Effects of NO/NH_3 on the generation of SO_3 over V_2O_5-WO_3/TiO_2 catalyst

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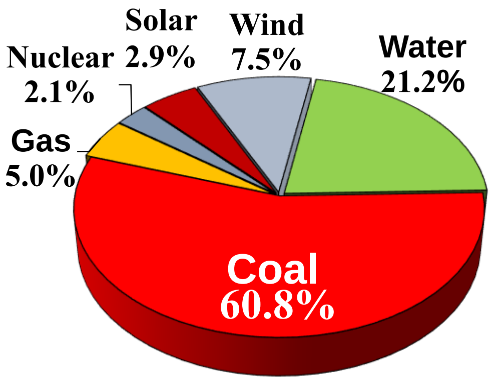
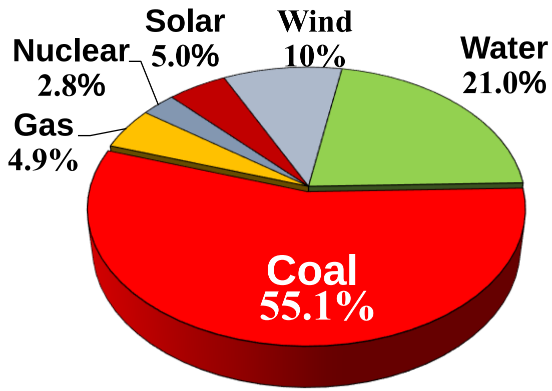
Background



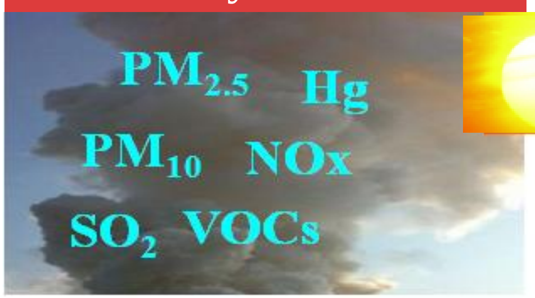
Composition of power installation in 2015



Composition of power installation in 2020

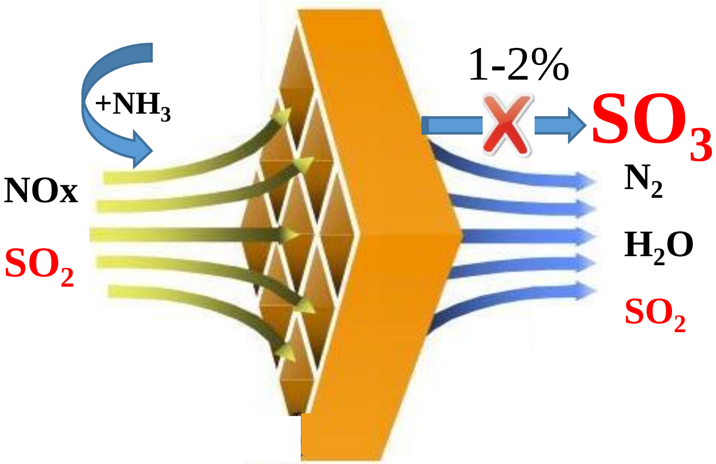
Coal-fired power still occupies the dominant position of China's power supply!

Primary emission



Secondary generation

Burning coal causes serious air pollution



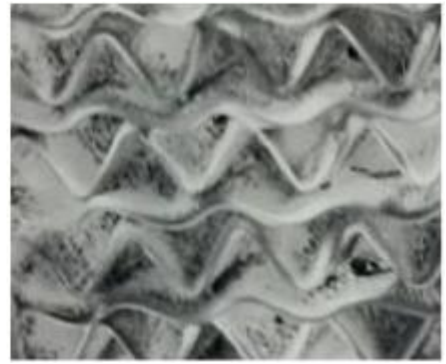
SCR catalyst has been widely used

Chen et al. (2016), Energy Policy
Ministry of Environmental Protection, 《China's Environmental Statistic Yearbook 2016》

Background

Air pollutant
Acid mists

ABS generation
Catalyst poisoning



Clogging
air preheater

Corrosion
equipment

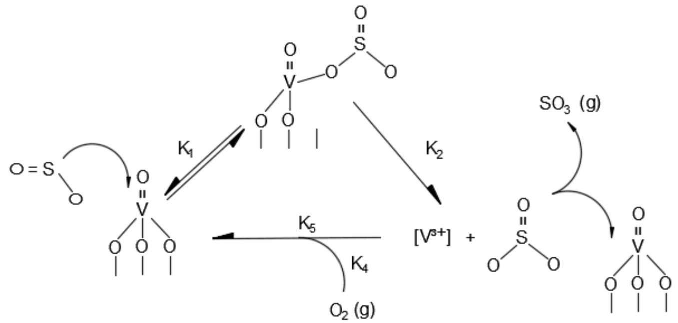
$$SO_3 + NH_3 + H_2O \rightarrow NH_4HSO_4$$
$$SO_3 + 2NH_3 + H_2O \rightarrow (NH_4)_2SO_4$$
} ABS

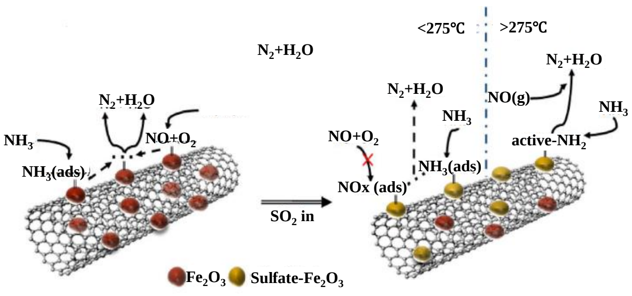
SO_3 seriously affects the safe and economic operation of coal-fired power plants

SO_3 control

- Flue gas treatment
  - WFGD — Not widely used
  - WESP — Not applicable for all power plants
  - Dry sorbent — negative effect on boiler still exist
- Source control
  - SCR process — One of the main generation of SO_3; Generation mechanism still unclear

Background





- Ti-O-V, V-O-V and V=O play roles in the oxidation of SO_2
- SO_2 sulfates the active components, changes NO*x* removal path

Different conclusions

- Svachula et al. : suppressed by H_2O and NH_3 slightly enhanced by NO
- Berndt et al. :NH_3 promoted (OH) and SO_2 reaction
- Dunn et al. : NH_3 strong inhibitory role; NO has smaller effect
- NH_3 and NO net-inhibitory effect NH_3:NO ratio greater than 0.4

The generation mechanism of SO_3 is still unclear!

Dunn et al. Catal. Today 51 (1999) 301-318.
Tang et al. Catal. Today (2017).
W. Jing et al. Catal. Commun. 56 (2014) 23-26.
Svachula et al. Ind. Eng. Chem. Res. 1993
Berndt et al. Atmos. Chem. Phys. 2010

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Materials and methods

Table 1. The chemical properties of catalyst A and catalyst B (wt.%).

Catalyst	V	W	Si	Ti	Al	S	Ca	Fe	Other
A	1.73	7.73	0.86	83.81	0.74	2.11	0.69	0.08	2.25
B	1.51	6.48	2.56	83.88	1.06	1.42	0.93	0.09	2.08

Table 2. The physical properties of catalyst A and catalyst B.

