ICMGP 2024

CAPE TOWN • SOUTH AFRICA • 21 - 26 JULY

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Catalytic Oxidation of Hg^0 Over Co-Based Mixed Metal Oxides Catalyst

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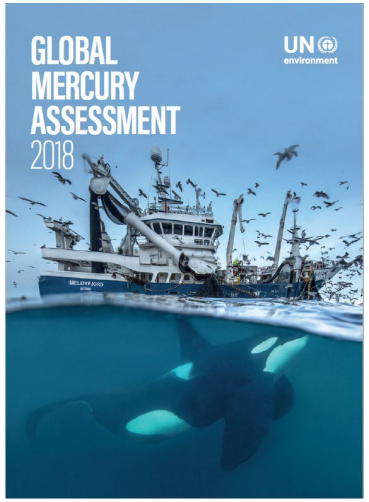
25/07/2024

Background

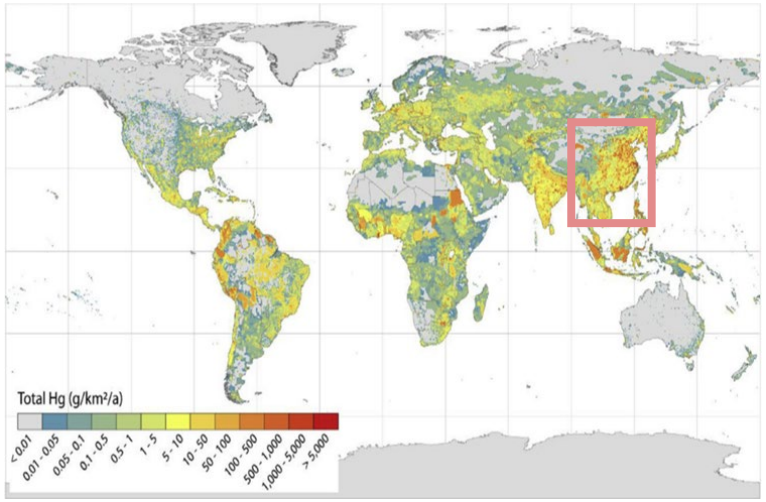
- China emits the most mercury, with **357.8 tons** in 2020.
- The composition of coal flue combustion gas is complex, and SCR catalysts are used to **synergically eliminate Hg^0 and NO_x**.



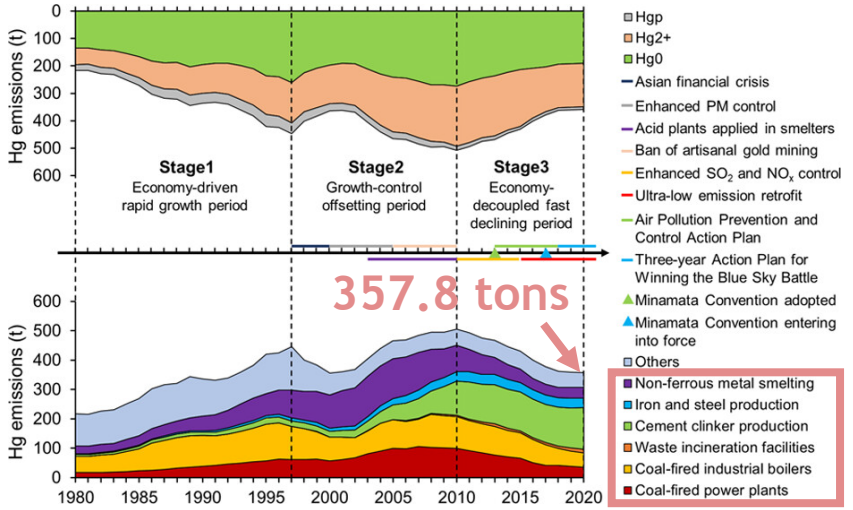
2015 year

20%

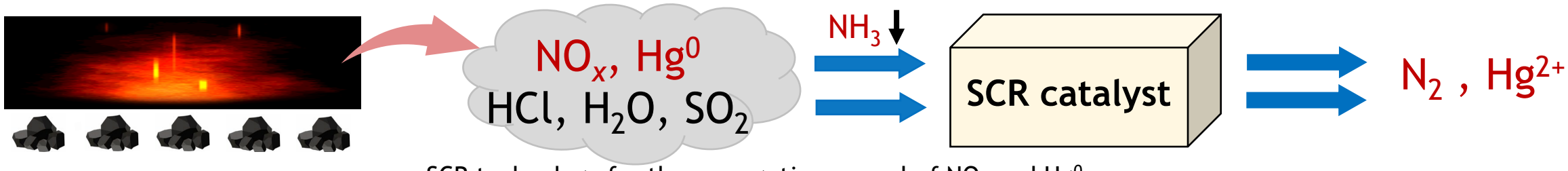
2010 year



Geospatial distribution of atmospheric mercury emissions from anthropogenic sources(2015)[1]



Hg emissions from different industries in China(2020) [2]

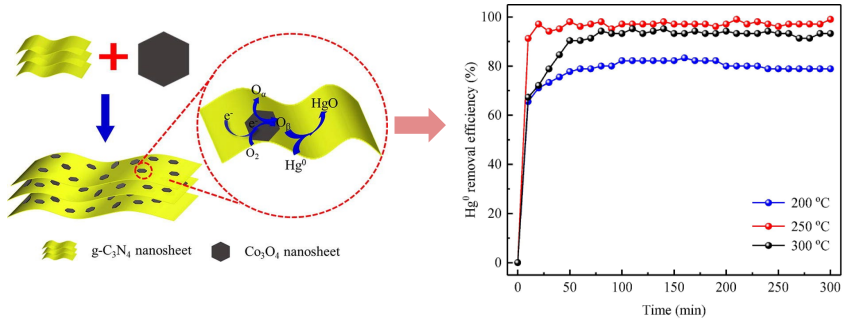


SCR technology for the synergetic removal of NO_x and Hg^0

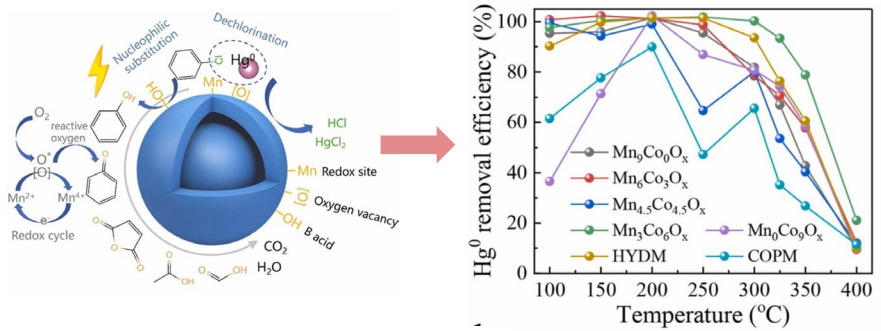
[1] UNEP. Global Mercury Assessment,2018.;[2] Zhang, et al, Environ. Sci. Technol. 2023, 57: 8660-8670.

