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Exploration of surface properties of Sb-promoted copper vanadate catalysts for selective catalytic reduction of NO_X by NH_3

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ABSTRACT

A way to fulfill efficient exploitation of desired catalytic nature provided by V oxide is to modify its chemical structure through the incorporation of secondary transition metal species. This paper reports the use of Cu as a modifier of high-valent V oxide (V_2O_5) to produce a class of copper vanadates and their utilization as active sites for the selective catalytic reduction of NO_X (X = 1 or 2) by NH_3 (NH_3-SCR). All catalysts contained ~2 nm-sized copper vanadate particles highly dispersed on anatase with desired vanadate phases. The anatase-supported $Cu_5V_2O_{10}$ provided a greater quantity of acid sites with improved redox character than $Cu_1V_2O_6$, $Cu_2V_2O_7$, and $Cu_3V_2O_8$, thereby exhibiting the greatest NH_3-SCR performance under ideal reaction conditions. Anatase-supported $Cu_3V_2O_8$, however, was found to possess the most preferred surface properties among the catalysts post sulfation. This was evidenced by NH_3-SCR runs of the catalysts under reaction conditions with H_2O and SO_2-including stream, where all catalysts were pre-sulfated by SO_2 and O_2 at elevated temperatures. The NH_3-SCR performance of the optimum $Cu_3V_2O_8$ on anatase was further promoted after sulfation of the catalyst with the optimum content of Sb promoter. The Sb promoter was verified to enhance the redox feature and minimize the interactions among catalyst surfaces and SO_2/ammonium (bi)sulfates during the NH_3-SCR, as evidenced by durability experiments. While showing N_2 selectivities as ~100% at ≤ 400 °C, the optimized Sb-promoted $Cu_3V_2O_8$ on anatase showed high NO_X conversions (≥ ~85%) at ≥ 220 °C and outperformed the control vanadia-tungstate on anatase, which was used to simulate a commercial catalyst. This paper remarks the exploration of the variable structures of metal vanadates can be a good strategy to discover high-performance catalytic solids for the reduction of NO_X species.

1. Introduction

Vanadium (V) oxides have shown appreciable potential as catalytic solids for various chemical transformations involving the scission/activation of C–H, C—O, N—H, N—O, or C—S bonds [1–3]. This is due to the *multi*-functional surface properties of V oxides to provide great redox character [4,5] and tunable Brönsted or Lewis acidity [6,7], all of which are possible through the alteration of the crystal structures of the V oxides [8–10]. It has been reported that the geometric or electronic features of V_2O_5 (V^{5+}) and VO_2 (V^{4+}) were favorable to provide greater amount of catalytic surface defects than V_2O_3 (V^{3+}) and its low-valent V analogues ($V^{\delta+}$, where $0 < \delta < 3$) [8–10]. Hence, high-valent V oxides (*i.e.*, V_2O_5 and VO_2) often outperformed their counterparts in various redox reactions [8,11–13].

Such examples can be found in the literature reports [8,11–13], among which the selective catalytic reduction of NO_X (X = 1 or 2) by NH_3 to form N_2 and H_2O is recently highly-profiled (denoted as NH_3-SCR in Fig. 1(a)) [14–17]. This recent interest is because of a major side-effect of NO_X, that is, it plays a role as a precursor in the formation of ultra-fine particulate matter, which causes severe air pollution [14–17]. For NH_3-SCR, high-valent V oxides exhibit moderate NO_X conversions and good N_2 selectivities at 300–400 °C [14–17]. This results from two primary roles of the multiple surface sites present in the high-valent V oxides, one of which is to provide Brönsted acid sites ($V^{5+}-OH$) or coordinatively unsaturated Lewis acid sites (V^{5+}) to bind with NH_3 *via* the formation of $V^{5+}-O^{-} \cdots NH_4^{+}$ or $V^{5+} \cdots NH_3$ (Fig. 1(b)) [18–21]. The other role of these V oxides has been reported to be the acceleration of NO_X turnover *via* redox cycle. Coordinatively-saturated V^{5+} sites ($V^{5+}=O$) first bind with NO to form $V^{4+} \cdots NO_2$ intermediates and are transformed into $V^{4+} \cdots OH$ upon the generation