Catalyst	Specific surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
A	50.04	0.25	20.11
B	65.99	0.32	19.17

power plants in China

Honeycomb catalyst

18–40 μm

Table 3. Experimental conditions for SO_3 generation.

	Temperature (℃)	Space velocity (h^{-1})	Experimental atmosphere
Space velocity	360	4 000-90 000	600ppm SO_2, 3%O_2 balanced with N_2
Temperature	280-400	10 000	600ppm SO_2, 3%O_2 balanced with N_2
NO concentration	360	10 000	0-1000ppm NO, 600ppm SO_2, 3%O_2 balanced with N_2
NH_3:NO	360	10 000	500 or 550ppm NH_3, 500ppm NO, 600ppm SO_2, 3%O_2, balanced with N_2

Materials and methods

SO_3 generation test

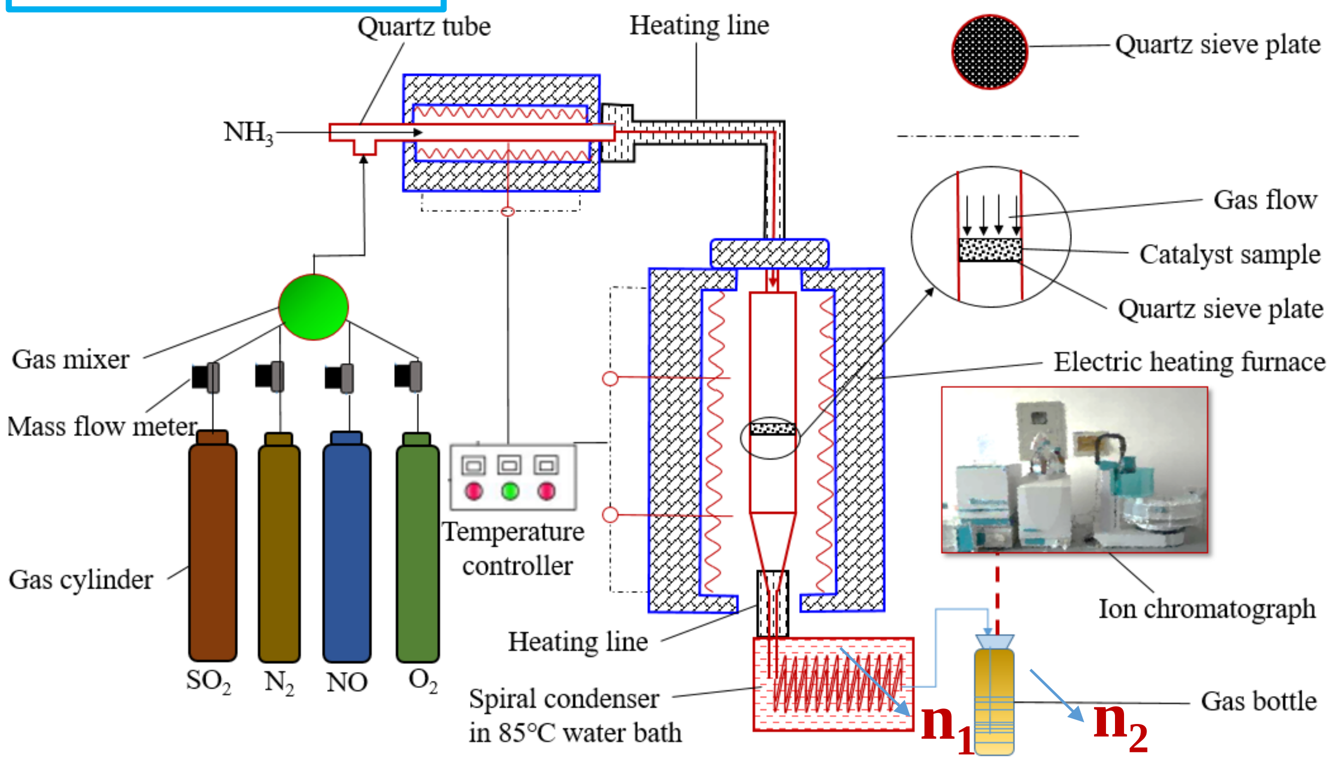

Fig. 1. SO_3 generation reaction system

Gas flow rate 1 000 ml/min

Residence time = 30 min

SO_3 generation amount:

$$\chi = n_1/(n_1 + n_2) \times 100\%$$

Catalyst Characterization

- In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)
- N_2 adsorption (BET)/X-ray fluorescence (XRF)/Scanning electron microscope (SEM)
- X-ray photoelectron spectroscopy (XPS)/SO_2 temperature-programmed desorption (TPD)

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Catalyst performance for SO_3 generation

Catalyst performance for SO_3 generation

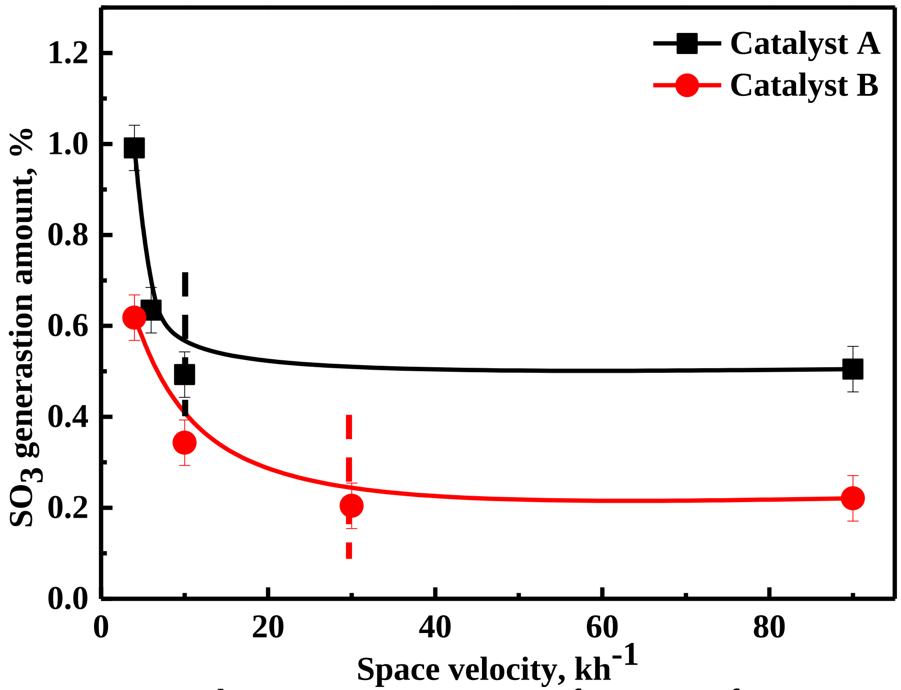


Fig. 2. The generation amount of SO_3 as a function of space velocity on catalyst A and B at 360℃.

