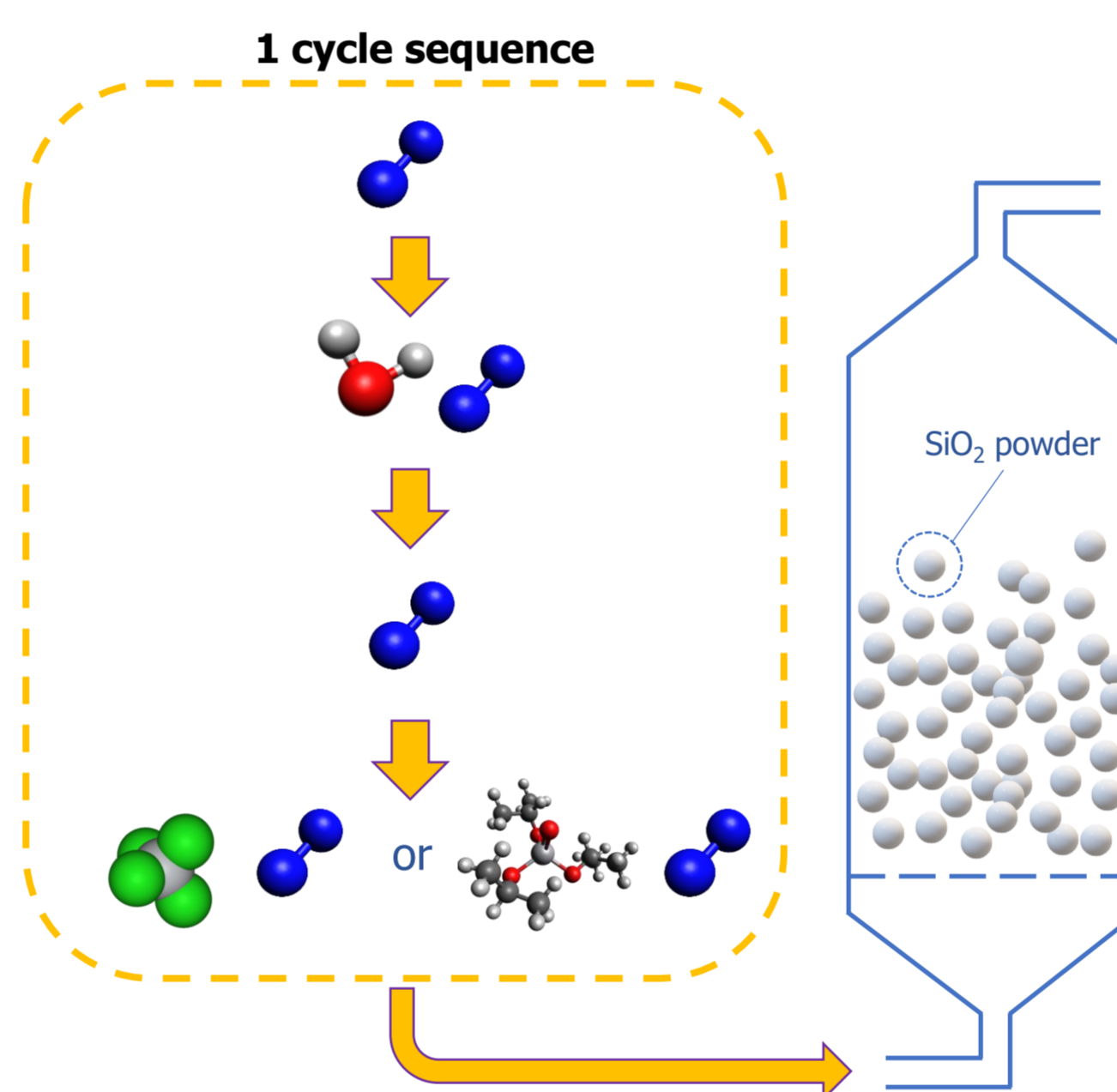
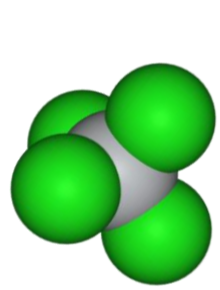
**Carrier gas:**  
Nitrogen (N<sub>2</sub>)



