

Reduction of SO₂ by NH₃ to Elemental Sulfur Over Transitional Metal Oxides Catalysts

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Abstract Mixed oxides , TiO₂-MeO_x (Me-V , Cr , Mn , Fe , Co , Ni , Cu) have shown high catalytic activity for the NH₃ decomposition reaction and the reduction of SO₂ by NH₃ to elemental sulfur. Co₃O₄-TiO₂ and Fe₂O₃-TiO₂ catalysts show higher catalytic activity than other catalysts at low temperature. Characterization by XRD indicates that transition metal sulfides are probably the most active. The mechanism of the reduction of SO₂ by NH₃ to elemental sulfur over TiO₂-MeO_x (Me-V , Cr , Mn , Fe , Co , Ni , Cu) catalysts is assumed.

Key words Transitional metal oxides ; Transitional metal sulfides ; NH₃ ; SO₂ ; Elemental sulfur

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1 Introduction

SO₂ is one of the most hazardous pollutants. Currently operating desulfurization^[1-3] process , based on the SO₂ scrubbing with lime or limestone , is a costly process requiring a large space with complicated facilities and disposal of the used sorbents. Direct catalytic oxidation of SO₂ to SO₃ , which is absorbed to H₂SO₄ , is an optional method ; however , it will essentially produce liquid production , which is very corrosive and difficult to transport. Other desulfurization processes , based on adsorption/regeneration system^[4-6] are under well development , yet all the techniques need a compact process to deal with the dissociative SO₂. Direct catalytic reduction of SO₂ to elemental sulfur has received much attention because it is easier to design and operate^[7-11]. The process can be applied directly to flue gases containing a small amount of oxygen or to the case where SO₂ in the flue gas is isolated or concentrated using a proper adsorption/regeneration system. SO₂ reduction with several reducing agents , including CO , CH₄ , H₂ and C , has been studied using several types of catalysts including alumina - supported transition met-

als^[12] , perovskite type oxides^[13] and mixed oxides containing La or Ce^[14,15].

In this paper , we report a new kind of reducing agent , ammonia. SO₂ reduction with NH₃ as reducing agent is very cheap , easy to operate and especially suitable for coal gas desulfurization. The last products are N₂ , H₂O and elemental sulfur , which will lead to no more pollution and high commercial values. We also reported new types of mixed oxide catalysts for this reaction system and the mechanism of the reduction of SO₂ by NH₃ to elemental sulfur over TiO₂-MeO_x (Me-V , Cr , Mn , Fe , Co , Ni , Cu) catalysts is assumed.

2 Experiment

V₂O₅ and TiO₂ were purchased from Tianjin Chemical Reagent Ltd. Cr , Mn , Fe , Co , Ni and Cu these six kinds of transition metal oxide catalysts were prepared by precipitation method. A solution of 1 mol/L NaOH was respectively dropped into aqueous solutions of corresponding transition metal nitrate and the precipitated slurry was dried at 120°C for 8 h in air and calcined at 450°C for 4 h in air. Proportionally (10% of V , Cr , Mn , Fe , Co , Ni ,

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Cu) mixed with TiO_2 , the mechanical mixture was prepared by gently mixing the two powders in a mortar for 15 min. It was then calcined at 1000°C for 10 h in air and ground and sieved to 0.250.45 mm size.

A vertical, fixed-bed reactor made of 8 mm pyrex tube was used for the reaction measurement. The reaction of SO_2 reduced by NH_3 to elemental sulfur was tested from 200 to 1000°C . The feed ($GHSV = 10000 \text{ h}^{-1}$) containing 4% NH_3 and 3% SO_2 in balanced N_2 was fed to the reactor containing 1.0 mL catalyst. A sulfur trap was attached at the effluent side of the reactor. The gaseous products were analyzed by GC4001 gas chromatograph equipped with a thermal conductivity detector. Because it only detected NH_3 , N_2 , SO_2 , H_2S and no NO_x , we assumed that NH_3 would not oxidized to NO_x in this system and SO_2 was only converted to elemental sulfur and H_2S . The conversion of NH_3 , SO_2 and the selectivity to elemental sulfur are defined as follows:

$$\text{NH}_3 \text{ conversion \%} = \frac{\text{NH}_3 \text{ in} - \text{NH}_3 \text{ out}}{\text{NH}_3 \text{ in}} \times 100$$

$$\text{SO}_2 \text{ conversion \%} = \frac{\text{SO}_2 \text{ in} - \text{SO}_2 \text{ out}}{\text{SO}_2 \text{ in}} \times 100$$

$$\text{Sulfur selectivity \%} = \frac{\text{SO}_2 \text{ in} - \text{SO}_2 \text{ out} - \text{H}_2\text{S}}{\text{SO}_2 \text{ in} - \text{SO}_2 \text{ out}} \times 100$$

Where NH_3 , SO_2 and H_2S represent the concentration of NH_3 , SO_2 and H_2S . The subscripts, "in" and "out", indicate the inlet and outlet position of the reactor. From 200°C to 1000°C , there was no conversion of NH_3 or SO_2 when the reactor contains on catalysts. Thus

its influence on the reaction test is neglected.

