

# Separate/simultaneous catalytic reduction of sulfur dioxide and/or nitric oxide by carbon monoxide over TiO<sub>2</sub>-promoted cobalt sulfides

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Received 23 April 2002; accepted 18 September 2002

## Abstract

TiO<sub>2</sub>-promoted cobalt sulfides, which were prepared by pre-sulfiding with H<sub>2</sub>S/H<sub>2</sub> the titanium–cobalt oxides prepared by coprecipitation method in order to get an intimate contact between them, were studied for the separate and simultaneous reduction of SO<sub>2</sub> and/or NO by CO. Physicochemical characterizations of the catalysts before and after reactions were conducted to disclose the reaction mechanism by means of XRD, BET, XPS and transient MS techniques. It is found that TiO<sub>2</sub>-promoted cobalt sulfides were more active catalysts for the reduction of SO<sub>2</sub> by CO than the mechanical mixtures of the components. There exists a strong synergistic promoted effect, which can be explained based on a COS enhanced redox mechanism proposed in the work. Furthermore, not only the addition of NO had little effect on this reaction, but also a combined reduction of SO<sub>2</sub> and NO by CO occurred in a gas mixture comprising very low concentrations of them. The reduction of NO is explained by a NO decomposition mechanism over sulfides with the formation of by-product, SO<sub>2</sub>, based on the MS results. There also exists a synergistic effect between cobalt sulfide and TiO<sub>2</sub>. The produced SO<sub>2</sub> can further be reduced over TiO<sub>2</sub> to sulfur, which might spill over to cobalt sites to regenerate cobalt sulfide. The SO<sub>2</sub> + NO + CO reaction was proposed to proceed via two separate reactions of SO<sub>2</sub> + CO and NO decomposition. However, the two reactions are interrelated. The reaction between CO and cobalt sulfide to produce COS intermediate is a necessity for the further reduction reaction of SO<sub>2</sub> on TiO<sub>2</sub>; while SO<sub>2</sub>, one of the products of NO decomposition on cobalt sulfide, is recovered to sulfur on TiO<sub>2</sub> by SO<sub>2</sub> + CO reaction. Lastly, CO<sub>2</sub> was found to promote the production of COS, but has little effect at levels around 1000 ppm. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** SO<sub>2</sub>; CO; NO; Cobalt sulfide; TiO<sub>2</sub>; Catalytic reduction

## 1. Introduction

Sulfur dioxide (SO<sub>2</sub>), nitric oxide (NO) and carbon monoxide (CO) are three major air pollutants. They are usually emitted as by-products of combustion

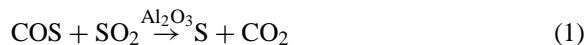
processes from industrial, transportation and domestic activities and, in many occasions, simultaneously. Various processes are now under operation or research to remove SO<sub>2</sub> and NO separately or simultaneously [1]. Irrespective of the commercialization of numerous wet-scrubbing processes [1], dry flue gas desulfurization is highly desirable. Compared to the oxidation of SO<sub>2</sub> into SO<sub>3</sub> and further production of dilute sulfur acid, direct catalytic reduction of SO<sub>2</sub>

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to elemental sulfur by various reductants such as CO, CH<sub>4</sub> or synthesis gas is emerging as a promising and high-effective technique [2]. However, the use of CH<sub>4</sub> as a reducing agent generally results in a much higher reaction temperature than CO [2,3]. Considering that the boiling point of elemental sulfur is 444.6 °C, the decrease of reaction temperature would become important and cost-effective.

The direct reduction of SO<sub>2</sub> by CO to elemental sulfur under dry conditions has been studied for a long time. Early developed are alumina-supported transition metals and oxides [4,5], but production of COS, which is much harmful than SO<sub>2</sub>, usually proceeds to a substantial extent on these catalysts. The COS formation could be lowered by using the perovskite LaTiO<sub>3</sub> [6], and even completely removed over La<sub>0.7</sub>Sr<sub>0.3</sub>CoO<sub>3</sub> catalyst [7]. Unfortunately, the perovskite-type catalysts lost their structure under reaction conditions. La<sub>2</sub>O<sub>2</sub>S was also reported to be active and selective above 500 °C [8,9]. Recently, Zhuang et al. [10] reported that complete conversion of SO<sub>2</sub> with negligible COS formation was achieved at 300 °C with CoMo/Al<sub>2</sub>O<sub>3</sub>. They suggested a COS intermediate mechanism:



