

Contents lists available at ScienceDirect

Applied Catalysis A, General



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

Sequentially prepared Mo-V-Based SCR catalyst for simultaneous Hg⁰ oxidation and NO reduction



Can Li^a, Vishnu Sriram^a, Zhouyang Liu^a, Dale Brewe^b, Joo-Youp Lee^{a,*}

^a Chemical Engineering Program, Department of Chemical and Environmental Engineering, University of Cincinnati, Cincinnati, OH, 45221-0012, United States ^b X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Argonne, IL, 60439, United States

ARTICLE INFO

Keywords: Mercury oxidation Nitrogen oxide reduction SCR catalyst Calcination temperature Bimetallic catalyst

ABSTRACT

Molybdenum (Mo)-vanadium (V)-based selective catalytic reduction (SCR) catalyst synthesized by the sequential impregnation of Mo and W followed by V was investigated for simultaneous elemental mercury (Hg⁰) oxidation and nitrogen oxide (NO) reduction in an existing SCR unit with respect to different TiO₂ phases, calcination temperatures, flue gas constituents, gas velocities, and reaction temperatures. Anatase phase TiO₂ and the calcination temperatures of 400 and 500 °C resulted in $\sim 69\%$ Hg⁰ oxidation at 10 ppmv HCl and 350 °C. The high calcination temperature of 700 °C resulted in TiO₂ phase transformation from anatase to rutile and agglomeration. The modified SCR catalyst prepared with the impregnation sequence of Mo and W followed by V using anatase TiO₂ and calcination temperature 500 °C showed $\sim 99\%$ Hg⁰ oxidation and 87% NO reduction conversions at an NH₃/NO molar ratio of 0.9 under 350 °C and 5,000 hr⁻¹ space velocity in typical subbituminous and lignite coal simulated flue gases. The effects of these parameters and conditions were further investigated using various characterization techniques including BET, TEM, XRD, NH₃ TPD and XAFS.

1. Introduction

Coal-fired power plants are considered to be responsible for over 30% (>44 tonnes) mercury emissions from all kinds of anthropogenic sources every year in the United States [1]. There exist three different types of mercury in coal combustion exhaust gas including particulate-bound (Hg^p), oxidized (Hg²⁺), and elemental (Hg⁰) [2]. Hg^p and Hg^{2+} can be easily separated using current conventional air pollution control systems, such as baghouse filter, electrostatic precipitator (ESP) and wet flue gas desulfurization (FGD) [3]. Nevertheless, it is very challenging to separate Hg⁰ species because it is highly volatile, very low in concentrations, and nearly insoluble in water. The Mercury and Air Toxics Standards (MATS) rule issued in 2012 the mercury emissions limits of 1.2 and 0.015 lb/TBtu (or 0.013 and 0.0002 lb/GWh) from existing and new coal-fired power plants, respectively. These regulation limits for existing and new coal-fired power plants are equivalent to \sim 90+ and \sim 99+% on a monthly rolling average basis, respectively. Therefore, the separation of Hg⁰ is imperative to successfully comply with the current stringent regulations.

Existing mercury control technologies in the market include sorbent

injection, fuel additives, selective catalytic reduction (SCR) optimization, and Hg²⁺ separation from wet FGD system. Sorbent injection uses raw or chemically-modified activated carbon to collect Hg⁰ and Hg²⁺ [2-4]. However, the cost is expensive [5]. Fuel additives including chlorine and bromine salts can be added to the power plant boiler to improve the Hg^0 oxidation capability [6–8]. However, it generally requires high halogen addition and can also cause a corrosion problem in the air preheater. Previous studies demonstrated that $\sim 15\%$ to 68% of Hg⁰ vapor could be converted into Hg²⁺ form over SCR catalyst with HCl. [9-11] Currently, SCR units and wet FGD systems have been equipped in most coal-fired power plants. The number of SCR and wet FGD unit installations has increased due to the Cross State Air Pollution Rule (CSAPR) regulating NO_{x} and SO_{2} emissions more stringently from fossil fuel-fired power plants in 27 states from 2012 in the United States. The Hg^0 to Hg^{2+} conversion over the SCR unit provides an opportunity to capture Hg^{2+} in a downstream wet FGD system to lower both mercury and NO_x emissions.

 $V_2O_5\text{-}WO_3$ or $V_2O_5\text{-}MoO_3$ supported on TiO_2 are widely used as commercial SCR catalysts to reduce NO_x [12–14]. Previous studies on Hg^0 oxidation over $V_2O_5\text{-}WO_3/TiO_2$ reported limited Hg^0 oxidation

https://doi.org/10.1016/j.apcata.2021.118032

Received 17 June 2020; Received in revised form 30 January 2021; Accepted 1 February 2021 Available online 5 February 2021 0926-860X/© 2021 Elsevier B.V. All rights reserved.

^{*} Corresponding author at: Chemical Engineering Program, Department of Chemical and Environmental Engineering, University of Cincinnati, Cincinnati, Ohio, 45221-0012, United States.

E-mail addresses: li2c2@mail.uc.edu (C. Li), sriramvu@mail.uc.edu (V. Sriram), liuzy@mail.uc.edu (Z. Liu), brewe@aps.anl.gov (D. Brewe), joo.lee@uc.edu (J.-Y. Lee).

capability under the condition of low HCl concentrations in sub-bituminous and lignite coal combustion flue gases. [9,15,16] To enhance the Hg⁰ oxidation capability under low HCl concentrations, additional active metals such as Mn, Ce, Ru, Cu, and Fe have been attempted to optimize conventional SCR catalyst formulas [17-24]. However, all the above modified catalysts need additional equipment installations or changes in different operating temperatures. A few studies have been taken to explore Hg^0 oxidation over V_2O_5 -MoO₃/TiO₂. A V₂O₅(5%)-MoO₃(5%)/TiO₂ catalyst synthesized using a sol-gel technique reported an up to 28% improvement in Hg⁰ oxidation activity relative to an in-house V2O5(5%)/TiO2 catalyst under 6%(v) O2 and no HCl at 350 °C [25]. A previous study using V₂O₅(5%)-MoO₃(5%)/TiO₂ reported that HCl and NO gases could positively affect Hg⁰ oxidation activity while H₂O, SO₂, and NH₃ gases showed an inhibitory effect [26]. The Hg⁰ oxidation activity of the catalyst was higher than that of a fresh commercial SCR catalyst (V2O5(3.30%)-WO3(2.27%)/TiO2) regardless of NH₃ under actual flue gas conditions [27].

