Simultaneous Catalytic Removal of VOCs and NO_x with the Dual-layered Catalyst of CoCeO_x and V₂O₅/TiO₂

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ABSTRACT

NO and volatile organic compounds (VOCs) are ones of exhaust with high irritation and toxicity, thus it is very necessary to develop a catalyst that can simultaneously remove them. In this study, a type of dual-layered catalyst has been prepared by combining CoCeO_x and V₂O₅/TiO₂ as different functional layers. The dual-layered catalyst was tested under NO, NH₃, propane and the mixing atmosphere, achieving great NO_x removal efficiency and good propane degradation under wide range temperature window. It is presented that NO conversion could reach 100% at 225°C and kept more than 80% at 175–300°C, while VOCs degradation reached 80% above 260°C. Moreover, the dual-layered catalyst with different construction is surveyed to reveal the mechanism included in this special construction. It is supposed that V₂O₅/TiO₂ layer possesses rich acid sites which adsorbs NH₃ as an ammonia buffer part and CoCeO_x layer provides good oxidizing ability to oxidize NO and propane. The combination moderates the competitive adsorption between NH₃ and propane which is the initial obstacle for multiple pollutants removal.

Keywords: Simultaneous removal of propane and NO, Dual-layered catalyst, Reaction mechanism, Cobalt cerium catalyst

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1 INTRODUCTION

The exhaust gas emitted from coal-fired power plants and vehicle is very complex, among which nitrogen oxides (NO_x) and volatile organic compounds (VOCs) are ones of the main air pollutants with the most severe irritation and toxicity (Zhao *et al.*, 2013; Kamal *et al.*, 2016). The emission of NO_x is always mixed with VOCs because of the incomplete combustion of the fossil fuels, which is assumed as a contribution to the photochemical smog and atmospheric oxidative pollution (Zhang *et al.*, 2018; Bilgen, 2014; Cheng *et al.*, 2016), dealing great harm to human health and ecological environment (Boningari and Smirniotis, 2016; Gholami *et al.*, 2020). Fortunately, selective catalytic reduction (SCR) is an effective method (Busca *et al.*, 1998) for the reduction of NO, with several metal oxides like TiO₂ (Liu *et al.*, 2018), CeO₂ (Zhang *et al.*, 2015; Tang *et al.*, 2016), Fe₂O₃ (Yu *et al.*, 2021) researched to obtain good reactive activity under working condition. For VOCs in traditional combustion process, several techniques like chemical adsorption (Yang *et al.*, 2019; Li *et al.*, 2020), photochemical degradation (Tobaldi *et al.*, 2021) are adopted effectively to remove organic air pollutants from flue gas, among which catalytic combustion is considered to be the most efficient way for VOCs abatement (Li *et al.*, 2019; Wang *et al.*, 2019). However, as widely accepted for most power plant only soluble VOCs is removed in wet technology, most of hydrophobic VOCs still remain to be released into atmosphere without any reduction (Li *et al.*, 2011). Therefore, it is very promising to explore a kind of catalyst that can simultaneously remove NO and VOCs in the SCR reaction zone.

In the past two decades, due to the complex process involved in the multiple pollutant degradation

