Short communication

Effect of support synthesis methods on structure and performance of VO$_x$/CeO$_2$ catalysts in low-temperature NH$_3$-SCR of NO

Thanh Huyen Vuong [a,b], Jörg Radnik [a], Matthias Schneider [a], Hanan Atia [a], Udo Armbruster [a], Angelika Brückner [a,*]

[a] Leibniz Institute for Catalysis at the University of Rostock, Albert-Einstein-Str. 29a, D-18059 Rostock, Germany
[b] School of Chemical Engineering, Hanoi University of Science and Technology, 1 Dai Co Viet, Hanoi 10000, Vietnam

ARTICLE INFO

ABSTRACT

CeO$_2$ supports were prepared by a citrate (C) or a precipitation method (P) before deposition of vanadia by wet impregnation to obtain supported V/CeO$_2$ catalysts. The V/CeO$_2$-P catalyst is more active, reaching $\approx$100% NO conversion and N$_2$ selectivity already below 225 °C at a space velocity of GHSV = 70,000 h^{-1}. XRD, UV-vis-DRS, Raman, pseudo-in-situ-XPS and operando-EPR spectroscopy revealed that this is due to higher surface area and a more effective incorporation of V sites into the support surface, which keeps them in their active valence states +5 and +4 and prevents reduction to inactive V^{3+} as observed on V/CeO$_2$-C.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts, used for selective catalytic reduction (SCR) of NO$_x$ in power plants, operate only at 300–500 °C which is too high for, e.g., diesel or lean-burn gasoline engines. Therefore, development of new catalysts [1,2] or improvement of vanadium-based catalysts [3,4] for low-temperature NH$_3$-SCR of NO$_x$ is needed, whereby vanadia supported on (modified) ceria appeared to be particularly effective [3,5–7]. With VO$_x$/Ce$_x$Zr$_{1-x}$O$_2$, we recently reached almost full NO conversion and N$_2$ selectivity around 200 °C at a space velocity of GHSV = 70,000 h^{-1} [8]. This was attributed to the formation of special —O—Ce–O–V(=O)–O–Zr–O– moieties supposed to support oxygen transport. In these moieties, the V sites shuttle reversibly between V^{5+} and V^{4+} while Ce and Zr species remained essentially tetravalent. Interestingly, we found that the same amount of vanadia deposited on differently prepared CeO$_2$ supports leads to catalysts of rather different performance. A sensitive dependence of the performance of ceria-based catalysts on the synthesis procedure was also observed in other reactions [9–11], for which ceria was prepared by hydrothermal [12], precipitation [9,13], citrate sol-gel [10,14], solution combustion [15], or microemulsion [11] protocols. It is supposed that, depending on the synthesis protocol, oxygen vacancies and structural defects are formed

that in turn influence the Ce^{4+}/Ce^{3+} redox behavior [16,17]. However, at least in NH$_3$-SCR, a detailed analysis of these relations has not yet been performed. This is the aim of the present study. To this end, we compare structure-reactivity relationships of two VO$_x$/CeO$_2$ catalysts in which 5 wt.% of V$_2$O$_5$ were deposited by the same procedure on CeO$_2$ supports prepared by precipitation (V/CeO$_2$-P) or a citrate sol-gel method (V/CeO$_2$-C). Synthesis, catalytic performance and selected characterization results of the latter catalyst have already been described in our recent paper [8] and are cited here only for comparison.

2. Experimental

CeO$_2$ supports were prepared by a sol-gel method from citric acid and cerium nitrate (CeO$_2$-C) [8,14], or by precipitation from cerium nitrate in aqueous ammonia (CeO$_2$-P) [9]. The V/CeO$_2$ catalysts with a nominal content of 5 wt.% V$_2$O$_5$ were prepared by wet impregnation of the calcined CeO$_2$ powders with a solution of ammonium metavanadate in oxalic acid.

Catalysts were characterized by X-ray diffraction (XRD) for their crystallinity, by inductively coupled plasma optical emission spectroscopy (ICP-OES) for chemical composition, by nitrogen adsorption for BET surface area and pore properties, by X-ray photoelectron spectroscopy (XPS) for their surface properties as well as by Raman, UV-vis diffuse reflectance and electron paramagnetic resonance (EPR) spectroscopy.

* Corresponding author.
E-mail address: angelika.brueckner@catalysis.de (A. Brückner).
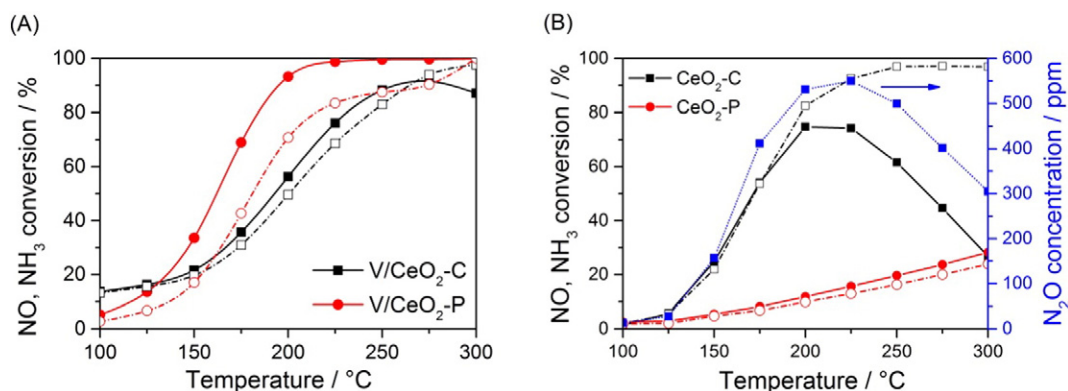
Fig. 1. NO (solid symbols and lines), NH$_3$ conversion (open symbols and dashed lines) over: (A) V/CeO$_2$-C (squares) and V/CeO$_2$-P (circles); (B) V-free CeO$_2$-C (squares) and CeO$_2$-P (circles); and N$_2$O concentration (solid squares and dotted lines) over V-free CeO$_2$-C as a function of temperature. Feed composition: 0.1% NO, 0.1% NH$_3$, 5% O$_2$/He, GHSV = 70,000 h^{-1}

Catalytic performance in NH$_3$-SCR of NO was measured between 100 and 300 °C with 100 mg catalysts and a feed composition of 0.1% NO, 0.1% NH$_3$, 5 vol.% O$_2$/He at a GHSV of 70,000 h − 1.