Our previous study reported that the modified SCR catalyst prepared using the impregnation sequence of Mo and W followed by V exhibited ~69% Hg⁰ oxidation activity at 10 ppmv HCl and 350 °C [28]. Meanwhile, the NO reduction activity was ~80% with respect to various metal loadings and impregnation sequences. The objective of this study is to examine the simultaneous Hg⁰ oxidation and NO reduction in terms of different TiO₂ phases, calcination temperatures, flue gas constituents, gas velocities, and reaction temperatures over our Mo-V-based SCR catalyst. Different characterization techniques were employed to understand potential relationships between the different preparation conditions and catalytic activities. The study results can provide fundamental understanding and scientific insights for simultaneous mercury and NO_x emissions control in an existing SCR system.

2. Experimental

2.1. Catalyst synthesis

In this work, our Mo-V-based SCR catalyst was synthesized using incipient wetness impregnation with different TiO_2 supports and calcination temperatures [29]. It is the most widely cited method for

supported metal oxide catalysts due to its simplicity and the ease of scalability [30]. Anatase TiO₂ (DT-51, from Cristal), mixed anatase/rutile TiO₂ (P25, from Sigma Aldrich) and rutile TiO₂ (STR-100W, from Sakai Chemical) were selected as the catalyst supports, respectively. Four different temperatures 400, 500, 600 and 700 °C were chosen as the calcination temperatures, respectively. The detailed synthesis procedures are shown in our previous publication [28]. The previous work demonstrated that the Mo-V-based SCR catalyst containing 0.5 wt.% V₂O₅, 7 wt.% MoO₃ and 3 wt.% WO₃ with the impregnation sequence of Mo and W followed by V (i.e. $MoO_3(7)+WO_3(3)\rightarrow V_2O_5(0.5)/TiO_2$) had the best activity. Therefore, the same impregnation sequence and loading percentages of the metals have been used to prepare the modified SCR catalyst samples with different TiO₂ supports and calcination temperatures. The synthesized samples were designated as $MoO_3+WO_3 \rightarrow V_2O_5/TiO_2 A B$, where A and B represented TiO₂ support and calcination temperature, respectively. Co-impregnation method was utilized to synthesize V-based conventional SCR catalyst with 0.5 wt.% V₂O₅ and 9 wt.% WO₃. This sample was denoted as V₂O₅+WO₃/TiO₂ DT-51 CT500. The pelletized catalyst was employed to conduct the catalytic activity test. The powdered catalyst was employed to carry out characterization analysis after grinding the pelletized catalyst.

2.2. Activity tests

The catalytic activity tests of the Mo-V-based SCR catalyst in terms of different TiO₂ supports and calcination temperatures were conducted in a fixed-bed reactor system as illustrated in Fig. 1 to evaluate their Hg⁰ oxidation and NO reduction efficiencies. Hg⁰ vapor was brought into the system by introducing 100 mL/min N₂ through a mercury permeation tube (VICI Metronics) located in a calibration gas generator oven (Dynacalibrator, VICI Metronics) and ~15 ppbv Hg⁰ was used as a typical inlet concentration. All of the simulated flue gas constituents regulated through mass flow controllers were produced using gas cylinders and specified in Results and Discussions part. Water vapor was fed into the system through controlling the temperature of a water bubbler. The total flow rate of the simulated coal combustion flue gas was fixed at 1 L/min. Typically, a quartz reactor with a 16 mm inner diameter containing ~1.72 g of catalyst pellets was used to conduct the activity



Fig. 1. Schematic of lab-scale fixed-bed reactor set-up.

Applied Catalysis A, General 614 (2021) 118032

tests. The quartz reactor was placed in the center of a vertical oven equipped with a temperature controller. These tests were run under a gas hourly space velocity (GHSV) of 40,000 hr⁻¹ at 350 °C to examine the catalytic activities of Hg⁰ oxidation and NO reduction in terms of different TiO₂ supports and calcination temperatures [16]. When the effect of GHSV on the activities was investigated, a different catalyst amount was used to set the GHSV inside the reactor.

During all the catalytic activity tests, a cold vapor atomic absorption spectrophotometer (CVAAS, Model 400A, Buck Scientific Inc.) combined with Ontario Hydro Method was used to measure mercury concentrations at the inlet and outlet of the system. Two different impinger solutions: 1 M KCl and 4%(w/v) KMnO₄/10% (v/v) H₂SO₄ were employed to collect oxidized mercury and Hg⁰ vapor, respectively. A Micro Emission Analyzer (Model 500, Enerac LLC) was employed to determine NO inlet and outlet concentrations. The activities of Hg⁰ oxidation and NO reduction were calculated based on the inlet and outlet Hg⁰ and NO concentrations as shown below.

$$Hg^{0} \text{ oxidation activity} = \frac{Hg^{0}_{\text{in}} - Hg^{0}_{\text{guil}}}{Hg^{0}_{\text{in}}} \times 100\%$$
(1)

NO reduction activity =
$$\frac{NO_{in}-NO_{out}}{NO_{in}} \times 100\%$$
 (2)

2.3. Catalyst characterization

The Brunauer-Emmett-Teller (BET) surface area, pore volume and pore diameter of the Mo-V-based SCR catalysts were determined at 77 K by nitrogen adsorption using Micromeritics ASAP 2020. The catalyst morphology was analyzed using a FEI CM 20 transmission electron microscope (TEM). Isopropyl alcohol (IPA) was utilized to spread the ground catalyst to ensure that the catalyst powder was uniformly dispersed over a copper grid for TEM analysis.

The X-ray powder diffraction (XRD) analysis was conducted under an X'Pert Pro MPD X-ray diffractometer to measure the crystalline structure of the samples. The XRD diffractometer was equipped with Cu K α radiation ($\lambda=0.1543$ nm). The ground catalyst powder was packed into a sample holder. The sample was scanned under a step time of 0.5 s in a range of 10° to 60° (20) with a step size of 0.02°.

Temperature-programmed desorption of NH₃ (NH₃-TPD) was conducted using AutoChem 2910 to determine the surface acidity of the sequentially modified SCR catalysts on different substrates. In a typical pretreatment process, ~100 mg catalyst was heated up to 500 °C with a ramp rate of 20 °C/min and held at this temperature for 1 hr under 20 mL/min He. Then, the sample was cooled down to room temperature and saturated with 4% NH₃ balanced with He at 30 mL/min for 30 min. At the end of the saturation procedure, pure He at 20 mL/min was used to flush over the sample for 30 min to remove weakly adsorbed NH₃. The thermal conductivity detector (TCD) signal was recorded while heating the sample up to 500 °C at a ramp rate of 15 °C /min in pure He for NH₃ desorption.