Because this reaction is more facile over titania than alumina [11], titania is supposed to be more suitable for the SO<sub>2</sub> + CO reaction. However, reports of Co<sub>3</sub>O<sub>4</sub>-TiO<sub>2</sub> mixed oxides [12] showed that complete SO<sub>2</sub> conversion took place nearly 100 °C higher than CoMo/Al<sub>2</sub>O<sub>3</sub> catalyst. The authors [12] also proposed the migration of intermediate, COS, from CoS<sub>2</sub> to TiO<sub>2</sub>, which then reacts with SO<sub>2</sub> or preferentially with TiO<sub>2</sub> to generate oxygen vacancies. Nevertheless, it is evident that simple mechanical mixture cannot provide a good interparticle intimacy allowing for very rapid diffusion between particles of any formed gas-phase intermediate. This was substantiated by a higher activity for the SO<sub>2</sub> + CO reaction over the pelletized catalysts with small particle sizes of components of iron powder and alumina than their simple mixture with large particle sizes [4].

The removal of NO has been extensively studied in the recent years for environmental protection. NO reduction by CO is one of the fundamental reactions

in the presence of CO, especially for the so-called three-way automotive catalysts (TWC). This reaction has been studied over noble metals [13–15], transition metals [16,17], perovskites [18,19] and mixed oxides [20]. However, few literatures have been concerned with the effects of SO<sub>2</sub> on the reaction. Since fuels often contain residual sulfur, any practical catalyst needs to be resistant to SO<sub>2</sub>. In general, SO<sub>2</sub> is thought to be the most important poison for lean NO<sub>x</sub> catalysts because of competing adsorption on the active sites of the catalyst with nitrogen oxide [21]. For instance, Gandhi and Shelef [22] found that the activity of NO reduction to N<sub>2</sub> over the γ-Al<sub>2</sub>O<sub>3</sub> supported Pt and Pd catalyst was completely suppressed by the presence of very low levels of SO<sub>2</sub>.

As to the simultaneous removal of SO<sub>2</sub> and NO, wet lime/limestone scrubbers for desulfuration and selective catalytic reduction of nitrogen oxides with NH<sub>3</sub> have been commercialized [23], but the combination processes are complicated and produce sufficient amount of solid/liquid wastes that require further disposal. Therefore, the dry type sorbent/catalyst for simultaneous removal of SO<sub>2</sub> and NO was developed [24–26]. Since SO<sub>2</sub> is oxidized to SO<sub>3</sub> and then fixed on the catalysts as sulfates in the process, the sulfated catalyst must be periodically removed for regeneration and repeated use. In these regards, direct catalytic reduction of SO<sub>2</sub> and NO to elemental sulfur and N<sub>2</sub> respectively by CO in a one-way process has been under development. Kittrell and coworkers [27–29] reported that alumina-supported transition metals were effective catalysts. Unfortunately substantial amounts of undesirable COS formed are required to be eliminated in another catalyst bed. Recently, La<sub>2</sub>O<sub>2</sub>S-CoS<sub>2</sub> [30] and ceria-based oxide catalysts [3] have also been reported to be active. Especially for the later, at 500 °C, in the presence of high content of water, sulfur yield and NO conversion were 77 and 100%, respectively. However, both of the two kinds of catalysts suffer from a high reaction temperature.

It is known that both CoS<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> have negligible activity for the SO<sub>2</sub> reduction by CO to elemental sulfur [8,12]. In a recent letter [31], we first reported cobalt sulfide and TiO<sub>2</sub>-promoted cobalt sulfide catalysts for NO decomposition and reduction by CO. Interestingly, the simultaneous catalytic reduction of NO and SO<sub>2</sub> by CO was conducted over TiO<sub>2</sub>-promoted cobalt sulfides. In this paper, the detailed results will

be reported, and especial attention is focused on the mechanism aspects of the reaction system.