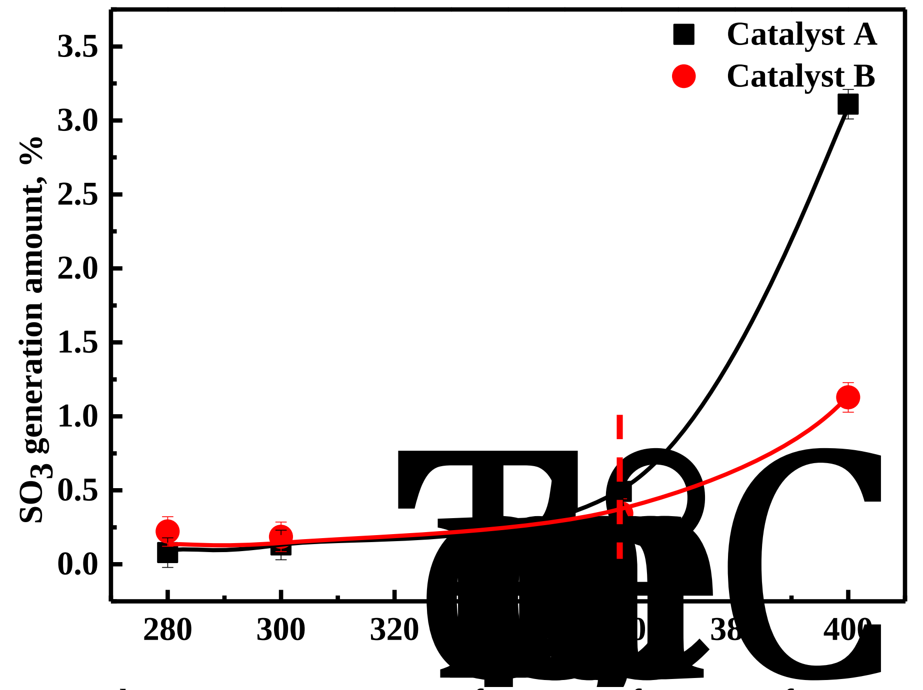


Fig. 3. The generation amount of SO_3 as a function of temperature on catalyst A and B with the space velocity of 10 000 h^{-1}.

- Catalyst A:

10 000 h^{-1} external diffusion eliminated

- Catalyst B:

30 000 h^{-1} external diffusion eliminated

reproducible comparison of the experiments

- 280 – 360 °C slightly increased

Catalyst A = Catalyst B

- > 360 °C significantly increased

Catalyst A> Catalyst B

Catalyst performance for SO_3 generation

Catalyst performance for SO_3 generation

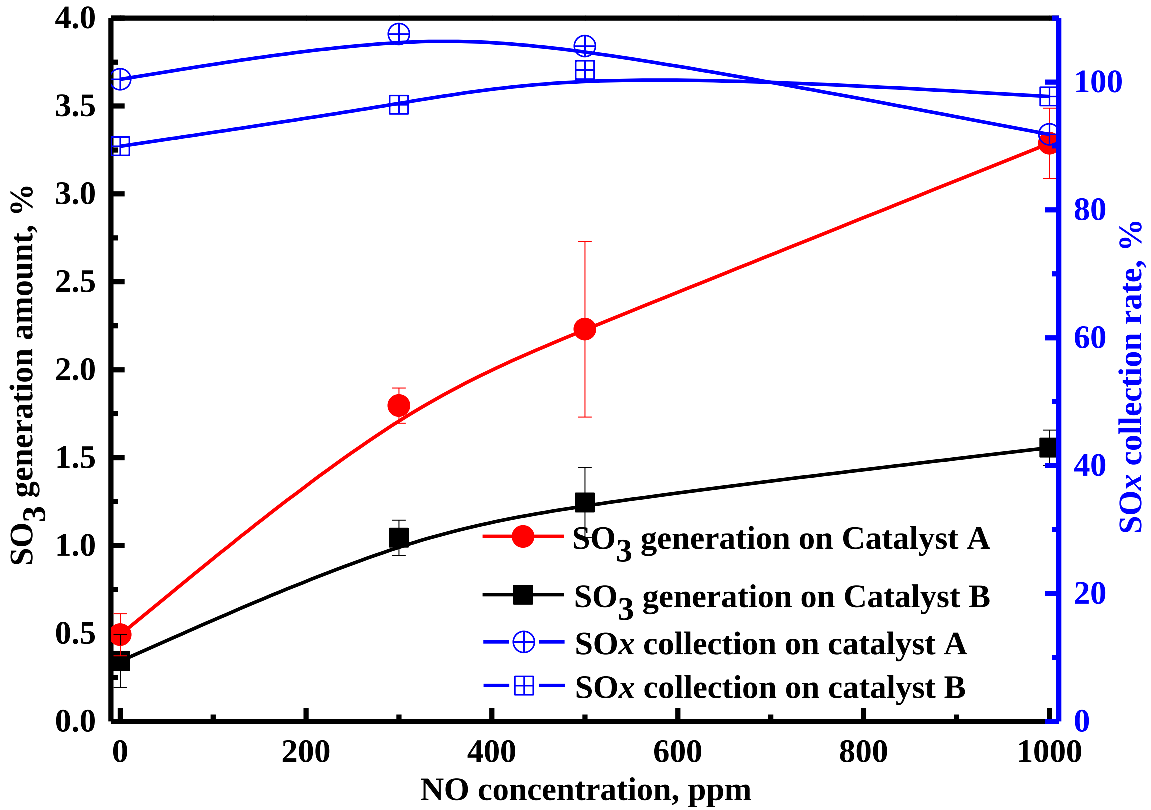


Fig. 4. The generation amount of SO_3 and total collection amount of SO*x* as a function of NO concentration on catalyst A and B at 360℃.

