Structure and performance of a \(V_2O_5-WO_3/TiO_2-SiO_2\) catalyst derived from blast furnace slag (BFS) for DeNO\(_x\)^†

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The titanium-bearing blast furnace slag (BFS), a solid waste with high TiO\(_2\) content (around 20%) and huge production (3.6 million tons per year), has caused serious environmental problems in China. The reuse of BFS in making DeNO\(_x\) catalysts has been confirmed to be promising because of its low cost and high effectiveness for DeNO\(_x\). In this work, four \(V_2O_5-WO_3/TiO_2-SiO_2\) samples from BFS and commercial Ti/Si were made with different amounts of \(Al_2O_3/Fe_2O_3/SO_4^{2-}\) dopants to reveal the unique structure effect of a slag-based catalyst on the catalytic behavior for DeNO\(_x\). Catalyst characterization clarified that the \(Al_2O_3/Fe_2O_3/SO_4^{2-}\) dopants from BFS may facilitate the formation of Ti—O—Si linkages with abundant structure defects. The structure possibly played a key role in acquiring a high surface area, well-dispersed active VO\(_x\) species, sufficient weak acid sites and a high amount of O\(_{ads}\) and V\(^{4+}\) species for the slag-based catalyst. These advantages in structure were confirmed by catalytic tests showing superior DeNO\(_x\) performances. Nonetheless, too many SO\(_4^{2-}\) dopants caused agglomeration of TiO\(_2\)-SiO\(_2\) particles, formation of strong acid sites and a high amount of O\(_{ads}\) species to negatively impact the DeNO\(_x\) activity, selectivity and catalyst lifetime.

1. Introduction

The vanadium-based catalysts, especially \(V_2O_5/TiO_2\) doped with WO\(_3\) or MoO\(_3\), have achieved great success in selective catalytic reduction (SCR) of NO with NH\(_3\) for their high activity and durability to SO\(_2\) poisoning.\(^1-14\) Nevertheless, this kind of catalyst has a relatively high price, which restricts their wide use in combustion facilities of small to middle scale. On the other hand, the blast furnace slag (BFS), which contains about 20 wt% TiO\(_2\), is a massive solid waste from the iron-steel industry. In China, it amounts 3.6 million tons per year, and would cause serious environmental problems without efficient treatment and reuse.\(^15,16\) Considering the reuse of BFS as a Ti source, we have for the first time proposed the preparation of V–W–Ti catalysts for flue gas denitration (DeNO\(_x\)) from the slag. The idea was confirmed to be effective to lower the cost of SCR catalysts and simultaneously provides a new pathway to fully utilize BFS.\(^17\)

Recent studies have shown that incorporation of some metal oxides such as Al\(_2O_3\), SiO\(_2\), Fe\(_2O_3\), and CeO\(_2\) into TiO\(_2\) support as mechanical promoters enhanced DeNO\(_x\) catalytic performance of the resulting catalysts because the promoters likely improve the dispersion and thermal stability of catalytic components.\(^7,18-23\) Especially, TiO\(_2\)-SiO\(_2\) has drawn particular attention because of its induced high DeNO\(_x\) activity and low SO\(_2\) oxidation activity. The structural advantages from doping SiO\(_2\) are its enhanced dispersion and stabilization effects on anatase TiO\(_2\) and VO\(_x\) species, together with the formation of more Bronsted acid sites needed for NO reduction.\(^5-7,19\) As a matter of fact, the TiO\(_2\)-SiO\(_2\) support with different TiO\(_2\)/SiO\(_2\) ratios can be easily prepared in one step from BFS as shown by our recent work.\(^24\) Besides providing low preparation cost as compared to methods based sol-gel or co-precipitation using pure chemicals, a distinguishing feature is its enabled high specific surface (427 m\(^2\) g\(^{-1}\)) and better DeNO\(_x\) performance in a wide temperature window of 250–400 °C for the prepared catalyst. However, the TiO\(_2\)-SiO\(_2\) support made from BFS has to contain some unavoidable dopant oxides such as Al\(_2O_3\) and Fe\(_2O_3\) to challenge the understanding of relationship between structure and function of the BFS-derived DeNO\(_x\) catalysts. It is thus necessary to deeply get insight into the structure of the BFS-derived catalysts for achieving their better applications.

The present work aims at revealing the structure effect of BFS-derived catalysts on their superior catalytic performance for DeNO\(_x\) by SCR. Two catalysts on TiO\(_2\)-SiO\(_2\) support but with different amounts of Al\(_2O_3/Fe_2O_3/SO_4^{2-}\) dopants were prepared from BFS by controls of H\(_2SO_4\) concentration and pH value in
precipitation. The other two samples for comparison were prepared by traditional co-precipitation or sol–gel method using commercial inorganic or organic Ti/Si chemicals. The SiO$_2$ content of all samples was nearly the same (about 0–10 wt%) as that in commercial SCR catalysts. The structure of catalysts was obtained through characterizations using XRD, TG, BET, XPS, TPR, SEM, TEM and FT-IR for both fresh and spent catalysts, and the relationship between structure and dopants was clarified through correlating catalytic performance for SCR of NO by NH$_3$ and catalyst structure. This is further expected to deeply understand the mechanism of BFS-based DeNO$_x$ catalysts for their good performance of flue gas denitration.

2. Experimental section

2.1. Catalyst preparation

Raw materials used for TiO$_2$–SiO$_2$ preparation included blast furnace slag (BFS), titanium(iv) chloride (TiCl$_4$) and colloidal silica (30 wt% SiO$_2$ in water), or tetrabutyl titanate (Ti(OCC$_4$H$_9$)$_4$) and tetraethyl orthosilicate (Si(OC$_2$H$_5$)$_4$). The BFS was water-quenched slag and from Panzhihua Iron & Steel Group Co., Ltd of China. Table 1 shows its composition obtained by XRF analysis. All other chemicals were all commercial products of reagent grade (Alfa Aesar). For comparison, a kind of commercial V–W–Ti SCR catalyst denoted as DKC ZERONOX® 993510537 was gotten from Chengdu Dongfang KWH Environmental Protection Catalyst Co., Ltd., China. This commercial monolithic honeycomb catalyst was crushed into powder and further evaluated to compare with the prepared catalysts.