X-ray absorption near-edge structure (XANES) spectroscopy was conducted at Argonne National Laboratory (ANL, Chicago, IL). The data were taken on the 20-BM-B Beamline from the Advanced Photon Source (APS) with a Si (111) monochromator. The energy scale was calibrated at 5,465 eV by a V metal foil. Three different vanadium references containing V_2O_5 , VO_2 and V_2O_3 were used to carry out the energy scale calibration. These references were finely pulverized using a mortar and evenly dispersed over Kapton tape. Then the folded tape was analyzed under transmission mode. Each sample was run at least three times to enhance the signal-to-noise ratio. Since the V concentration on synthesized SCR catalysts was low and the interference between V and Ti, a larger amount of sample was packed in a sample holder. To analyze V in fresh modified SCR catalysts with different TiO₂ supports and calcination temperatures, these modified SCR samples were finely pulverized using a mortar and put into a Teflon holder. Then, the samples were tested in fluorescence mode. Each sample was run at least 8 scans to enhance the signal-to-noise ratio.

3. Results and Discussions

3.1. Effects of preparation parameters on activities of Hg^0 oxidation and NO reduction

3.1.1. Effects of TiO₂ supports

 TiO_2 is a widely used substrate resistant to metal sulfate formation in coal combustion flue gas containing SO_2 . TiO_2 -based catalysts are stable and has a resistance to sulfation in the SCR process [31,32]. To explore the effects of different TiO_2 phases on simultaneous Hg^0 oxidation and NO reduction, the three different TiO_2 supports of anatase DT-51, 75 wt. % anatase/25 wt.% rutile P25, and rutile STR-100W were selected.

The activities of simultaneous Hg^0 oxidation and NO reduction over the Mo-V-based SCR catalysts with different TiO_2 phases were tested under a simulated lignite and sub-bituminous coal combustion flue gas condition and the activity results are exhibited in Fig. 2. For Hg^0 oxidation, among these three catalysts, anatase TiO_2 DT-51 supported Mo-V-based SCR catalyst exhibited the highest Hg^0 oxidation activity (~53% at 5 ppmv HCl and ~69% at 10 ppmv HCl) and NO reduction activity (~80%). When P25 was employed as a support, Hg^0 oxidation activity decreased to ~32% at 5 ppmv HCl and ~56% at 10 ppmv HCl,



Fig. 2. Activity test results of Mo-V-based SCR catalysts for Hg^0 oxidation (a) and NO reduction (b) in terms of different TiO_2 supports (DT-51*, P25 and STR-100W). Experimental conditions: 15 ppbv Hg^0 , 300 ppmv NO, 270 ppmv NH₃ (molar ratio of NH₃ to NO = 0.9), 200 ppmv SO₂, 3%(v) O₂, 10%(v) H₂O, 12% (v) CO₂ balanced with N₂ at T = 350 °C and GHSV = 40,000 hr⁻¹. Note: * [28].

respectively. In the meantime, the NO reduction activity was kept the same at ~80% for both supports. When rutile STR-100W was used, the catalyst almost lost its Hg⁰ oxidation ability and also showed the significantly decreased NO reduction activity of ~49%. This result shows that anatase phase TiO₂ should be used as a support for simultaneous Hg⁰ and NO removal.

3.1.2. Effects of calcination temperatures

Calcination temperature is an important factor during SCR catalyst preparation. Because calcination temperature can affect phase transformation and active metal dispersion, it can influence SCR catalyst activity [33-35]. To probe the effect of calcination temperatures on simultaneous Hg⁰ oxidation and NO reduction, four different calcination temperatures were selected. The activities of simultaneous Hg⁰ oxidation and NO reduction over the Mo-V-based SCR catalysts with different calcination temperatures were tested under a simulated flue gas and the test results are exhibited in Fig. 3. For Hg⁰ oxidation, when the calcination temperatures were 400 and 500 °C, it showed the highest Hg⁰ oxidation activity (~53% at 5 ppmv HCl and ~69% at 10 ppmv HCl). With calcination temperature increasing to 600 °C, the Hg⁰ oxidation conversion was reduced to 39% at 5 ppmv HCl and 55% at 10 ppmv HCl, respectively. Once the calcination temperature was enhanced to 700 °C, the modified catalyst almost lost the capability to oxidize Hg⁰. For NO reduction, all of the catalysts showed the comparable NO reduction

activity of ~80% at all calcination temperatures except at 700 °C showing the lowest NO reduction activity of ~54%. Therefore, lower temperature of 400 or 500 °C would be an optimal calcination temperature for synthesizing the Mo-V-based SCR catalyst. The effects of calcination temperatures were studied using multiple characterization techniques in Section 3.3.

3.2. Effects of experimental conditions on activities of ${\rm Hg}^0$ oxidation and NO reduction

The activities of $MoO_3+WO_3\rightarrow V_2O_5/TiO_2$ DT-51 CT500 prepared using anatase TiO₂ DT-51 as the support and 500 °C as the calcination temperature were investigated in terms of flue gas constituents, gas velocities, and reaction temperatures using a fixed-bed reactor system.

3.2.1. Effect of O_2

100

 O_2 plays a significant part during the catalytic process. The effects of O_2 on simultaneous Hg⁰ oxidation and NO reduction are shown in Fig.4. With an O_2 concentration increasing from 3 to 9%(v), Hg⁰ oxidation activity enhanced from 69% to 81%. It demonstrated that O_2 was crucial to Hg⁰ oxidation and had a positive effect. This result clearly shows that O_2 is required for Hg⁰ oxidation. However, considering a typical range of $\sim 3-6\%$ O_2 concentration was not significant. Meanwhile, NO reduction activity was ~80% with respect to different O_2 concentrations.





Fig. 3. Activity test results of Mo-V-based SCR catalysts for Hg^0 oxidation (a) and NO reduction (b) in terms of different calcination temperatures (400, 500, 600 and 700 °C). Experimental conditions: 15 ppbv Hg^0 , 300 ppmv NO, 270 ppmv NH₃ (molar ratio of NH₃ to NO = 0.9), 200 ppmv SO₂, 3%(v) O₂, 10%(v) H₂O, 12%(v) CO₂ balanced with N₂ at T = 350 °C and GHSV = 40,000 hr⁻¹.

Fig. 4. Effect of O₂ on simultaneous Hg⁰ oxidation (a) and NO reduction (b) over Mo-V-based SCR catalyst MoO₃+WO₃ \rightarrow V₂O₅/TiO₂ DT-51 CT500. Experimental conditions: 15 ppbv Hg⁰, 300 ppmv NO, 270 ppmv NH₃ (molar ratio of NH₃ to NO = 0.9), 200 ppmv SO₂, 10 ppmv HCl, 10%(v) H₂O, 12%(v) CO₂ balanced with N₂ at T = 350 °C and GHSV = 40,000 hr⁻¹.

C. Li et al.

3.2.2. Effect of SO₂

When SO_2 concentration was raised from 200 to 2000 ppmv, the catalytic activities of Hg^0 oxidation and NO reduction did not significantly change as shown in Fig.5. This means that the modified SCR catalyst is very robust and can be used in a wide range of SO_2 concentrations.