with various reactive mechanisms, multiple pollutants removal in flue gas is a still common problem to deal with although a large number of catalysts removing NO_x and VOCs separately have been developed very fast (Chen *et al.*, 2020; Sun *et al.*, 2020). In recent years, synergistic control of NO_x and VOCs in flue gas could now be achieved by catalyst combined with chemical trapping. Lin *et al.* (2009) found that BaAlO_4 catalyst could attain the reduction of NO_x and oxidation of VOCs at the same time. The results showed that NO_x adsorbed on the surface forms nitrate species, while VOCs and active oxygen formed $\text{C}(\text{O})$. Then the nitrate species oxidized VOCs to CO_2 , and reduced to N_2 and N_2O itself. Mori *et al.* (2014) reported that $\text{Cu}/\text{BaO}/\text{La}_2\text{O}_3$ could reduce NO_x and VOCs simultaneously, in which soot could act as a solid-phase reducing agent to promote the reduction of NO. Some researchers have surveyed on the HC-SCR of NO with hydrocarbons as reducing agents in order to further investigate the simultaneous removal of VOCs and NO_x . Habib *et al.* (2014) surveyed Cu/Y catalyst using propylene as the reducing agent, and the propylene oxidation activity at 290°C was close to 100% with 73% for NO_x conversion, 98% for N_2 selectivity. Colpini *et al.* (2013) tested the SCR denitration performance of propane on vanadium-based catalysts with different supports. It was found that 10 wt% V/TiO_2 catalyst showed the best catalytic performance, but only 50.8% NO_x could be reduced with very low (10%) conversion of propane as well at 400°C . Chansai *et al.* (2014) used octane and methanol to trigger the SCR process on $\text{Ag}/\text{Al}_2\text{O}_3$ catalysts. The results showed that the NO conversion rate at 250°C could reach to 53%, with 83% for methanol degradation. In summary, multi-pollutants removal can be achieved through the combination of active sites with different functions, but the efficiency of which still needs to be promoted with unclear reaction mechanism.

In our previous work, we found that improvement of SCR reactivity could be realized by utilizing the oxidizing properties of cobalt-cerium oxide (denoted as CoCeO_x) catalyst and the acidity of the $\text{V}_2\text{O}_5/\text{TiO}_2$. Moreover, we also revealed that oxidation ability was the dominant property to enhance the degradation performance for VOCs (Hu *et al.*, 2021). Therefore, we propose a dual-layered structure to achieve an effective collocation with different functional areas, enhancing its total activity for NO_x and VOCs removal.

In this work, we developed a new dual-layered structural catalyst to realize simultaneous removal of VOCs and NO_x . We selected CoCeO_x catalyst and $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst for layered construction, investigated the synergistic effect to each other between two layers, and consequentially put forward an interaction mechanism between propane oxidation reaction and SCR. As a result, this kind of dual-layered structure made it better to remove both NO and propane compared with single catalyst, which achieved the severe demand for efficient and simultaneous removal of propane and NO_x .

2 METHODS

2.1 Catalyst Preparation

The CoCeO_x catalysts in this work were prepared by citric acid complexation method. Appropriate amounts of $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ were dissolved in deionized water with stirring. Added citric acid in a molar ratio of 1.5:1 to the solution, then reacting at 80°C till the solution turned into a dark red gel. Then the mixture was dried at 110°C for 12 h, calcined at 450°C for 4 h.

The $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts in this work were prepared by incipient wetness impregnation, with NH_4VO_3 (Sinopharm Chemical Reagent Co., Ltd.) being precursors. TiO_2 (Degussa P25) was used as supports. Details of the impregnation procedure was presented as below. NH_4VO_3 and oxalic acid were dissolved in ionized water at a molar ratio of 1:2, aging overnight. Then, 5g P25 was added into NH_4VO_3 solution with vigorous stirring, then under ultrasonic treatment for 20 minutes. The mixture was aged overnight, centrifuged, dried at 110°C for 12 hours and calcinated at 500°C for 5 hours sequentially.

2.2 Dual-layered Catalyst Preparation

Dual-layered catalyst was built up in the Quartz tube with 6mm inner diameter with particle size controlled in 40-60 mesh. The samples were introduced with different ratio and structure. Different modes were presented in Fig. 1. The dual-layered set was detailed as below: 30 mg oxidation catalyst and 30 mg SCR catalyst were filled into two layers, separated by quartz wool.

Fig. 1. Different samples for dual-layered catalyst.

Mode 1 referred to SCR catalyst as former part along the direction of gas flow, and oxidation catalyst in the latter layer. Mode 2 had the layered arrangement opposite to Mode 1. Since the two catalysts did not interact with each other, they would not affect the surface structure and chemical properties to one another directly.