- Relative high SO*x* collection
- NO promoted the generation of SO_3 apparently

Catalyst performance for SO_3 generation

Catalyst performance for SO_3 generation

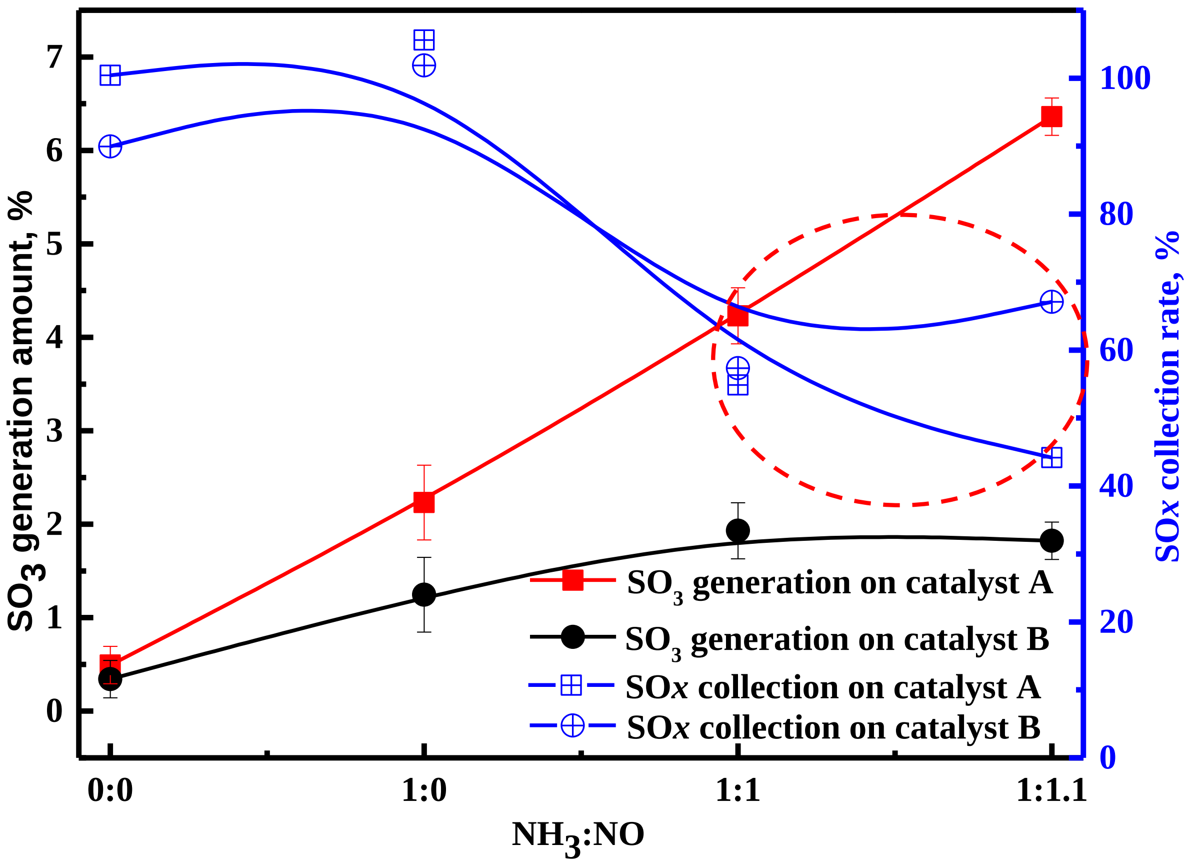


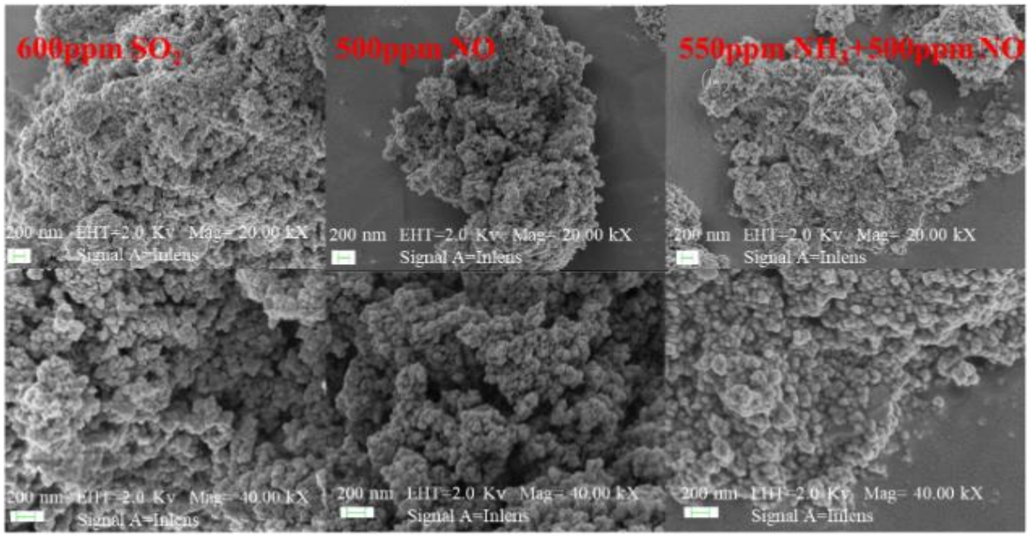
Fig. 5. The generation amount of SO_3 and total collection amount of SO*x* as a function of NO:NH_3 concentration on catalyst A and B at 360℃

- NH_3+NO further increased the generation of SO_3
- Collection amount of SO*x* decreased significantly

Catalyst characterization

Catalyst physical characteristics

(a)



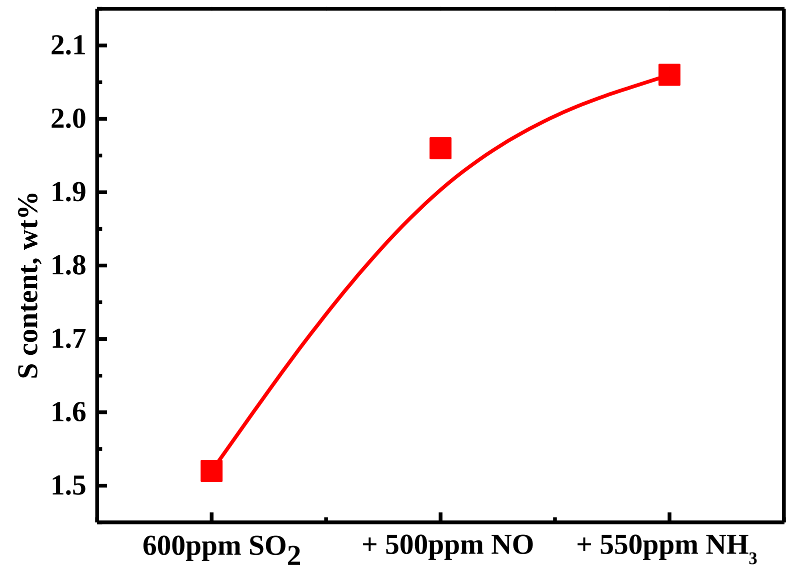


Fig. 6. (a). SEM image of catalyst A after reacted; (b). The content of S on catalyst A after reacted

Table 4. The physical properties for catalyst A after reacted under different conditions.

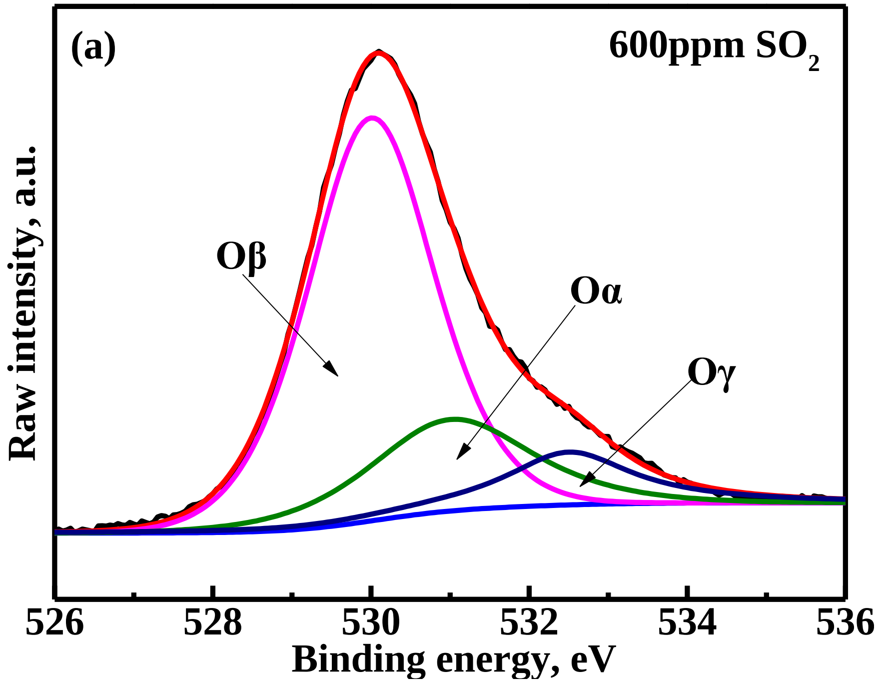
	Surface area (m^2/g)	Pore Volume (cm^3/g)	Pore size (nm)
Catalyst A	50.04	0.25	20.11
SO_2	48.15	0.23	19.37
SO_2+ NO	52.69 ↑	0.25 ↑	18.70 ↓
SO_2+ NO+ NH_3	17.38 ↓	0.19 ↓	43.65 ↑

