The effects of Bi$_2$O$_3$ on the selective catalytic reduction of NO by propylene over Co$_3$O$_4$ nanoplotes

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Bi$_2$O$_3$/Co$_3$O$_4$ catalysts prepared by the impregnation method were investigated for the selective catalytic reduction of NO by C$_3$H$_6$ (C$_3$H$_6$-SCR) in the presence of O$_2$. Their physicochemical properties were analyzed with SEM, XRD, H$_2$-TPR, XPS, PL and IR measurements. It was found that the deposition of Bi$_2$O$_3$ on Co$_3$O$_4$ nanoplotes enhanced the catalytic activity, especially at low reaction temperature. The SO$_2$ tolerance of Co$_3$O$_4$ in C$_3$H$_6$-SCR activity was also improved with the addition of Bi$_2$O$_3$. Among all catalysts tested, 10.0 wt% Bi$_2$O$_3$/Co$_3$O$_4$ achieved a 90% NO conversion at 200 °C with the total flow rate of 200 mL min$^{-1}$ (GHSV 30 000 h$^{-1}$). No loss in its C$_3$H$_6$-SCR activity was observed at different temperatures after the addition of 100 ppm of SO$_2$ to the reaction mixture. These enhanced catalytic behaviors may be associated with the improved oxidizing characteristics of 10.0 wt% Bi$_2$O$_3$/Co$_3$O$_4$. XRD results showed that Bi$_2$O$_3$ entered the lattice of Co$_3$O$_4$, resulting in the formation of lattice distortion and structural defects. H$_2$-TPR results showed that the reduction of Co$_3$O$_4$ was promoted and the diffusion of oxygen was accelerated with the addition of Bi$_2$O$_3$. XPS measurements implied that more Co$^{3+}$ formed on the 10.0% Bi$_2$O$_3$/Co$_3$O$_4$ catalysts. The improved oxidizing characteristics of the catalyst with the addition of Bi$_2$O$_3$ due to the synergistic effect of the nanostructure hybrid, thus enhanced the C$_3$H$_6$-SCR reaction and hindered the oxidization of SO$_2$. Therefore, the 10.0% Bi$_2$O$_3$/Co$_3$O$_4$ catalyst exhibited the highest NO conversion and strongest SO$_2$ tolerance ability.

1 Introduction

Lean burn engines, which are generally used in gasoline and diesel powered vehicles, are more fuel-efficient than the stoichiometric gasoline engines. They also effectively reduce unburned hydrocarbons, CO$_2$ and CO in exhausts. However, lean burn engines operate with a large excess of air, leading to a significant concentration of oxygen in the exhausts, where the noble-metal three-way catalysts cannot work well to reduce nitrogen oxides (NOx). A large amount of NO$_x$ produced by lean burn engines leads to serious air pollution and public health problems.

In order to control NO$_x$ emission under the lean burn conditions, selective catalytic reduction of NO by hydrocarbons (e.g., propylene) has been undertaken and reported in the literatures as one potential application (HC-SCR). Many classes of catalysts, including supported noble metals (e.g., Pt, Au), metal oxides (e.g., Ag$_2$O, CuO, SnO$_2$, CoO (ref. 15–18)) and zeolite types (ZSM-5, MCM-41 (ref. 20)) have been investigated. In general, the noble metals are active and stable even at lower temperature, but the formation of N$_2$O is undesirable by using such precious metals, particularly, platinum-based catalysts. The zeolite-based catalysts were low thermal stability. Among metal oxides catalysts, cobalt oxides (e.g., Co$_3$O$_4$) are considered as one promising catalyst for HC-SCR due to its high catalytic activity. When combined with other oxides, such as CeO$_2$, ZrO$_2$, Al$_2$O$_3$, sulphated ZrO$_2$, the catalytic performances of the cobalt oxide catalyst could be improved as reported. These results implied that the chemical environment around cobalt oxide plays a crucial role in controlling the overall activity of cobalt containing catalysts in SCR reactions.

Bi$_2$O$_3$, a common oxide semiconductor, is widely used in the fields of chemical engineering and electronics such as NO detection and the oxidation or ammoxidation of propylene. In the oxidation/ammoxidation of propene over bismuth/molybdate catalyst, bismuth was thought to involve the rate-determining hydrogen abstraction from propylene, exhibiting its mild oxidizing characteristics. This property might be also beneficial for the partial oxidation of propylene in C$_3$H$_6$-SCR for NO reduction. Therefore, it is of considerable interest to explore the application of Bi$_2$O$_3$ in the reduction of NO with propylene.