3 Results and discussion

3.1 Catalytic activity for the ammonia decomposition

To find a catalytic system that is effective for NH_3 - SO_2 reaction, first we test its activity for NH_3 decomposition. Fig.1 shows the conversion of NH_3 as a function of temperature. The profile of each catalyst has a common characteristic, S shape curve, caused by the pre-reduction of transition metal oxides; however, the activity of different catalysts varies greatly. Based on the 50% NH_3 conversion, the reaction temperature of each catalyst is: 600°C , 500°C , 550°C , 420°C , 400°C , 420°C , 410°C ; the activity in turn is: $\text{Co}_3\text{O}_4 > \text{CuO} > \text{Fe}_2\text{O}_3 \approx \text{NiO} > \text{Cr}_2\text{O}_3 > \text{MnO} > \text{V}_2\text{O}_5$. Based on the 100% NH_3 conversion, the reaction temperature of each catalyst is: 880°C , 790°C , 800°C , 650°C , 640°C , 700°C , 690°C ; The activity in turn is: $\text{Co}_3\text{O}_4 > \text{Fe}_2\text{O}_3 > \text{CuO} > \text{NiO} > \text{Cr}_2\text{O}_3 > \text{MnO} > \text{V}_2\text{O}_5$. Every catalyst has high activity for ammonia decomposition from 300°C to 900°C . The catalyst of Co_3O_4 - TiO_2 and Fe_2O_3 - TiO_2 also has high activity at low temperature. Some researchers tried to make a relation between the catalyst activity and its reductivity^[16-18], i.e., the high activity of Ni/MgO or Ni/ Al_2O_3 supported catalysts is coherent with their low reductive extent during reaction; but in our experiment, it is different that CoO- TiO_2 and Fe_2O_3 - TiO_2 catalysts have high activity and high reductive extent. Thus, it is assumed that the

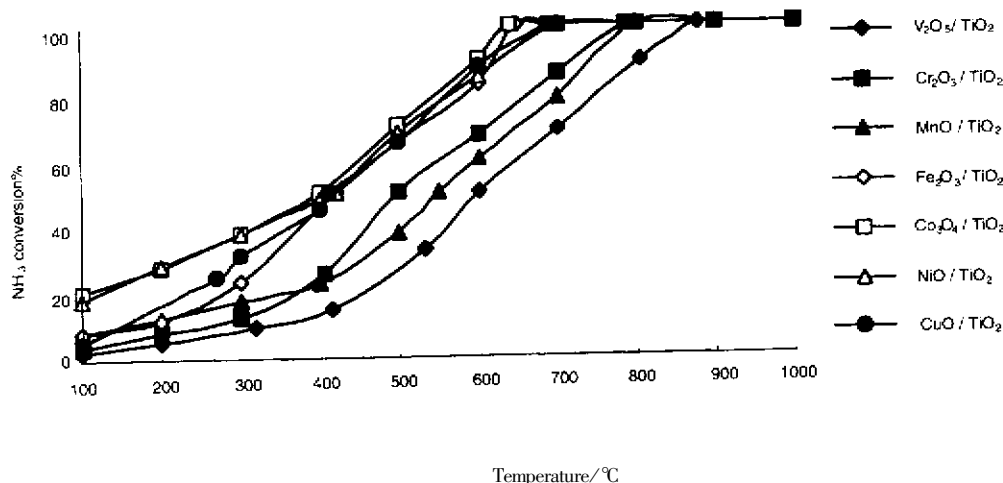


Fig.1 Effect of temperature on NH_3 conversion

ammonia decomposition is completed from a different mechanism on these mixed oxides catalysts.

3.2 Catalytic activity for the ammonia decomposition reaction

Fig.2 shows the conversion of SO₂ as a function of reaction temperature. Except for Cr₂O₃-TiO₂ catalyst, each activity profile appears S shape. The phenomena that the catalytic activity varies greatly before and after a certain temperature indicate that the active phase varies during the NH₃-SO₂ reaction. Characterization by XRD indicates that, except for Cr₂O₃-TiO₂ catalyst, each catalyst has been sulfidated with different extent, and each produced sulfide has single valence state, i. e., V₃S₄, MnS, NiS, FeS or multi-valence state, i. e., Cu₂S, CuS and Co₉S₈, Co₃S₄, CoS₂. Thus it is assumed that the active phase for NH₃-SO₂ reaction is probable transition metal sulfides.