- NH_3 block pores
- NH_4HSO_4 generation

Catalyst characterization

Catalyst chemical characteristics

529.0–530.1 eV lattice oxygen (Oβ)
530.6–531.0 eV chemisorbed oxygen (Oα)
532.4–533.0 eV chemisorbed water (Oγ)



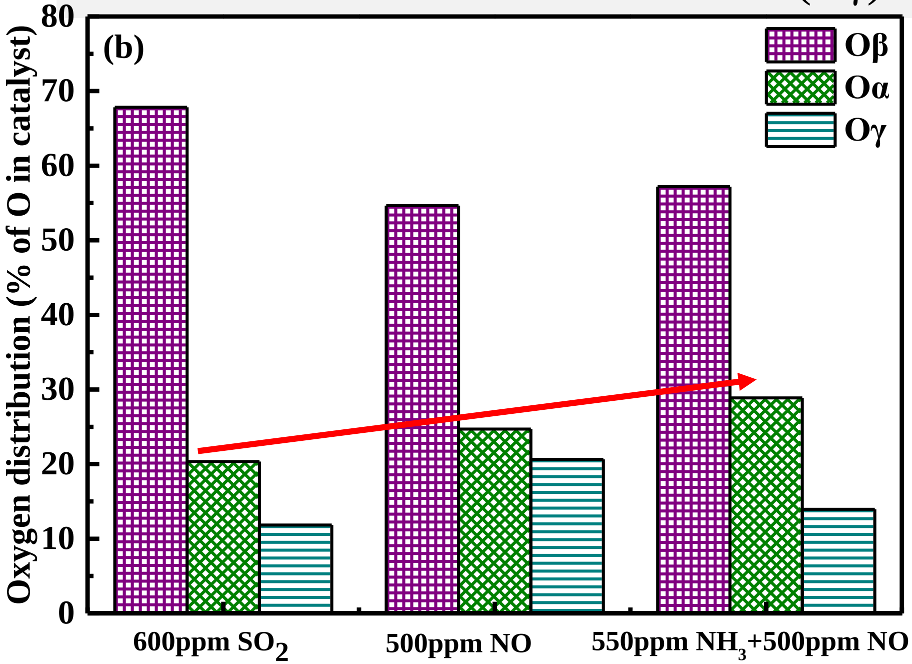


Fig. 7. (a). O1s XPS spectra of catalyst A exposed in 600 ppm SO_2, 3% O_2 balanced with N_2 at 360 ℃; (b). Oxygen distribution on catalyst B after reacted under 600 ppm SO_2, 3% O_2, 500ppm NO, 500ppm NH_3 balanced with N_2 at 360 ℃.

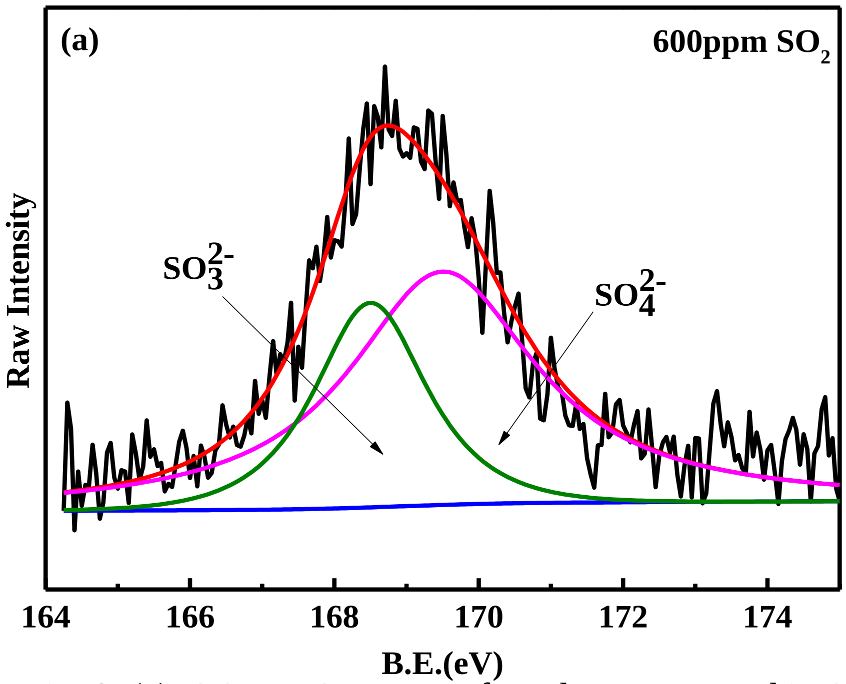
Oα plays a substantial role in the reaction due to its higher mobility than the lattice oxygen

- proportion of surface oxygen slightly increased with NO addition in flue gas
- proportion of surface oxygen further increased with NH_3 addition in flue gas

Catalyst characterization

Catalyst chemical characteristics

168.7 eV	SO_3^{2-}	SO_2 adsorption products
169.2 eV	SO_4^{2-}	SO_3 adsorption products



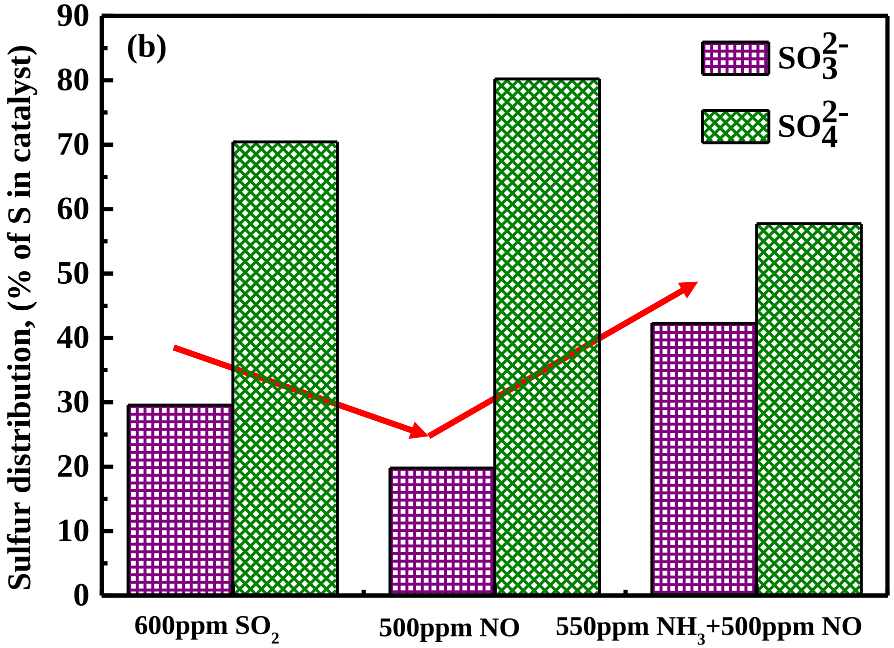


Fig. 8. (a). S 2p XPS spectra of catalyst A exposed in 600 ppm SO_2, 3% O_2 balanced with N_2 at 360 ℃; (b). Oxygen distribution on catalyst B after reacted under 600 ppm SO_2, 3% O_2, 500ppm NO, 500ppm NH_3 balanced with N_2 at 360 ℃.