For more experimental details see Supporting information SI-A.

3. Results and discussion

3.1. Catalytic behavior

From Fig. 1B it is evident that already the pure supports show some activity in the catalytic reaction. While NO and NH$_3$ conversion is low over the whole temperature range on support CeO$_2$-P, sample CeO$_2$-C shows almost similar conversion around 200 °C as the corresponding catalyst V/CeO$_2$-C. However, above 200 °C undesired NH$_3$ combustion and N$_2$O formation reduce NO conversion and N$_2$ selectivity. Thus, both pure supports show detrimental catalytic behavior and are therefore not further considered here.

Catalyst V/CeO$_2$-C is much less active than V/CeO$_2$-P, reaching a maximum NO conversion of 90% at only 275 °C which even drops at higher temperature due to undesired oxidation of NH$_3$ (Fig. 1A). In contrast, V/CeO$_2$-P reaches full conversion already at 225 °C and remains stable. In due course, we present the results of a comprehensive characterization study to find out reasons for this different behavior.

Above 200 °C, NO conversion declines markedly and a rather high concentration of undesired N$_2$O is formed (Fig. 1B). In the following section, we present the results of a comprehensive characterization study of the catalysts to find out reasons for their different behavior.

3.2. Catalyst characterization

XRD patterns of both CeO$_2$-C and CeO$_2$-P supports show the characteristic peaks of the cubic fluorite structure (Fig. SI-1). They are sharper and more intense for CeO$_2$-C due to its larger mean crystallite size and a smaller strain derived by the Williamson-Hall equation [18] (Table 1, SI-A). The strain in CeO$_2$-P is about twice as high as in CeO$_2$-C which might

promote oxygen mobility inside the support. Deposition of vanadia does not lead to any changes, indicating that highly dispersed and/or amorphous VO$_x$ surface species dominate in both samples. However, the Raman spectra of both catalysts show some weak bands of V$_2$O$_5$ nanocrystals too small to be detectable by XRD [19] (Fig. SI-2). The bulk V/Ce atomic ratios are similar and close to the nominal value corresponding to 5% of V$_2$O$_5$ (Table 1). The BET surface area and pore volume of CeO$_2$-P and V/CeO$_2$-P are significantly higher than those of CeO$_2$-C and V/CeO$_2$-C. This might be due to the fact that the P-samples are mesoporous while the C-samples are non-porous or macroporous [20] (Fig. SI-3).

The UV-vis-DR spectra of the pure supports show bands below 250 nm, around 280 and 350 nm. The first is usually assigned to O^{2-} → Ce^{3+} charge-transfer (CT) transitions while the latter two arise from O^{2-} → Ce^{4+} CT and interband transitions (Fig. 2) [18,21]. For CeO$_2$-P, the intensity below 250 nm is higher suggesting a higher content of Ce^{3+} which, for maintaining electroneutrality, must create oxygen vacancies. This is supported by the fact that the absorption edge of CeO$_2$-P (E$_g$ = 2.72 eV) is red-shifted compared to CeO$_2$-C for which E$_g$ = 3.00 eV is close to the bulk value of CeO$_2$ (3,15 eV) [22], as well as by Raman data discussed below. Such red shift is caused by a drop in lattice symmetry due to increased disorder, which may result from small nanoparticles with abundant surface defects and/or replacement of Ce by other metal ions with different diameter [18,21]. It agrees with the smaller crystallite size and higher strain of CeO$_2$-P (Table 1).

Deposition of vanadia on these supports leads to an increase of absorbance below 400 nm, characteristic for O^{2-} → V^{5+} CT bands of VO$_x$ single sites and small V$_x$O$_y$ clusters [23]. The weak shoulder extending from 400 to 500 nm in sample V/CeO$_2$-C might arise from few V$_2$O$_5$ nanocrystals [24], which are evident, too, from the Raman spectra. Interestingly, a marked red shift of the absorption edge is observed for V/CeO$_2$-P. One could suppose that this is due to a higher V site agglomeration in this sample, since it has been shown previously that the absorption edge energy of V$_x$O$_y$-containing oxides decreases with the number of V-O-V bridges [25]. However, the Raman spectra in Fig. SI-2 do not

Table 1
Bulk V/Ce ratio[a], chemical composition crystallite size, specific surface area and pore volume, band gap energy of supports and catalysts.

Sample	V/Ce ratio[a]	Mean crystallite size[b] (nm)	Strain[b]	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Band gap energy (eV)[c]
CeO$_2$-C		24.3	0.00138	12.7	0.026	3.00
CeO$_2$-P		14.1	0.00265	61.2	0.060	2.72
V/CeO$_2$-C	0.100			11.5	0.043	2.58
V/CeO$_2$-P	0.092			45.4	0.053	2.25

[a] From ICP.

[b] From XRD using the Williamson-Hall equation (see SI-A).

[c] From UV-vis-DRS.