In the present study, Co$_3$O$_4$ nanoplotes and Bi$_2$O$_3$/Co$_3$O$_4$ were prepared with the solvothermal and impregnation method respectively. Their catalytic performances in the NO reduction by C$_3$H$_6$ in the presence of O$_2$ were investigated. The catalysts...
were characterized with X-ray diffraction (XRD), temperature programmed reduction with hydrogen (H\textsubscript{2}-TPR), and X-ray photoelectron spectra (XPS). The effects of Bi\textsubscript{2}O\textsubscript{3} on the selective catalytic reduction of NO by propylene over Co\textsubscript{3}O\textsubscript{4} nanoplates were expected to be elucidated.

2 Experimental

2.1 Preparation of Co\textsubscript{3}O\textsubscript{4} and Bi\textsubscript{2}O\textsubscript{3}/Co\textsubscript{3}O\textsubscript{4}

The Co\textsubscript{3}O\textsubscript{4} support was synthesized via the solvent-thermal method, 50 mmol CoCl\textsubscript{2} solution (200 mmol L\textsuperscript{-1}, Sinopharm Chemical Reagent Co. China) and 25 mL of NaOH (2 mol L\textsuperscript{-1}, Sinopharm Chemical Reagent Co. China) were added to a round-bottom flask, ultrasonicated for about 20 minutes to obtain a light brown uniform suspension. And then the suspension was transferred into a stainless steel autoclave with Teflon liner. The autoclave was sealed and maintained at 120 °C for 12 h. The obtained product was collected after washing with deionized water for several times, finally calcined at 500 °C for 5 h in air (S1).

The Bi\textsubscript{2}O\textsubscript{3}/Co\textsubscript{3}O\textsubscript{4} catalysts with different Bi\textsubscript{2}O\textsubscript{3} contents were synthesized by impregnation method as followed: 0.0155 g Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O and 20 mL 3% NH\textsubscript{3}·H\textsubscript{2}O were added into a round-bottom flask, ultrasonicated for about 20 minutes to obtain a white uniform suspension. After that, the Co\textsubscript{3}O\textsubscript{4} support (S1) were added in the suspension, ultrasonicated for about 15 minutes to make it homogeneously distributed in the suspension. The suspension was then dried at 80 °C with continuous stirring for 1 h, further heated at 120 °C for 12 h followed by calcination at 500 °C in air for 4 h, yielding the 5.0 wt% Bi\textsubscript{2}O\textsubscript{3}/Co\textsubscript{3}O\textsubscript{4} catalyst (S2). 10.0 wt% Bi\textsubscript{2}O\textsubscript{3}/Co\textsubscript{3}O\textsubscript{4} (S3) and 15.0 wt% Bi\textsubscript{2}O\textsubscript{3}/Co\textsubscript{3}O\textsubscript{4} (S4) were prepared with 0.0310 g and 0.0465 g Bi(NO\textsubscript{3})\textsubscript{3}·5H\textsubscript{2}O respectively. In addition, the physical mixture of 10% Bi\textsubscript{2}O\textsubscript{3} nanoparticles and Co\textsubscript{3}O\textsubscript{4} support was also prepared and labeled as S5. As references, classical catalysts 4% Ag/Al\textsubscript{2}O\textsubscript{3} and 2% Pt/Al\textsubscript{2}O\textsubscript{3} were prepared to compare the catalytic performance of the Bi\textsubscript{2}O\textsubscript{3}/Co\textsubscript{3}O\textsubscript{4} catalysts.

2.2 Catalytic activity tests

C\textsubscript{3}H\textsubscript{6}-SCR over the catalysts was carried out at atmospheric pressure in a fixed-bed quartz reactor (diameter = 10 mm). 0.1 g catalyst was used in each run with a reaction mixture composed of 200 ppm NO, 200 ppm C\textsubscript{3}H\textsubscript{6}, 100 ppm SO\textsubscript{2} (when needed) and 10 vol% O\textsubscript{2} in balance gas N\textsubscript{2}. The total flow rate was 200 mL min\textsuperscript{-1}, corresponding to a GHSV 30 000 h\textsuperscript{-1}. Reaction temperature ranges from 100 to 500 °C. The concentration of NO was continuously measured by a NO analyzer (Thermo Environmental Instruments Inc., model 42c), which monitors NO, NO\textsubscript{2}, and NO\textsubscript{x} (NO\textsubscript{x} represents NO + NO\textsubscript{2}). The removal efficiency of NO was calculated as NO removal (%) = (1 – C/C\textsubscript{0}) \times 100\%, where C and C\textsubscript{0} are concentrations of NO in the outlet and inlet, respectively.