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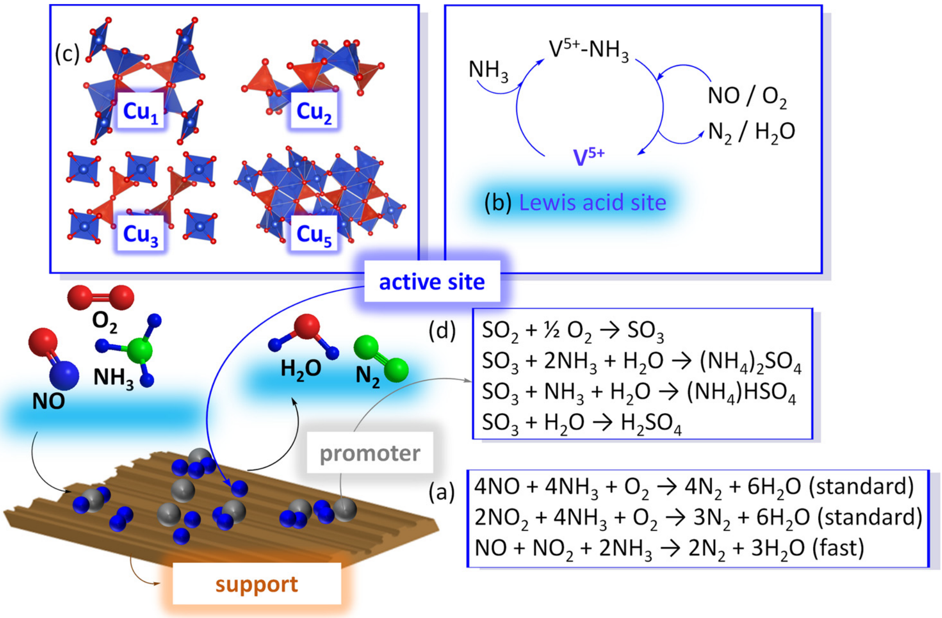

Fig. 1. Schematic representation of selective catalytic reduction of NO_X by NH_3 (NH_3-SCR). Stoichiometry in 'ball-and-stick' is not considered for simplicity. (a) Standard SCR and fast SCR. (b) Surface reaction mechanism on VO_X-based catalytic surface including Lewis acid sites. In (b), reaction stoichiometry is ignored for simplicity. (c) Crystal structures of copper vanadates such as $Cu_1V_2O_6$ (Cu_1), $Cu_2V_2O_7$ (Cu_2), $Cu_3V_2O_8$ (Cu_3), and $Cu_5V_2O_{10}$ (Cu_5). (d) A series of reactions accounting for the generation of ammonium (bi) sulfates (ABS).

of two products (*i.e.*, N_2 and H_2O). This terminates the cycle *via* oxidation, recovering $V^{5+} = O$ while releasing H_2O [18,19,21]. Aforementioned catalytic roles of the surface V^{5+} sites can be further improved when utilizing tungsten oxide (WO_3) and anatase (TiO_2) as a promoter and support, respectively [22,23]. WO_3 helps 1) to suppress the generation of bulk polymeric V aggregates [24] and 2) to retain Brönsted acid sites even at NH_3-SCR temperatures greater than 300 °C [25], whereas catalytic surfaces can accommodate surface-mobile, labile oxygen species to facilitate redox cycle during NH_3-SCR [26,27]. Notably, these benefits could aid in commercializing V_2O_5-WO_3/TiO_2 catalysts for mobile/stationary NO_X emission control units [14–17].

To synthesize a catalyst that outperforms V_2O_5-WO_3/TiO_2 for NH_3-SCR, it is promising to modify V_2O_5 through the incorporation of the secondary metal species (*e.g.*, Ce, Fe, or Mn), leading to the formation of a novel, interesting class of bimetallic V oxides such as $CeVO_4$, $FeVO_4$ and MnV_2O_6 [28–32]. These bimetallic oxides have higher melting points than V_2O_5 and are expected to circumvent the sublimation of toxic V during NH_3-SCR (*i.e.*, 850 °C for $FeVO_4$; 1030 °C for MnV_2O_6; 690 °C for V_2O_5) [33–35]. In conjunction with providing a larger quantity of Brönsted acid sites than V_2O_5, $CeVO_4$ has been reported to 1) stabilize the surface V^{5+} species [28] and 2) accelerate NO_2 production from NO by surface Ce^{4+} species, which could help spur the *so-called* 'fast SCR' (Fig. 1(a)) [28]. In addition, $FeVO_4$ has been shown to incorporate a large quantity of surface defects available to adsorb or activate reactants because of the presence of unique Fe^{3+}-O-V^{5+} linkages [30].