The TiO$_2$–SiO$_2$ supports used in making DeNO$_x$ catalysts were prepared from different precursors according to the technical routes shown in Fig. S1 (see ESI†). The first support denoted as S-BFS-1 was prepared from BFS by, in succession, digesting the slag in 70 wt% H$_2$SO$_4$ at 90 °C for 3 h; hydrolyzing the resulting solution containing TiOSO$_4$/Si at pH = 1 and 110 °C for 5 h, washing the obtained H$_2$TiO$_3$ slurry using H$_2$O, aqueous NH$_3$ (10 wt%) and H$_2$O again, and finally drying the filter cake to obtain the TiO$_2$–SiO$_2$ support. The second BFS-based support with different amounts of Al$_2$O$_3$/Fe$_2$O$_3$/SO$_4^{2-}$ dopants (S-BFS-2) was obtained via a similar procedure but its slag digestion used 60 wt% of H$_2$SO$_4$, hydrolysis did not have any pH adjustment and slurry washing to pH = 7 by using only distilled water. The detailed procedure for preparing the BFS-based supports can be found in our previous publications.

Commercial Ti and Si precursors were also used to synthesize TiO$_2$–SiO$_2$ by co-precipitation and sol–gel methods. Following literature reports, TiCl$_4$ and colloidal silica were used in co-precipitation, and the resulting precipitate was washed with distilled water and aqueous NH$_3$ to get S-CP-TiCl$_4$. Another TiO$_2$–SiO$_2$ support (S-SG-Organic) was made by sol–gel method from Ti(OCC$_4$H$_9$)$_4$ and Si(OC$_2$H$_5$)$_4$ precursors. All samples had the similar SiO$_2$ content and were calcined at 600 °C for 4 h in air to obtain catalyst supports.

With the preceding TiO$_2$–SiO$_2$ supports, all DeNO$_x$ catalysts were obtained by impregnating 5 wt% WO$_3$ and 2 wt% V$_2$O$_5$. The impregnation slurry was continuously stirred at 60 °C until it became a paste. Then the paste was dried at 110 °C for 10 h and calcined at 600 °C for 4 h to get the V$_2$O$_5$–WO$_3$/TiO$_2$–SiO$_2$ catalysts. Four catalysts were prepared and denoted as BFS-1, BFS-2, CP-TiCl$_4$ and SG-Organic according to their different raw materials and synthesis methods used in preparing the TiO$_2$–SiO$_2$ supports.

2.2. Characterization and evaluation

Nitrogen adsorption/desorption isotherms were obtained using an ASAP 2020 (Micromeritics Instrument Corp.) working at 77 K. For all samples measured, they were degassed in vacuum at 150 °C for 6 h in prior to BET measurement. The Brunauer–Emmett–Teller (BET) equation was used to calculate the specific surface area (S$_\text{BET}$) from the recorded isotherms. Pore size distribution was calculated from the adsorption curve using the Barrett–Joyner–Halenda (BJH) model. The nitrogen adsorption volume at a relative pressure (P/P$_0$) of 0.994 was adopted in determining the pore volume and average pore size. The X-ray diffraction (XRD) pattern was performed in the 2θ angle from 10° to 90° on a D/Max-RB diffractometer (Rigaku Corp., Tokyo, Japan) having a Cu K$_\alpha$ radiation. FT-IR spectra were taken using a Tensor 27 (Bruker, Germany) in 400–4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$. For this, 1.0 mg dry powder was dispersed into 100 mg IR transmissive material (KBr), which was further pressed to obtain the transparent disks used for measurement.

The bulk chemical composition of blast furnace slag and all the prepared supports were determined in an Axios X-ray fluorescence (XRF) spectrometer (PANalytical X’pert). The composition and oxidation state of elements presented on the surface of prepared catalysts were obtained using a X-ray photoelectron spectroscopy (XPS) working on an ESCALAB 250Xi electron spectrometer from Thermo Fisher Scientific Corporation (USA) using 100 W Al K$_\alpha$ radiation (h$\nu$ = 1486.6 eV). A catalyst sample was put into its sample holder in advance and further degassed overnight at room temperature at a pressure of 10$^{-9}$ mbar. Binding energies were corrected by referring to the binding energy 284.8 eV for C 1s. For all samples not containing carbon, such a C 1s signal in XPS spectra was from their adventitious carbon.

Surface morphology and cross-sectional structure of all prepared supports were characterized using a JSM-7001F scanning electron microscope (SEM) of JEOL (Japan) working at an accelerating voltage of 10 kV, and further a JEM-2100 transmission electron microscopy (TEM) ofJEOL working at 200 kV. All TEM samples were on a copper-supported carbon polymer grid, and a sample was formed by placing a few droplets (onto the grid) of a suspension made by dispersing ground sample into ethanol and in turn drying the droplets in room condition. The bulk and surface compositions of vanadium element in catalysts were determined using the Inductively Coupled

| Table 1 Chemical composition of blast furnace slag (mass%) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| TiO$_2$ | SiO$_2$ | MgO | CaO | Al$_2$O$_3$ | Fe$_2$O$_3$ | SO$_4^{2-}$ | Others | Particle size |
| 20.87 | 23.18 | 10.32 | 26.96 | 13.83 | 1.36 | 1.67 | 1.81 | <0.2 mm |
Plasma-Optical Emission Spectrometry (ICP-OES, ICAP 6300, USA) and Energy Dispersive X-ray Spectroscopy (EDS) attached to a JSM-7001F SEM, respectively.