Background

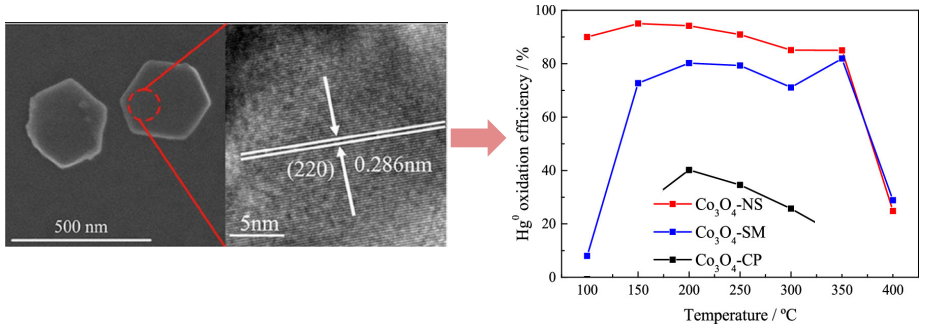
➢ The Co_3O_4 and modified Co-based catalysts are excellent candidates for Hg^0 oxidation.



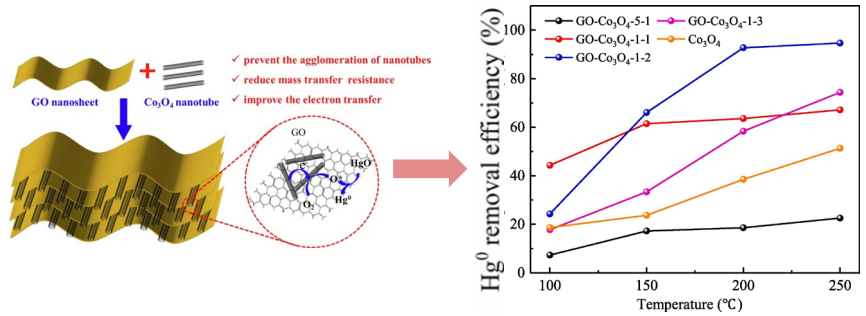
The Hg^0 oxidation of Co_3O_4/NS-g-C_3N_4[1]



The Hg^0 oxidation of $MnCo_2O_4$[2]



The Hg^0 oxidation of Co_3O_4 nanosheets[3]

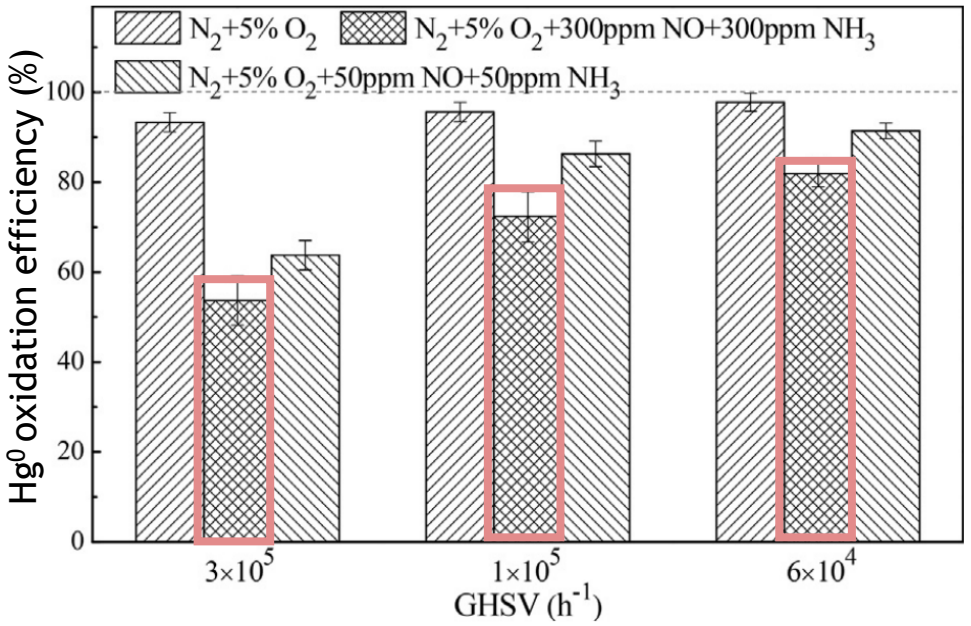


The Hg^0 oxidation of GO-Co_3O_4[4]

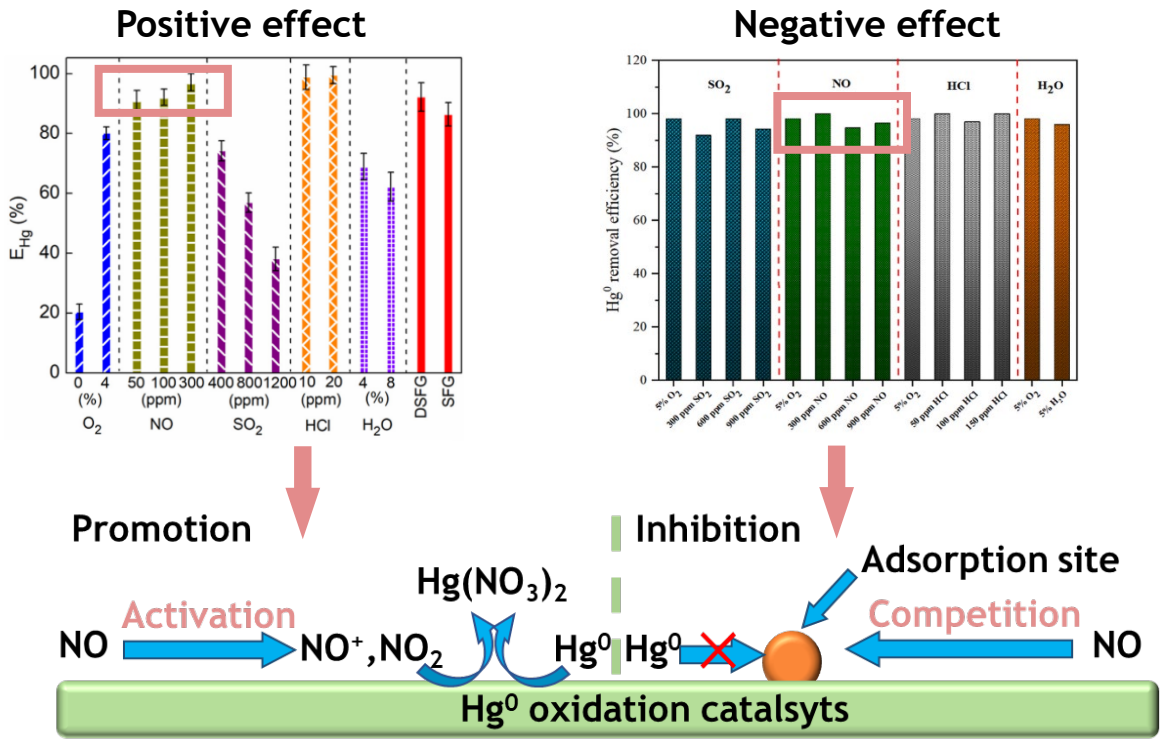
[1] Wang, et, al, Fuel, 2022, 324: 124660.;[2] Shi, et al, J. Hazard. Mater., 2023, 443, 130179; [3] Zhu, et, al, Environ. Sci. Technol. 2020, 54: 8601-8611.; [4] Zhang, et al, Sep. Purif. Technol, 2023, 320: 124014.;