3.2.3. Effect of molar ratio of NH₃ to NO

NH₃/NO molar ratio is an important factor affecting Hg⁰ oxidation and NO reduction activities because NH3 can competitively adsorb with HCl. A ratio between 0 and 1.1 is used in the field to minimize an NH₃ slip of <5 ppmv to avoid the formation of ammonium sulfate [36,37]. The effects of NH₃/NO molar ratio on the simultaneous removal activities of Hg⁰ and NO over MoO₃+WO₃ \rightarrow V₂O₅/TiO₂ DT-51 CT500 catalyst were tested under a simulated flue gas and the test results are exhibited in Fig. 6. When an NH₃/NO molar ratio increased over the range of 0.3 to 0.9, the Hg⁰ oxidation activity was almost constant or slightly decreased from 73% to 69% (Fig. 6 (a)). However, with a further increase from 0.9 to 1.1, the Hg⁰ oxidation activity significantly started to decrease from 69% to 59%. On the other hand, as NH₃/NO molar ratio increased from 0 to 1.1, the NO reduction activity almost linearly enhanced from 0 to 95%. The NO reduction activity is found to be almost primarily dependent on the NH₃/NO molar ratio and to be insensitive to the rest of the parameters studied above.



Fig. 5. Effect of SO₂ on simultaneous Hg⁰ oxidation (a) and NO reduction (b) over MoO₃+WO₃ \rightarrow V₂O₅/TiO₂ DT-51 CT500. Experimental conditions: 15 ppbv Hg⁰, 300 ppmv NO, 270 ppmv NH₃ (molar ratio of NH₃ to NO = 0.9), 3%(v) O₂, 10 ppmv HCl, 10%(v) H₂O, 12%(v) CO₂ balanced with N₂ at T = 350 °C and GHSV = 40,000 hr⁻¹.



Fig. 6. Effect of NH₃/NO molar ratios on simultaneous Hg⁰ oxidation (a) and NO reduction (b) over MoO₃+WO₃→V₂O₅/TiO₂ DT-51 CT500. Experimental conditions: 15 ppbv Hg⁰, 300 ppmv NO, 200 ppmv SO₂, 3%(v) O₂, 10 ppmv HCl, 10%(v) H₂O, 12%(v) CO₂ balanced with N₂ at T = 350 °C and GHSV = 40,000 hr⁻¹.

3.2.4. Effect of GHSV

The effects of GHSV on the simultaneous removal activities of Hg^0 and NO over $MoO_3+WO_3\rightarrow V_2O_5/TiO_2$ DT-51 CT500 catalyst were tested under the same combustion flue gas conditions and the test results are exhibited in Fig. 7. With a decrease in the GHSV from 40,000 hr⁻¹ to 5,000 hr⁻¹, the Hg^0 oxidation activities enhanced from 53% to 93% at 5 ppmv HCl and from 69% to 99% at 10 ppmv HCl under the flue gas conditions. On the other hand, the NO reduction activities slightly increased from ~80% to 87% over a range of 5–10 ppmv HCl. It shows that the space velocity has an obvious impact on Hg^0 oxidation.

3.2.5. Effect of temperature

A typical operating temperature window of the SCR unit is between 300-400 °C in coal-fired power plants. The activities of simultaneous Hg⁰ oxidation and NO reduction over the Mo-V-based SCR catalyst were tested between 300 and 400 °C and the test results are exhibited in Fig. 8. With an increase in temperature from 300 °C to 400 °C, Hg⁰ oxidation activities was reduced from 81% to 38%. It indicated that in the typical SCR operating temperature window, lower temperature was beneficial to oxidize Hg⁰. Meantime, the NO reduction activities of this Mo-V-based SCR catalyst was quite constant at ~80% within the same temperature range. An in-house V-based SCR catalyst V₂O₅+WO₃/TiO₂ DT-51 CT500 was also evaluated to compare with the Mo-V-based SCR catalyst. The conventional V-based SCR catalyst showed lower Hg⁰ oxidation activities within a typical SCR operating temperature window



Fig. 7. Effect of GHSV on simultaneous Hg^0 oxidation (a) and NO reduction (b) over $MoO_3+WO_3 \rightarrow V_2O_5/TiO_2$ DT-51 CT500. Experimental conditions: 15 ppbv Hg^0 , 300 ppmv NO, 270 ppmv NH₃ (molar ratio of NH₃ to NO = 0.9), 200 ppmv SO₂, 3%(v) O₂, 10%(v) H₂O, 12%(v) CO₂ balanced with N₂ at T = 350 °C.

between 300 and 400 °C. The activities difference in Hg⁰ oxidation for these two catalyst samples decreased with an increase in temperature. Lower temperature could facilitate more HCl adsorption onto the catalyst surface and thus Hg⁰ oxidation could be kinetically limited by HCl adsorption [24]. The conventional V-based SCR catalyst also showed a comparable NO reduction activity at ~80%.

3.3. Characterization

3.3.1. BET

Since the activities were significantly different with respect to different TiO₂ supports and calcination temperatures, the BET surface area, pore volume and average pore diameter were examined by nitrogen adsorption-desorption isotherms as listed in Table 1. The catalyst samples with different TiO₂ supports showed slightly lower surface areas and pore volumes after doping metals. The loadings of V, Mo and W metals only insignificantly vary the surface areas and pore values of the Mo-V-based SCR catalysts with different TiO₂ supports. These BET surface area and pore volume values were still in the range of $36-120 \text{ m}^2/\text{g}$ and $0.17-0.31 \text{ cm}^3/\text{g}$ of typical SCR catalysts, respectively [11,15,38].

The SCR catalyst sample prepared onto P25 had a surface area lower than that onto DT-51. The SCR catalyst sample onto rutile STR-100W had surface area, pore volume and size comparable to that onto anatase DT-51 although its activities were much lower (Fig. 2). Therefore, anatase phase TiO_2 was selected as a support for our Mo-V-based



Fig. 8. Effect of reaction temperatures on simultaneous Hg^0 oxidation (a) and NO reduction (b) over Mo-V-based SCR catalyst $MoO_3+WO_3\rightarrow V_2O_5/TiO_2$ DT-51 CT500 and $V_2O_5+WO_3/TiO_2$ DT-51 CT500. Experimental conditions: 15 ppbv Hg^0 , 300 ppmv NO, 270 ppmv NH₃ (molar ratio of NH₃ to NO = 0.9), 200 ppmv SO₂, 3%(v) O₂, 10 ppmv HCl, 10%(v) H₂O, 12%(v) CO₂ balanced with N₂ and GHSV = 40,000 hr⁻¹.

Table 1

BET surface area, pore volume and average pore diameter measurements for Mo-V-based SCR catalysts.