## 2. Experimental

### 2.1. Catalyst preparation

TiO<sub>2</sub>-promoted cobalt oxides (TiO<sub>2</sub>:Co<sub>3</sub>O<sub>4</sub> = 1:4, 1:1, 4:1, weight ratio) were prepared by coprecipitation method. The stoichiometric mixed solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Ti(SO<sub>4</sub>)<sub>2</sub> and that of ammonia were simultaneously dropped into de-ionized water under vigorous agitation, and then the solution was aged for 30 min. The resultant precipitates were dried at 120 °C over night and calcined at 500 °C for 5 h in air. Pure titanium and cobalt oxides were also prepared by the same procedures mentioned above, and by using one of the precursors. An oxide catalyst was in situ sulfided in a flow of 5 vol.% H<sub>2</sub>S in H<sub>2</sub> gas at 400 °C for 1 h, then cooled down to room temperature with Ar purge to eliminate adsorbed H<sub>2</sub>S.

### 2.2. Reaction studies

The reaction was carried out in a fixed-bed flow reactor. The 0.3 g of 40–60 mesh oxide catalyst powder was packed in the reactor and in situ pre-sulfided. The model flue gases employed are shown in Table 1. Unless otherwise specified, the gas flow rate was held constant at 40 cm<sup>3</sup>/min. In some experiments, CO<sub>2</sub> was added to the feed gas. The products in the effluent stream were analyzed by a quadruple mass spectrometry (LZL-204, Beijing Analytical Instrument Plant). Elemental sulfur was condensed at room temperature. The SO<sub>2</sub> and NO conversions were calculated on the basis of differences between the inlet and outlet SO<sub>2</sub> and NO intensities, respectively. The data for

steady-state activity of the catalysts were collected after 1.5 h testing.

### 2.3. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku D/max 2000 diffractometer employing Cu K $\alpha$  radiation.

The BET specific surface area was measured with a Micromeritics ASAP-2010 instrument.

X-ray photoelectron spectroscopy (XPS) analyses were performed with a VG ESCALAB5 system.

The transient response technique was also used to elucidate the reaction mechanism. First, Ar flowed through the catalyst at the desired temperature, and the concentration step change Ar/NO + Ar, Ar/NO + CO + Ar, Ar/SO<sub>2</sub> + NO + CO + Ar was then enforced by switching a four-way valve.

The mass-to-charge (*m/e*) ratios were monitored by MS as follows: SO<sub>2</sub> (64), NO (30), CO and N<sub>2</sub> (28), CO<sub>2</sub> and N<sub>2</sub>O (44), NO<sub>2</sub> (46), COS (60).

## 3. Results

### 3.1. XRD analysis of fresh catalysts

Fig. 1 shows the X-ray diffraction patterns for titanium–cobalt oxides (1:4, 1:1, 4:1) calcined at 500 °C for 5 h. For comparative purposes, the XRD patterns of pure titanium and cobalt oxides at the same preparation procedure were also included, which showed the crystallite structures of Co<sub>3</sub>O<sub>4</sub> and anatase TiO<sub>2</sub>, respectively. It was noted that no diffraction peaks assigned to TiO<sub>2</sub> were observed in a 1:4 sample, suggesting either a high dispersion of TiO<sub>2</sub> or an incorporation of titanium ions into Co<sub>3</sub>O<sub>4</sub>

Table 1

Typical SO<sub>2</sub> and NO compositions of flue gas emitted from combusting coal with sulfur of 1–3 wt.% and model flue gas employed, GHSV = 8000 h<sup>-1</sup>, balance gas Ar

Components	Actual flue gas, [32] (ppm)	Feed compositions employed (ppm)		
		Separate reduction of SO <sub>2</sub> by CO to S	Separate reduction of NO by CO to N <sub>2</sub>	Simultaneous reduction of SO <sub>2</sub> and NO to S and N <sub>2</sub>
SO <sub>2</sub>	200–2000	1050	–	525
NO	200–2000	–	1025	520
CO		2085	2085	2085