Background

➢ Technical challenge :



Hg^0 oxidation efficiency in SCR atmosphere containing NH_3[1]



Study on the interaction between Hg^0 and NO[2-4]

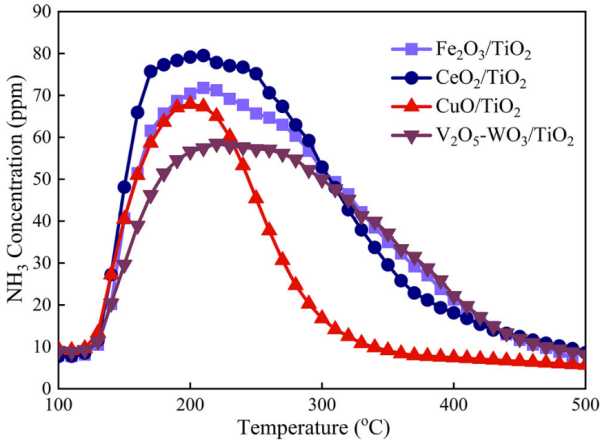
1. The flue gas components(such as NH_3) have a negative impact

2. Simultaneous catalysis of Hg^0 and NO is very different

[1] Wang, et al, Appl. Surf. Sci., 2018, 436: 1022-10129.; [2] Wang, et al, J. Hazard. Mater.,2021, 415: 125692.; [3] Zhou, et al, Fuel., 2018, 225: 134-139.; [4] Yang, et al, Chem. Eng. J., 2019, 1656-1666.

The regulation of basic sites for improving the resistance to NH_3 of Co-based catalyst

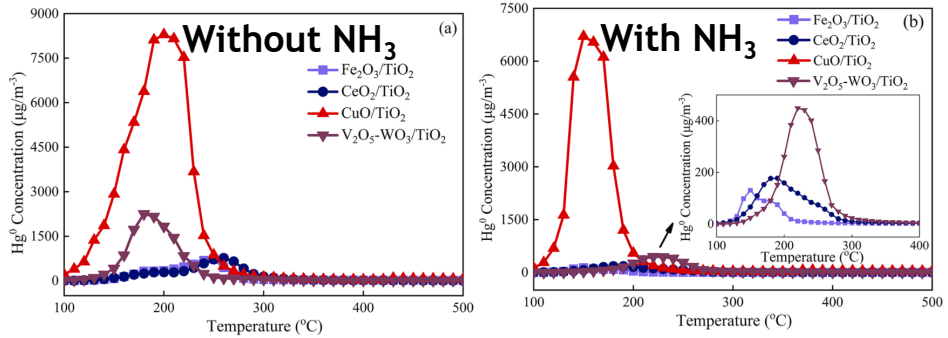
- The regulation of weak acidic sites enabled the catalyst to have the superior Hg^0 adsorption capacity in the presence of NH_3.
- The resistance to NH_3 might be improved by **the regulation of basic sites**.



NH_3-TPD in different component

The ratio of weak/strong acidic sites

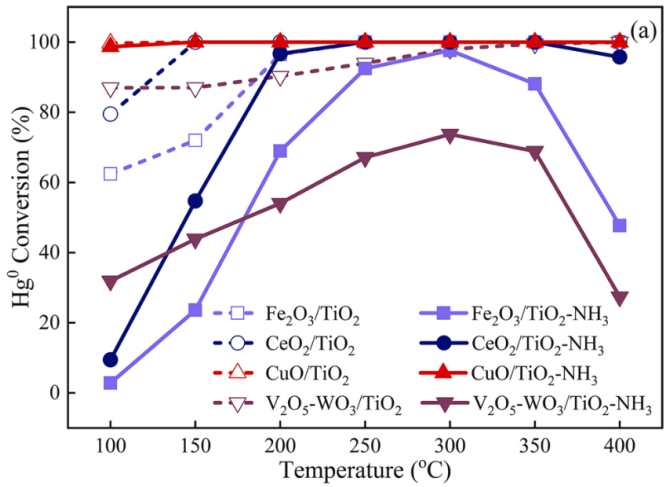
Catalysts	BET surface area (m^2/g)	Weak acidic sites/strong acidic sites
Fe_2O_3/TiO_2	50.3	2.14
CeO_2/TiO_2	44.4	2.60
CuO/TiO_2	33.6	4.97
V_2O_5-WO_3/TiO_2	55.1	1.74



Hg^0-TPD in different component

Hg^0 desorption quantity on the different catalyst

Catalysts	Desorption quantity (μg/g) (without NH_3)	Desorption quantity (μg/g) (with NH_3)	Percentage decrease (%)
Fe_2O_3/TiO_2	2.50	0.35	86.0
CeO_2/TiO_2	2.85	0.74	74.0
CuO/TiO_2	28.60	15.25	46.7
V_2O_5-WO_3/TiO_2	5.98	1.37	77.1

