Applied Catalysis B: Environmental 234 (2018) 318–328

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Induced effect of tungsten incorporation on the catalytic properties of $CeVO_4$ systems for the selective reduction of NO_x by ammonia

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ARTICLE INFO

Keywords:
Ammonia
$CeV_{1-x}W_xO_4$ mixed oxides
Fast-SCR
Selective catalytic reduction
NO_x

ABSTRACT

The SCR performances of aged W-doped $CeVO_4$ catalysts were investigated in fast-, NO_2- and standard conditions. Bulk $CeV_{1-x}W_xO_4$ catalysts were prepared in soft conditions, according to a hydrothermal synthesis route at 180 °C leading to the *ad hoc* tetragonal structure. The aging procedure consisted in exposing the samples to 10 vol.% H_2O diluted in air at 600 °C. The impact of this aging process was investigated as a function of tungsten loading, with x varying in the range 0.02–0.15. A clear beneficial effect is distinguishable at high temperature, i.e., above 300 °C, associated to a sharp selectivity enhancement irrespective of the operating conditions and tungsten loading. On the contrary, a slight detrimental effect on the reaction rate is clearly discernible in standard-conditions below 300 °C. It was found that the thermal aging induces more extensive diffusion of V^{5+} species assisted by the presence of substituted W^{6+}. It was also demonstrated that tungsten diffuses more readily than V^{5+} leading ultimately to a significant surface enrichment and the formation of $Ce_4W_9O_{33}$ mixed oxide evidenced from XRD and Raman spectroscopy. Hence, tungsten would rather act as a stabilizer than promoter avoiding the sintering of monomeric VO_x species to more active polyvanadate species but also less selective. The gain observed in selectivity at high temperature can be equally explained by a greater stabilization of Brønsted acid sites and the preservation of the dispersion of monomeric vanadate species preventing the occurrence of ammonia oxidation.

1. Introduction

Supported vanadium catalysts on titania, doped by various metal oxide additives [1,2] are currently used for the ammonia Selective Catalytic Reduction (SCR). Now, V_2O_5-WO_3/TiO_2 is recognized as a benchmark for the abatement of NO_x from stationary emission sources [3,4]. The optimal composition of vanadium and tungsten is generally below 2 wt.% and 10 wt.%, respectively, corresponding to a remarkable selectivity behavior in the presence of a large excess of oxygen [3,5]. In fact, such an optimization in the past three decades was not an easy task and has been the subject of numerous investigations [6–11], which sometimes led to controversial statements regarding the nature of active and selective vanadium species as a function of their coverage. Today, there is a general agreement which emphasizes the fact that isolated VO_x species, stabilized in distorted tetrahedral environment, can polymerize to more active metavanadates species at increasing vanadium loading but becoming at the same time less selective than isolated vanadium species. On the contrary, the role of tungsten still remains unclear leading to conflicting viewpoints for explaining the specific interactions between tungsten, vanadium and/or TiO_2 which can originate significant improvements in the selectivity and in the acidic properties of the surface through the formation of Brønsted acid sites [3]. Alemany et al. [12] previously suggested that tungsten would act as spectator allowing a closer proximity of isolated vanadium oxo centers to form most active dimeric V—O—V structures. On the contrary, Kompio et al. [13] found that tungsten would mainly originate a dilution effect, privileging an intimate mixing between tungsten and vanadia instead of the formation of oxidic vanadium islands. Hence, according to Alemany et al. [12], tungsten would mainly act as stabilizer rather than promoter in agreement with previous investigations [14]. However, a closer interaction between W and V can also lead to more reducible vanadium species which can attest improved redox properties of vanadium moieties.