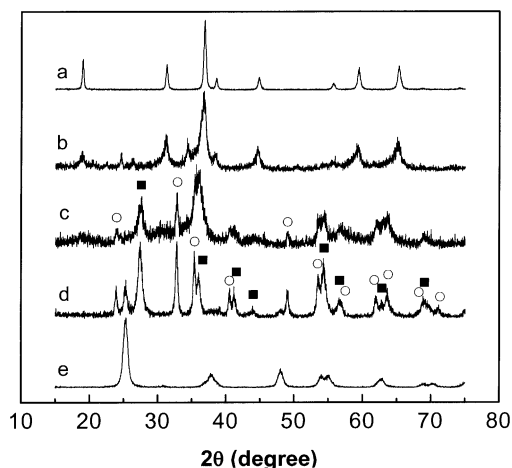


Fig. 1. XRD patterns of fresh catalysts. (a)  $\text{Co}_3\text{O}_4$ ; (b)  $\text{TiO}_2:\text{Co}_3\text{O}_4 = 1:4$ ; (c)  $\text{TiO}_2:\text{Co}_3\text{O}_4 = 1:1$ ; (d)  $\text{TiO}_2:\text{Co}_3\text{O}_4 = 4:1$ ; (e) anatase  $\text{TiO}_2$ . (■) Rutile, (○)  $\text{CoTiO}_3$ .

lattice. On the other hand, rutile rather than anatase  $\text{TiO}_2$  and a new phase,  $\text{CoTiO}_3$ , were formed in a 1:1 sample. This is very important, because pure  $\text{TiO}_2$  calcined at the same temperature showed anatase, as shown in Fig. 1e. The addition of cobalt ions promoted the transformation of anatase to rutile [33], and hence increased the oxygen vacancies in the bulk [34]. While oxygen vacancy and mobility are thought to be important properties for the reduction of both  $\text{SO}_2$  [35] and  $\text{NO}$  [36] by  $\text{CO}$ . In addition to rutile and  $\text{CoTiO}_3$ , a small amount of anatase was formed in a 4:1 sample. The BET surface areas of all samples were present in Table 2.

### 3.2. Activity of $\text{TiO}_2$ -promoted cobalt sulfides

#### 3.2.1. Separate reduction of $\text{SO}_2$ by $\text{CO}$

$\text{SO}_2$  and  $\text{CO}$ , at a low concentration, did not react with each other in absence of a catalyst even at temperatures as high as  $950^\circ\text{C}$  [4]. As mentioned above,

Table 2

BET areas of the catalysts prepared

Samples (weight ratio)	BET surface area ( $\text{m}^2/\text{g}$ )
$\text{Co}_3\text{O}_4$	23
$\text{TiO}_2:\text{Co}_3\text{O}_4 = 1:4$	64
$\text{TiO}_2:\text{Co}_3\text{O}_4 = 1:1$	53
$\text{TiO}_2:\text{Co}_3\text{O}_4 = 4:1$	54
$\text{TiO}_2$	109

neither  $\text{Co}_3\text{O}_4$  nor  $\text{CoS}_x$  was active for the reaction (8, 12), but rutile  $\text{TiO}_2$  was confirmed to show activity only above  $400^\circ\text{C}$  [12].

Fig. 2 shows the  $\text{SO}_2$  conversion (a), selectivity towards elemental sulfur (b) and  $\text{COS}$  formation (c) as a function of temperature for  $\text{TiO}_2$ -promoted cobalt sulfides in the separate reduction of  $\text{SO}_2$  by  $\text{CO}$ . It is evident that adding 20 wt.%  $\text{TiO}_2$  (1:4 sample) to the inactive  $\text{Co}_3\text{O}_4$  ( $\text{CoS}_x$ ) improved the catalytic activity significantly. At  $300^\circ\text{C}$ , 86%  $\text{SO}_2$  conversion and 100% selectivity to sulfur with no  $\text{COS}$  formation were observed. The maximum activity was obtained with 50 wt.%  $\text{TiO}_2$  in the catalyst (1:1 sample). Catalyst with a high content of  $\text{TiO}_2$  (4:1 sample), which is known to present a small proportion of anatase phase, was found to be less active at temperatures below  $400^\circ\text{C}$ . However, the  $\text{SO}_2$  conversion will be higher than that of 1:4 sample when the reaction temperature was above  $400^\circ\text{C}$ , but still less than that of 1:1 sample.