Thermogravimetry (TG) coupled with differential scanning calorimetry (DSC) was conducted on a Labsys Evo STA 1600 (Setaram Instrumentation) to characterize the weight change and endothermal–exothermal characteristics of TiO2-based supports and catalysts. The heating curves (TG/DSC) were recorded under inert atmosphere of argon at a heating rate of 10 °C min⁻¹ in the range of 30–1000 °C. The presence of sulfate species in the sample was evaluated from the weight loss in the range in which the release of SO2 occurred. Both NH3-TPD and H2-TPR experiments were performed on an AutoChem II-2920s V5.02 equipment (Micromeritics Instrument Corp.) to obtain the surface acidity and redox properties of a sample. After loading 0.1 g sample into its quartz U-tube reactor and purged with He, the sample was heated from room temperature to 300 °C at 10 °C min⁻¹ and maintained at this temperature for 60 min in He. Then, the sample was cooled to 80 °C, followed by NH3 adsorption for 1 h (10 vol% NH3 in He), and finally heated to 600 °C at 10 °C min⁻¹ to obtain NH3-TPD curve in 50 mL min⁻¹ pure He. For H2-TPR analysis the sample was cooled to 90 °C and followed by heating it to 1000 °C at 20 °C min⁻¹ in H2–He (10 vol% H2) gas at 50 mL min⁻¹. The released NH3 or consumed H2 were continuously detected using a mass spectrometer (Proline MS, Ametek).

Catalytic activity for SCR of NO by NH3 was evaluated in an atmospheric quartz fixed bed reactor of 15 mm in internal diameter. The tested catalyst was powder of 0.15–0.2 mm in sizes, and the used simulated flue gas contained 0.06 vol% NO, 0.048 vol% NH3, 3 vol% O2, 5 vol% H2O, 0.06 vol% SO2, and balanced with N2. The tested model flue gases included NO–O2–N2, NO–O2–H2O–N2 and NO–O2–H2O–SO2–N2, and for each kind of gas its total flow rate through the reactor was kept at 400 mL min⁻¹ (STP) to give a high Gas Hourly Space Velocity (GHSV) of 100 000 h⁻¹. The tested reaction temperature was in 150–500 °C and under each condition the test was last for 60 min. Molar concentrations for feeding and reacted gases were continually monitored in an ABB-AO2020 on-line flue gas analyzer (ABB). The realized NO conversion was calculated according to the measured inlet and outlet NO concentrations by

$$\text{NO conversion} (\%) = \frac{\text{NO}_\text{in} - \text{NO}_\text{out}}{\text{NO}_\text{in}} \times 100.$$

3. Results and discussion

3.1. Characterization of TiO2–SiO2 supports

**XRF analysis.** Table 2 shows the chemical compositions of all TiO2–SiO2 supports. Their SiO2 content was all about 9.3 wt%, but the slag-based samples contained some unavoidable dopants such as Fe2O3, Al2O3 and SO4²⁻. With controlled hydrolytic pH and aqueous NH3 washing (10 wt%), the S-BFS-1 support contained 1.38% Fe2O3, 0.59% Al2O3 and 0.39% SO4²⁻, whereas S-BFS-2 prepared without aqueous NH3 washing had significantly less Fe2O3 (0.31%) and Al2O3 (nearly zero) but more SO4²⁻. This amount variation for Fe2O3 and Al2O3 dopants in slag-based samples were subject to the solubility of such species in hydrolytic solution with a certain pH value.28,29 Both S-CP-TiCl4 and S-SG-Organic samples contained only TiO2 and SiO2.

<table>
<thead>
<tr>
<th>Support</th>
<th>TiO2</th>
<th>SiO2</th>
<th>Fe2O3</th>
<th>Al2O3</th>
<th>SO4²⁻</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-BFS-1</td>
<td>87.72</td>
<td>9.17</td>
<td>1.38</td>
<td>0.59</td>
<td>0.39</td>
<td>0.75</td>
</tr>
<tr>
<td>S-BFS-2</td>
<td>87.18</td>
<td>9.3</td>
<td>0.31</td>
<td>—</td>
<td>2.97</td>
<td>0.24</td>
</tr>
<tr>
<td>S-CP-TiCl4</td>
<td>90.67</td>
<td>9.21</td>
<td>—</td>
<td>0.12</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>S-SG-Organic</td>
<td>90.72</td>
<td>9.28</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
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</table>

**Textural characteristics.** Fig. 1 and Table 3 show the results of BET analysis for all supports. Fig. 1 shows the obvious difference for all supports in the N2 adsorption/desorption isotherms and pore size distribution (PSDs) curves. All supports exhibit irregular pore shape and type-IV isotherms in Fig. 1a (IUPAC classification) to characterize the mesoporous feature.33,34 Both SiO2 and other oxide dopants like Al2O3, Fe2O3 caused S-BFS-1 to have mesoporous structure with high BET area (282.30 m² g⁻¹) and high pore volume (0.609 cm³ g⁻¹). For S-BFS-2, its high SO4²⁻ content and low Al2O3 and Fe2O3 contents led to the meso–macro PSDs having lowered surface area (137.91 m² g⁻¹) and pore volume (0.293 cm³ g⁻¹). The large mesopores and even macropores in 20–100 nm on S-BFS-2 might be from the packing of secondary aggregates.28 Also, the crystalline size detected by XRD obviously increased from 11.9 nm for S-BFS-1 to 16.6 nm for S-BFS-2. All these indicated that the Al2O3 and Fe2O3 dopants possibly prohibited aggregation of crystallites to resist the reduction in surface area during high-temperature calcination and thus facilitated the formation of highly mesoporous structure.4,35,36 However, the presence of SO4²⁻ worked oppositely. Literature reviews30,31 showed that the titania catalysts with high specific surface areas are well suited for selective catalysis because of their more available active sites. For S-CP-TiCl4 and S-SG-Organic made using commercial reagents (without Al2O3 and Fe2O3 dopants), they had lowered BET area and pore volume in comparison with S-BFS-1, although S-BFS-1 had more sulfate. Especially for S-CP-TiCl4 (made with the similar method as for S-BFS-1), it had the much smaller BET surface area, pore volume and pore size. Thus, there are great advantages for preparing high-surface-area TiO2–SiO2 supports from BFS.

