Supporting Information for

Unveiling the role of microwave induction on V_2O_5 @AC catalyst with enhanced activity for low temperature NH₃-SCR reaction: Experimental and DFT study

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Content

S1. Catalysts preparation

S1.1. Acid pretreatment of AC support

A commercial activated carbon (AC) (Ningxia Huahui Activated Carbon Co.Ltd) was pretreated in HNO₃ solution (30%) at 60 °C for 1 h during continuous stirring. Then, the material was filtrated and washed with deionized water until the pH reached up to 7, and finally dried at 120 °C for 6 h.

S1.2. 3V₂O₅@AC catalysts preparation

The $3V_2O_5@AC$ catalysts were synthesized by microwave-assisted wet impregnation method. In brief, a certain amount of oxalic acid was dissolved in 30 mL of deionized water, then ammonium metavanadate (NH₄VO₃) was added to the solution. After stirring for 30 min, the beaker containing the preoxidized AC impregnated with the above light green aqueous solution was placed in the modified domestic microwave oven (xianghu, China, XH-200A, 2.45 GHz) with different microwave power. After the impregnation for 1 h, the samples were dried at 120 °C for 5 h. Subsequently, the sample was calcined at 500 °C for 5 h in the flow of N₂ and preoxidized at 250 °C for 2 h in the static air atmosphere. The obtained catalysts were denoted as $3V_2O_3@AC-X$ (X = 100, 200, 300, and 350 W), where X represented the microwave power. While for the $3V_2O_5@AC$ catalyst, the slurry was stirred at 60 °C for 1 h in a water bath, afterwards, the sample was dried and calcined like the above synthetic procedure. The loading of V₂O₅ on each V₂O₅@AC and V₂O₅@AC-X catalysts is 3 wt.%. Finally, all of the samples were compressed into tablet form and sieved to 40-60 mesh before use.

S2. Catalysts characterization

The textural characteristics of samples were measured by N₂ adsorption and desorption at liquid nitrogen temperature (-196 °C) on a Micromeritics ASAP 2020. Before each analysis, samples were pre-degassed at 250 °C for 4 h to remove physically adsorbed species. The specific surface area of the catalysts was evaluated using the Brunauer–Emmett–Teller (BET) method, and the average pore size and the volume were analyzed by using the Barrett-Joyner-Halenda (BJH) model.

The morphologies of samples were characterized by Scanning Electron Microscopes (Hitachi Regulus8100, Japan) equipment. The samples were fixed onto silicon wafers and to be dried in a vacuum atmosphere and then treated by gold sputtering.

The crystal structures of the catalysts were determined on an X-ray diffractometer (Bruker/AXS D8 Advance) with Cu K α ($\alpha = 0.15406$ nm) radiation at 40 kV and 40 mA. The samples were scanned from 10 to 80° (2 θ) with a step size of 0.02°. Raman spectra were collected on a spectrometer (Horiba, JYT64000) under ambient conditions and a laser with a wavelength of 532 nm as the excitation source.

 H_2 -TPR (Hydrogen-temperature programmed reduction) profiles were collected on a chemisorption apparatus (Micromeritics Auto Chem II 2920). Prior to the TPR experiments, the 50 mg sample was loaded into a quartz reactor and pretreated in pure N_2 (> 99.999%, 50 mL min⁻¹) at 300 °C for 60 min. When the baseline remained unchanged, the TPR profile of the catalyst was collected by heating the sample from 40 to 900 °C in a flow of 10% H₂/Ar (40 mL min⁻¹) at a heating rate of 10 °C min⁻¹. The consumption of H₂ was monitored continuously by a thermal conductivity detector.

NH₃-temperature programmed desorption (NH₃-TPD) experiments were carried out over a chemisorption apparatus (Micromeritics Auto Chem II 2920). The samples were preheated to 450 °C under a helium flow for 60 min, and then cooled to 40 °C for NH₃ adsorption. A stream containing 10% NH₃/He (30 mL min⁻¹) was introduced for 1 h to achieve the adsorption equilibrium. Then the samples were purged with He for 1 h to remove the weakly adsorbed NH₃. The profiles of the catalyst were recorded as the sample was heated from 40 to 900 °C at a rate of 10 °C min⁻¹. And the procedure of NO-TPD was similar to NH₃-TPD just replaced NH₃ with NO + O₂.