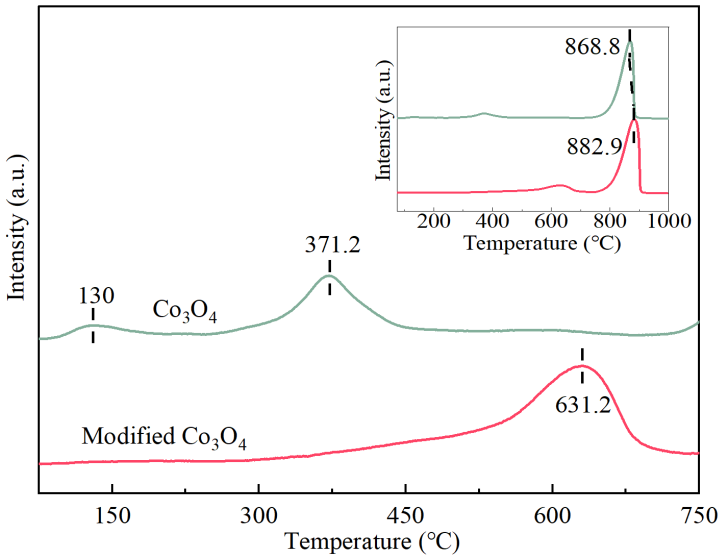


Hg^0 oxidation activity of different catalysts

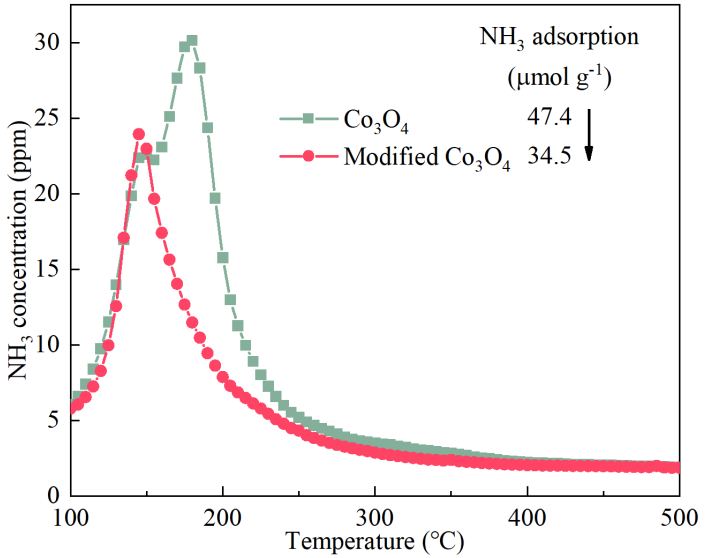
Li J, et al, Catalysis Today. 2021,376: 276-284.

The regulation of basic sites for improving the resistance to NH_3 of Co-based catalyst

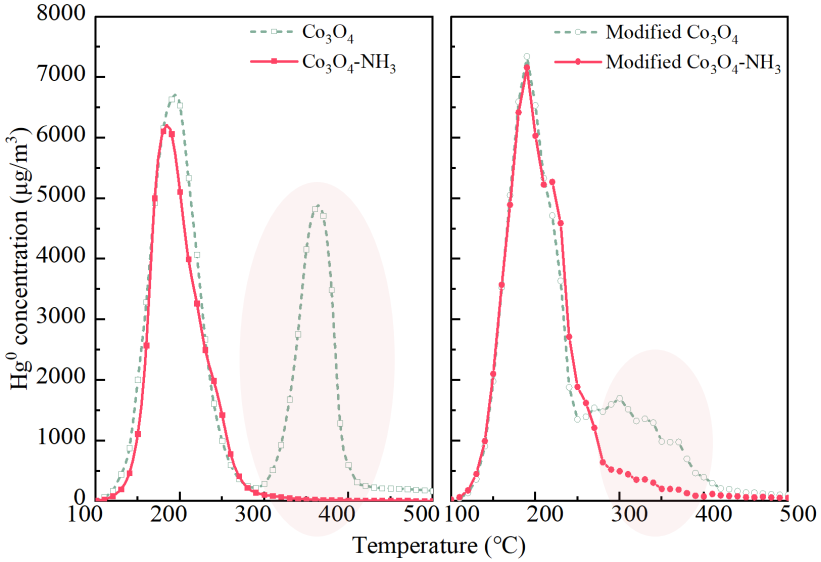
- The strength of basic sites over catalyst were enhanced, which enabled the modified Co_3O_4 to be less susceptible to NH_3(**NH_3 adsorption capacity decreased by ~27%**).
- The inhibitory effect of ammonia on mercury adsorption on modified Co_3O_4 could be **greatly weakened**.