2.3 Catalytic Characterization

X-ray photoelectron spectroscopy (XPS) spectra was tested using a Thermo ESCALAB 250 instrument (Al K α X-ray radiation, $h\nu = 1486.6$ eV). C1s binding energy with (284.8 eV) was set as reference binding energy. H₂ temperature-programmed reduction (H₂-TPR) and O₂ temperature-programmed desorption (O₂-TPD) experiments were performed on a Micromeritics Autochem II 2920 analyzer. For H₂-TPR, the prepared catalysts (45 mg) were pretreated in N₂ at 450°C for 30 min. After cooling to 50°C, the temperature was increased linearly to 800°C at a heating rate of 10°C min⁻¹, where the atmosphere was 10% H₂/Ar flow (30 mL min⁻¹). For O₂-TPD, 50 mg catalyst were pretreated in 20% O₂/He (30 mL min⁻¹) at 400°C for 30 min, then cooled down to room temperature. After continuously purging in a He flow for 30 min, the catalysts were heated up to 900°C in He flow at a rate of 10°C min⁻¹.

In-situ DRIFT was tested by Nicolet NEXUS 6700 infrared spectrometer to survey the information of the surface functional groups as well as the reactive species adsorbed on surface during the catalytic reaction. The spectrometer is equipped with an MCT/A detector with a resolution of 4 cm⁻¹ and scanning range of 4000–400 cm⁻¹. The spectral signal was averaged after 16–32 scans. The acquisition time of a single spectrum was about 1 min.

2.4 Catalytic Activity Test

The catalytic activity was tested by a fixed-bed reactor as mentioned in Section 2 that 150 mg catalyst was placed in a quartz tube reactor for every sample (i.d. = 6 mm). The reaction condition for SCR was consistent of 1000 ppm NH₃, 1000 ppm NO and 10% O₂ with GHSV = 90,000 mL g⁻¹ h⁻¹ in He atmosphere. Propane was used as the target gas for VOCs testing. The reaction condition for propane oxidation was consistent of 800 ppm propane and 10% O₂ with GHSV = 90,000 mL g⁻¹ h⁻¹ under He atmosphere. The concentration of reactants and products were analyzed online by a Fourier transform infrared spectroscopy (FTIR) Gas Analyzer (Gasmeter Dx4000, Finland).

In SCR reaction, the NO conversion rates, X_{NO} , and selectivity of N₂, S_{N_2} , were calculated according to the following formula:

$$X_{NO} = \left(1 - \frac{[NO]_{out}}{[NO]_{in}} \right) \times 100\% \quad (1)$$

$$S_{N_2} = \left(1 - \frac{2[N_2O]_{out} + [NO_2]_{out}}{[NO]_{in} + [NH_3]_{in}} \right) \times 100\% \quad (2)$$

where, $[\text{NO}]_{\text{in}}$ and $[\text{NO}]_{\text{out}}$ referred to NO concentration at inlet and outlet respectively, $[\text{NH}_3]_{\text{in}}$ represented the NH_3 concentration at inlet; $[\text{N}_2\text{O}]_{\text{out}}$ and $[\text{NO}_2]_{\text{out}}$ referred to concentration of N_2O and NO_2 at outlet.

In propane oxidation, conversion of propane, $X_{\text{C}_3\text{H}_8}$ and selectivity of CO_2 , S_{CO_2} were calculated as below:

$$X_{\text{C}_3\text{H}_8} = \left(1 - \frac{[\text{C}_3\text{H}_8]_{\text{out}}}{[\text{C}_3\text{H}_8]_{\text{in}}} \right) \times 100\% \quad (3)$$

$$S_{\text{CO}_2} = \frac{[\text{CO}_2]_{\text{out}}}{[\text{C}_3\text{H}_8]_{\text{in}} - [\text{C}_3\text{H}_8]_{\text{out}}} \times 100\% \quad (4)$$

where $[\text{C}_3\text{H}_8]_{\text{in}}$ and $[\text{C}_3\text{H}_8]_{\text{out}}$ refer to C_3H_8 concentration at influx and outflux, $[\text{CO}_2]_{\text{out}}$ stands for CO_2 concentration at outflux.

The reaction rate of propane oxidation, r , could be calculated by the conversion rate, $X_{\text{C}_3\text{H}_8}$ according to the following formula (Ren *et al.*, 2016):

$$r = \frac{1\% F_{\text{C}_3\text{H}_8} X_{\text{C}_3\text{H}_8}}{22.4 W_{\text{cat}}} \quad (5)$$

where, $F_{\text{C}_3\text{H}_8}$ stands for the velocity of (L s^{-1}), W_{cat} represented the mass of catalyst (g).