X-ray photoelectron spectroscopy (XPS) was performed on an X-ray photoelectron spectrometer (Thermal Scientific, ESCALAB 250 XI) using Al Kα radiation operating at an accelerating power of 15 KW. The C 1s peak at 284.8 eV was considered as a reference for the binding energy calibration.

In situ diffuse reflectance infrared transform spectroscopy (*in situ* DRIFTS) experiments were conducted to identify surface adsorbed species and intermediate species on the presented catalysts using FTIR spectrometer (Bruker Tensor II) with BaF_2 windows, which is equipped with liquid N₂ cooled high-sensitive MCT detector. Prior to each experiment, the sample was pretreated at 300 °C for 1 h in a flow of 30 mL min⁻¹ He (> 99.999%) and then cooled to 50 °C. Afterward, the background

spectrum was recorded in a continuous He (> 99.999%, 50 mL min⁻¹) atmosphere and was subtracted from the sample spectrum. Subsequently, the sample was exposed to a flow of 30 mL min⁻¹ of 1000 ppm NH₃ or 1000 ppm NO + 6% O₂ for 1 h for saturation adsorption and purified with He (> 99.999%, 50 mL min⁻¹) to remove NH₃/NO from the gas phase and physical adsorption at 100 °C, and the spectra were recorded at 50 °C with different reaction times. All spectra were collected from 4000 to 400 cm⁻¹ by accumulating 32 scans with a resolution of 4 cm⁻¹.

S3. Catalyst activity test

The SCR activity measurements were carried out in a fixed-bed quartz flow reactor containing 1 mL catalyst of 40-60 mesh at atmospheric pressure. The reaction condition was controlled as follows: 1000 ppm NO, 1000 ppm NH₃, 6% O₂, 10% H₂O (when used), 300 ppm SO₂ (when used), and the balance gas is N₂. The total flow rate of the feed gas was 500 mL·min⁻¹ and the gas hourly space velocity (GHSV) was approximately 30,000 h⁻¹. The concentrations of NO was continuously measured using a Signal NO_x analyzer and N₂O was monitored using a Bruker Tensor 27 FTIR spectrometer. The reaction system was maintained at each reaction temperature for 30 min before analysis. The equations to calculate NO_x conversion and N₂ selectivity were as follows:

$$NO_x \text{ conversion } (\%) = \left(1 - \frac{[NO_x]_{out}}{[NO_x]_{in}}\right) \times 100$$
(S1)

$$N_2 \text{ selectivity (\%)} = (1 - \frac{[NO_2]_{out} + 2[N_2O]_{out}}{[NO]_{in} + [NH_3]_{in}}) \times 100$$
(S2)

S4. Computational methods and constructed models

Periodic density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP)¹. The projector augmented wave (PAW) method combined with a plane wave basis set was used to describe the core and valence electrons². The exchange correlation effects are investigated within the generalized gradient approximation according to Perdew, Burke, and Ernzerhof (GGA-PBE)³. The spin-polarized calculations were also taken into account and the cutoff energy was set to 400 eV. All structures were relaxed until the forces over each atom were smaller than 0.05 eV Å⁻¹ and a Monkhorst-Pack k point of $2 \times 2 \times 1$ was selected for the Brillouin zone integration. The Hubbard correction (DFT + U) was applied to solve the strong electron correlation in the transition metal atoms, where the U = 3 eV was adopted in all calculations ⁴. The dispersion correction (DFT-D3) was implemented. V₂O₅ surface structure was constructed by using a (2 × 2) supercell and a vacuum thickness of the model was set to 15 Å to prevent other periodic cell from influencing the reaction.

The V_2O_5 model and adsorbed molecule were also optimized geometrically by VASP, and the adsorbed energy of those molecules are calculated following the formula:

$$\Delta E_{ad} = E_{system} - E_{surface} - E_{adsorbate}$$
(S3)

Wherein, E_{system} represents the calculated electronic energy of the given geometry containing the V₂O₅ and the adsorbed molecules, E_{model} is the calculated energy for V₂O₅ model, and $E_{adsorbate}$ is the electronic energy for the adsorbate attached to the V₂O₅ model like NO, NH₃, NO₂, and O₂. Note that the lower value for ΔE_{ad} indicates the stronger interaction between the adsorption substrate and reactants.