The basic sites



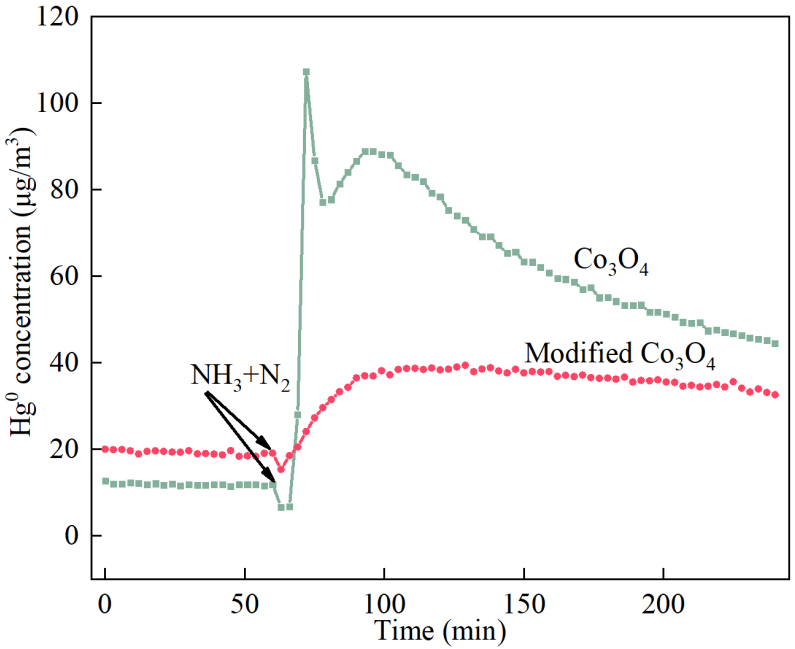
The NH_3 adsorption



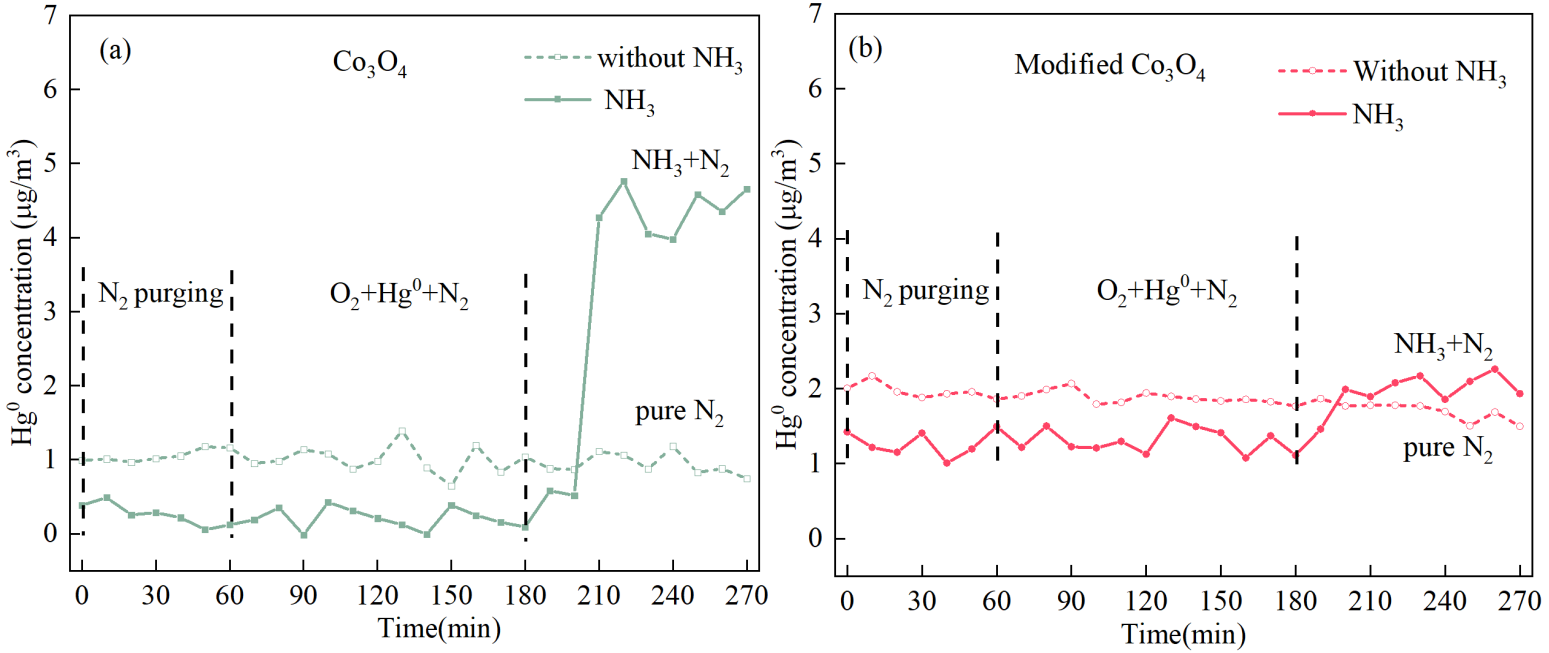
Hg^0-TPD

The regulation of basic sites for improving the resistance to NH_3 of Co-based catalyst

- The regulation of basic sites **decreased the competitive adsorption** between NH_3 and Hg^0.
- Modified Co_3O_4 catalyst was more resistant to NH_3, which decreased the reduction of NH_3 for Hg^{2+} at high temperature.



Desorption of Hg^0 from Co_3O_4 and modified Co_3O_4 catalysts by NH_3 at 100 ℃



Reduction effect of NH_3 on Co_3O_4 and modified Co_3O_4 catalysts: (a), (b) Transient response at 300 ℃; (c), (d) Hg^0-TPD

1 Background

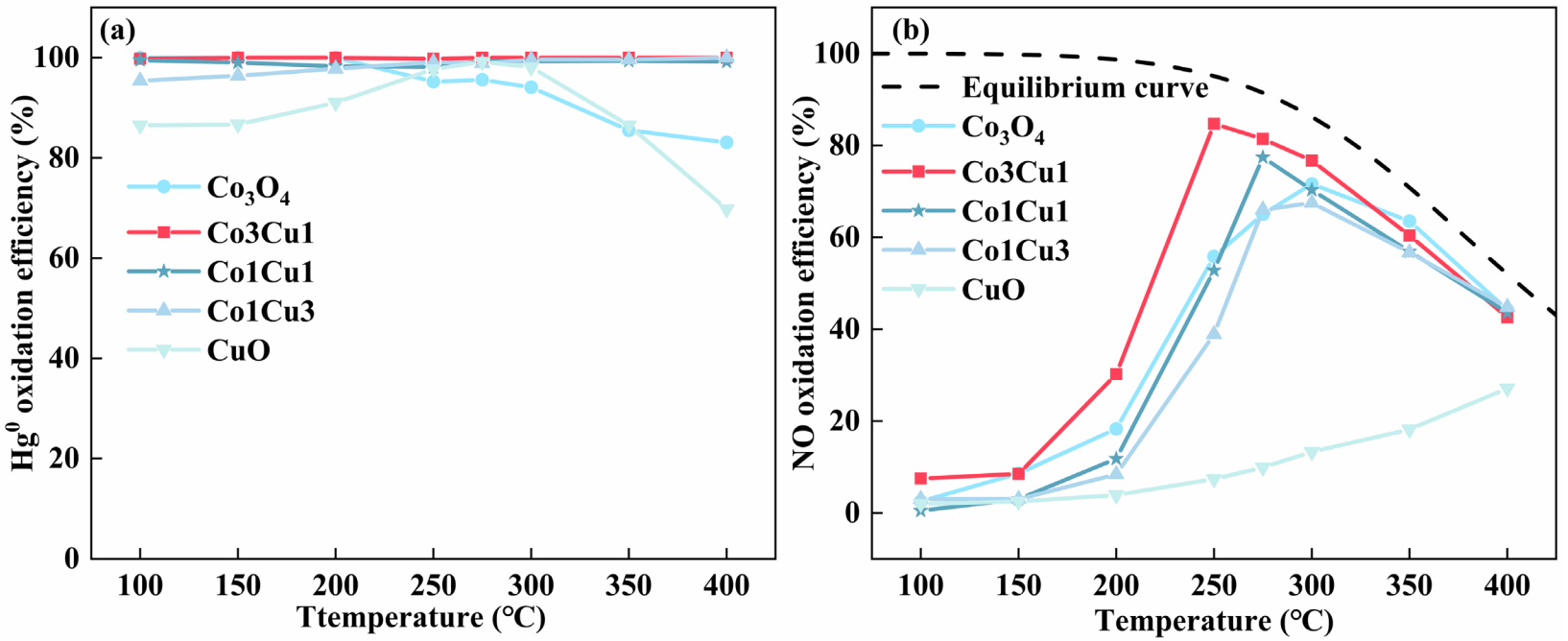
2 The regulation of basic sites for improving the resistance to NH_3 of Co-based catalyst

3 Co_xCu_y metal oxides catalyst for simultaneous catalysis of Hg^0 and NO

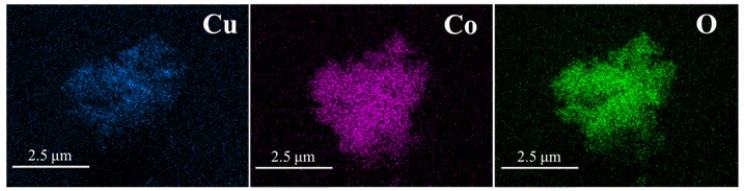
4 Conclusions

Co_xCu_y metal oxides catalyst for simultaneous catalysis of Hg^0 and NO

- The molar ratio of Co to Cu had an **optimal ratio of 3:1**
- The Co3Cu1 catalyst exhibited nearly 100% Hg^0 oxidation efficiency at 100-400 ℃ and 84% NO oxidation efficiency at 250 ℃



The Hg^0-NO simultaneous oxidation efficiency: (a) Hg^0 oxidation efficiency, (b) NO oxidation efficiency. (200 ppm NO, 110 μg m^{-3}, 4% O_2, 10 ppm HCl, N_2 balance, 1 L min^{-1} gas flow, GHSV=70000 h^{-1})