- SO_2 content reduced with NO

⇧

reacted with SO_2

⇧

NO adsorbed species formed

- SO_2 content increased with NH_3

⇧

unfavorable to SO_2 diffusion

⇧

NH_3 decrease pore structure

Catalyst characterization

SO_2 desorption characteristics

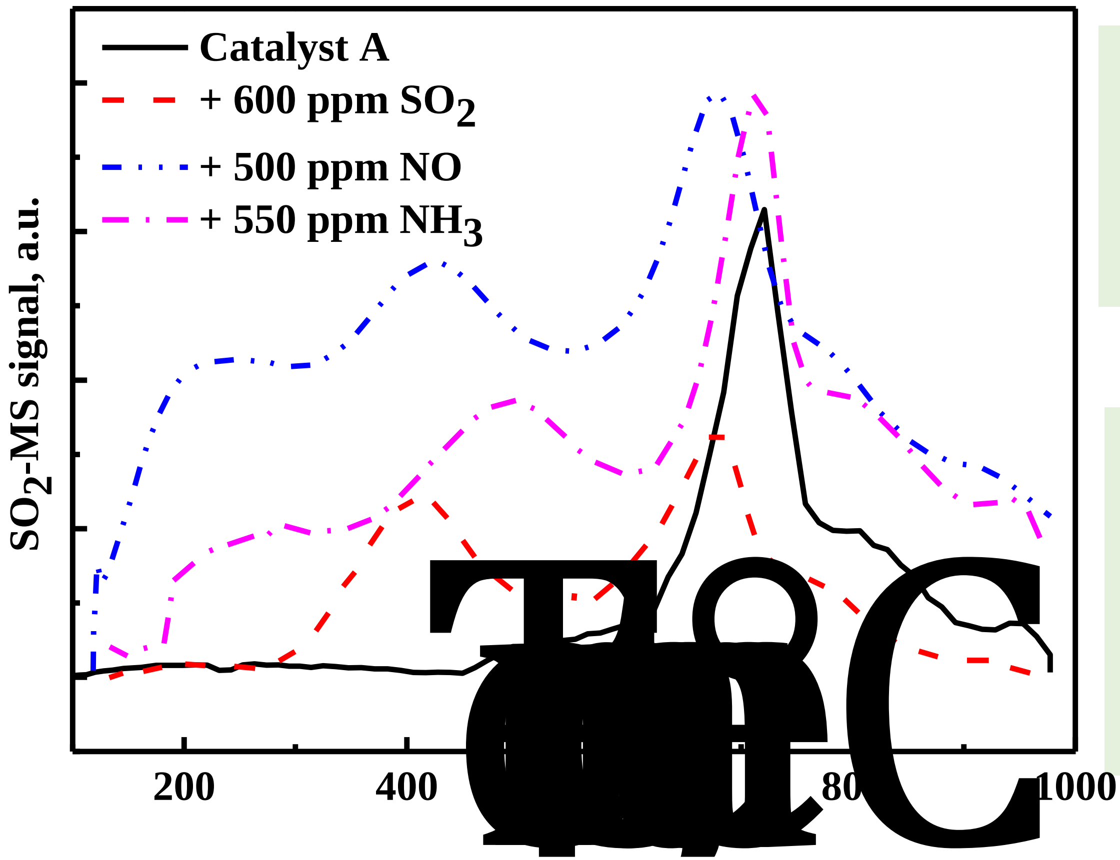


Fig. 9. SO_2 TPD of catalyst A exposed in 600 ppm SO_2, 3% O_2, 500ppm NO (when added), 500ppm NH_3 (when added) balanced with N_2 conditions.

- NO significantly promotes the adsorption of SO_2 on the catalyst
- NH_3+NO also promotes SO_2 adsorption, but the adsorption of SO_2 would lower than that in NO atmospheres

In situ DRIFT study

Adsorption of SO_2 on catalyst

3678 cm^{-1} OH vibration of V^{5+}-OH; 1359 cm^{-1} weak adsorption of SO_2; 1344 cm^{-1} adsorbed SO_2 (SO_3^{2-}); 1376 cm^{-1} $VOSO_4$; 1276 cm^{-1} HSO_4^-; 1620-1660 cm^{-1} H_2O, 1315 cm^{-1} surface sulfate; 1510 cm^{-1} adsorbed SO_3; 1420-1440 cm^{-1} surface sulfates

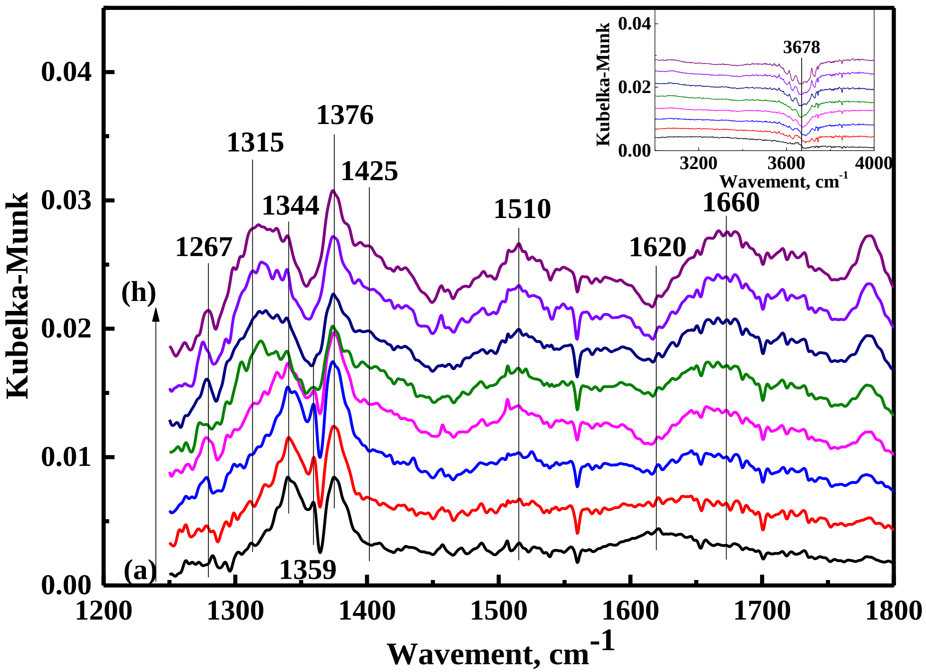


Fig. 10. DRIFTS spectra of catalyst A exposed to 600ppm SO_2 balanced with N_2 at 360℃ 10min, 20min, 40min and 60min (a-d), and then exposed to 3%O_2 balanced N_2 10min, 20min 40min and 60min (e-h).