3 RESULTS AND DISCUSSION

3.1 Performance of Dual-layered Catalyst

Co-based catalyst had good redox performance under low-temperature range but with low selectivity in high-temperature, while vanadium-based catalyst had good acidity with low activity in low-temperature condition. By optimizing the superb activity of single layer detailed in Fig. S1, we chose the CoCeO_x (with the molar ratio of Co and Ce equals to 9:1) as the oxidation catalyst in the upper layer and the $\text{V}_2\text{O}_5/\text{TiO}_2$ (with 1%wt V_2O_5 loading amount) as the SCR catalyst in the lower layer with volume ratio at 1:1 referred to Mode 1 in Fig. 1.

The SCR performance for dual-layered catalyst was surveyed, where Mode 1 was adopted as ' $\text{CoCeO}_x + \text{V}_2\text{O}_5/\text{TiO}_2$ ' for this whole article below. Fig. 2 showed the activity results and product distribution of the dual-layered catalyst. At temperature of 150°C , NO conversion rate of $\text{CoCeO}_x + \text{V}_2\text{O}_5/\text{TiO}_2$ reached 65%. As temperature increased from 150°C to 225°C , the NO conversion gradually increases from 65%, reaching 100% at 225°C . For temperature between 175 – 300°C , $\text{CoCeO}_x + \text{V}_2\text{O}_5/\text{TiO}_2$ maintained good performance where NO conversion was kept higher than 80%. Compared with $\text{V}_2\text{O}_5/\text{TiO}_2$, the active window for SCR moved nearly 150°C to the left. Furthermore, $\text{CoCeO}_x + \text{V}_2\text{O}_5/\text{TiO}_2$ attained far better activity than that of CoCeO_x at 200 – 300°C . This might be due to the acidity of $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst, which trapped a large amount of NH_3 on the up-stream position. The inhibiting of NH_3 oxidation gave sufficient reducing agent in reactive atmosphere above 250°C , helping dual-layered catalyst obtain a wide range of active temperature. The product distribution for $\text{CoCeO}_x + \text{V}_2\text{O}_5/\text{TiO}_2$ was shown in Fig. 2(b). It was obvious that all by-products were below 100 ppm between 175°C and 300°C , indicating that NO was mainly converted to N_2 .

In addition, as oxidation ability was one of promotions for VOCs degradation under NH_3 atmosphere, we surveyed the NH_3 oxidation ability for every sample. The result was shown in Fig. 3(a). $\text{CoCeO}_x + \text{V}_2\text{O}_5/\text{TiO}_2$ performed a strong catalytic oxidation of NH_3 ability above 200°C , extremely better than the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst but similar to CoCeO_x . The NH_3 oxidation product distribution for dual-layered was presented in Fig. 3(b). It was obvious that below 200°C , NH_3 was gradually oxidized to N_2 , NO and N_2O with increasing temperature; When temperature rose to 300°C , the remaining NO and N_2O could be further oxidized to NO_2 . Compared with pure CoCeO_x catalyst, the proportion of NO and N_2O was much less with more NH_3 oxidized to N_2 .

Fig. 2. SCR performance of CoCeO_x + V₂O₅/TiO₂ on (a) NO conversion, (b) product distribution, NH₃ concentration: 1000 ppm, NO concentration: 1000 ppm; GHSV: 90,000 mL g⁻¹ h⁻¹; catalyst dosage: 150 mg.

Fig. 3. (a) NH₃ oxidation performance of CoCeO_x + V₂O₅/TiO₂, (b) product distribution of NH₃ oxidation for CoCeO_x + V₂O₅/TiO₂. NH₃ concentration: 1000 ppm; GHSV: 90,000 mL g⁻¹ h⁻¹; catalyst dosage: 150 mg.