EDS

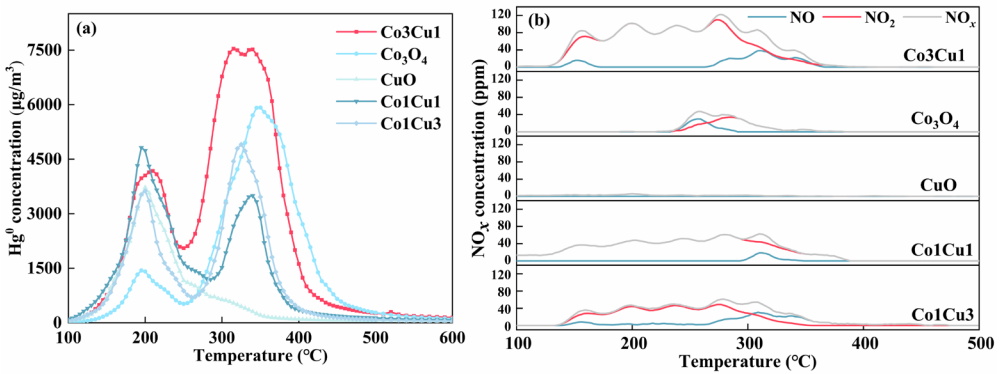
Catalyst	Co(w%)	Cu(w%)
Co3Cu1	62.10	19.78
Co1Cu1	43.91	39.10
Co1Cu3	20.36	67.42

The ICP for Co_xCu_y catalysts with different molar ratios

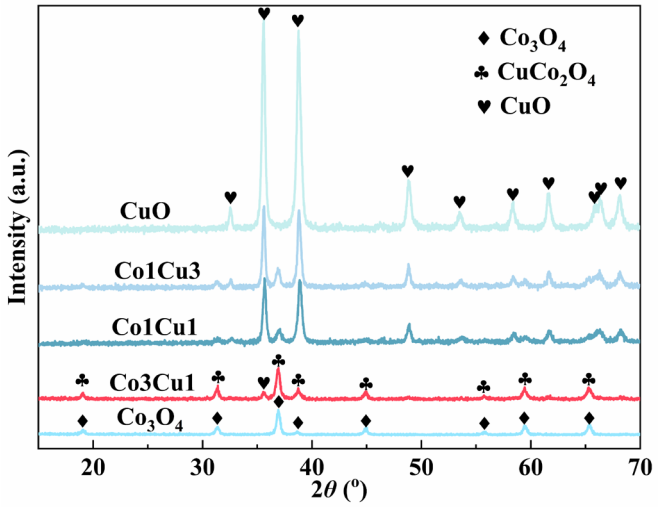
Qiu, et, al, Catalysis Today, 2024, 439: 114801.

Co_xCu_y metal oxides catalyst for simultaneous catalysis of Hg^0 and NO

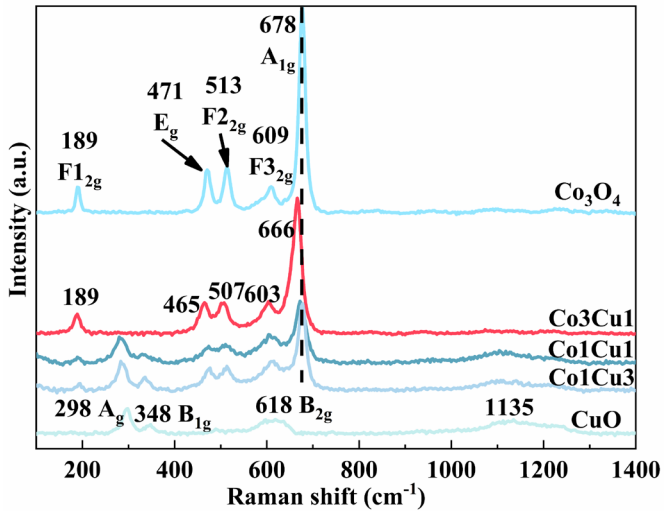
- The Hg^0 adsorption of Co3Cu1 catalyst was greatly improved, and NO was more easily activated.
- The $CuCo_2O_4$ spinel phase was formed on the Co3Cu1 catalyst.



Hg^0-TPD(a) and NO_x-TPD(b) curves of Co_xCu_y catalysts



XRD



Raman

The Hg^0 and NO_x adsorption capacity

Catalysts	Hg^0 Adsorption (μg g^{-1})	NO_x Adsorption (μmol g^{-1})
Co_3O_4	747..4	14.3
Co3Cu1	1155.2	92.9
Co1Cu1	609.0	55.3
Co1Cu3	574.5	48.5
CuO	326.3	3.7

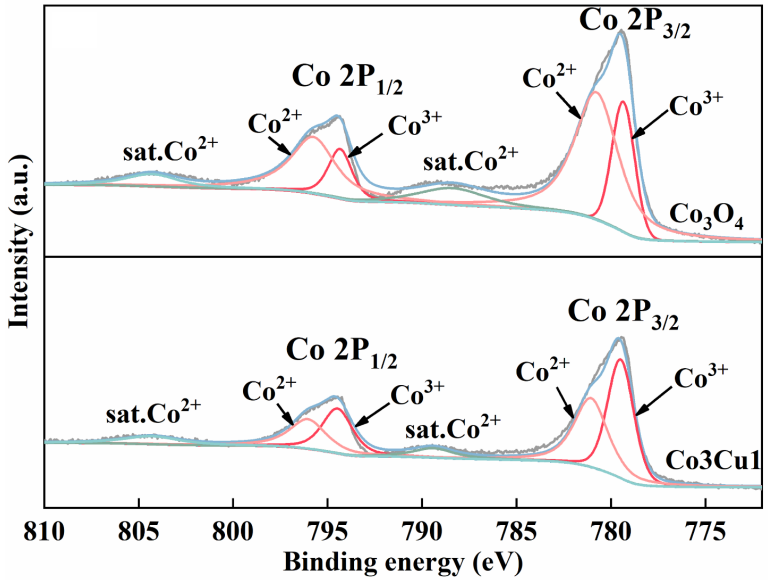
BET

Catalysts	Co_3O_4	Co3Cu1	Co1Cu1	Co1Cu3	CuO
BET specific surface area (m^2 g^{-1})	23.0	26.2	13.1	14.3	8.4