The electron density difference could be used to describe the charge transfer on the catalyst surface during the reaction. The electron density difference $(\Delta \rho)$ was expressed by the formula (S4):

$$\Delta \rho = \rho_{adsorbate/surface} - \rho_{adsorbate} - \rho_{surface}$$
(S4)

where $\rho_{adsorbate/substrate}$ was the total electron density of the adsorption system. $\rho_{adsorbate}$ and $\rho_{surface}$ denoted the unperturbed electron densities of the adsorbate and catalyst surface, respectively.

S5. NH₃-SCR activity comparisons

	NO	Reaction		
Sample	conversion	temperature	Reaction conditions	Reference
	(%)	(°C)		
4.71Fe ₂ O ₃ /AC	85	200	$[NO] = [NH_3] = 500 \text{ ppm},$	5
			$[O_2] = 11\%$, GHVS = 12,000 h ⁻¹	
5.17V ₂ O ₅ /AC	80	200	$[NO] = [NH_3] = 500 \text{ ppm},$	6
			$[O_2] = 5\%, GHVS = 12,000 \text{ h}^{-1}$	
5V ₂ O ₅ /AC	75	200	$[NO] = [NH_3] = 500 \text{ ppm},$	7
			$[O_2] = 5\%, GHVS = 12,000 h^{-1}$	
1V ₂ O ₅ /AC	55	200	$[NO] = 500 \text{ ppm} [NH_2] = 600 \text{ ppm}$	8
			$[O_2] = 3.4\%$, GHSV = 40.000 h ⁻¹	
5V ₂ O ₅ /AC	80			
		-		
5V ₂ O ₅ -3WO ₃ /AC	70	200	$[NO] = 500 \text{ ppm}, [NH_3] = 560 \text{ ppm},$	9
		$[O_2] = 3.3\%, \text{GHSV} = 36,000$		
5V2O5-5ZrO2/AC	67			
3V ₂ O ₅ /AC	72	200	$[NO] = [NH_3] = 500 \text{ ppm},$	10
			$[O_2] = 3.1\%$, GHVS = 15,000 h ⁻¹	
3V ₂ O ₅ /ASC	81	200	$[NO] = [NH_3] = 1000 \text{ ppm},$	11
			$[O_2] = 2\%$, GHSV = 12,000 h ⁻¹	11
3V ₂ O ₅ @AC-300	83	200	$[NO] = [NH_3] = 1000 \text{ ppm},$	Present
			$[O_2] = 6\%, \text{GHSV} = 30,000 \text{ h}^{-1}$	work

Table S1. NH_3 -SCR activity comparisons with the carbon-based catalysts.



S6. Physicochemical property characterization

Fig. S1. (a-e) N_2 adsorption-desorption isotherms and (f) pore size distributions of $3V_2O_5@AC$ and $3V_2O_5@AC$ -X catalysts.

S7. XPS results



Fig. S2. XPS survey spectrum of $3V_2O_5@AC$ and $3V_2O_5@AC$ -300 catalysts.

As demonstrated in Fig. S2, both $3V_2O_5$ @AC and $3V_2O_5$ @AC-X catalysts exhibited similar XPS survey spectra. From the signal peak, it can find that the C, V, and O elements existed in $3V_2O_5$ @AC and $3V_2O_5$ @AC-300 catalysts¹².



Fig. S3. The corresponding reactants adsorption structure of (a, b) NO, (c, d) NH₃, (e, f) O₂, and (g, h) NO₂ on V₂O₅ and V₂O₅-O_v samples. (Color scheme: • V, • O, and • N, and • H)



Fig. S4. The charge difference distribution and Projected density of states (PDOS) of NO₂ on V_2O_5 sample, wherein yellow (blue) represented the accumulation (depletion) of electron. (Color scheme: • V, • O, and • N)



Fig. S5. The total density of states (TDOS) of the NO (a and e), NH_3 (b and f), O_2 (c and g), and NO_2 (d and h) adsorbed on V_2O_5 and V_2O_5 - O_v samples.

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