**Co-reactant:**  
Water (H<sub>2</sub>O)



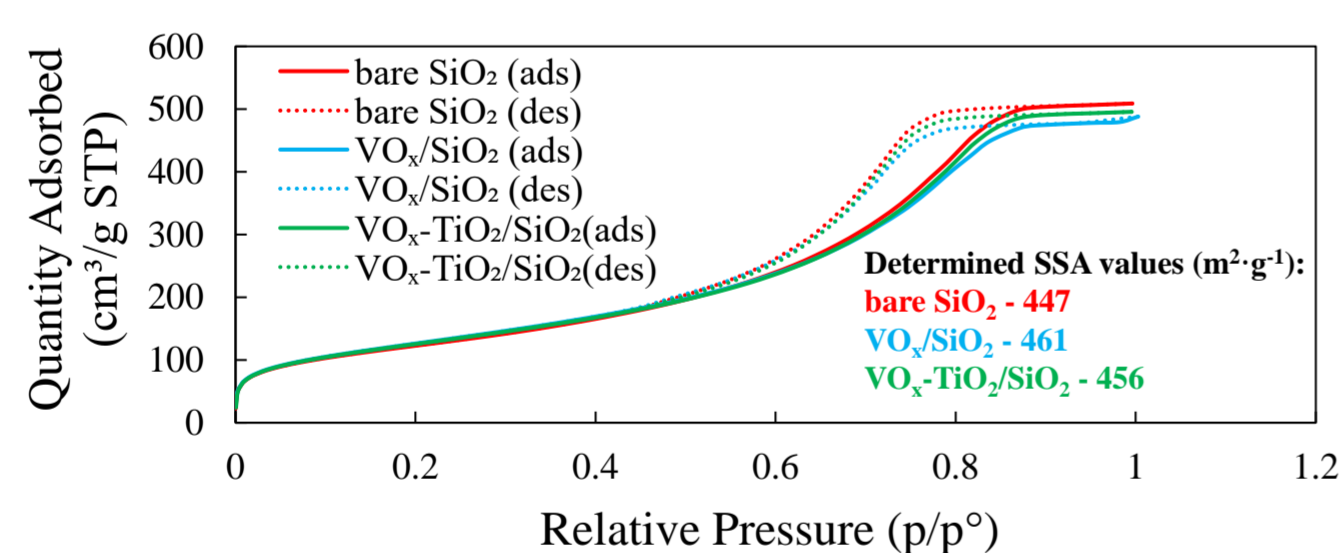
**Titanium precursor:**  
Titanium tetrachloride (TiCl<sub>4</sub>)



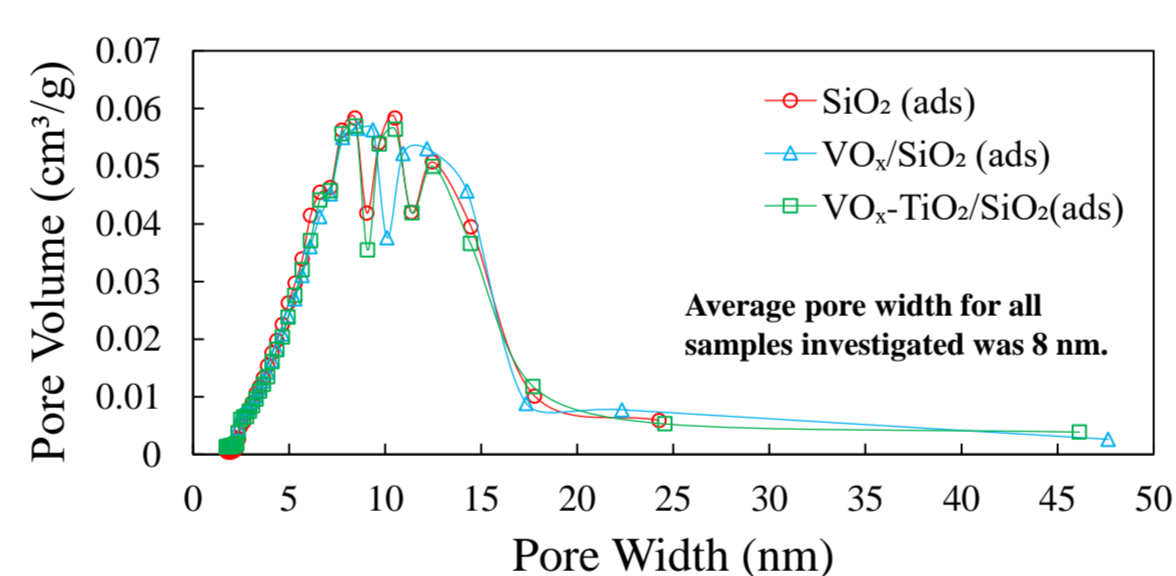
Fluidized bed atomic layer deposition technique has been used to prepare a highly dispersed VO<sub>x</sub>-based oxide catalysts for NH<sub>3</sub>-SCR de-NO<sub>x</sub>