Secondly, we tested another type of dual-layered catalyst (the V₂O₅/TiO₂ catalyst in the upper layer, the CoCeO_x catalyst in the lower layer, with volume ratio at 1:2, denoted as Mode 4 for its propane oxidation reactivity under different atmosphere in order to investigate the performance of simultaneous removal and synergistic mechanism of dual-layered catalyst.

As shown in Fig. 4, with C₃H₈ fed only, T₅₀ (the temperature that 50% reactant is reacted) and T₉₀ (the temperature that 90% reactant is reacted) for propane oxidation were 232°C and 263°C, respectively. If we introduced NH₃ simultaneously, the activity for propane oxidation would be greatly reduced and the temperature of T₅₀, T₉₀ rose 53°C and 47°C higher respectively. It was proposed that the activation of C-H bond in adsorbed propane was the rate-determining step in propane oxidation, while the activation of N-H bond breaking took the initial step in NH₃ oxidation. The C-H bond energy in propane reached 401.3 kJ mol⁻¹ higher than that of N-H bond in NH₃ (391 kJ mol⁻¹), which meant that propane might be more difficult to be activated than NH₃. As a result, propane and NH₃ were in competitive adsorption for the active sites when two reactants were added to the reactor at the same time. Thus, the conversion rates of propane and NH₃ were both lower than single layer reacting separately.

Fig. 4. The influence of gas components on propane oxidation performance of CoCeO_x. NH₃ concentration: 1000 ppm, NO concentration: 1000 ppm, propane concentration 800ppm; GHSV: 90,000 mL g⁻¹ h⁻¹; catalyst dosage: 150 mg.

Fig. 5. HC-SCR activity (a) under propane and NO atmosphere, (b) without propane. NH₃ concentration: 1000 ppm, NO concentration: 1000 ppm, propane concentration: 800 ppm; GHSV: 90,000 mL g⁻¹ h⁻¹; catalyst dosage: 150 mg.

In another perspective for NO influence, we introduced C₃H₈ with NO into the reactive atmosphere. As shown in Fig. 4, the T₅₀ and T₉₀ for propane oxidation were at 248°C and 276°C, performing slightly lower activity than C₃H₈ alone. The NO-deduced inhibition on propane oxidation was significantly weaker than that caused by NH₃, because propane could be adsorbed and activated more easily than NO. Moreover, NO + O₂ was a higher oxidizing atmosphere but the curve was shifted to higher temperature, indicating that the lattice oxygen was the relevant species in propane oxidation. If C₃H₈, NH₃ and NO were all introduced in the reactive atmosphere, activity of dual-layered catalyst went back to a high level especially at 275–350°C. It might be attributed to that SCR react in different sites to propane oxidation, helped reducing the competitive adsorption of NH₃ and NO with propane.

It was widely accepted that C₃H₈ could be used as a reducing agent to react with NO in HC-SCR (Moreno-González *et al.*, 2017). Therefore, we proposed that C₃H₈ acted as reducing agent, beneficial for NO reduction at high temperature. It was shown in Fig. 5 that the dual-layered catalyst had excellent SCR activity no matter whether C₃H₈ existed. We supposed that NH₃ was mainly adsorbed on acid sites while C₃H₈ was mainly adsorbed and activated on redox sites. In summary, the

simultaneous existence of NH_3 and NO could reduce the activity inhibition, caused by competitive adsorption, of propane oxidation, promoting the synergistic removal of multiple pollutants.

3.2 Mechanism for NO Oxidation and Propane Degradation

From the results of propane oxidation and our previous work (Zhang *et al.*, 2019), it could be seen that the CoCeO_x layer in the dual-layered catalyst performed outstanding redox performance for propane oxidation and NH_3 oxidation. Otherwise as widely accepted that acidity also played a vital role in the performance of the SCR reaction, NH_3 adsorption and desorption experiment was adopted to detect the acidity of the catalyst surface shown in Fig. 6.