2.3 Catalysts characterization

Scanning electron microscopy (SEM) images were taken on a Hitachi S4800 scanning electron microscope operating at 5.0 kV. X-ray powder diffraction (XRD) was carried out on Brukeraxs D8 Discover (Cu Kα = 1.5406 Å). The scanning rate is 1° min\textsuperscript{-1} in the 2θ range from 20 to 80 degree. The reducibility of Bi\textsubscript{2}O\textsubscript{3}/Co\textsubscript{3}O\textsubscript{4} catalysts was estimated by temperature programmed reduction with hydrogen analysis (H\textsubscript{2}-TPR). The experiments were carried out with a Micromeritics 2910 apparatus using H\textsubscript{2}/Ar (3/97, v/v) gas with a total flow rate of 15 mL min\textsuperscript{-1}. In each run, 0.030 g of the catalyst was previously activated at 500 °C for 30 min under air, and then cooled to RT. TPR started with the introduction of the mixture of H\textsubscript{2} and Ar. The catalyst was heated from room temperature (RT) to 1000 °C (10 °C min\textsuperscript{-1}). H\textsubscript{2} consumption was continuously monitored with the thermal conductivity detector. X-ray photoelectron spectra (XPS) of the catalysts were measured in a VG Multilab 2000 spectrometer by using Al Kα (1486.6 eV) radiation as the X-ray source. Photoluminescence (PL) measurement was carried out on a Shimadzu RF-5301 PC fluorescence spectrophotometer. Raman spectra were recorded using a Horiba Jobin-Yvon Lab Ram HR800 Raman microspectrometer, with an excitation laser at 514 nm.

3 Results

3.1 Scanning electron microscope (SEM) observation and XRD analysis

Co\textsubscript{3}O\textsubscript{4} nanoplates with different dimensions were observed on the support Co\textsubscript{3}O\textsubscript{4} (S1), shown in Fig. 1(a). Fig. 1(b–d) presented Bi\textsubscript{2}O\textsubscript{3}/Co\textsubscript{3}O\textsubscript{4} catalysts with different Bi\textsubscript{2}O\textsubscript{3} loading amounts. It was shown that Bi\textsubscript{2}O\textsubscript{3} nanoparticles with dimension ca. 20 nm were supported on Co\textsubscript{3}O\textsubscript{4}. And the crystal size of Bi\textsubscript{2}O\textsubscript{3} slightly increased with increasing Bi\textsubscript{2}O\textsubscript{3} loading amount from 5% to 15%.

Fig. 2(A) shows the XRD patterns of the synthesized Co\textsubscript{3}O\textsubscript{4} and Bi\textsubscript{2}O\textsubscript{3}/Co\textsubscript{3}O\textsubscript{4} catalysts. It can be seen that the Co\textsubscript{3}O\textsubscript{4} support possessed the characteristic peaks of Co\textsubscript{3}O\textsubscript{4} (JCPDS 73-1701, a = 5.45 Å). Besides the characteristic peaks of Co\textsubscript{3}O\textsubscript{4}, the diffraction peaks due to Bi\textsubscript{2}O\textsubscript{3} (JCPDS 22-515, a = 10.94 Å and c = 11.28 Å) were also observed on Bi\textsubscript{2}O\textsubscript{3}/Co\textsubscript{3}O\textsubscript{4} catalysts which became sharper with the increase of Bi\textsubscript{2}O\textsubscript{3} loading amount. It was suggested that the crystal size of Bi\textsubscript{2}O\textsubscript{3} was bigger on the catalyst with higher loading amount of Bi\textsubscript{2}O\textsubscript{3}, which was consistent with the SEM observations. Moreover, the diffraction peaks of Co\textsubscript{3}O\textsubscript{4} over Bi\textsubscript{2}O\textsubscript{3}/Co\textsubscript{3}O\textsubscript{4} catalysts behaved a slight shift towards lower degree in comparison with that of Co\textsubscript{3}O\textsubscript{4}, shown in Fig. 2(B). It indicated that the Bi\textsuperscript{3+} inserted the lattice of Co\textsubscript{3}O\textsubscript{4} in the preparation process, and changed the lattice parameter of Co\textsubscript{3}O\textsubscript{4} due to the different radius of Bi and Co atoms. At the same time, the characteristic peak of Co\textsubscript{3}O\textsubscript{4} became weak obviously after the deposition of Bi\textsubscript{2}O\textsubscript{3}, which revealed the reduction of crystal size. It was implied that the insertion of Bi\textsubscript{2}O\textsubscript{3} induced the structure defect of Co\textsubscript{3}O\textsubscript{4} and suppressed the growth of crystal.