**XRD analysis.** The XRD patterns compared in Fig. 2 show that TiO2 in all supports presents as anatase crystal form (JCPDS 21-1272).23,35,36 Estimation according to the Scherrer's formula based on the (101) diffraction peak found that the anatase crystallites are in sizes of 11.3–16.6 nm (see Table 3). Of them, the crystallite size of S-BFS-1 (containing Al2O3/Fe2O3 dopants) is about 11.3 nm, very close to that of pure TiO2–SiO2 made with organic materials. The sulfate in S-BFS-2, however, caused a slight growth of titania crystallinity to have thus its reduced BET surface area and big crystallite size, as similarly reported by M. Kobayashi et al.27 Overall, the supports from
BFS had higher crystallinity than the samples made with organic precursors did, possibly due to the heat intolerance in calcination of the latter. Thus, the origin (nature) of precursor and preparation procedure affected the crystallization characteristics of TiO$_2$.

**Thermal analysis.** Fig. 3 shows the TG and DSC profiles of calcined TiO$_2$–SiO$_2$ supports in a temperature range of 30–1000 °C with a heating rate of 10 °C min$^{-1}$ in argon. The thermal event at 30–200 °C can be correlated to the DSC endothermic peak at around 100 °C to indicate the removal of physically adsorbed water. There was not obvious weight loss and an exothermic peak when further increasing temperature to 600 °C, indicating the completion of amorphous-anatase phase transformation for all supports and there was not organic matters trapped inside the pores of S-SG-Organic.

Comparing S-BFS-1, S-CP-TiCl$_4$ and S-SG-Organic, the TG diagram of S-BFS-2 had a distinctively big weight loss peak in 550–800 °C to show the decomposition of sulfate species (see Table 2). Besides, the DSC heating curves in 600–1000 °C revealed that varying the transition point of anatase to rutile due to the introduction of dopants showed influence of dopants on kinetics of anatase-to-rutile transformation taking place via changes of oxygen vacancies in a support.

**SEM images.** Fig. 4 displays SEM (also TEM) micrographs of all support samples. In Fig. 4a–d (SEM), all synthesized TiO$_2$–SiO$_2$ supports possess a rough porous surface, and the samples S-BFS-1 (a), S-CP-TiCl$_4$ (c) and S-SG-Organic (d) show shaped agglomerates composed of asymmetric plate-like particles. The S-BFS-2 (b) exhibits micro spherical morphology with heavy aggregation, possibly from breakage of its structure into small pieces of matters in sintering due to its high sulfate content. For slag-based supports containing unavoidable Fe$_2$O$_3$ dopant, one can see a dense elemental distribution of Ti in their SEM images and EDS mappings of Ti and Fe shown in Fig. S2 and S3 (ESI$^\dagger$). This reveals the presence of underlying TiO$_2$ substrate and uniform Fe dispersion on the entire TiO$_2$ substrate.

**Table 3**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Textural properties of support</th>
<th>Elemental composition of catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B.E.T. (m$^2$ g$^{-1}$)</td>
<td>Pore size (nm)</td>
</tr>
<tr>
<td>S-BFS-1</td>
<td>282.30</td>
<td>8.62</td>
</tr>
<tr>
<td>S-BFS-2</td>
<td>137.91</td>
<td>8.50</td>
</tr>
<tr>
<td>S-CP-TiCl$_4$</td>
<td>164.07</td>
<td>6.95</td>
</tr>
<tr>
<td>S-SG-Organic</td>
<td>150.66</td>
<td>3.04</td>
</tr>
</tbody>
</table>

$^a$ Crystallite size of TiO$_2$ was calculated from X-ray diffraction (XRD) data. $^b$ Actual bulk concentration was obtained by inductively coupled plasma (ICP). $^c$ Surface composition was obtained from energy dispersive X-ray spectroscopy (EDS) attached to SEM.
EDS spectra further suggested that the ferric elements were not aggregated, complying with the absence of Fe₂O₃ peak in XRD patterns shown in Fig. 2. Both S-CP-TiCl₄ and S-BFS-1, prepared via the same co-precipitation method, displayed the similar morphology to indicate that starting material has not obvious effect on morphology of the resulting support. Overall, the surface morphology of synthesized support obviously varied with the treatment method, either co-precipitation or sol-gel synthesis. The particles from sol-gel method (S-SG-Organic) showed some layered stacking structure with less rough surface than the co-precipitation method did.

TEM images. As shown by TEM images in Fig. 4e–h, all TiO₂–SiO₂ supports had spherical primary particles without any coating on surface. Mesopore structure features can be clearly seen to indicate high surface area and high adsorptive capacity. The S-BFS-1 had the best dispersion to show small particle sizes, while serious aggregation occurred to S-BFS-2 to form large particle sizes. The results well agree with the BET results in Fig. 1. For all samples, SiO₂ particles and impurities were not clearly identified and their non-uniform distributions were observed in the TEM images. A high-resolution transmission electron microscopic study (HR-TEM) was performed to observe the distribution of crystalline titania (Fig. S2–S5(a) in ESI†). All the observed lattice fringes of TiO₂–SiO₂ nanoparticles show a d-spacing of 0.360 nm, just corresponding to the (101) lattice fringes of anatase TiO₂ (d = 0.352 nm, JCPDS No. 21-1272). In summary, one can see from the TEM and SEM images that the dopants and synthetic route remarkably affected the morphologies and nano-micron structure of the prepared TiO₂–SiO₂ supports, and the S-BFS-1 support had the best dispersion of its precursors.