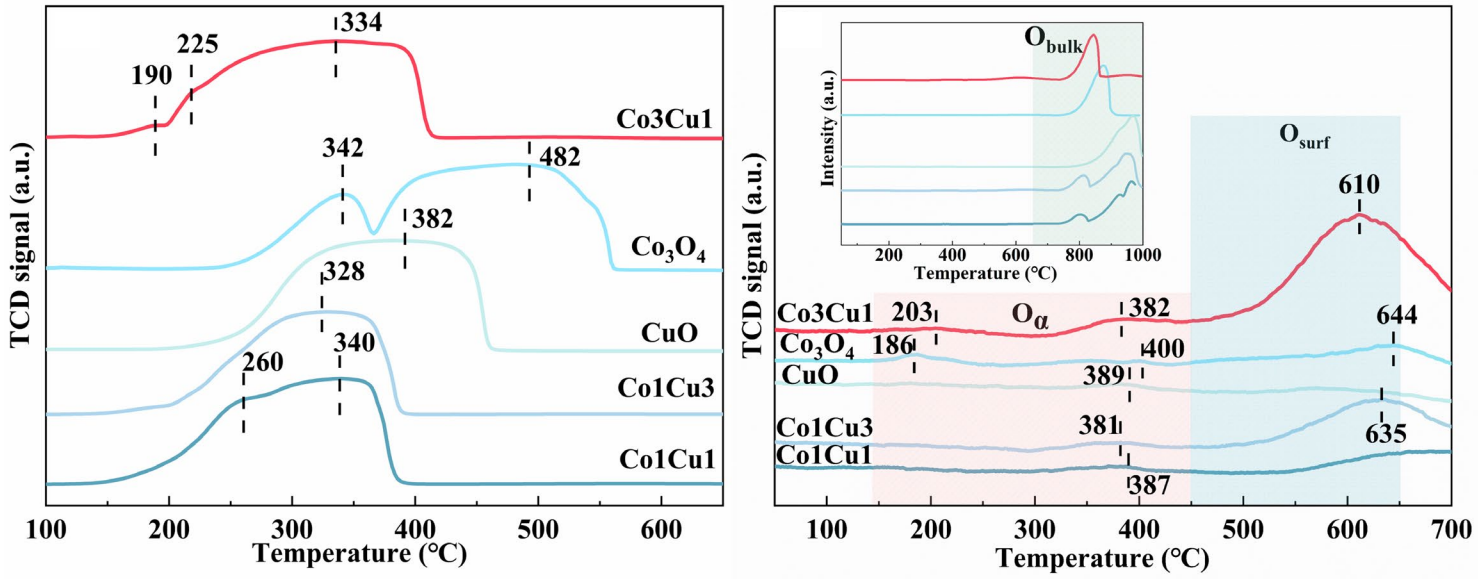
Qiu, et, al, Catalysis Today, 2024, 439: 114801.

Co_xCu_y metal oxides catalyst for simultaneous catalysis of Hg^0 and NO

- The **ratio of Co^{3+}** was increased by ~24% over Co3Cu1 catalyst.
- The Co3Cu1 catalyst exhibited lowest reduction peak temperatures(**190 ℃**) and excellent oxygen mobility of surface lattice oxygen species (**610 ℃**).



Co 2p XPS spectra

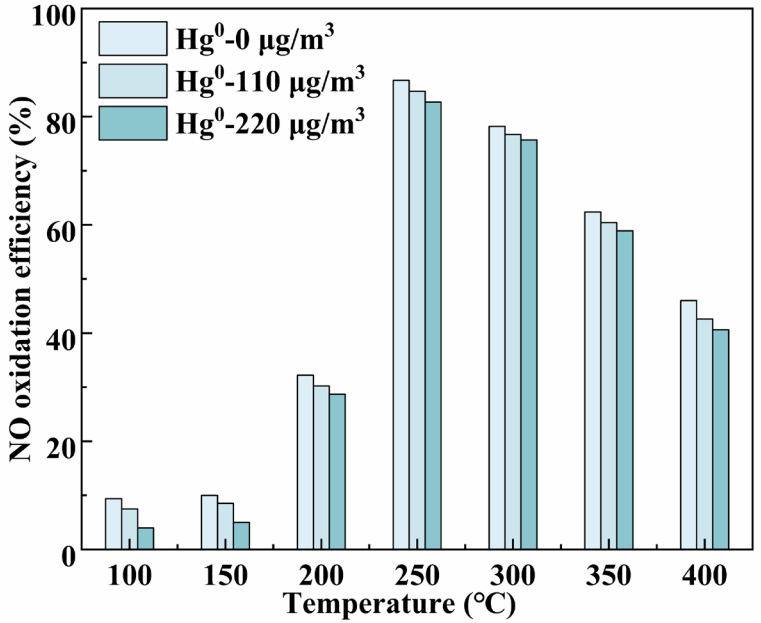


H_2-TPR and O_2-TPD profiles of Co_xCu_y catalysts

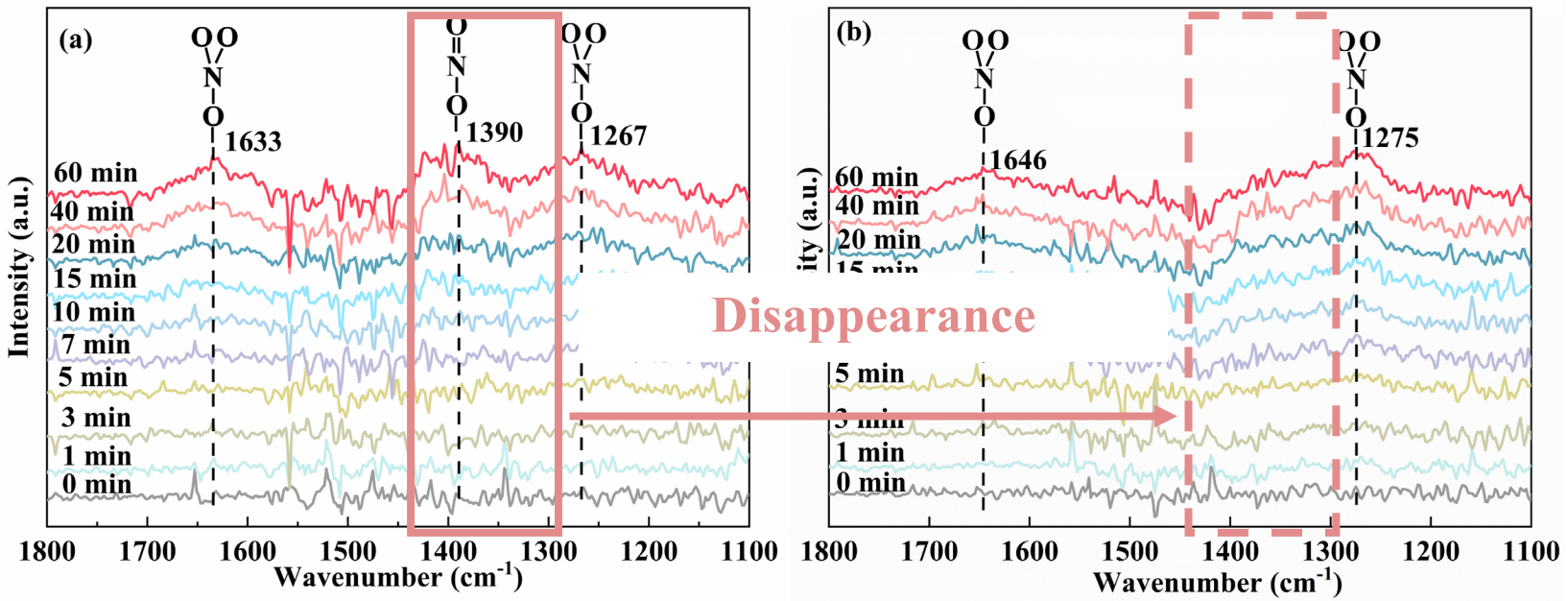
Qiu, et, al, Catalysis Today, 2024, 439: 114801.