3.2 Temperature-programmed reduction by hydrogen (H\textsubscript{2}-TPR)

The H\textsubscript{2}-TPR profiles of Co\textsubscript{3}O\textsubscript{4}, Bi\textsubscript{2}O\textsubscript{3} and Bi\textsubscript{2}O\textsubscript{3}/Co\textsubscript{3}O\textsubscript{4} catalysts were shown in Fig. 3. For the reduction of Bi\textsubscript{2}O\textsubscript{3}, a sharp peak
was observed at ca. 490 °C, implying the reduction of Bi³⁺ in a narrow temperature range. A broad reduction peak from 330 to 460 °C with a large shoulder at the lower reduction temperature (ca. 380 °C) appeared on Co₃O₄ support (S1). Many researchers reported that the reduction of Co₃O₄ was a two-step reduction process involving the intermediate reduction of CoO.

Two main clear reduction peaks respectively located around 186 °C and 310–480 °C were shown in the TPR spectra. The low temperature TPR peak was associated with the reduction of Co³⁺ to Co²⁺, and the peak at high temperature was the subsequent reduction of CoO to metallic cobalt. In the TPR spectrum of Co₃O₄ synthesized in the present work, there are no obvious two peaks probably due to an abroad particle size distribution as shown in SEM observation. The large shoulder at 376 °C (peak I) in Fig. 3 should be attributed to the reduction of Co³⁺ to Co²⁺, and main reduction peak (peak II) is ascribed to the reduction of CoO to metallic cobalt.

The reduction process of Bi₂O₃/Co₃O₄ catalysts (S2–S4) became complicated with the introduction of Bi₂O₃. The reduction peak at 487 °C became wider and shifted towards to the lower temperature, especially on the Bi₂O₃/Co₃O₄ catalyst with the highest Bi loading amount (S4). In addition, two new peaks around 342 °C (peak I) and 402 °C (peak II) respectively ascribed to the reduction of Co³⁺ to Co²⁺, Co²⁺ to metallic Co appeared on Bi₂O₃/Co₃O₄ catalysts (S2–S4). Compared with the bulk Co₃O₄ (S1), both the reduction peak of Co³⁺ and that of Co²⁺ shifted to lower temperature after the deposition of Bi₂O₃, implying the promoted reduction of Co₃O₄. Moreover, the larger reduction peak I than peak II on S2–S4 samples indicated that the ratio of Co³⁺/Co²⁺ was higher on S2–S4 samples than that on the Co₃O₄ (S1). It revealed that the deposition of Bi₂O₃ on Co₃O₄ affected the oxidized state of cobalt in the synthesized Co₃O₄, more Co³⁺ were present on the supported samples (S2–S4) than the pure Co₃O₄.

3.3 X-ray photoelectron spectroscopy (XPS)

XPS measurements were carried out on Co₃O₄ and 10.0% Bi₂O₃/Co₃O₄ catalysts to examine the influence of Bi₂O₃ on the surface electronic state of Co₃O₄. The Co 2p and O 1s XPS profiles are shown in Fig. 4. In the Co 2p (Fig. 4(a)), the main peaks located at 779.6–781.3 eV and 794.8–796.5 eV are ascribed to Co 2p3/2 and Co 2p1/2 spin-orbital peaks, respectively. It was well-known that the spin–orbit splitting value for Co³⁺ compounds is 15.0 eV, 15.1–15.3 eV for the mixed-valence Co₃O₄. Here, the spin–orbit splitting values of Co 2p for Co₃O₄ and 10.0% Bi₂O₃/Co₃O₄ are the same, 15.2 eV, which is close to that of mixed-valence Co₃O₄. So the cobalt species on both S1 and S3 should be Co₃O₄, agreeable with the XRD and TPR results.