FT-IR analysis. The FT-IR spectra in Fig. 5 for all supports demonstrate a large and intense band within 3200–3600 cm⁻¹ to indicate the presence of OH group on TiO₂–SiO₂ surface and also a sharp peak at 1635 cm⁻¹ to refer to the O–H stretching vibration in water. The broad adsorption peak located in 400–
600 cm$^{-1}$ represents the characteristic vibration of Ti–O bonds in Ti–O–Ti$^{5,37,45}$. An absorption band extending from 1000 to 1300 cm$^{-1}$ shows the asymmetric and symmetric stretching of Si–O–Si bridge, and a minor feature around 960 cm$^{-1}$ can be associated with the vibrations of Si–O–Ti linkage. Thus, a substitution of Si for Ti has occurred in the prepared TiO$_2$–SiO$_2$ supports.$^{35,45}$ Besides, the absorption band within 1000–1300 cm$^{-1}$ is more intensive for the sulfated S-BFS-2 sample, indicating the vibration overlapping of Si–O–Si and S=O bonds, where the latter is associated with sulfate groups and anchored to TiO$_2$–SiO$_2$ surface.$^{39,46}$

In summary, the supports made with the co-precipitation method, as compared to the sol–gel synthesis, displayed the similar morphological features and their rough porous surface provided the larger surface area. On the other hand, the dopants also greatly influenced the structure of synthesized TiO$_2$–SiO$_2$ such as size of crystallites, porous textures and particle agglomeration. The dopants Al$_2$O$_3$ and Fe$_2$O$_3$ (as in S-BFS-1) facilitated mesoporous structure, enlarged BET surface area as well as mesoporous size because they inhibited the growth of anatase TiO$_2$ grain by their existence on TiO$_2$ boundary. The presence of SO$_4^{2-}$ made the TiO$_2$–SiO$_2$ support easy to agglomerate to form meso–macro pores, having thus the obviously low surface area for S-BFS-2. These difference in porosity, surface area and crystallinity parameters of TiO$_2$–SiO$_2$ supports will greatly impact the catalysts made with them for SCR of NO with NH$_3$ (flue gas DeNO$_x$).

### 3.2. Evaluation of catalysts for DeNO$_x$

Denitration catalysts were prepared by impregnated 2 wt% V$_2$O$_5$ and 5 wt% WO$_3$ onto the preceding TiO$_2$–SiO$_2$ supports having different structures, properties and Fe$_2$O$_3$/Al$_2$O$_3$/SO$_4^{2-}$ dopants amounts. The SEM images and EDS spectra as well as mappings of Ti/V elements in Fig. S2–S5(b–e) shown in ESI† confirmed that all prepared V$_2$O$_5$–WO$_3$/TiO$_2$–SiO$_2$ catalysts were composed of Ti, Si, Al, Fe, O, V, W elements, and the main active element V was highly dispersed into the lattice of entire TiO$_2$ substrate.$^{14}$ The ICP-OES and EDS results shown that all the catalysts had the similar bulk vanadium contents of about 1.1 wt% but different surface V concentrations (Table 3), showing essentially the varied interactions between V$_2$O$_5$ and support for different catalysts.$^{13,14}$ In the following, DeNO$_x$ performance was evaluated to correlate the structure and dopants of supports with the catalytic performance for SCR of NO by NH$_3$.

Fig. 6 shows the results of DeNO$_x$ performance over catalysts prepared using the preceding supports. At the same reaction conditions, all prepared catalysts except for BFS-2 enabled higher NO reduction than the reference DKC commercial catalyst did in the reaction temperature of 250–450 °C. The realized NO removal over DKC below 70% but it had an acceptably wide temperature window for DeNO$_x$. The BFS-1 catalyst exhibited the best catalytic activity by having about 74% NO conversion in 300–450 °C under an NH$_3$/NO ratio of 0.8 and GHSV of 100 000 h$^{-1}$. The manifested activity for CP-TiCl$_4$ was between BFS-1 and SG-Organic catalysts. Although BFS-2 contained the highest sulfate, it showed the lowest activity among all prepared catalysts. Referring to the support compositions in Table 2, one can conclude that the proper amounts of Fe$_2$O$_3$ and Al$_2$O$_3$ dopants in catalytic support facilitated NH$_3$-SCR reactions over V$_2$O$_5$–WO$_3$/TiO$_2$–SiO$_2$ catalysts. Earlier studies have shown that the incorporation of Al$_2$O$_3$ (ref. 20, 21 and 47) of up to 10 wt% and Fe$_2$O$_3$ (ref. 4, 11 and 48) of up to 3 wt% into the TiO$_2$ support are beneficial to NO reduction in NH$_3$-SCR, and the catalyst has better thermal stability in comparison with conventional V$_2$O$_5$/TiO$_2$ catalysts. Thus S-BFS-1 support should be a promising candidate for making inexpensive and highly active catalyst for flue gas DeNO$_x$. Also, one can infer that the activity for DeNO$_x$ of TiO$_2$–SiO$_2$ supported catalysts was mainly subject to the dopants in support other than the precursors (materials) and preparation method. The presence of Fe$_2$O$_3$ (ref. 4 and 11) and Al$_2$O$_3$ (ref. 20 and 21) would positively work on DeNO$_x$ performance of the resulting catalyst, but too much SO$_4^{2-}$ (about 3 wt%) in support would lead to adverse impacts. Literature studies$^{37,49,50}$ have reported that the presence of about 1 wt% sulfate in TiO$_2$ and TiO$_2$–SiO$_2$ supports would promote NH$_3$-SCR performance of the resulting catalyst because of its increase in catalyst acidity and facilitation in oxidation of NO into nitrate and transformation of monomeric vanadate into polymeric vanadate on catalyst surface.