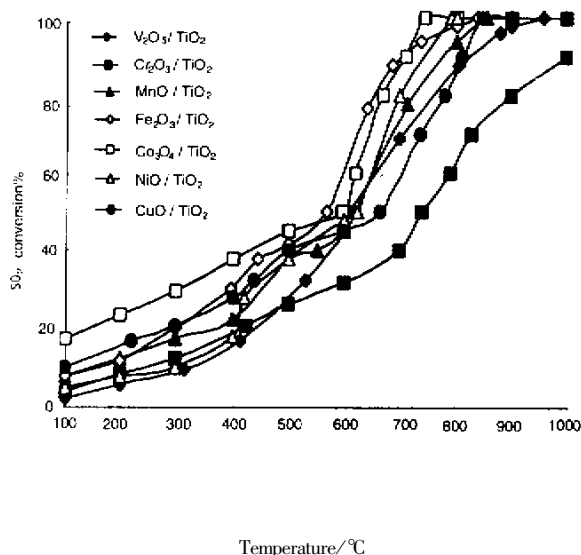
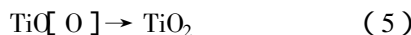
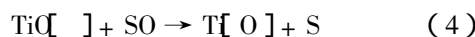
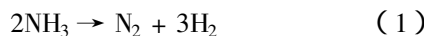


Fig.2 Effect of temperature on SO₂ conversion

Based on the 50% SO₂ conversion, the reaction temperature of each catalyst is: 610°C, 740°C, 620°C, 570°C, 595°C, 625°C and 665°C; the activity in turn is: Fe-Ti > Co-Ti > V-Ti > Mn-Ti > Ni-Ti > Cu-Ti > Cr-Ti. Based on the 100% SO₂ conversion, the reaction temperature of each catalyst is: 960°C, higher than 1000°C, 855°C, 840°C, 740°C, 790°C and 780°C; the activity in turn is: Co-Ti > Ni-Ti > Cu-Ti > Fe-Ti > Mn-Ti > V-Ti > Cr-Ti. It also shows that at low temperature the activity of Cu-Ti catalyst is higher than Co-Ti catalyst, yet at high

temperature it reversed. Combined with XRD results we assume that because CuO is easier to be sulfidated than CoO and becomes higher sulfidity CuS, the activity of CuO is then higher at low temperature; on the other hand, CoO is more difficult to be sulfidated than CuO and becomes multi-valence state sulfides, i. e., Co₉S₈, Co₃S₄ and CoS₂. When the reaction processes from 300°C to 700°C in about five hours, the sulfidation of CoO is almost complete. Thus the activity of CoO is higher at high temperature. It is interesting that Cr₂O₃-TiO₂ catalyst is very different from other six kinds of catalysts. At the temperature of 1000°C, the conversion of SO₂ is only 87%. It is probably because Cr₂O₃-TiO₂ catalyst is very difficult to be sulfurized and there is no phase of sulfides after the reaction. Thus the redox mechanism of NH₃-SO₂ is assumed.



First, on the Cr₂O₃ catalyst ammonia is decomposed to H₂ (1). Then TiO₂ is reduced by H₂ to produce oxygen vacancies on the surface of TiO₂ (2). It is oxygen vacancies that reduce SO₂ to elemental sulfur (3), (4). As the reaction temperature increases sufficiently high, a fast incorporation of [O] to the lattice and equilibrium shift to the right in Eq.(5) results in the absence of oxygen vacancies and then it is difficult to reduce SO₂.

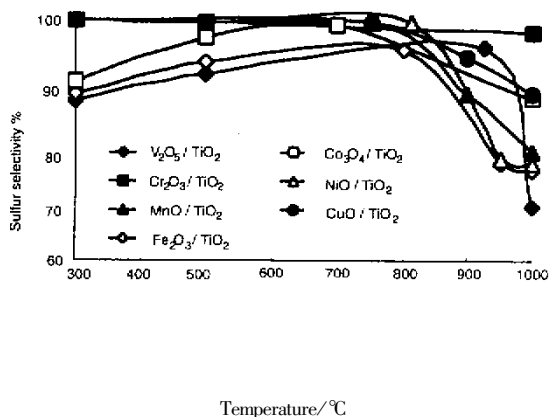


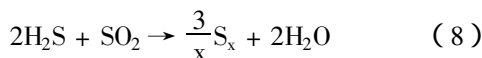
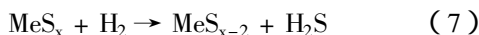
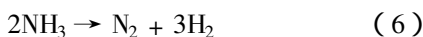
Fig.3 Effect of temperature on sulfur selectivity