Based on the restriction that Co 2p3/2 binding energies of Co²⁺ and Co³⁺ components are 781.3 eV and 779.6 eV, respectively, the spin–orbit doublet splitting is 15.2 eV with a fixed ratio of 2/1 for the 2p3/2-to-2p1/2 peak area, the Co 2p spectra of S1 and S3 can be fitted to the Co²⁺ (peak II and IV) and Co³⁺ (peak I and III) components. The satellite peak of Co²⁺ and that of Co³⁺ in Co₃O₄ were also respectively observed at 787.0 eV and 791.0 eV, Fig. 4 shows that the peak areas of peak I and III increased with the addition of Bi₂O₃, implying that the surface Co³⁺ and the surface content ratio of Co³⁺/Co²⁺...
increased with the addition of Bi$_2$O$_3$. More Co$^{3+}$ was present on 10.0% Bi$_2$O$_3$/Co$_3$O$_4$ (S3) than the bulk Co$_3$O$_4$ support (S1), as consistent with the TPR results.

The O 1s XPS spectra of Co$_3$O$_4$ and Bi$_2$O$_3$/Co$_3$O$_4$ catalysts are shown in Fig. 4(b). For the Co$_3$O$_4$ sample, there are two peaks (I and II). The peak I located at ~530.1 eV is attributed to the surface lattice of Co$_3$O$_4$, and the peak II at ~531.5 eV is associated with OH$^-$ groups.$^{14}$ In the case of 10.0% Bi$_2$O$_3$/Co$_3$O$_4$, besides the peak I and II, one new peak at ~532.8 eV appeared, which should be related to the contribution of the oxygen from Bi$_2$O$_3$.

### 3.4 Photoluminescence (PL) and Raman spectra

PL emission spectra originating from the recombination of free charge carriers are useful to reveal the migration, transfer and separation of photogenerated charge carriers. Fig. 5 shows photoluminescence emission spectra of different catalysts at room temperature. All samples show one luminescence peak centered at about 358 nm, which can be attributed to the radiative recombination of charge carriers. The pure Co$_3$O$_4$ has the strongest PL emission peak. This charge recombination process of Co$_3$O$_4$ can be greatly inhibited by the deposition of Bi$_2$O$_3$ on
Co$_3$O$_4$. 10.0% Bi$_2$O$_3$/Co$_3$O$_4$ (S3) has the lowest PL emission peak, which is associated with its structural imperfection. The structural imperfection originating from the insertion of the Bi$^{3+}$ into the lattice of Co$_3$O$_4$, as evidenced by XRD, increased the number of structural defects (e.g., oxygen vacancies), which could capture the electrons or holes, thus resulting in low radiative PL emission.

Fig. 6 shows the Raman spectra of 10.0% Bi$_2$O$_3$/Co$_3$O$_4$ (S3), pure Co$_3$O$_4$ (S1) and Bi$_2$O$_3$. For the pure Co$_3$O$_4$, the Raman peak at 655 cm$^{-1}$ was corresponded to the symmetry of Co$_3$O$_4$. 10.0% Bi$_2$O$_3$/Co$_3$O$_4$ gave the similar Raman spectra with Co$_3$O$_4$, while the characteristic peaks of Bi$_2$O$_3$ could not be detected. Compared with Co$_3$O$_4$, the Raman peaks on 10.0% Bi$_2$O$_3$/Co$_3$O$_4$ shifted to the lower frequencies with stronger intensities, which associated with the lattice distortion or residual stress of the spinel structure. The XRD results showed that part of Bi$_2$O$_3$ entered the lattice of Co$_3$O$_4$ over 10.0% Bi$_2$O$_3$/Co$_3$O$_4$, leading to the lattice distortion and lattice defect. The highly defective structure formed on 10.0% Bi$_2$O$_3$/Co$_3$O$_4$ could accelerate the adsorption and activation of O$_2$, which was suggested to be related to the better catalytic performance.