Catalyst	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)
TiO ₂ (DT-51)*	72	0.38	20.2
TiO ₂ (P25)	51	0.31	24.8
TiO2 (STR-100W)	67	0.37	22.4
$MoO_3+WO_3\rightarrow V_2O_5/TiO_2$	65	0.26	15.7
DT-51 CT500*			
$MoO_3+WO_3 \rightarrow V_2O_5/TiO_2$	42	0.27	26.2
P25 CT500			
$MoO_3+WO_3\rightarrow V_2O_5/TiO_2$	62	0.33	27.7
STR-100W CT500			
$MoO_3+WO_3\rightarrow V_2O_5/TiO_2$	69	0.25	14.3
DT-51 CT400			
$MoO_3+WO_3\rightarrow V_2O_5/TiO_2$	48	0.21	17.7
DT-51 CT600			
$MoO_3+WO_3\rightarrow V_2O_5/TiO_2$	5	0.01	8.9
DT-51 CT700			

Note:

[28]; CT: calcination temperature.

SCR catalyst.

When the calcination temperature of the samples onto anatase DT-51 was 400 and 500 $^{\circ}$ C, the surface areas, pore volumes, and pore sizes were not significantly reduced. With the calcination temperature increasing to 600 $^{\circ}$ C, they started to significantly decrease. At the calcination temperature of 700 $^{\circ}$ C, they were almost close to zero. These results lead to additional examinations by images and X-ray-based techniques.

3.3.2. TEM

The images of TEM from the raw TiO_2 supports and Mo-V-based SCR catalysts based on different TiO_2 supports are shown in Fig. 9. After doping onto the support, the modified SCR catalyst samples retained almost the same physical structure as the raw supports, which was consistent with BET results. From the TEM images, some grain particles were found from the catalyst surfaces for all the three modified SCR catalysts (b, d, f). Since the loading quantity of V or W metals were rather lower than those needed to generate the theoretical monolayers, these grain particles are most likely derived from Mo as observed from previous studies. [28,39,40]

The TEM images of raw anatase DT-51 TiO₂ support and Mo-V-based SCR catalysts in terms of different calcination temperatures are exhibited in Fig. 10. The Mo-V-based SCR catalysts showed the morphological structure similar to the raw TiO₂ support when the calcination temperature was 400, 500 or 600 °C. The only difference was visible grain

particles formed over the samples. With the calcination temperature increasing to 700 °C, the TiO₂ support particle dimension dramatically increased from ~30 nm to ~180 nm. Meanwhile, the small grain particles on the catalyst surface disappeared, suggesting that the calcination temperature of 700 °C led to the agglomeration of the support and the active metals. This is consistent with the very low surface area and pore volume of the sample prepared at 700 °C. The poor catalytic activities are very likely attributed to this agglomeration phenomenon taking place at 700 °C.

3.3.3. XRD

The XRD patterns of the raw TiO_2 (anatase DT-51, 75% anatase/25% rutile P25, and rutile STR-100W) supports and the catalyst samples synthesized at 500 °C are exhibited in Fig. 11. All the TiO_2 supports demonstrated their XRD patterns consistent with the information provided from the manufacture. All of the Mo-V-based SCR catalysts did not show any visible peaks for the active metals, suggesting that they were likely in the amorphous phase or evenly spread over the TiO_2 support beyond the detection limit of XRD technique. [12]

The XRD patterns of the Mo-V-based SCR catalysts prepared on the anatase DT-51 TiO₂ support with respect to different calcination temperatures are exhibited in Fig. 12. For the Mo-V-based SCR catalysts synthesized at 400, 500 and 600 °C, no visible peaks for V₂O₅, MoO₃, and WO₃ were detected, suggesting the amorphous phase or uniform dispersion. Nevertheless, with the calcination temperature increasing to



Fig. 9. TEM images of Mo-V-based SCR catalysts in terms of different TiO₂ supports: (a) TiO₂ (DT-51)*; (b) MOO₃+WO₃ \rightarrow V₂O₅/TiO₂ DT-51 CT500*; (c) TiO₂ (P25); (d) MOO₃+WO₃ \rightarrow V₂O₅/TiO₂ P25 CT500; (e) TiO₂ (STR-100W); (f) MOO₃+WO₃ \rightarrow V₂O₅/TiO₂ STR-100W CT500. Scale bars: 20 nm. Note: * [28].



Fig. 10. TEM images of Mo-V-based SCR catalysts in terms of different calcination temperatures: (a) TiO₂ (DT-51)*; (b) MoO₃+WO₃ \rightarrow V₂O₅/TiO₂ DT-51 CT400; (c) MoO₃+WO₃ \rightarrow V₂O₅/TiO₂ DT-51 CT500*; (d) MoO₃+WO₃ \rightarrow V₂O₅/TiO₂ DT-51 CT600; (e) MoO₃+WO₃ \rightarrow V₂O₅/TiO₂ DT-51 CT700; (f) MOO₃ + WO₃ \rightarrow V₂O₅/TiO

700 °C, the peaks at 27°, 36°, 41°, 44°, 54° and 57° belonging to the rutile phase were visible, indicating the transition from the anatase to rutile phase happened due to the high calcination temperature [33–35]. The phase transformation from anatase to rutile seems to lead to the major activities difference shown in Fig. 3. A peak at 23° was from MoO₃. At 700 °C, small MoO₃ grain particles agglomerated into larger sizes, which was detectable by XRD. This could also lead to a negative impact on Hg⁰ oxidation and NO reduction.

3.3.4. NH3 TPD

The adsorption of NH₃ onto the catalyst surface is an important step during SCR process. Therefore, the surface acidity of the samples with different substrates was investigated using NH₃-TPD as shown in Fig. 13. For all of the three modified SCR catalysts with different TiO₂ supports, they all started to desorb NH₃ from ~60 °C. As temperature increased, the NH₃ desorption peak reached a maximum and then gradually decreased. Overall, the desorption of NH₃ occurred with a broad shape within a wide temperature range of ~60–450 °C. It indicated that several adsorbed NH₃ species with different thermal stability were present on the catalyst surface.

For the $MoO_3+WO_3\rightarrow V_2O_5/TiO_2$ STR-100W CT500 catalyst, it showed ~0.18 mmol desorbed NH₃/g catalyst with a maximum NH₃ desorption peak at ~168 °C. However, the NH₃ species adsorbed onto

the one with STR-100W was thermally unstable within a typical SCR operating temperature range of ~300-400 °C and only a slight amount of NH₃ was desorbed in this temperature range. When DT-51 was used, a broader NH₃ desorption spectrum at higher temperatures was obtained. A total amount of NH₃ desorbed increased to \sim 0.23 mmol/g catalyst. More importantly, the sample showed higher thermal stability for adsorbed NH₃ between 300 and 400 °C, which could be used to reduce gaseous NO in the typical SCR operating temperature range. When P25 TiO2 with 75% anatase and 25% rutile phases was used, the desorption spectrum showed a characteristic between anatase DT-51 and rutile STR-100W substrates with an estimated amount of NH3 desorbed of \sim 0.18 mmol/g catalyst. More specifically, the desorbed amount of NH₃ at 350 °C were in the order of MoO₃+WO₃ \rightarrow V₂O₅/TiO₂ DT-51 CT500 > $MoO_3+WO_3 \rightarrow V_2O_5/TiO_2 P25 CT500 > MoO_3+WO_3 \rightarrow V_2O_5/TiO_2 STR-$ 100W CT500. These results are consistent with our NO reduction performance differences shown in Fig. 2.