The generation of N$_2$O during NH$_3$-SCR was also tested. At temperatures above 350 °C, ammonia would be partially oxidized to N$_2$O,$^{37,39}$ but only negligible N$_2$O (3 ppm) was formed at 450 °C over DKC (see Fig. 6). The formed N$_2$O amount at 350–500 °C over all catalysts followed a sequence of BFS-2 > CP-TiCl$_4$ ≈ SG-Organic > BFS-1 > DKC. In term of composition and structure features, the low emission of N$_2$O at high temperatures over BFS-1 catalyst should be related to its presence of Al$_2$O$_3$ and Fe$_2$O$_3$ dopants. Hence, the type of dopants is critical to achieve the expected high N$_2$ selectivity of catalyst for SCR of NO by NH$_3$.

The tolerance to poisoning of SO$_2$ and steam was tested by feeding 5 vol% steam and 600 ppm SO$_2$ at 300 °C in a stable SCR reaction lasting for a few hours under GHSV of 100 000 h$^{-1}$. As shown in Fig. 7, the presence of both SO$_2$ and H$_2$O in the reactant [fed] gas caused obvious loss of DeNO$_2$ activity from the case with only H$_2$O (steam) feed. Having only 5 vol% H$_2$O in gas...
the absolute drop of NO conversion was 2.6%, 3.5% respectively over the BFS-1, CP-TiCl₄ catalysts, meanwhile the deactivation nearly was not seen over sulfated TiO₂-SiO₂ supported catalyst (BFS-2). The interaction of sulfate species with adsorbed water can cause the formation of Brønsted acid sites to promote the NH₃ adsorption, which may compensate the degree of the loss of its DeNOₓ efficiency. Stopping H₂O feed, NO conversions were fully reversible for all catalysts, indicating that this inhibition is due to competitive adsorption of H₂O and NH₃ on active sites.

Feeding SO₂ and steam simultaneously revealed that the realized NO conversion was stable but further dropped by 8%, 10% respectively for BFS-1 and CP-TiCl₄ catalysts from the flue gas without presence of SO₂ and steam, furthermore shutting off the feeding of both SO₂ and steam, their DeNOₓ activity were recovered quickly to their initial high value. At the analogous reaction conditions, the activity over BFS-2 dropped by 12.7% and decreased gradually afterwards, besides its recovery of catalytic performance was gradual and the performance could not rebound to the original after cutting off SO₂ and steam in fed gas. Thus, high sulfate content in catalyst is not good for tolerance to the poisoning of steam and SO₂ because the formed Bronsted acid sites and long-term exposure to SO₂ containing in flue gas can lead to the formation of ammonium sulfates (NH₄HSO₄ and (NH₄)₂SO₄) on catalysts easily, which would cause similar deactivation for all catalysts. In summary, the impurities Al₂O₃/Fe₂O₃ (excluding SO₄²⁻) not only enhanced DeNOₓ activity and selectivity of the prepared catalyst but also positively affected the resistance of the catalyst to poisoning by water and SO₂ in SCR of NO. Obviously, BFS-1 is the most active and robust catalyst for DeNOₓ application to actual flue gases.

Correlating with structure of catalyst supports found that the preceding catalytic activities for DeNOₓ increased with increasing the surface area of supports. Indeed, large pore volume and high surface area of a catalyst would improve its catalytic activity by facilitating spread of reactant molecules (NO) or reaction intermediates to active sites in catalyst’s mesostructure framework. The catalyst BFS-1 showed high NO reduction capability (about 74% reduction) at 300–450 °C under high GHSV of 100 000 h⁻¹. Agglomeration observed on BFS-2 reduced its BET surface and also blocked some active sites, which caused thus the instability of the catalyst in gas containing both of steam and SO₂. Thus, the texture and morphology of support importantly affect the catalytic performance of V₂O₅-WO₃/TiO₂–SiO₂ for DeNOₓ by NH₃. The BFS-1 catalyst with the relatively low crystallinity exhibited the best DeNOₓ activity, possibly owing to its special acid sites and large BET surface area to have highly dispersed vanadia on catalyst surface, as further justified below.

### 3.3. Justification of catalytic activities

**NH₃-TPD.** Comparing the profiles of temperature programmed desorption of ammonia (NH₃-TPD) in Fig. 8 shows clearly different acidic sites for catalysts having different contents of Al₂O₃/Fe₂O₃/SO₄²⁻ dopants. While BFS-2 containing high SO₄²⁻ content displayed two broad NH₃ desorption regions below and above 400 °C to refer to weak and strong acid sites, the other catalysts exhibited only one broad and asymmetric peak below 400 °C to represent weak acid sites. The clarification in Fig. 8 and data in Table 4 show actually that the impurities in slag-based catalysts caused strong acid sites on catalyst surface in comparison with those prepared from commercial Ti/Si sources. The highest amount of desorbed NH₃ occurred at temperatures of 100–400 °C for BFS-1. For BFS-2 its strong acidic sites occurred at 400–600 °C due to the strong interaction between sulfate anion and titanium cation which causes the titanium cation to be more positively charged ions. Accordingly there were few weak acid sites for BFS-2, showing that the strong acid sites are formed by reducing weak acid sites, causing strong adsorption and oxidation of NH₃ to hinder the SCR reaction for NO as evidenced in Fig. 6. Weak acidic sites are beneficial to DeNOₓ activity by their retaining of NH₃ for SCR reaction. This was confirmed by correlating the DeNOₓ activity and amount of weak acid sites such that BFS-1 had the highest amount of weak acid sites and also the best DeNOₓ performance. The presence of unavoidable sulfate species in CP-TiCl₄ prepared by co-precipitation using H₂SO₄...
Table 4 Results of NH3-TPD and H2-TPR experiments for all prepared DeNOx catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Weak acid</th>
<th>Strong acid</th>
<th>Total</th>
<th>VOx reduction</th>
<th>WOx reduction</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFS-1</td>
<td>0.317</td>
<td>—</td>
<td>0.317</td>
<td>0.316</td>
<td>0.126</td>
<td>0.442</td>
</tr>
<tr>
<td>BFS-2</td>
<td>0.073</td>
<td>0.075</td>
<td>0.148</td>
<td>0.299</td>
<td>0.071</td>
<td>0.370</td>
</tr>
<tr>
<td>CP-TiCl4</td>
<td>0.210</td>
<td>—</td>
<td>0.210</td>
<td>0.158</td>
<td>0.169</td>
<td>0.327</td>
</tr>
<tr>
<td>SG-Organic</td>
<td>0.139</td>
<td>—</td>
<td>0.139</td>
<td>0.122</td>
<td>0.067</td>
<td>0.189</td>
</tr>
</tbody>
</table>