At the beginning, we introduced 900 ppm NH_3 at 50°C to be adsorbed till saturated, then purged N_2 in to remove the weakly adsorbed NH_3 , subsequently increasing the temperature to 500°C at $10^\circ\text{C min}^{-1}$. A strong NH_3 desorption peak was observed near 175°C with concentration of 65 ppm. The peak I at $150\text{--}200^\circ\text{C}$ represented the desorption of physically adsorbed NH_3 , while the peak II at 250°C referred to weakly chemically adsorbed NH_3 , with the peak III at 350°C the strong chemisorption peak of NH_3 (Gao *et al.*, 2011; Hu *et al.*, 2017). Peak I and peak II reached 60% and 35% respectively, which were much higher than 5% of peak III. Therefore, CoCeO_x catalyst was mainly affected by physical adsorption and weak chemical adsorption with much fewer strong acid sites.

In-situ DRIFTS spectroscopy was adopted to perform NH_3 adsorption and desorption experiments to survey the surface acidity on CoCeO_x catalyst. The results were shown in Fig. 7(a). The peak at 1230 cm^{-1} and 3200 cm^{-1} was related to NH_3 adsorbed on Lewis acid site, and that of 1480 cm^{-1} referred to Brønsted acid sites (Hadjiivanov, 2000; Chen *et al.*, 2010). It was depicted that Lewis and Brønsted acid sites on the surface of CoCeO_x catalyst had basically the same adsorption strength for NH_3 . In addition, the vibration peak of hydroxyl group was observed at $3600\text{--}3750\text{ cm}^{-1}$, which indicated that NH_3 was firstly adsorbed on hydroxyl group forming NH_4^+ .

In order to study the entire SCR reaction mechanism, more experiments of in-situ DRIFTS were used to analyze the intermediate reaction species. Fig. 7(b) showed the in-situ infrared spectrum where NO and O_2 were introduced with pre-adsorbed NH_3 at 200°C . It was revealed that after purging with pure N_2 for 30 minutes, a significant NH_3 adsorption peak signal was still observed with both Brønsted acid site and Lewis acid sites. As 1000 ppm NO and 10% O_2 fluxed in, NH_3 adsorption peak signal decayed rapidly, where adsorbed NH_3 species reacted with the NO . After the influx of $\text{NO} + \text{O}_2$ for 5 minutes, new vibration peak signals began to appear at 1260 cm^{-1} and 1600 cm^{-1} increasingly, which indicated NH_3 was totally consumed. Furthermore, the vibration peak at 1260 cm^{-1} could be regarded as nitrate species, while the peak at 1600 cm^{-1} could be attributed to nitrite and adsorbed NO_2 (Ruggeri *et al.*, 2014, 2015). It was obvious that at the moment adsorbed NH_3 species was consumed completely, NO would be rapidly oxidized on the

Fig. 6. The NH_3 -TPD experiment of the CoCeO_x catalyst. (a) Detailed processes of the NH_3 adsorption and desorption, (b) the result of NH_3 -TPD. NH_3 concentration: 900 ppm, the heating rate of desorption is $10^\circ\text{C min}^{-1}$.

Fig. 7. In-situ DRIFTS spectrum results of CoCeO_x under (a) temperature programmed NH₃ desorption, (b) pre-adsorbed NH₃ introduced with NO + O₂, (c) pre-adsorbed NO + O₂ introduced with NH₃. NH₃ concentration: 1000 ppm, NO concentration: 1000 ppm; O₂ concentration: 10%, GHSV: 90,000 mL g⁻¹ h⁻¹.

surface of the CoCeO_x catalyst. Fig. 7(c) showed the in-situ infrared spectrum where NH₃ were introduced with pre-adsorbed NO and O₂ at 200°C. After NH₃ introduction, the nitrate and nitrite peak showed negligible change. There was no reaction between nitrate and NH₃ as the adsorption and activation of NH₃ played the vital role in low temperature SCR.

In-situ infrared spectroscopy was adopted to for C₃H₈ temperature-programmed reaction experiment on the CoCeO_x to identify the reactive species on the catalyst surface. The results were shown in Fig. 8(a). Introducing propane at 50°C for 30 minutes, it could be found that the peak corresponding to hydroxyl group at 3373 cm⁻¹ was rising, as well as the peak between 1450–1550 cm⁻¹ representing the COO⁻ group asymmetry vibration. In addition, the peak at 1175 cm⁻¹ represented carbonate species with bidentate coordination, and the peak at 1259 cm⁻¹ was related to the swing vibration of the C-H bond (Vayssilov *et al.*, 2011). As the temperature rose, the C-H bond vibration gradually decreases, while the COO⁻ vibration peak firstly went up and then began to be vanished above 150°C. It was revealed that the activated C-H bond would be converted into COO⁻ and finally decomposed into CO₂. In absence of gas-phase O₂, the oxidative decomposition process of propane could still be observed. It was clear that the oxygen required for propane oxidation mainly came from the oxygen species adsorbed on the catalyst surface, following the MvK reaction mechanism.