Given the benefits of bimetallic V oxides as catalytic sites for the NH_3-SCR stated above, here we synthesized a series of bimetallic copper vanadate phases active to NH_3-SCR, all of which are well-defined in the CuO-V_2O_5 binary phase diagram such as $Cu_1V_2O_6$, $Cu_2V_2O_7$, $Cu_3V_2O_8$, and $Cu_5V_2O_{10}$ [33,36]. These are denoted as Cu_1, Cu_2, Cu_3, and Cu_5 for simplicity, whereas commercially-available mesoporous anatase (*i.e.*, DT51) was employed as a support to disperse the copper vanadates. Note that an anatase-supported copper vanadate catalyst was previously synthesized for NH_3-SCR by D. Zhang and co-workers [32]. Albeit it showed good NH_3-SCR performance, this catalyst contained mixed bulk phases of CuO, Cu_1, and Cu_2 [32]. Thus, this remains a critical question: 'Which phase among copper vanadate phases does show outstanding NH_3-SCR performance?' This paper details our efforts to answer this question by testing three major hypotheses, which are specified below.

All vanadates crystallize in the *monoclinic* crystal system [33], which allows for the exclusion of different bulk phase-driven geometric effects on the NH_3-SCR performance. Interestingly, Cu_1 consists of distorted octahedral VO_6 sub-units: The V species in Cu_1 are coordinatively saturated by six oxygen atoms and thus are not accessible to NH_3 [33,36]. In contrast, other structures consist of tetrahedral VO_4 sub-units, where the local V environment is open and therefore accessible to NH_3 (Fig. 1(c)) [33,36]. We, therefore, constructed our first hypothesis: 'Cu_2, Cu_3, and Cu_5 can outperform Cu_1 because of the enhanced NH_3 accessibility to the open V^{5+} sites compared to those in Cu_1 during NH_3-SCR.' We also established our second hypothesis such that 'The different atom connectivities of copper vanadates affect the amount of Brönsted acid sites or redox sites present in the resulting catalysts, leading to different NH_3-SCR performance.'

To further promote the NH_3-SCR performance of the catalysts at ≤ 300 °C, the catalysts must be resistant to SO_2 and its derivatives [37–41]. In the course of NH_3-SCR, SO_2 can be oxidized to form SO_3 and sequentially react with NH_3 and H_2O to form ammonium (bi) sulfates (ABS), as illustrated in Fig. 1(d) [37–41]. The ABS species then poison the catalyst surface, limiting the NO_X/NH_3 accessibility during NH_3-SCR [37–41]. This motivated us to use antimony (Sb) as a promoter for the catalysts. Our choice of Sb is based on our previous studies, which have clarified the ability of Sb to reduce the binding energy between catalytic surfaces and SO_2/ABS species [39,41–44]. Our third hypothesis is that 'The NH_3-SCR performance of the catalysts can be maximized by optimizing the Sb composition, where the synergistic effect among copper vanadates and Sb species is predominant.' All catalysts were synthesized, characterized, and tested for the NH_3-SCR to test our three hypotheses. A control, simulating a commercial V_2O_5-WO_3/TiO_2 catalyst, was also synthesized for comparison and tested for NH_3-SCR.

2. Material and methods

2.1. Chemicals

All chemicals were used as-received: $Cu(NO_3)_2{\cdot}3H_2O$ (Daejung, ≥ 99.0%), NH_4VO_3 (Junsei, ≥ 99.0%), $(NH_4)_6H_2W_{12}O_{40}{\cdot}xH_2O$ (Aldrich, 99.99% trace metal basis), $Sb(CH_3COO)_3$ (Alfa Aesar, 97%), DT51 (Cristal Global Co.), $C_2H_2O_4{\cdot}2H_2O$ (Junsei, 99.5–100.2 %), and glacial acetic acid (J. T. Baker, ≥ 99.9%). All gases were purchased from Shinyang: N_2, O_2, Ar, He, 5 vol. % NO/N_2, 5 vol. % NH_3/N_2, 5 vol. % SO_2/N_2, 5 vol. % SO_2/He, 10 vol. % H_2/Ar, 5 vol. % O_2/He, 10 vol. %

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