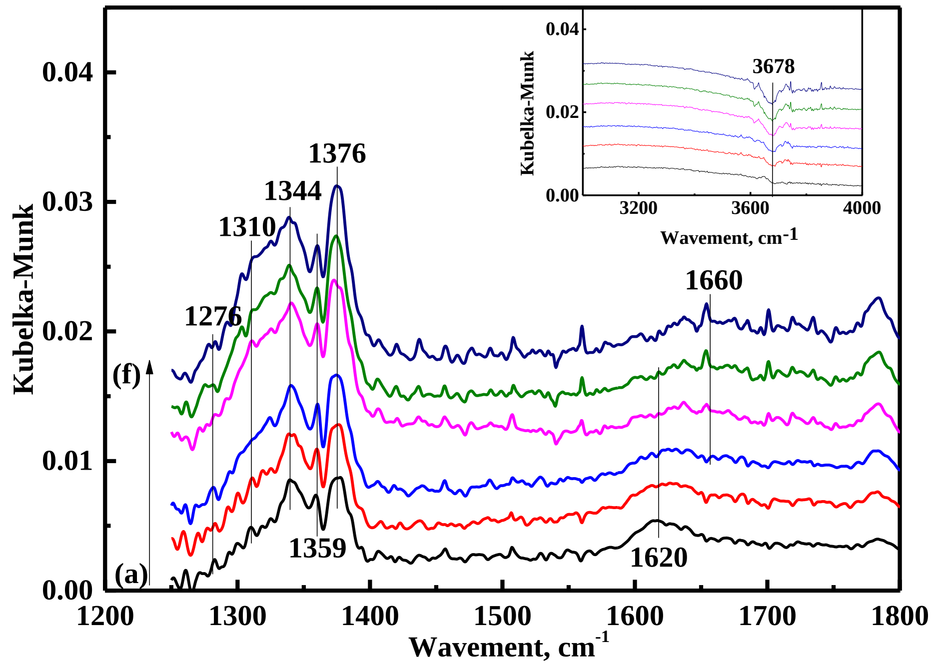


Fig. 11. DRIFTS spectra of catalyst A exposed to 600 ppm SO_2, 3% O_2 balanced with N_2 at 360℃ 10min, 20min, 30min, 40min, 50min and 60min (a-f)

- SO_2 could be adsorbed on catalyst in the forms of SO_3^{2-}
- SO_3^{2-} can react with V^{5+}-OH to form $VOSO_4$ and HSO_4^-, which will further converted to SO_3

In situ DRIFT study

Adsorption of NO+SO_2+O_2 on catalyst

1325-1340 cm^{-1} bridged NO_2^- species; 1415 cm^{-1} water-solvated nitrate; 1540 cm^{-1} monodentate nitrate

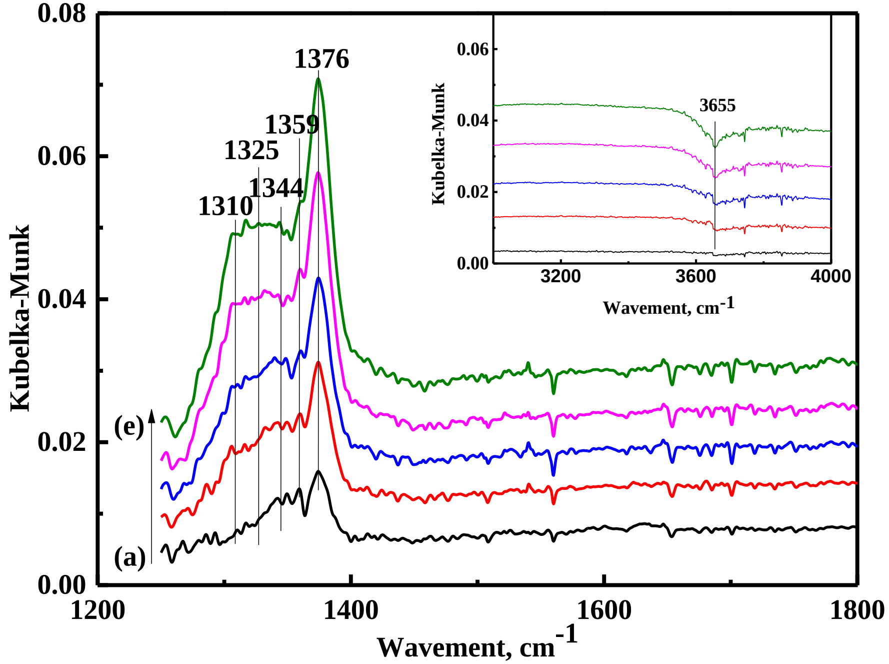


Fig. 12. DRIFTS spectra of catalyst A exposed to 600ppm SO_2, 3% O_2, 500ppm NO balanced with N_2 at 360℃ 2 min, 10 min, 20 min, 40 min and 60 min (a-e).

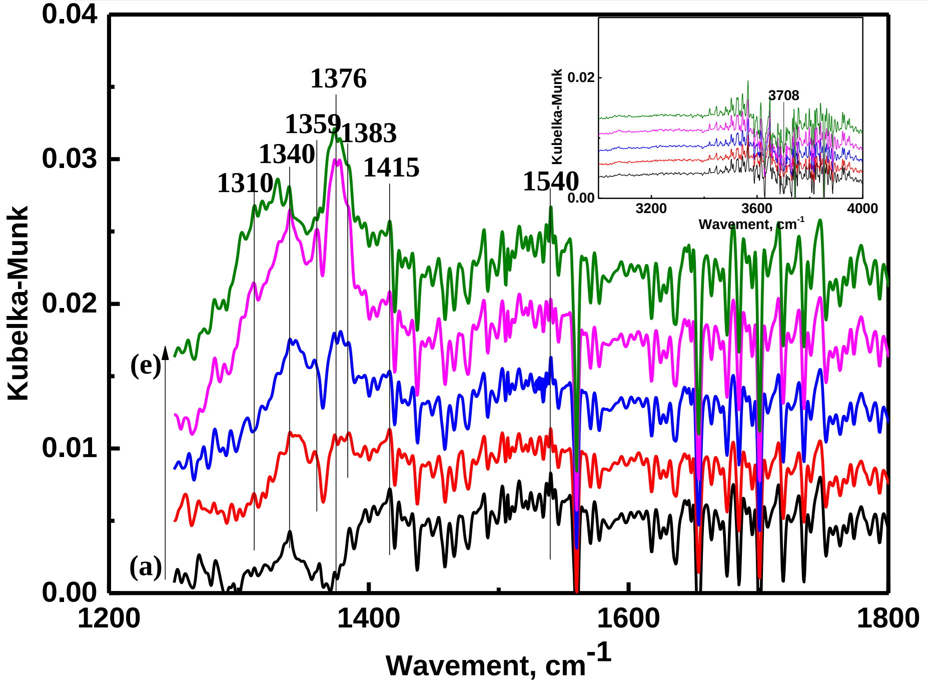


Fig. 13 DRIFTS spectra of catalyst A exposed to 500ppm NO balanced with N_2 at 360℃ 30 min (a), and then exposed to 600ppm SO_2 balanced with N_2 at 360℃ 2 min, 10 min, 40 min and 60 min (b-e).