Fig. 3 shows the selectivity of elemental sulfur as a function of reaction temperature. It indicates that the selectivity of these mixed oxides catalysts is higher than the supported and perovskite catalysts. According to presentment of different profile, these seven selectivity profiles could be separated into three types. The first kind includes Co-Ti, Fe-Ti and V-Ti catalysts and the profile has a maximum selectivity lower than 100%. The second includes Cu-Ti, Fe-Ti and V-Ti catalysts and they have high selectivity at the beginning of NH₃-SO₂ reaction, yet after certain temperature the selectivity decreases greatly. The third is Cr-Ti catalyst whose selectivity is almost 100%. According to the definition of selectivity to wards elemental sulfur, it is assumed that there produces no H₂S on the Cr₂O₃-TiO₂ catalyst, which further confirmed the redox mechanism of NH₃-SO₂ reaction. It is more interesting to find that the break point of the first and the second types of catalysts is consistent with the temperature of 100% SO₂ conversion, showed in Table 1.

Table 1 Comparison of the temperature of 100% SO₂ conversion on the break point of sulfur selectivity

No.	Catalysts	Temperature of 100% SO ₂ conversion/°C	Break point of sulfur selectivity/°C
1#	V ₂ O ₅ -TiO ₂	960	925
2#	Cr ₂ O ₃ -TiO ₂	100(87%)	No break-point
3#	MnO-TiO ₂	855	860
4#	Fe ₂ O ₃ -TiO ₂	840	810
5#	CoO-TiO ₂	710	700
6#	NiO-TiO ₂	790	790
7#	CuO-TiO ₂	850	855

Thus the modified redox mechanism on the six kinds of catalysts is assumed.



First, after the process of sulfurization, the transition metal oxides is converted to transition metal sulfides, MS_x, on which there exists two reactor(6), (7); on the TiO₂ there processes Claus reaction(8). The sulfur produced via the reactor(8) replenishes the sulfur vacancies of the reduced transition metal sulfide(MS_x) via the reaction(9). Additionally, because the transition metals bonding with sulfur is weaker than with oxygen, the sur-

face sulfur is more mobile and easier to bond with H₂ to produce sulfur vacancies and the intermediate-H₂S. The produced sulfur vacancies exchanging with surface sulfur and the Claus reaction on TiO₂ catalyst will enhance the formation of elemental sulfur; thus, the selectivity of elemental sulfur on these catalysts is much higher than on the Cr₂O₃-TiO₂ catalyst.

3.3 Stability test of CoO-TiO₂ catalyst

To test the stability of the catalyst for the reduction of SO₂ by NH₃ to elemental sulfur, we select Co₃O₄-TiO₂ catalyst to react under the above conditions continuously for 48 h since Co₃O₄-TiO₂ catalyst has the highest SO₂ conversion and the elemental sulfur selectivity in the seven types of catalyst we researched. The reaction temperature is accorded to 50% and 100% SO₂ conversion which is respectively 595°C and 740°C, and the accorded sulfur selectivities are 98% and 96%. The result is shown in Fig. 4.

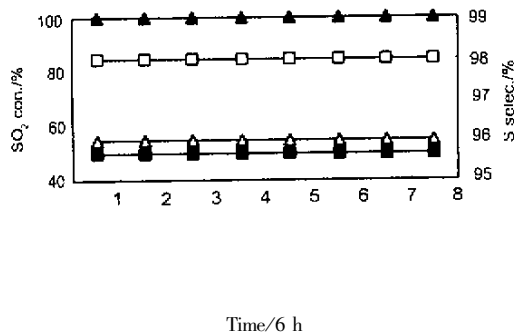


Fig. 4 Stability of Co₃O₄-TiO₂ catalyst for 48 h

3.4 Characterization by X-ray diffraction

Table 2 shows the structure change of the seven

Table 2 XRD results of mixed oxides catalysts before/after reaction

Catalysts	Phases before reaction	Phases after reaction
1# V-TiO ₂	V ₂ O ₅ , TiO ₂	V ₃ S ₄ , TiO ₂
2# Cr-TiO ₂	Cr ₂ O ₃ , TiO ₂	Cr ₂ O ₃ , TiO ₂
3# Mn-TiO ₂	MnO, TiO ₂	MnS, TiO ₂
4# Fe-TiO ₂	Fe ₂ O ₃ , TiO ₂	FeS, TiO ₂
5# Co-TiO ₂	Co ₃ O ₄ , TiO ₂	Co ₉ S ₈ , Co ₄ S ₃ , Co ₃ S ₄ , CoS ₂ , TiO ₂
6# Ni-TiO ₂	NiO, TiO ₂	NiS, TiO ₂
7# Cu-TiO ₂	CuO, TiO ₂	Cu ₂ S, CuS, TiO ₂