Acid caused more adsorbed NH4+ to participate in SCR reaction and had thus higher NOx reduction than SG-Organic catalyst did. In summary, the difference in DeNOx activity for all compared catalysts having the same SiO2 content should be correlated with their different weak acidities that determine the ability to retain adsorbed NH3. For S-BFS-1, its high BET surface area acquired from its Al2O3/Fe2O3 dopants and proper sulfate content (0.4 wt%) caused the catalyst to have abundant weak acid sites and thus good DeNOx performance. The too much SO42− in support can convert a part of weak acid sites into inert strong acidic sites to decrease DeNOx activity as S-BFS-2 performed.

H2-TPR. Fig. 9 shows the H2-TPR diagrams for all catalysts, and their corresponding amounts of consumed H2 were summarized in Table 4. A two-step reduction profile was observed with their T_max at 431–471 °C and 718–863 °C and representations of active V2O5 and promoter WO3, respectively. The samples made from slag exhibited the highest H2 consumption in H2-TPR, indicating its more reducible metal oxides on catalyst surface or the higher reducibility for slag-based catalysts. On the other hand, the shift of reduction peak for active VOx reflects the difficulty in changing its valence during DeNOx reactions. The lower reduction temperature of VOx species, the higher catalytic activity was achieved. For BFS-1, it had the lowest T_max to reduce VOx species and the highest H2 consumption in H2-TPR, indicating its more reducible active VOx species and thus higher DeNOx efficiency clarified in Fig. 6. In comparison, the BFS-2 catalyst with the highest T_max for reducing VOx species manifested the worst DeNOx performance so that CP-TiCl4 and SG-Organic catalysts had the intermediate catalytic activity for DeNOx to respond their intermediate T_max for reducing VOx species. Considering its high BET surface area, the low reduction temperature and many reducible sites for BFS-1 may be owing to its highly dispersed VOx species on catalyst surface.

XPS. Fig. 10a–d show the electron binding energies of Ti 2p, Si 2p, O 1s and V 2p XPS peaks of V2O5−WO3/TiO2−SiO2 catalysts determined using XPS analysis. All peaks were fitted by Gaussian–Lorentz curves. One may see that the reported electron binding energies agree well with other reports. From the XPS spectra of Ti 2p in Fig. 10a we can see that the binding energies (BE) of Ti 2p1/2 and Ti 2p3/2 refer to Ti4+ in TiO2, which are respectively higher than 458.7 and 464.4 eV for pure TiO2. A downward shift (to be slightly lower) of Si 2p BE was detected in Fig. 10b, as compared to 103.4 eV for pure SiO2 which indicates a decrease in the effective positive charge on Si. These essentially revealed the strong interaction between TiO2 and SiO2 in TiO2−SiO2 support. Since Ti has greater affinity to oxygen than Si does, some Si–O bands disappeared to promote the formation of Ti–O bands on surface and thus to reduce the binding energy of Si 2p. Combining the results of XPS and FT-IR (Fig. 5) suggests the formation of Ti–O–Si linkages in the prepared catalyst, as also reported elsewhere. There were obvious upward shift of Ti 2p and downward shift of Si 2p for BFS-1 in comparison with the other three samples, referring to more Ti–O–Si linkages and better interspersion of Ti–Si components in this support. This well accounts for the high BET area, small particle size and weak crystallization for BFS-1.

Fig. 10c shows interesting feature of O 1s XPS spectra. All catalysts are characterized by complex profiles to indicate the presence of different oxygen chemical bonds. The BE around 533 eV is attributed to the surface adsorbed oxygen (denoted as O_ads), such as O2− or O− belonging to defect-oxide or hydroxyl-like group. Another peak located around 530 eV corresponds to the lattice oxygen atom O2− (denoted as O_latt), indicating a mainly single chemical environment surrounding the photo emitting oxygen. Against the O_latt for catalyst based on pure TiO2, the upward shifts in BE of O 1s peak for all other catalysts clarified a substitution of Ti atoms by other higher electronegativity elements like Si, Al, Fe, S. For BFS-2, the upward shift of O 1s peak was more pronounced, as recognized from the broad O_ads peak, which reflects a more electronegative environment around oxygen atom due to the strong electron affinity by S6+ in SO42−.
Table 5 shows the surface O$_{\text{ads}}$/O ratios of all samples. The slag-based catalysts had notably high O$_{\text{ads}}$/O ratios. The more O$_{\text{ads}}$ on surface should result from the more defects created by the Al$_2$O$_3$, Fe$_2$O$_3$, $\text{SO}_4^{2-}$/C0 dopants. The O$_{\text{ads}}$ is usually considered to be beneficial for NO oxidation into NO$_2$ in SCR reactions, thereby facilitating “fast SCR” reaction and enhancing DeNO$_x$ efficiency at low temperatures.$^{5,18}$ Thus, the more surface adsorbed oxygen O$_{\text{ads}}$ should be responsible for the better catalytic performance of BFS-1. However, a very high O$_{\text{ads}}$/O ratio, such as for BFS-2, means an excessive oxidation ability, which is harmful to SCR reaction owing to its induced strong ammonia oxidation that forms nitrogen oxide byproducts to narrow the temperature window of SCR and to generate more N$_2$O (Fig. 6).$^{56}$