- NO would absorb on catalyst in different forms
- NO promoted the adsorption of SO_2 and the generation of $VOSO_4$ species
- NO inhibited the generation of HSO_4^-

In situ DRIFT study

Adsorption of $NH_3+SO_2+O_2$ on catalyst

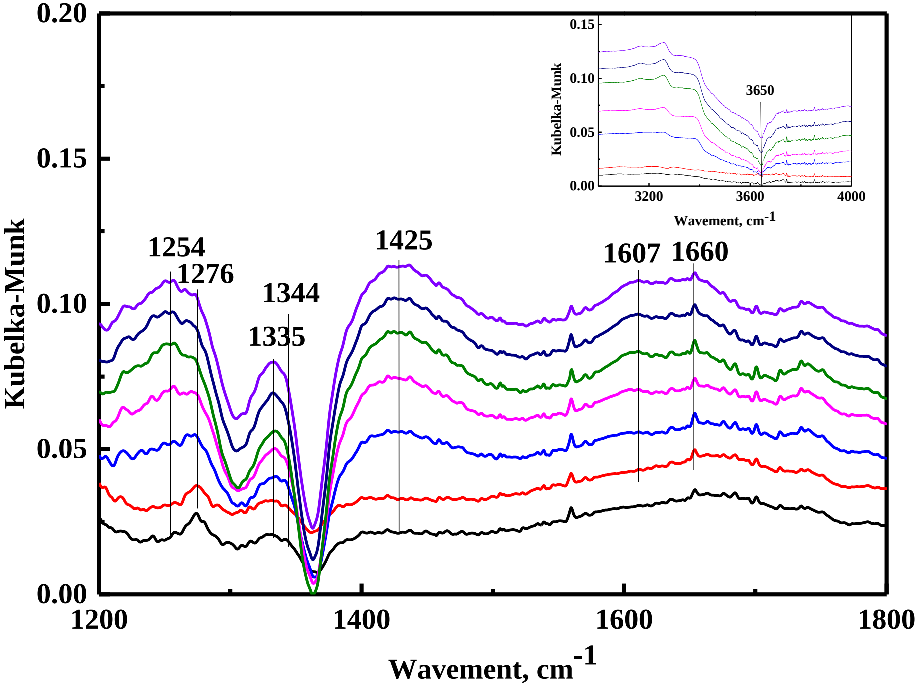


Fig. 14. DRIFTS spectra of catalyst A exposed to 600ppm SO_2, 500ppm NH_3, 3%O_2 balanced with N_2 at 360℃ 2min, 4min, 8min, 10min, 20min, 40min and 60min (a-g).

1335 cm^{-1} bending vibration of NH_2; 1254 cm^{-1} coordinated NH_3 on Lewis acid sites; 1425 ammonium ions bond to Bronsted acid sites; 1607 cm^{-1} coordinated NH_3 on Lewis acid sites

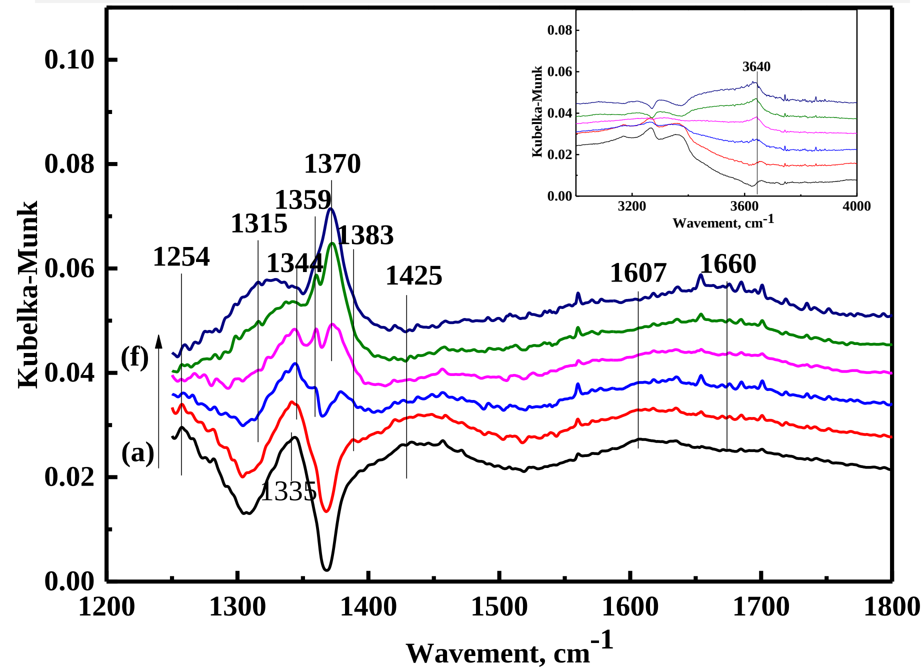


Fig. 15. DRIFTS spectra of catalyst A exposed to 500ppm NH3, 3%O_2 balanced with N_2 at 360℃ 30min (a), and then exposed to 600ppm SO_2 balanced with N_2 at 360℃ 2min, 10min, 20min, 40min and 60min (b-f).

- NH_3 would adsorb on catalyst in different forms
- NH_3 promotes the generation of HSO_4^- on catalyst, which exist in the form of NH_4HSO_4

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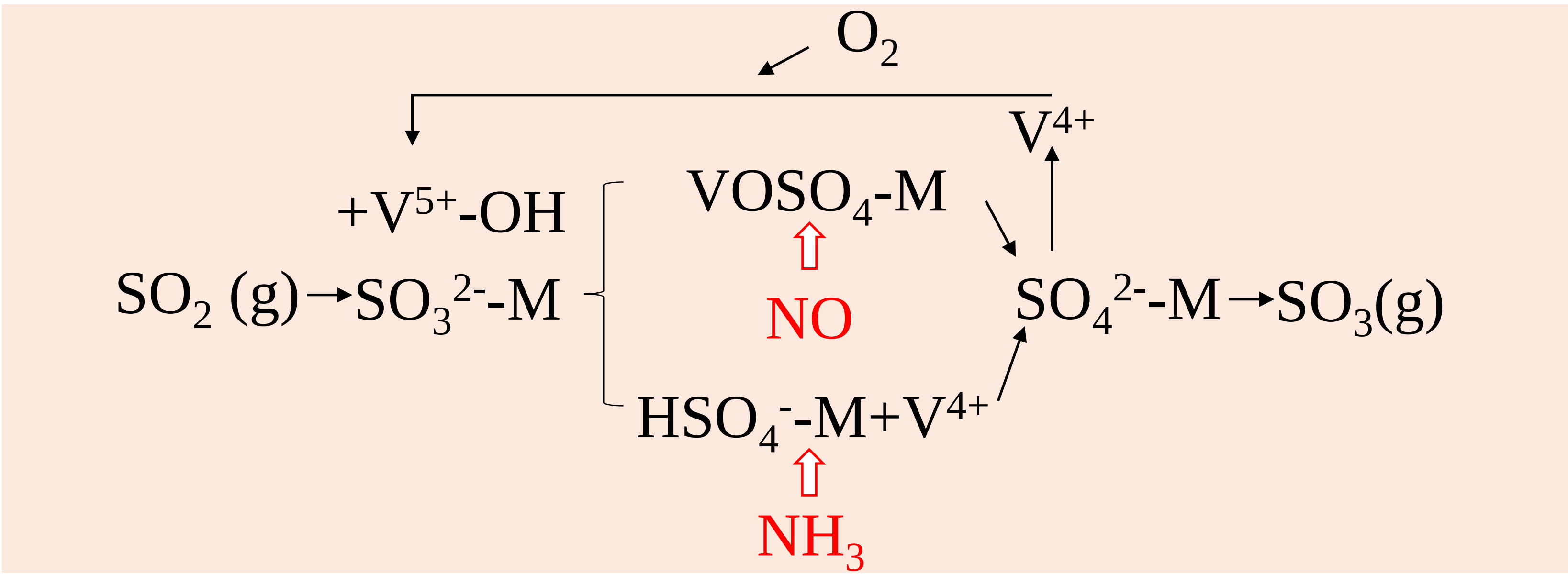
Conclusions

The generation path of SO_3 on catalyst



- The generation of SO_3 on catalyst is promoted by NO and NH_3.
- NH_3 leads to a significant reduction of the catalyst specific surface area.
- NO and NH_3 both increase the proportion of Oα and adsorption of SO_2.

Acknowledgments

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Thanks!
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