3.3 Analysis on Function of CoCeO_x Layer in Dual-layered Catalyst

In order to reveal the influence of catalyst contact on the total activity, we added a quartz wool layer as the transforming barrier in the middle of the two catalysts. The layout structure is

Fig. 8. In-situ DRIFTS spectrum results of CoCeO_x under (a) C_3H_8 , (b) $\text{C}_3\text{H}_8 + \text{O}_2$. Propane concentration: 800 ppm, NO concentration: 1000 ppm, O_2 concentration: 10%; GHSV: $90,000 \text{ mL g}^{-1} \text{ h}^{-1}$.

shown in Fig. 9(a). The corresponding SCR reaction performance was shown in Fig. 9(b). The results showed that the SCR activity of dual-layered catalyst with quartz wool (Mode 2) was significantly lower than that without quartz wool (Mode 1) below 300°C . It was worth noting that the result of Mode 2 was extremely similar to that of pure $\text{V}_2\text{O}_5/\text{TiO}_2$, indicating that the synergistic effect between the CoCeO_x and the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts was dominant for dual-layered SCR activity.

To clarify the synergistic effect in this dual-layered structure, we surveyed the effects on the removal of propane and NO_x by tuning filling construction of dual-layered catalyst shown in Fig. 10. Then we introduced C_3H_8 and NO mixed gas flow to test the comprehensive performance for multiple pollutant removal.

Fig. 11(a) showed the propane oxidation activity of different modes. It could be found that both modes showed great and similar propane oxidation performance, with slight superior of Mode 1 than Mode 2. At 275°C , propane reduction of Mode 1 reached ghs% which was much higher than 71% of Mode 2. We have known that during oxidation process, metal sites firstly gained electrons from the adsorbed gas molecular, then lattice oxygen provided O atoms to help break the chemical bond to complete the reactive cycle. So the good acidity of vanadium helped $\text{V}_2\text{O}_5/\text{TiO}_2$ layer in Mode1 trap amounts of NH_3 to prevent the competitive adsorption in CoCeO_x

Fig. 9. (a) Layered structure before and after adding quartz wool. Mode 1: The $\text{V}_2\text{O}_5/\text{TiO}_2$ in the upper layer and the CoCeO_x in the lower layer. Mode 2: the same dual-layered structure with silica wool in the middle of two layers. (b) NO conversion with addition of Quartz wool. NH_3 concentration: 1000 ppm, NO concentration: 1000 ppm; O_2 concentration: 10%, GHSV: $90,000 \text{ mL g}^{-1} \text{ h}^{-1}$.

Fig. 10. Schematic diagram for dual-layered catalyst with different filling order. Mode 1: V_2O_5/TiO_2 in the upper layer and $CoCeO_x$ in the lower layer. Mode 3: $CoCeO_x$ in the upper layer and V_2O_5/TiO_2 in the lower layer.

Fig. 11. The influence of filling order to (a) propane oxidation, (b) SCR reaction; Byproduct generation of (c) N_2O , (d) NO_2 . Propane concentration: 800ppm, NH_3 concentration: 1000 ppm, NO concentration: 1000 ppm; O_2 concentration: 10%, GHSV: 90,000 $mL\ g^{-1}\ h^{-1}$.

layer between NO and propane. Fig. 11(b) depicted the SCR activity for two modes. The results showed that the impact of layer order on SCR was far stronger than on propane oxidation. At 175–325°C, Mode 1 had shown consistent superior SCR activity with NO conversion rate above 85%. But for Mode 2, it did not show any difference with Mode 1 Below 175°C, both reaching about 80%; For temperature at 225–275°C, NO conversion rate declined rapidly to 0% with temperature increasing.