Parameters	Deposited material	VO <sub>x</sub>	TiO <sub>2</sub>
Number of cycles		1; 3; 6; 12	1
Exposure time by metal precursor per 1 cycle, min		20; 60; 150	1
Exposure time by co-reactant per 1 cycle, min		20; 60; 150	1
Purge time, min		5	5
Volumetric gas flow rate, l/min		0.4	0.4
Temperature of the precursor bubbler, °C		60	~23 (Room temperature)
Temperature of the co-reactant bubbler, °C		~23	~23
Temperature inside the Reactor, °C		150	90

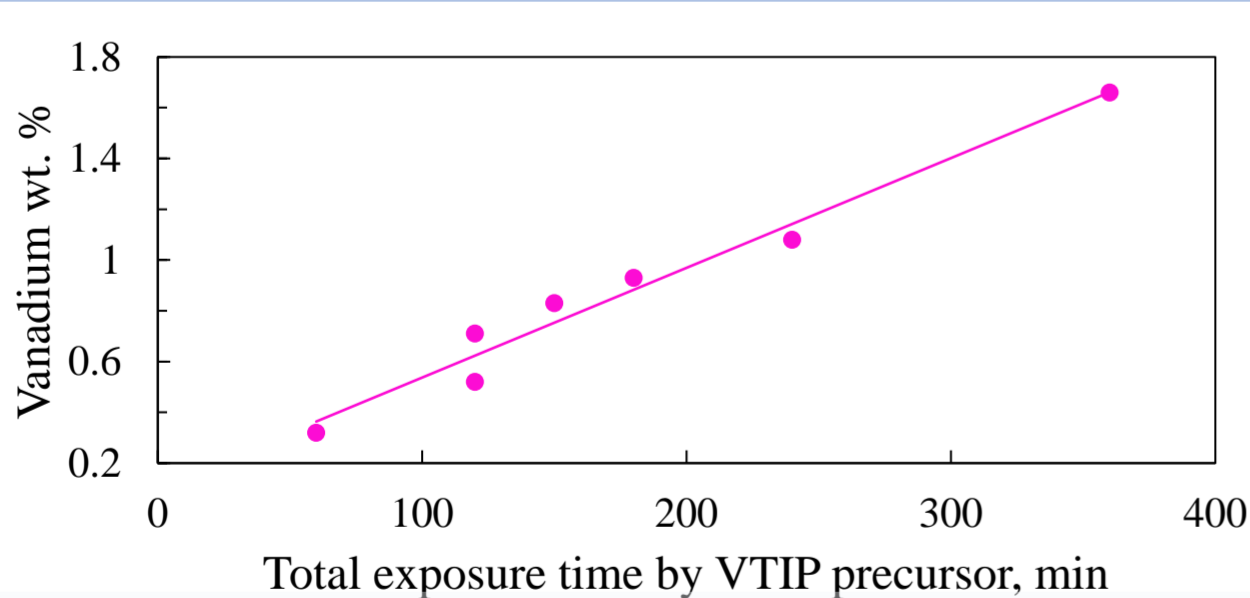