3.3.5. XANES

Previous studies reported inconsistent results for V oxidation state changes using X-ray photoelectron spectroscopy (XPS) with respect to different calcination temperature. [41–44] In this study, XANES was employed to investigate the oxidation states and speciations of V from the fresh catalyst samples on different TiO_2 supports. Due to the



Fig. 11. XRD patterns of Mo-V-based SCR catalysts on different TiO₂ supports calcined at 500 °C: (a) Anatase TiO₂ DT-51*; (b) Anatase/rutile TiO₂ P25; (c) Rutile TiO₂ STR-100W; (d) $MoO_3+WO_3\rightarrow V_2O_5/TiO_2$ DT-51 CT500*; (e) $MoO_3+WO_3\rightarrow V_2O_5/TiO_2$ P25 CT500; (f) $MoO_3+WO_3\rightarrow V_2O_5/TiO_2$ STR-100W CT500. Note: * [28].



Fig. 12. XRD patterns of $MoO_3+WO_3 \rightarrow V_2O_5/TiO_2$ DT-51 with respect to different calcination temperatures: (a) Anatase TiO₂ DT-51*; (b) Rutile TiO₂ STR-100W; (c) $MoO_3+WO_3 \rightarrow V_2O_5/TiO_2$ DT-51 CT400; (d) $MoO_3+WO_3 \rightarrow V_2O_5/TiO_2$ DT-51 CT500*; (e) $MoO_3+WO_3 \rightarrow V_2O_5/TiO_2$ DT-51 CT500; (f) $MoO_3+WO_3 \rightarrow V_2O_5/TiO_2$ DT-51 CT700. Note: * [28].

interference between V and Ti, 0.5 wt.% V_2O_5 used in the Mo-V-based SCR formula was too low to conduct XAFS characterization. Therefore, V_2O_5 loading was raised from 0.5 to 2 wt.%. Fig. 14 exhibits V K-edge XANES spectra of the Mo-V-based SCR catalyst in terms of different TiO₂ supports with 2 wt.% V_2O_5 and vanadium oxide references. All the fresh catalyst samples had distinct pre-edge peaks, but the post-edge part was not differentiable. A comparison of the spectra of the catalyst samples with those of the V_2O_3 , VO_2 and V_2O_5 standard samples suggests that the oxidation state of vanadium oxide consists of V^{5+} and V^{4+} .

To quantify the V oxidation states in the Mo-V-based SCR catalysts, linear combination fitting (LCF) analysis was employed. The derivative XANES spectra and LCF results are exhibited in Fig. 15, and the quantitative speciation data acquired are summarized in Table 2. The spectrum of the V₂O₃ standard with V³⁺ was completely deviated from those of the catalyst samples during the LCF analysis, and thus the V₂O₃ standard was ruled out from the analysis. When the MoO₃+WO₃→V₂O₅/



Fig. 13. NH_3 -TPD spectra of Mo-V-based SCR catalysts with different TiO_2 supports (DT-51, P25 and STR-100W).



Fig. 14. Vanadium K-edge XANES spectra of Mo-V-based SCR catalyst samples with different TiO_2 supports (DT-51*, P25 and STR-100W) and standard reference vanadium oxide samples. Note: * [28].

TiO₂ DT-51 CT500 spectrum (Fig. 15(a)) was fitted with those of the references, the vanadium oxides could comprise 53.1% V⁵⁺ and 46.9% V⁴⁺. When P25 and STR-100W were chosen as the supports, the content of V⁵⁺ slightly decreased to 49.3% and 47.1%, respectively. It seems that TiO₂ supports could not lead to significant differences on vanadium oxidation state. The significant Hg⁰ oxidation and NO reduction activity differences may not be derived from the vanadium oxidation state change with respect to different TiO₂ supports.

Fig. 16 exhibits V K-edge XANES spectra of the Mo-V-based SCR catalyst samples based on different calcination temperatures with 2 wt. % V₂O₅ and vanadium oxide references. LCF was employed to quantify the V oxidation states from the fresh Mo-V-based SCR catalysts with different calcination temperatures. The derivative XANES spectra and LCF results are shown in Fig. 17, and the quantitative speciation data acquired are summarized in Table 3. The analysis for the MoO₃+WO₃→V₂O₅/TiO₂ DT-51 CT 400 °C sample (Fig. 17(a)) showed 52.2% V⁵⁺ and 47.8% V⁴⁺. When the calcination temperature increased to 500 °C, the content of V⁵⁺ slightly increased to 53.1%. However, as the calcination temperatures increased to 600 °C and 700 °C, the content of V⁵⁺ dramatically decreased to 43.9% and 34.3%, respectively. This is in agreement with the catalytic activity differences (Fig. 3). As the calcination temperature increased from 400 or 500 °C, the Hg⁰ oxidation activities decreased from ~53% to ~39% at 5 ppmv HCl and

5485



Fig. 15. LCF results for vanadium species of Mo-V-based SCR catalysts with different TiO₂ supports: (a) Fresh MoO₃+WO₃ \rightarrow V₂O₅/TiO₂ DT-51 CT500*; (b) Fresh MoO₃+WO₃ \rightarrow V₂O₅/TiO₂ P25 CT500; (c) Fresh MoO₃+WO₃ \rightarrow V₂O₅/TiO₂ STR-100W CT500. Note: * [28].

Tabl	e 2									
LCF	results	for	vanadium	species	of	Mo-V-based	SCR	catalysts	with	different
TiO ₂	suppor	rts.								