Co_xCu_y metal oxides catalyst for simultaneous catalysis of Hg^0 and NO

- The **inhibitory effect** of Hg^0 on NO oxidation was very limited
- The disappearance of band at 1390 cm^{-1} indicated that the pretreatment of Hg^0 **might cover the adsorption sites of nitrite species** on the surface of Co3Cu1 catalyst



The effects of Hg^0 concentration on NO oxidation. (200 ppm NO, 4% O_2, 10 ppm HCl, N_2 balance, 1 L min^{-1} gas flow, GHSV=70000 h^{-1})

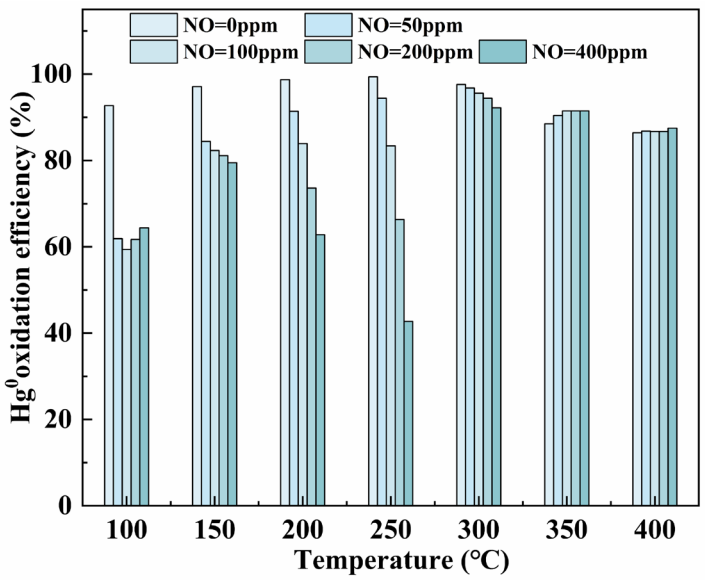


In-situ DRIFTs spectra of NO adsorption over Co3Cu1 catalyst at 100 ℃: (a) Fresh catalyst; (b) After the pretreatment of Hg^0.

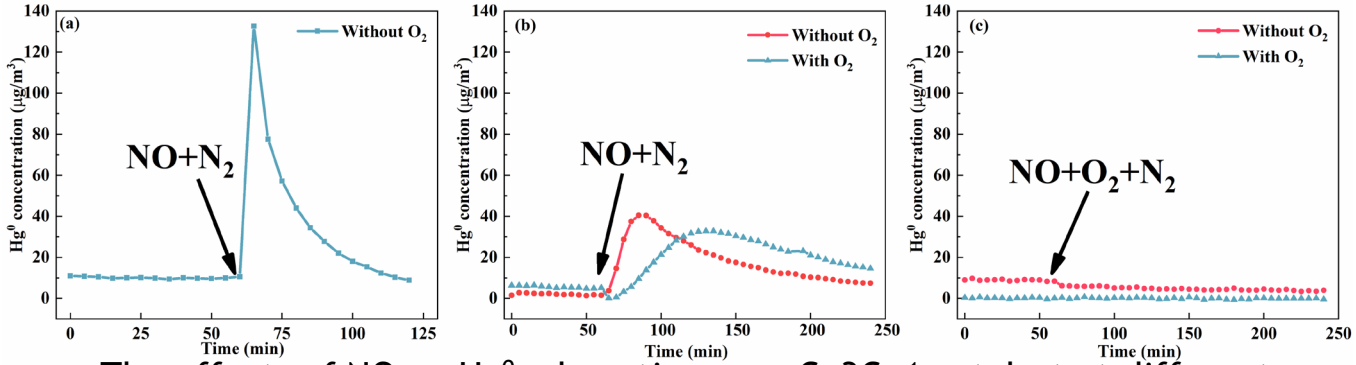
Qiu, et, al, Catalysis Today, 2024, 439: 114801.

Co_xCu_y metal oxides catalyst for simultaneous catalysis of Hg^0 and NO

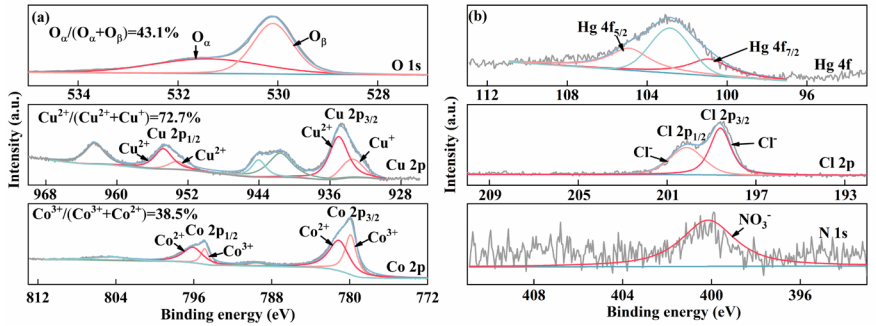
- The Hg^0 oxidation activities **were decreased** when added NO at 100-300 ℃
- There were **competitive adsorption** between Hg^0 and NO, which might be weakened by introducing sufficient O_2.The **Oα and the redox cycle of Co^{3+} + Cu^{+} ↔ Co^{2+}+ Cu^{2+}** were involved in reaction.



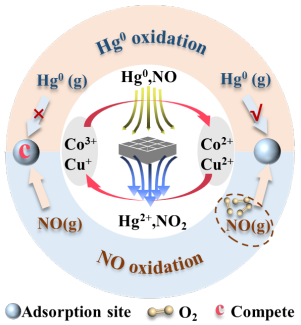
The effects of NO concentration on Hg^0 oxidation. (110 μg m^{-3} Hg^0, 4% O_2, 10 ppm HCl, N_2 balance, 500 mL min^{-1} gas flow, GHSV=630000 h^{-1})



The effects of NO on Hg^0 adsorption over Co3Cu1 catalyst at different temperatures: (a) 100 ℃; (b) 250 ℃; (c) 250 ℃.



The XPS spectra after reaction



The reaction mechanism

Qiu, et, al, Catalysis Today, 2024, 439: 114801.

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Conclusions

- The competitive adsorption between Hg^0 and NH_3 over Co-based catalyst could be weakened by the regulation of basic sites. It resulted in the negative effect of NH_3 on Hg^0 oxidation was decreased .

- Co3Cu1 catalyst was an excellent candidate for Hg^0-NO simultaneous oxidation.

- The Hg^0 could be crowded out when introduced the NO. However, the inhibitory effect of NO on Hg^0 oxidation might be weakened by introducing sufficient O_2.

This is my **united, loving** research group!

Thank you

Huazhen Chang, Lei Qiu, Rong Xiao
Renmin University Of China
25/07/2024