catalysts before and after the NH₃-SO₂ reaction. Except for Cr₂O₃-TiO₂ catalyst, other catalysts appear to experience sulfidation, i.e., Co₃O₄ is transformed to CoS₂ under reaction conditions.

4 Conclusions

Mixed oxides, MeO_x (Me-V, Cr, Mn, Fe, Co, Ni, Cu) with TiO_2 , have been developed for the SO_2 reduction by NH_3 to elemental sulfur. Compared to other catalysts that have been developed so far, the catalysts have higher activity for SO_2 conversion and selectivity to elemental sulfur. For the ammonia decomposition reaction, all the catalysts have shown high catalytic activity for the NH_3 conversion between a wide range from 300°C to 900°C; CoO-TiO_2 and $\text{Fe}_2\text{O}_3\text{-TiO}_2$ catalysts show higher catalytic activity than other catalysts at low temperature. For the NH_3 decomposition Claus reaction, the SO_2 conversion increased with the temperature; Characterization by XRD indicates that, during the $\text{NH}_3\text{-SO}_2$ reaction, the active phase of all the catalysts have experienced sulfidation except for $\text{Cr}_2\text{O}_3\text{-TiO}_2$ catalyst. It is probable that the most active phase is transition metal sulfides for the SO_2 reduction by NH_3 to elemental sulfur. The mechanism of the reduction of SO_2 by NH_3 to elemental sulfur over $\text{TiO}_2\text{-MeO}_x$ (Me-V, Cr, Mn, Fe, Co, Ni, Cu) is assumed.

References

[1] Makansi J. *Power*, 1993, **137**:23

- [2] John N A. *Appl. Catal. B*, 1992, **1**:221
 [3] Vincent K, Roland E M. *Chem. Eng.*, 1995, (2):74
 [4] Heisel M, Linde G. 1989, US, 4, 795, 620
 [5] Kretchmer R A, Hinrichs L M. 1986, US, 4, 612, 177
 [6] Chung J S. *Catal. Today*, 1997, **35**:37
 [7] Murdock D L. *Process Design, Dev.*, 1974, **13**:254
 [8] Moody D C, Ryan R R, Salazar K V. *J. Catal.*, 1981, **70**:221
 [9] Paik S C, Chung J S. *Appl. Catal. B*, 1995, **5**:233
 [10] Paik S C, Chung J S. *Appl. Catal. B*, 1996, **8**:267
 [11] Mulligan D J, Dberk D. *Ind. Eng. Chem. Res.*, 1989, **28**:926
 [12] Khallafalla S E, Hass L A. *J. Catal.*, 1972, **24**:115
 [13] Hibbert D B, Champbell R H. *Appl. Catal.*, 1988, **41**:273
 [14] Liu W, Sarofim A F. *Appl. Catal. B*, 1994, **4**:167
 [15] Ma J, Fang M. *J. Catal.*, 1996, **158**:251
 [16] Mulligan D J, Berk D. *Ind. Eng. Chem. Res.*, 1992, **31**:119.
 [17] Sarlis J, Berk D. *Chem. Eng. Common*, 1996, **140**:73
 [18] Goetz V N, Sood A, Kittredll J R. *Eng. Chem. Prod. Res. Dev.*, 1974, **13**:110

过渡金属氧化物催化剂上 NH_3 分解 Claus 反应机理研究

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摘要: 运用浸渍法制备了七种过渡金属氧化物催化剂. 对于 NH_3 分解反应均可获得很高的 NH_3 转化率; 对于 NH_3 分解 Claus 反应则可以获得较高的 SO_2 转化率和单质硫选择性. 通过比较发现 $\text{Co}_3\text{O}_4\text{-TiO}_2$ 和 $\text{Fe}_2\text{O}_3\text{-TiO}_2$ 催化剂的低温活性比较高. 经过 XRD 表征发现在 NH_3 分解 Claus 反应中, 催化剂的活性相可能是过渡金属硫化物. 结合活性评价和 XRD 表征结果提出了 NH_3 分解 Claus 反应的机理.

关键词: 共沉淀法; 过渡金属氧化物; 过渡金属硫化物; NH_3 分解 Claus 反应

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