Samples	V ₂ O ₅ (V ⁵⁺) (%)	VO ₂ (V ⁴⁺) (%)	Ratio of V^{5+} to V^{4+}
Fresh MoO ₃ +WO ₃ →V ₂ O ₅ /TiO ₂ DT- 51 CT500*	53.1 ± 2.0	$\textbf{46.9} \pm \textbf{2.0}$	1.13
Fresh MoO ₃ +WO ₃ →V ₂ O ₅ /TiO ₂ P25 CT500	$\textbf{49.3} \pm \textbf{2.2}$	$\textbf{50.7} \pm \textbf{2.2}$	0.97
Fresh MoO ₃ +WO ₃ →V ₂ O ₅ /TiO ₂ STR- 100W CT500	$\textbf{47.1} \pm \textbf{2.3}$	$\textbf{52.9} \pm \textbf{2.3}$	0.89

Note: * [28].

from $\sim 69\%$ to $\sim 55\%$ at 10 ppmv HCl. When the calcination temperature was 700 $^\circ\text{C},$ the catalyst almost completely lost its Hg^0 oxidation activity and decreased NO reduction activity from $\sim 80\%$ to $\sim 54\%$. During the Hg⁰ oxidation and NO reduction process, V⁵⁺ was reduced to V^{4+} based on our previous proposed mechanism [28]. Low V^{5+}/V^{4+} ratio correlates with low catalytic activity with an increase in calcination temperature. In addition to the physical agglomeration (Fig. 10) and the anatase to rutile phase change in TiO₂ (Fig. 12) under different calcination temperatures, the significant activity difference could also be attributed to a change in the V oxidation state. Throughout this study, rutile-phase TiO₂ was found to degrade both Hg⁰ oxidation and NO reduction activities. Previous studies reported that degraded NO reduction activity of V-based SCR catalyst over the rutile phase is very likely attributed to crystallographic misfit between V₂O₅ and rutile TiO₂ [45–48]. Although low V^{5+}/V^{4+} ratio can help account for the degraded activities over rutile TiO2, it is not currently well understood about the



Fig. 16. Vanadium K-edge XANES spectra of Mo-V-based SCR catalyst samples with respect to different calcination temperatures (400, 500*, 600 and 700 $^{\circ}$ C) and standard reference vanadium oxide samples. Note: * [28].

role of rutile TiO₂.

4. Conclusions

In this study, the effects of preparation parameters including TiO_2 supports and calcination temperatures for Mo-V-based SCR catalysts on



Fig. 17. LCF results for vanadium species of Mo-V-based SCR catalysts with respect to different calcination temperatures: (a) Fresh $MoO_3+WO_3\rightarrow V_2O_5/TiO_2 DT-51$ CT400; (b) Fresh $MoO_3+WO_3\rightarrow V_2O_5/TiO_2 DT-51$ CT500*; (c) Fresh $MoO_3+WO_3\rightarrow V_2O_5/TiO_2 DT-51$ CT600; (d) Fresh $MoO_3+WO_3\rightarrow V_2O_5/TiO_2 DT-51$ CT700. Note: * [28].

Table 3

LCF fitting results for vanadium species of Mo-V-based SCR catalysts with respect to different calcination temperatures.

Samples	V ₂ O ₅ (V ⁵⁺) (%)	VO ₂ (V ⁴⁺) (%)	Ratio of V ⁵⁺ to V ⁴⁺
Fresh MoO ₃ +WO ₃ →V ₂ O ₅ /TiO ₂ DT- 51 CT400	52.2 ± 2.8	$\textbf{47.8} \pm \textbf{2.8}$	1.09
Fresh MoO ₃ +WO ₃ →V ₂ O ₅ /TiO ₂ DT- 51 CT500*	53.1 ± 2.0	$\textbf{46.9} \pm \textbf{2.0}$	1.13
Fresh MoO ₃ +WO ₃ →V ₂ O ₅ /TiO ₂ DT- 51 CT600	$\textbf{43.9} \pm \textbf{2.6}$	56.1 ± 2.6	0.78
Fresh MoO ₃ +WO ₃ →V ₂ O ₅ /TiO ₂ DT- 51 CT700	$\textbf{34.3} \pm \textbf{1.8}$	65.7 ± 1.8	0.52

Note: * [28].

simultaneous Hg⁰ oxidation and NO reduction were systematically investigated for the first time. Among different TiO₂ supports (anatase DT-51, mixed anatase/rutile phase P25 and rutile STR-100W) and four different calcination temperatures (400, 500, 600 and 700 °C), a combination of anatase phase TiO₂ and the calcination temperatures of 400 °C and 500 °C showed the best activities of simultaneous Hg⁰ oxidation and NO reduction. When rutile phase or the high calcination temperature of 700 °C was used to prepare the Mo-V-based SCR catalyst, the catalyst lost almost its capability to oxidize Hg⁰ and decreased NO reduction activity by ~30%. Different TiO₂ phase showed noticeable differences in the morphology. The calcination temperature of 700 °C could lead to the TiO₂ phase transformation from anatase to rutile and the agglomeration of active metals with TiO₂. The content of V⁵⁺ decreased with an increase in rutile TiO₂ content or calcination temperature.

Our Mo-V-based SCR catalyst using anatase TiO_2 as the support and 500 °C as the calcination temperature preferred lower reaction temperature in a typical SCR operating temperature of 300–400 °C. It showed good SO₂ resistance in a wide range tested up to 2,000 ppmv SO₂

under a simulated sub-bituminous and lignite coal combustion flue gas. O_2 had a positive impact on Hg^0 oxidation and NH_3 had a negative effect on Hg^0 oxidation. With the molar ratio of NH_3/NO in a range of 0 to 1.1, the Hg^0 oxidation activity decreased and NO reduction activity increased. An increase in GHSV could significantly enhance Hg^0 oxidation, but slightly improve NO reduction. When the low space velocity of 5,000 hr⁻¹ was used, the Hg^0 oxidation activity could achieve up to 99% under a typical sub-bituminous and lignite coal combustion flue gas condition. Compared to an in-house conventional V-based SCR catalyst, our Mo-V-based SCR catalyst showed much higher Hg^0 oxidation activity and comparable NO reduction activity. It has the potential to meet the stringent regulations for mercury and NO emissions in coal combustion flue gas using Mo-V-based SCR catalyst in an existing SCR unit.

CRediT authorship contribution statement

Can Li: Validation, Formal analysis, Investigation, Data curation, Writing - original draft, Visualization. **Vishnu Sriram:** Validation, Formal analysis, Investigation, Data curation. **Zhouyang Liu:** Validation, Formal analysis, Investigation, Data curation. **Dale Brewe:** Validation, Formal analysis. **Joo-Youp Lee:** Conceptualization, Methodology, Validation, Investigation, Resources, Writing - review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This study was supported by the National Science Foundation, NSF CAREER Grant # 1151017. The authors greatly appreciate their

financial support. This research used resources of the Advanced Photon Source, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science by Argonne National Laboratory, and was supported by the U.S. DOE under Contract No. DE-AC02-06CH11357, and the Canadian Light Source and its funding partners.