In order to verify why there was a significant SCR reactivity difference between two sequences, product distribution of the reaction process was analyzed shown in Fig. 11(c). It could be seen that the N_2O and NO_2 generated in Mode 1 kept in low concentration in the entire temperature range, and NO was mostly reduced to N_2 . On the contrary, Mode 2 produced a large amount of N_2O at 225–275°C, which means a severe side reaction had been triggered and that NH_3 was directly oxidized resulting in low SCR activity. It was worth noticing that although the conversion rate of NO returned up slightly above 300°C, the activity was still not satisfied because this increase was mainly due to the oxidation from NO to NO_2 . Obviously, the V_2O_5/TiO_2 should be set before the $CoCeO_x$ for multiple pollutant removal.

As mentioned above, the V_2O_5/TiO_2 layer inhibited the competitive adsorption on the $CoCeO_x$ to promote entire catalytic activity. Thus, we consequently adjusted the bed thickness of V_2O_5/TiO_2 layer to further investigated the mechanism. Under the consistent mass of total catalyst, the ratio of the V_2O_5/TiO_2 to $CoCeO_x$ was changed to 1:2 denoted Mode 4.

The catalytic activity with different bed thicknesses on propane is shown in Fig. 12. The results showed that T_{50} and T_{90} were at 240°C and 268°C, respectively, which was slightly better than Mode 1. The larger proportion of $CoCeO_x$ provided more active sites for propane oxidation, enhancing the oxidation activity. Fig. 13(b) showed the SCR result with different bed thicknesses. It was presented that both Mode 1 and Mode 2 had good SCR reactivity with NO conversion rate above 80% at 175–325°C. The superior activity was attributed to that the V_2O_5/TiO_2 catalyst participated as a temporary NH_3 buffer area, where adsorbed NH_3 species was firstly trapped to avoid over flow of NH_3 . When these adsorbed NH_3 species diffused downwards and reached the interface between layers, NH_3 was quickly reacted on $CoCeO_x$ with abundant NO, rather than further deep oxidation. Therefore, dual-layered catalyst could attain superior low-temperature activity and N_2 selectivity.

4 CONCLUSIONS

In this paper, we developed a new dual-layered $CoCeO_x + V_2O_5/TiO_2$ with high VOCs removal efficiency and good low-temperature denitration performance, of which the V_2O_5/TiO_2 was set on the upper layer, and the $CoCeO_x$ on downside. NO conversion of dual-layered catalysts could

Fig. 12. Dual-Layered catalysts with different bed thicknesses.

Fig. 13. The influence of different bed thicknesses on (a) propane oxidation, (b) SCR reaction. Propane concentration: 800 ppm, NH_3 concentration: 1000 ppm, NO concentration: 1000 ppm; O_2 concentration: 10%, GHSV: $90,000\text{ mL g}^{-1}\text{ h}^{-1}$.

reach 100% at 225°C and kept more than 80% below 300°C, while VOCs degradation reached 80% above 260°C.

In order to investigate the interaction mechanism for dual-layered catalyst, we examined both layers for their contribution to simultaneous removal under multiple pollutant atmosphere and various mode with different structure is surveyed such as catalyst packing form, bed thickness and particle size were adopted. It was revealed that V_2O_5/TiO_2 possesses rich acid sites which could tunable attract NH_4^+ and $CoCeO_x$ provides good oxidizing ability to oxidize NO and propane. The combination of the two moderate the competitive adsorption between NH_3 and propane which is the initial obstacle for $CoCeO_x$ to quickly remove multiple pollutants simultaneously. Moreover, compared with the lack of strong acid sites in the $CoCeO_x$ catalyst, the V_2O_5/TiO_2 catalyst adsorbed more NH_3 as a transparent buffer area to adjust the ammonia concentration in down-streamed $CoCeO_x$ oxidation layer, avoiding prior oxidation of NH_3 on $CoCeO_x$ surface.

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DISCLAIMER

The authors declare no conflict of interest.

SUPPLEMENTARY MATERIAL

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