The XPS spectra in Fig. 10d presents the chemical states of vanadium. In all prepared catalysts, two peaks representing V$^{5+}$ and V$^{4+}$ were detected in the range of 516.4–517.1 eV and 515.7–516.2 eV, respectively.$^{57}$ Table 5 listed surface atom concentrations and peak-fitting results of O 1s and V 2p spectra. We can see that BFS-1 had the highest surface V to indicate the best dispersion of vanadium species in the catalyst. Combining with the BET results in Fig. 1, the surface V signals are well related with the BET area of the four catalysts, meaning that high BET area is in favor of dispersion and exposure of vanadium species. Moreover, the non-stoichiometric V$^{4+}$ species can improve the NO reduction ability of catalyst due to its high mobility and activation of electron transfer.$^{5,7,21}$ Consequently, the realized DeNO$_x$ efficiency for all catalysts are proportionally correlated with the amount of V$^{4+}$/V ratio on their surfaces shown in Table 5. The BFS-1 catalyst had the highest BET area, best dispersion of surface vanadium species and largest V$^{4+}$/V ratio, thus it was rich in active vanadium sites on its surface to ensure its good catalytic performance in SCR of NO. Furthermore, Table 3 shows that the surface V/Ti ratio of BFS-1, CP-TiCl$_4$ and SG-Organic catalysts were higher than their bulk ratios, suggesting that V$_2$O$_5$ was mainly dispersed on their catalyst surface. The surface V/Ti ratio of BFS-2 was lower than its bulk ratio, implying that its vanadium mainly existed in the inside of catalysts.$^{57}$ The BFS-2 catalyst had consequently poor DeNO$_x$ performance as was tested.

**Spent catalyst analysis.** Table 6 summarized the textural characteristics ($S_{\text{BET}}$ and $V_{\text{pore}}$) of fresh and spent BFS-1, BFS-2 and CP-TiCl$_4$ catalysts, where the spent ones refer to 70 h

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Surface atomic concentration (at.%)</th>
<th>Surface atomic ratios$^a$, %</th>
<th>O$_{\text{ads}}$/O</th>
<th>V$^{4+}$/V</th>
</tr>
</thead>
<tbody>
<tr>
<td>BFS-1</td>
<td>22.28 9.86 64.78</td>
<td>48.24 80.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BFS-2</td>
<td>13.18 19.09 66.26</td>
<td>63.02 48.89</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CP-TiCl$_4$</td>
<td>20.63 11.26 65.51</td>
<td>40.96 69.15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SG-Organic</td>
<td>19.46 12.17 65.19</td>
<td>34.83 60.66</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Calculated from the ratio of peak area of XPS spectra.
exposure to SO2 and steam at 250 °C. They all showed decrease in catalyst surface area, corresponding to the drop in catalytic activity when exposed to SO2 and steam. There should be some solid materials formed during SCR reaction in flue gas containing SO2 and H2O which blocks or collapses pores of catalyst. The more decrease in pore volume would lead to more deactivation species deposited on catalyst. There are two possible kinds of such deactivation species. The reaction between SO2 or sulfate and NH3 forms (NH4)2SO4 and NH4HSO4 at low temperatures to block pores by deposition, while some active metal oxides may be sulfated by SO2 to form stable sulfate species to destroy pore structure. The most serious poisoning suffering for BFS-2 in Fig. 7 was further verified by the high amount of sulfate existing on its spent catalyst (see TG data in Table 6). The weight loss at 250–550 °C represents the decomposition of ammonium sulfate salts, which was observed only for spent BFS-2 catalyst. Considering its high SO42− content and abundant strong acid sites in 400–600 °C shown by NH3-TPD experiment, this catalyst is easier to accommodate irreversible ammonium salts during SCR of NO, which thus decreased catalyst lifetime and was hard to regenerate. The meso-macro PSDs of BFS-2 would also facilitate accommodation of ammonium salts during SCR. For mesoporous BFS-1 and CP-TiCl4 catalysts that had only weak acid sites, their ammonium salts in pores could be evaporated to greatly restore blocked pores and surfaces, thereby recovering their DeNOx activity after stopping the SO2 and steam feed into the tested flue gas. The mass loss occurred at 500–850 °C provided an evidence for the sulfate ions incorporated into TiO2 lattice (stable metal sulfates). This also decreased the pore volume of catalysts, especially for spent BFS-2, and suggested structure damage and irreversible deactivation of BFS-2 catalyst for SCR of NO.

As a summary, we can see that all spent catalyst lost their surface area in comparison with their fresh catalysts due to the formation of sulfate salts, especially for BFS-2 catalyst. This is the primary reason for the irreversible deactivation of catalyst for SCR of NO. On the other hand, too much doped SO42− in catalyst such as BFS-2 and too many strong acid sites would cause serious generation of ammonium sulfate species to block active sites and collapse pore structure of catalyst. With suitable content of SO42− dopant (below 1 wt%) in BFS-1, it increased NH3 adsorption capacity and surface Oads/O ratio to improve the DeNOx performance.

4. Conclusions

Four V2O5–WO3/TiO2–SiO2 samples with different amounts of Al2O3/Fe2O3/SO42− dopants prepared from blast furnace slag (BFS) containing Ti/Si and also commercial Ti/Si sources were characterized to reveal the relationship among performance, structure and preparation method of catalyst. Results shown that the BFS-based catalysts with proper amounts of Al2O3/Fe2O3/SO42− dopants exhibited excellent catalytic activity, selectivity and stability to ensure the high NO reduction capability (about 74% reduction) at temperatures of 300–450 °C and NH3/NO ratio of 0.8. The performance is much better than that realized by the catalyst made by co-precipitation or sol–gel methods using commercial Ti/Si sources. Characterization demonstrated that the Al2O3/Fe2O3 dopants acquired from using BFS prevented agglomeration of TiO2 lattice (stable metal sulfates). This also decreased the pore volume of catalysts, especially for spent BFS-2, and suggested structure damage and irreversible deactivation of BFS-2 catalyst for SCR of NO.

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