## Results



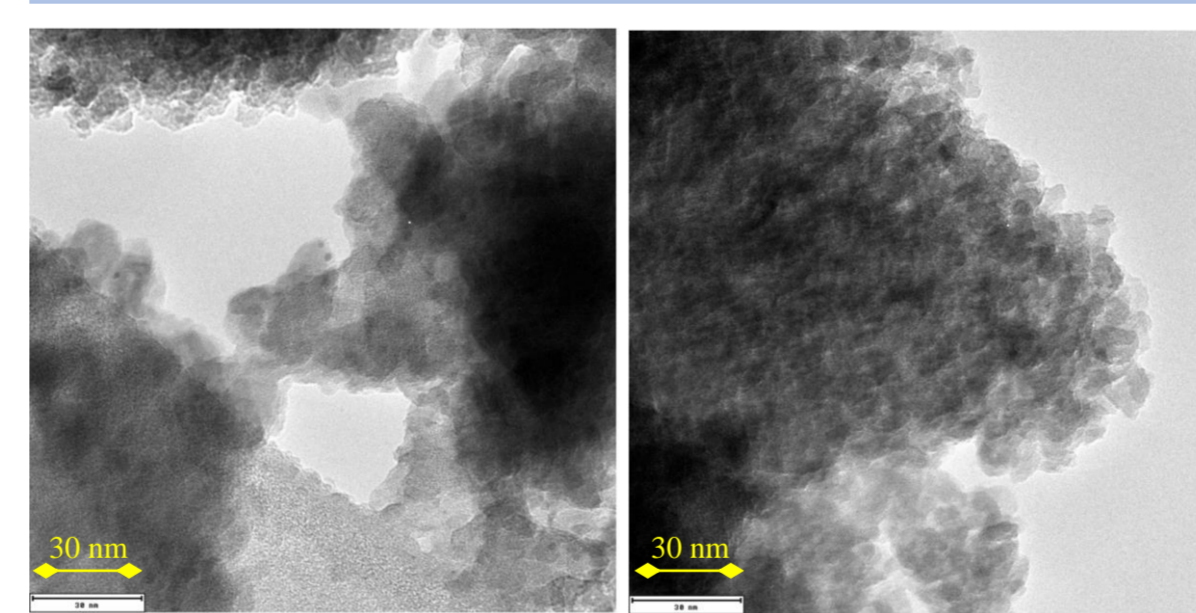
Nitrogen adsorption/desorption isotherm of bare SiO<sub>2</sub>, as-prepared VO<sub>x</sub>/SiO<sub>2</sub> (1.66 wt.%) and VO<sub>x</sub>-TiO<sub>2</sub>/SiO<sub>2</sub> (1 wt.%; 0.15wt.%)



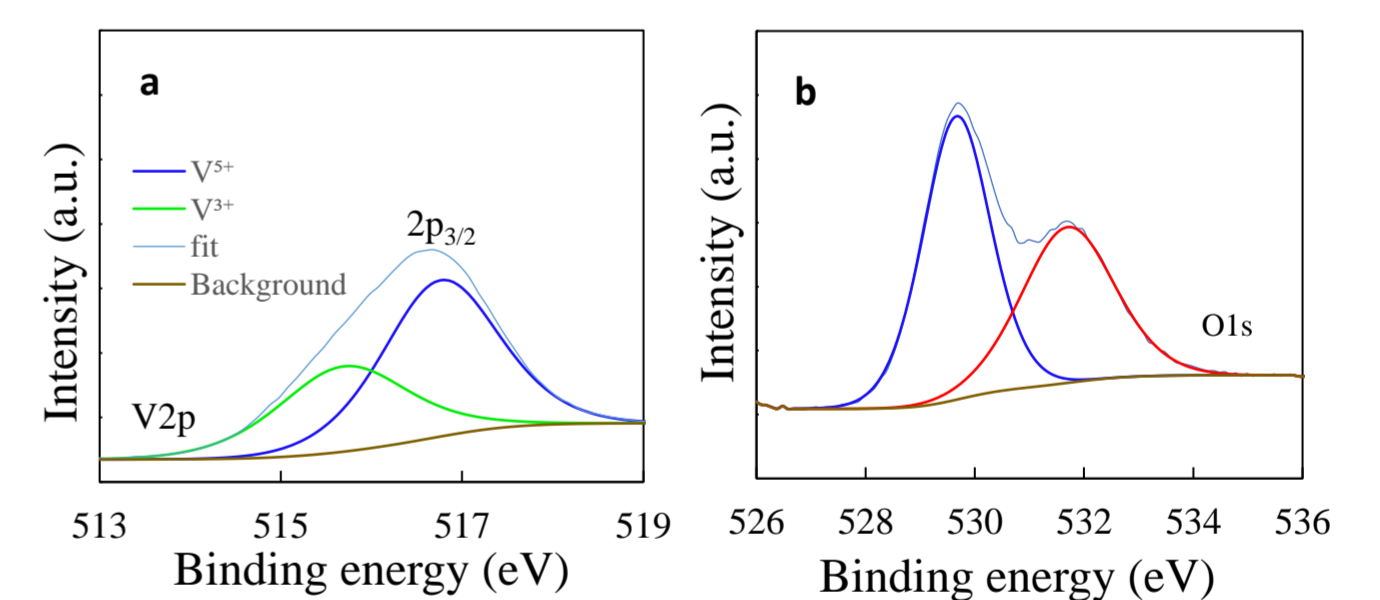
Pore distribution of bare SiO<sub>2</sub>, as-prepared VO<sub>x</sub>/SiO<sub>2</sub> (1.66 wt.%) and VO<sub>x</sub>-TiO<sub>2</sub>/SiO<sub>2</sub> (1 wt.%; 0.15wt.%)