### 3.5 Catalytic performance

Fig. 7 depicted the NO conversions over the Bi$_2$O$_3$/Co$_3$O$_4$ catalysts with different Bi$_2$O$_3$ contents (S1–S4), the physical mixture of 10% Bi$_2$O$_3$ nanoparticles and Co$_3$O$_4$ support (S5), 4% Ag/Al$_2$O$_3$ and 2% Pt/Al$_2$O$_3$ reference catalysts within the reaction temperature range of 100–500 °C. Co$_3$O$_4$ and Bi$_2$O$_3$/Co$_3$O$_4$ catalysts showed higher NO reduction activity than those of Ag/Al$_2$O$_3$ and Pt/Al$_2$O$_3$, especially Bi$_2$O$_3$/Co$_3$O$_4$ catalysts. The conversion of NO over Co$_3$O$_4$ support (S1) firstly increased with reaction temperature, reached the maximum conversion (ca. 60%) at ca. 300 °C and then decreased at higher temperature. The NO conversion was further increased with the addition of Bi$_2$O$_3$ into Co$_3$O$_4$ with the activity order: Co$_3$O$_4$ (S1) < 5.0% Bi$_2$O$_3$/Co$_3$O$_4$ (S2) < 15.0% Bi$_2$O$_3$/Co$_3$O$_4$ (S4) < 10.0% Bi$_2$O$_3$/Co$_3$O$_4$ (S3). Among all catalysts tested, 10.0% Bi$_2$O$_3$/Co$_3$O$_4$ (S3) possessed the highest activity for NO conversion in the reaction temperature window, reaching ca. 90% NO conversion at 200 °C. NO conversion under the lower reaction temperature (100–250 °C) over S3 also reached the highest among the catalysts tested. In contrast, the mixture of 10% Bi$_2$O$_3$ nanoparticles and Co$_3$O$_4$ support (S5) showed lower activity than S1 and S3. It was indicated that the interaction between Bi$_2$O$_3$ and Co$_3$O$_4$ in S3 is not the simply physical mixture like S5. The chemical interaction between them took place in S3 and should contribute the admirable catalytic performance of S3 in the C$_3$H$_6$-SCR reaction.

SO$_2$ usually exists in the diesel engine exhaust. So it is necessary to investigate the SO$_2$ tolerance of the catalyst in C$_3$H$_6$-SCR. Fig. 8 exhibited the effects of 100 ppm SO$_2$ co-fed in the reaction gas on the NO conversions over the catalysts at the different reaction temperatures. NO conversion over the S3
(10% Bi$_2$O$_3$/Co$_3$O$_4$) catalyst clearly did not change in the wide reaction window. The steady-state NO conversion reached 90.3% on S3 at 250 °C in the presence and absence of SO$_2$. In contrast, NO conversion decreased from 65.8% to 35.7% at 300 °C on the Co$_3$O$_4$ support (S1) when 100 ppm SO$_2$ was contained in the feed gas. NO conversions at other reaction temperatures also reduced in the presence of SO$_2$. These results obviously suggested that 10% Bi$_2$O$_3$/Co$_3$O$_4$ exhibited good resistibility against SO$_2$ that coexists with NO and C$_3$H$_6$ in the reaction mixture.

Fig. 9 shows the SO$_2$ durability of 10% Bi$_2$O$_3$/Co$_3$O$_4$ catalyst with the reaction time at the optimum reaction temperature 200 °C in the C$_3$H$_6$-SCR of NO. When NO conversion reached to the maximum (89.3%), 100 ppm SO$_2$ was added in the reaction system, NO conversion immediately decreased. It was probably due to the competitive adsorption of NO and SO$_2$ on the active site. 20 min later, NO conversion reduced to 63.6%. After that, NO conversion recovered to 85.7%, and maintained at ca. 88% through the whole reaction period of 90 min. This result further illustrates the outstanding SO$_2$ resistibility of 10% Bi$_2$O$_3$/Co$_3$O$_4$ in the long time-reaction.

4 Discussions

In this study, the deposition of Bi$_2$O$_3$ with the proper loading amount on Co$_3$O$_4$ nanoplates enhanced NO conversion over Co$_3$O$_4$, especially at low reaction temperature (<200 °C). 10.0% Bi$_2$O$_3$/Co$_3$O$_4$ catalyst also showed the strong resistibility against SO$_2$ in the feed gas. XRD results showed Bi$_2$O$_3$ could enter the lattice of Co$_3$O$_4$, and promote the formation of the lattice distortion and structural defect as demonstrated by PL spectra and IR spectra. The H$_2$-TPR and XPS results showed that more Co$^{3+}$ appeared with the deposition of Bi$_2$O$_3$. These changes were probably related to the promotive effects of Bi$_2$O$_3$ in the C$_3$H$_6$-SCR reaction.