More recently, V_2O_5-WO_3/TiO_2 catalysts were developed for automotive applications especially the urea-Selective Catalytic Reduction (urea-SCR). It is obvious that today, there is a strong renewed interest

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https://doi.org/10.1016/j.apcatb.2018.04.059
Received 20 February 2018; Received in revised form 19 April 2018; Accepted 23 April 2018

likely associated to this latter practical application [13,15,16] in order to promote the tolerance of V_2O_5-WO_3/TiO_2 catalysts to contaminants in fossil fuels and biodiesel, as well as their hydrothermal resistance. Indeed, well-dispersed vanadia species are usually sensitive to thermal sintering above 650 °C. Their aggregation can ultimately lead to V_2O_5 clusters that can sublime in the temperature conditions and enhance the formation of undesired N_2O. These phenomena considerably limit their automotive applications [17,18].

Recent developments of bulk vanadium-free catalysts led to successful achievements with the discovery of hydrothermally stable CeO_2-WO_3/TiO_2 compared to benchmarks up to 670 °C exposed in 5 vol.% water in air for 64 h [19]. Previous attempts also demonstrated that the incorporation of rare earths to V_2O_5-WO_3/TiO_2 prevents a loss of specific surface through the transformation of anatase to rutile and favors the formation of more thermally stable rare earth vanadate species [20]. Recently, iron vanadates supported on titania (9 wt.% $FeVO_4$/TiO_2) revealed improved performances thanks to a high dispersion of $FeVO_4$, a higher density of defective sites and electronic inductive effects between Fe^{3+} and V^{5+} [21]. Interestingly, the authors explained that the peculiar properties of those catalysts were ascribed to VO_x surface enrichment originating high ammonia-SCR activity and durability [21,22]. Such explanations match correctly with our recent observations on bulk $CeVO_4$-SCR catalysts: Unreducible V^{5+} species stabilized in tetrahedral geometry of the zircon-type structure of $CeVO_4$ can diffuse at the surface and aggregate into more reducible polymeric species [23]. Such reconstructions led to unprecedented performances at 200 °C compared to homologous supported VO_x/CeO_2 catalyst [24] reflected by a sharp increase of the normalized rates, shifting from 11.9 to 171.5 $\mu mol\,s^{-1}\,m^{-2}$, for the standard-SCR [23]. This rate enhancement was found closely dependent on the aging conditions and could be viewed as the stabilization of more stable segregated 2D-VO_x species than those currently obtained on more classical alumina and silica supports conventionally prepared via a simple wet impregnation method. Such stronger interactions have been already characterized, allowing higher dispersion limit reaching 9–12 V atoms per nm^2 of ceria support [25]. The coexistence of ceria with vanadia sample can also lead to more complex surface properties ascribed to V—O—V and V—O—Ce surface structures that can also originates diverse acidic and redox sites [26].

The present study deals with the incorporation of tungsten to $CeVO_4$ catalysts for the selective reduction of NO_x by ammonia. Particular attention will be paid to the impact of W in monitoring the nature of dispersion of segregated oxidic vanadium species and their relative stability especially if tungsten can act as spectator playing the role of spacer and/or modifying the relative reactivity of VO_x entities through the formation of mixed metallic oxide compounds that could enhance the Brønsted acidity suggested as a crucial parameter in SCR catalysis.

2. Experimental

2.1. Catalyst preparation

$CeV_{1-x}W_xO_4$ were prepared according to a classical hydrothermal route as described elsewhere [27,28]. First, Na_3VO_4 (99.98% Sigma-Aldrich) was dissolved in 50 ml of dionized water under vigorous stirring. An aqueous solution of nitric acid (3 M) was added dropwise until reaching a pH value of 1.8 corresponding to the stabilization of ${VO_2}^+$ cations. Afterwards, an aqueous solution obtained from the dissolution of $Ce(NO_3)_3.6H_2O$ and $(NH_4)_6H_2W_{12}O_{40}.xH_2O$ precursors (supplied by Sigma-Aldrich) was added to the former solution containing ${VO_2}^+$ cations. An aqueous solution of sodium hydroxide (1 M) was added dropwise to enable the precipitation of the hydroxide precursors. The suspension thus obtained, with pH stabilized at 8.5, was hydrothermally treated at 180 °C for 24 h, to promote the formation of the zircon-type structure for $CeV_{1-x}W_xO_4$ mixed oxides with x varying in the range 0–0.15. The solid samples were recovered by centrifugation, abundantly washed with dionized water and finally with ethanol. After drying in air at 80 °C for 24 h, freshly-prepared samples, labeled *"fresh"* $CeV_{1-x}W_xO_4$, were aged at 600 °C, exposed to a gas mixture composed of 10 vol.% H_2O diluted in air with a space velocity of 0.024 g h L^{-1}. The elemental analysis, performed by Energy Dispersive X-ray Spectroscopy, did not reveal detectable loss of vanadium and tungsten induced by the thermal aging under wet atmosphere.