The weight loading of vanadium as a function of total exposure time (based on ICP-OES results)



TEM images of as-prepared VO<sub>x</sub>/SiO<sub>2</sub> (1.66 wt.%)



The V2p<sub>3/2</sub> and O1s spectra of as-prepared (a,b) and calcined at 400°C (c,d) VO<sub>x</sub>/SiO<sub>2</sub> (1.66 wt.%) catalysts

## Conclusions

According to XPS spectra V<sub>2</sub>O<sub>3</sub> and V<sub>2</sub>O<sub>5</sub> species were identified with the predominance of vanadium (V) compounds (V<sub>2</sub>O<sub>3</sub>/V<sub>2</sub>O<sub>5</sub> ratio was 1.6 and 6.3 for as-prepared and calcined samples, respectively), indicating the suitability of the prepared VO<sub>x</sub>-based catalysts for NH<sub>3</sub>-SCR de-NO<sub>x</sub>. The BET analysis revealed that the specific surface area of silica gel powder was not reduced as a result of atomic layer deposition (determined SSA values were 447 m<sup>2</sup>·g<sup>-1</sup>, 461 m<sup>2</sup>·g<sup>-1</sup> and 456 m<sup>2</sup>·g<sup>-1</sup> for bare SiO<sub>2</sub>, VO<sub>x</sub>/SiO<sub>2</sub> and VO<sub>x</sub>-TiO<sub>2</sub>/SiO<sub>2</sub>, respectively), meaning that active VO<sub>x</sub> species with loading of up to 1.66 wt.% were highly dispersed on the carrier surface without clogging the pores. The high dispersion of VO<sub>x</sub> species was also confirmed by TEM results where precise identification of particles was problematic. Thus, it was supposed that VO<sub>x</sub> was deposited in a form of very small particles (less than 3 nm in size) without aggregation, which should positively affect the NO<sub>x</sub> conversion efficiency. The average pore size observed by N<sub>2</sub> adsorption method for all samples investigated was ca. 8 nm, while the cumulative pore volume was equal to 0.8 cm<sup>3</sup>·g<sup>-1</sup>, 0.76 cm<sup>3</sup>·g<sup>-1</sup> and 0.78 m<sup>2</sup>·g<sup>-1</sup> for bare SiO<sub>2</sub>, VO<sub>x</sub>/SiO<sub>2</sub> and VO<sub>x</sub>-TiO<sub>2</sub>/SiO<sub>2</sub>, respectively. All the results obtained demonstrate the high potential of ALD for preparation of NH<sub>3</sub>-SCR de-NO<sub>x</sub> catalysts being characterized by highly distributed active species on porous substrates with a complex structure and a high surface area.

## References

- [1] European Environment Agency, Air quality in Europe - 2019 report. 2019. 99 pp.
- [2] Gao, F. Tang X., Yi H., Zhao S., Li C., Li J., Shi Y., Meng X. 2017. A review on selective catalytic reduction of NO<sub>x</sub> by NH<sub>3</sub> over Mn-based catalysts at low temperatures: catalysts, mechanisms, kinetics and DFT calculations, Catalysts 7(7).
- [3] Brandon J. O'Neill, David H. K. Jackson, Jechan Lee, Christian Canlas, Peter C. Stair, Christopher L. Marshall, Jeffrey W. Elam, Thomas F. Kuech, James A. Dumesic, and George W. Huber. 2015. Catalyst design with atomic layer deposition, ACS Catalysis 5:1804-1825.