References

- [1] C. Wiedinmyer, H. Friedli, Environ. Sci. Technol. 41 (2007) 8092–8098.
- [2] J.H. Pavlish, E.A. Sondreal, M.D. Mann, E.S. Olson, K.C. Galbreath, D.L. Laudal, S. A. Benson, Fuel Process. Technol. 82 (2003) 89–165.
- [3] R. Meij, Water Air Soil Pollut. 56 (1991) 21–33.
- [4] M.A. Abu-Daabes, N.G. Pinto, Chem. Eng. Sci. 60 (2005) 1901–1910.
- [5] A.P. Jones, J.W. Hoffmann, D.N. Smith, T.J. Feeley, J.T. Murphy, Environ. Sci. Technol. 41 (2007) 1365–1371.
- [6] Y. Zhuang, J.S. Thompson, C.J. Zygarlicke, J.H. Pavlish, Fuel 86 (2007) 2351–2359.
- [7] Y. Yang, W. Xu, Y. Wu, J. Xiong, T. Zhu, X. Zhou, L. Tong, RSC Adv. 6 (2016) 59009–59015.
- [8] Q. Zhou, Y.-F. Duan, S.-L. Zhao, H.-F. Du, C. Zhu, M. She, H.-Q. Wei, Energy Fuels 29 (2015) 5267–5273.
- [9] Y. Cao, Z. Gao, J. Zhu, Q. Wang, Y. Huang, C. Chiu, B. Parker, P. Chu, W. Pan, Environ. Sci. Technol. 42 (2007) 256–261.
- [10] Y. Zhuang, J. Laumb, R. Liggett, M. Holmes, J. Pavlish, Fuel Process. Technol. 88 (2007) 929–934.
- [11] S. He, J. Zhou, Y. Zhu, Z. Luo, M. Ni, K. Cen, Energy Fuels 23 (2009) 253–259.
 [12] L. Casagrande, L. Lietti, I. Nova, P. Forzatti, A. Baiker, Appl. Catal. B 22 (1999)
- 63-77.
- [13] I. Nova, L. Lietti, L. Casagrande, L. Dall'Acqua, E. Giamello, P. Forzatti, Appl. Catal. B 17 (1998) 245–258.
- [14] G. Busca, L. Lietti, G. Ramis, F. Berti, Appl. Catal. B 18 (1998) 1-36.
- [15] H. Kamata, S. Ueno, T. Naito, A. Yukimura, Ind. Eng. Chem. Res. 47 (2008)
- 8136-8141. [16] S. Niksa, N. Fujiwara, J. Air Waste Manage. Assoc. 55 (2005) 1866-1875.
- [17] H. Li, C. Wu, Y. Li, J. Zhang, Appl. Catal. B 111 (2012) 381–388.
- [18] J. Zhou, W. Hou, P. Qi, X. Gao, Z. Luo, K. Cen, Environ. Sci. Technol. 47 (2013) 10056–10062.
- [19] L. Zhao, C. Li, J. Zhang, X. Zhang, F. Zhan, J. Ma, G. Zeng, Fuel 153 (2015) 361–369.

- [20] N. Yan, W. Chen, J. Chen, Z. Qu, Y. Guo, S. Yang, J. Jia, Environ. Sci. Technol. 45 (2011) 5725–5730.
- [21] Z. Liu, C. Li, V. Sriram, J.-Y. Lee, D. Brewe, Fuel Process. Technol. 153 (2016) 156–162.
- [22] Z. Liu, V. Sriram, C. Li, J.-Y. Lee, Catal. Sci. Technol. 7 (2017) 4669-4679.
- [23] V. Sriram, C. Li, Z. Liu, M. Jafari, J.-Y. Lee, Chem. Eng. J. 343 (2018) 244-257.
- [24] H. Wang, B. Wang, Q. Sun, Y. Li, W.Q. Xu, J. Li, Catal. Commun. (2017).
 [25] B. Zhao, X. Liu, Z. Zhou, H. Shao, C. Wang, J. Si, M. Xu, Chem. Eng. J. 253 (2014)
- 508–517. [26] B. Zhao, J. Han, L. Qin, W. Chen, Z. Zhou, F. Xing, New J. Chem. 42 (2018)
 - 20190–20196.
 [27] B. Zhao, X.W. Liu, Z.J. Zhou, H.Z. Shao, C. Wang, M.H. Xu, Fuel Process. Technol. 134 (2015) 198–204.
 - [28] C. Li, D. Brewe, J.Y. Lee, Appl. Catal. B (2020) 118854.
 - [29] K. Nochi, M. Yonemura, M. Kiyosawa, Mercury oxidation catalyst and method for producing the same, US 8288309 B2, Washington, DC: U.S. Patent and Trademark Office, 2012.
 - [30] J. Regalbuto, Catalyst Preparation: Science and Engineering, CRC Press, 2007.
 - [31] L.J. Alemany, F. Berti, G. Busca, G. Ramis, D. Robba, G.P. Toledo, M. Trombetta, Appl. Catal. B 10 (1996) 299–311.
 - [32] J. Chen, R. Yang, Selective catalytic reduction of NO with NH₃ on SO₄⁻²/TiO₂ superacid catalyst, J. Catal. 139 (1993) 277–288.
 - [33] J. Kim, K.C. Song, S. Foncillas, S.E. Pratsinis, J. Eur. Ceram. Soc. 21 (2001) 2863–2872.
 - [34] J. Ovenstone, K. Yanagisawa, Chem. Mater. 11 (1999) 2770–2774.
 - [35] J. Zhang, Q. Xu, Z. Feng, M. Li, C. Li, Angew. Chem. Int. Ed. 47 (2008) 1766–1769.
 - [36] H. Gutberlet, B. Schallert, Catal. Today 16 (1993) 207–236.
 - [37] I.Y. Lee, D.W. Kim, J.B. Lee, K.O. Yoo, Chem. Eng. J. 90 (2002) 267-272.
 - [38] Z.Y. Liu, V. Sriram, J.Y. Lee, Appl. Catal. B 207 (2017) 143–152.
 - [39] G. Deo, I.E. Wachs, J. Catal. 146 (1994) 323–334.
 - [40] I.E. Wachs, Catal. Today 27 (1996) 437–455.
 - [41] B.M. Reddy, P. Lakshmanan, A. Khan, J. Phys. Chem. B 108 (2004) 16855-16863.
 - [42] X. Gu, J. Ge, H. Zhang, A. Auroux, J. Shen, Thermochim. Acta 451 (2006) 84–93.
 - [43] B.M. Reddy, K.N. Rao, G.K. Reddy, P. Bharali, J. Mol. Catal. A Chem. 253 (2006)
 - 44–51.
 [44] B.M. Reddy, B. Chowdhury, I. Ganesh, E. Reddy, T. Rojas, A. Fernandez, J. Phys. Chem. B 102 (1998) 10176–10182.
 - [45] A. Vejux, P. Courtine, J. Solid State Chem. 23 (1978) 93–103.
 - [46] N.N. Nair, T. Bredow, K. Jug, J. Phys. Chem. B 109 (2005) 12115-12123.
 - [47] G. Centi, E. Giamello, D. Pinelli, F. Trifiro, J. Catal. 130 (1991) 220-237.
 - [48] J.W. Choung, I.-S. Nam, S.-W. Ham, Catal. Today 111 (2006) 242-247.