2.2. Physicochemical characterization

2.2.1. Bulk characterization

X-Ray diffraction (XRD) measurements were carried out on a Bruker AXS D8 Advance diffractometer in Bragg-Brentano geometry fitted with a LynxEye Super Speed detector. XRD patterns were recorded with Cu Kα radiation (λ = 0.154 nm, 40 kV, 30 mA) in the 10–80° 2θ range with a 0.02° 2θ step.

Raman spectroscopy analysis was performed on a Labram HR Jobin Yvon spectrometer. Spectra were recorded by using an excitation wavelength of 532 nm. The calibration was systematically checked by a silicon line at 520 cm^{-1}.

H_2-Temperature-Programmed Reduction experiments (H_2-TPR) were performed on a Micromeritics Autochem II 2920 instrument with a flow of 5 vol.% H_2 diluted in Ar and at constant gradient temperature of 10 °C min^{-1}.

The ^{51}V magic angle spinning nuclear magnetic resonance (MAS-NMR) experiments were performed at 210.4 MHz on a 18.8 T AVANCE III Bruker NMR spectrometer. The spectra were acquired with a 3.2 mm probehead with a spinning frequency of 22 kHz, a 0.5 µs pulse length (corresponding to a $\pi/12$ flip angle), 1024–2048 transients and a recycle delay of 0.5 s. Additional experiments were performed at a spinning frequency of 20 kHz to discriminate between the isotropic signals and the spinning sidebands (denoted with (*) in the following). The ^{51}V chemical shifts were referred to $VOCl_3$ solution as 0 ppm.

Continuous wave electronic paramagnetic resonance (CW-EPR) experiments were acquired on an X-band ELEXYS E580 Bruker spectrometer at room temperature with 256 transients, 2 mW of microwave power and 2 G of modulation amplitude.

2.2.2. Surface characterization

Specific surface area was calculated from N_2 physisorption measurements at −196 °C with a Flowsorb III device. Prior physisorption, samples were cleaned at 100 °C for 1 h under a flow of helium at ambient pressure.

X-ray Photoelectron Spectroscopy (XPS) analysis was performed on an AXIS Ultra DLD Kratos spectrometer fitted with a mono-chromatized aluminium source for excitation (150 W). Binding energies (B.E.) values were calibrated compared to the O 1s B.E. centered at 530.5 eV as internal reference.

Ammonia adsorption-desorption experiments were carried out on a Micromeritics Autochem II 2920 instrument. Ammonia concentration in the outlet mixture was monitored by an Omnistar™ Pfeiffer Mass Spectrometer. Prior to experiments, the samples were outgassed under helium at 500 °C. Temperature-programmed desorption experiments were performed under He on pre-adsorbed samples at 100 °C with a temperature ramp of 10 °C min^{-1}.

Infrared spectra recorded during pyridine adsorption-desorption experiments were recorded on a Nicolet Protégé 460 infrared spectrometer equipped with MCT detector (4 cm^{-1}). The samples were preliminary outgassed under vacuum (10^{-5} mbar) at 450 °C. Pyridine adsorption was performed at room temperature up to saturation coverage. IR spectra were recorded at after desorption under vacuum at different temperatures. The normalized concentration of Lewis and Brønsted acid sites were quantified based on the integrated IR bands taking into account absorption coefficients of respectively 1.5 cm μmol^{-1} and 1.8 cm μmol^{-1} [29].