Scheme 1 illustrated the mechanistic investigations for the HC-SCR reactions in the previous literatures.$^{17,36,37}$ According to these findings, the reactants (C$_3$H$_6$, NO and NO$_2$) are supposed to be first adsorbed on the active sites over the catalyst surface. Subsequently, the adsorbed nitrates formed via NO oxidation by O$_2$. C$_3$H$_6$ was also activated to form C$_x$H$_y$O$_z$ species such as formate, acetate and so on. As these C$_x$H$_y$O$_z$ species become available, nitrates subsequently reacted with them to yield nitrogen-containing organic species, such as NCO species. The final step would be the interaction of NOC intermediates with NO$_2$ (NO, NO$_x$), decomposing into N$_2$, CO$_2$ and H$_2$O as final products. This proposed reaction process reveals the crucial role of O$_2$ in the feed gas and the importance of oxidizing characteristics of the catalyst surface.

In our work, PL and IR results showed that more oxygen vacancies were produced on the Co$_3$O$_4$ after the doping of Bi$_2$O$_3$. The vacancy could accelerate the adsorption, activation and diffusion of oxygen, which was suggested to be available for the oxidation reactions involved in HC-SCR. The doped Bi$_2$O$_3$ also increased the Co$^{3+}$ concentration on the surface. The richness of Co$^{3+}$ could promote the adsorption and activation of NO and (or) C$_3$H$_6$. What is more is the mild oxidizing characteristics of

![Fig. 8 SO2 resistibilities of Co3O4 (S1) and 10.0% Bi2O3/Co3O4 (S3) with the reaction temperature.](image8)

![Fig. 9 NO conversion over 10.0% Bi2O3/Co3O4 (S3) before and after the addition of SO2 (reaction temperature: 200 °C).](image9)

Scheme 1 The promotive effects of Bi$_2$O$_3$ on NO reduction by propene over Co$_3$O$_4$ catalyst.
bismuth oxide in the selective oxidation and ammoxidation of propene to acrolein and acrylonitrile. It will accelerate the formation of C₃H₆-SCR reaction, favored the activation of C₃H₆ and NO, and then enhanced the following NCO intermediate formation and its decomposition with reaction with NOₓ to N₂.

About poisoning HC-SCR catalyst with SO₂, the previous studies reported that the suppression effect of SO₂ on the SCR catalyst could attributed to the formation of sulphate on the catalyst. The presence of surface SO₄²⁻ groups blocked the formation of nitrate and decreased the amount of adsorbed nitrates. Thus it hindered the transformation of NOC species and decreased the catalytic activity. In our work, the presence of 100 ppm SO₂ in the feed gas decreased the NO conversion over Co₃O₄ catalyst, while the SO₂ tolerance of Bi₂O₃/Co₃O₄ was strong. 10% Bi₂O₃/Co₃O₄ showed the good stability when SO₂ involved in the C₃H₆-SCR reaction. Therefore, the combination of surface oxygen mobility and the partial oxidation of propene activation of C₃H₆. The activation of C₃H₆ over 10% Bi₂O₃/Co₃O₄ showed the good stability when SO₂ in the feed hardly affected the catalytic performance of 10% Bi₂O₃/Co₃O₄.

5 Conclusions

The optimum Bi₂O₃ loading on the Co₃O₄ nanoplates for the C₃H₆-SCR of NO was about 10%, giving the best catalytic activity, especially at low reaction temperature, as well as the strongest SO₂ tolerance. The decoration of moderate Bi₂O₃ on Co₃O₄ influenced the oxidation state of Co₃O₄, facilitate the surface oxygen mobility and the partial oxidation of propene involved in the C₃H₆-SCR reaction. Therefore, the combination of Co₃O₄ with Bi₂O₃ is more active than Co₃O₄. The addition of 100 ppm SO₂ to the feed hardly affected the catalytic performance of 10% Bi₂O₃/Co₃O₄.

Conflicts of interest

There are no conflict to declare.

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