#### 3.2.2. NO decomposition and reduction by $\text{CO}$ over cobalt sulfide

MS signals during the first contact with  $\text{NO}$  of cobalt sulfide ( $\text{CoS}_x$ ) at  $350^\circ\text{C}$  are plotted in Fig. 3a. The instantaneous  $\text{N}_2$  and  $\text{N}_2\text{O}$  response curves showed that cobalt sulfide was active in  $\text{NO}$  decomposition in the absence of  $\text{CO}$  in the gas phase. However the sulfur-containing species,  $\text{SO}_2$  ( $m/e = 64$ ), was observed. The delayed response of  $\text{SO}_2$  indicated that the oxygen from  $\text{NO}$  decomposition was first taken up by the highly reduced catalyst, and then reacted with sulfur species on the catalyst surface, that is the only known reservoir of sulfur for the solid. The catalytic activity of  $\text{NO}$  decomposition into  $\text{N}_2$  decreased with time. Introducing the reducing agent,  $\text{CO}$ , although cannot completely eliminate the formation of  $\text{SO}_2$  (Fig. 3b), a steady state with more than 90%  $\text{NO}$  conversion at  $350^\circ\text{C}$  was maintained for a longer time. No  $\text{COS}$  formation was due to the depletion of sulfur species available to react with  $\text{CO}$ .

#### 3.2.3. NO decomposition and reduction by $\text{CO}$ over $\text{TiO}_2$ -promoted cobalt sulfides after $\text{SO}_2 + \text{CO}$ reaction

Fig. 4 shows the transient MS results of  $\text{TiO}_2$ -promoted cobalt sulfides after  $\text{SO}_2 + \text{CO}$  reaction towards  $\text{NO}$  decomposition (a) and  $\text{NO} + \text{CO}$  reaction (b, c and d). In Fig. 4a, a rather long steady state

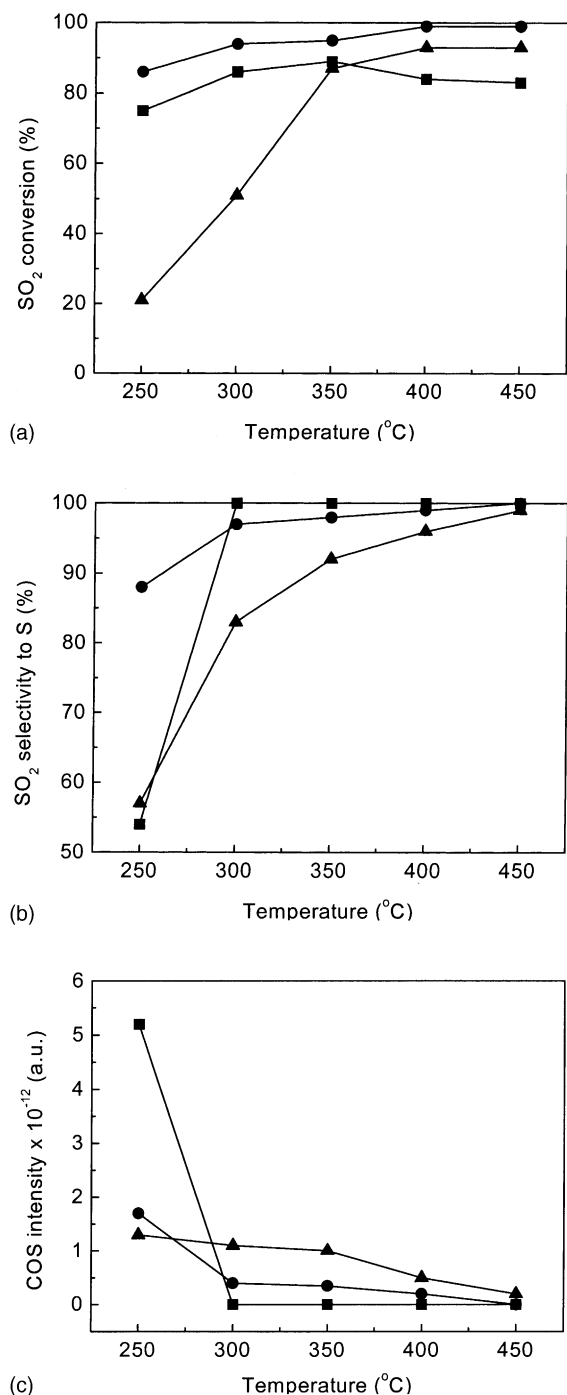


Fig. 2. SO<sub>2</sub> conversion (a), selectivity to elemental sulfur (b) and COS formation (c) as a function of temperature for pre-sulfided Ti-Co oxides (SO<sub>2</sub> 1050 ppm; CO 2085 ppm; Ar, GHSV = 8000 h<sup>-1</sup>). (■) 1:4; (●) 1:1; (▲) 4:1.

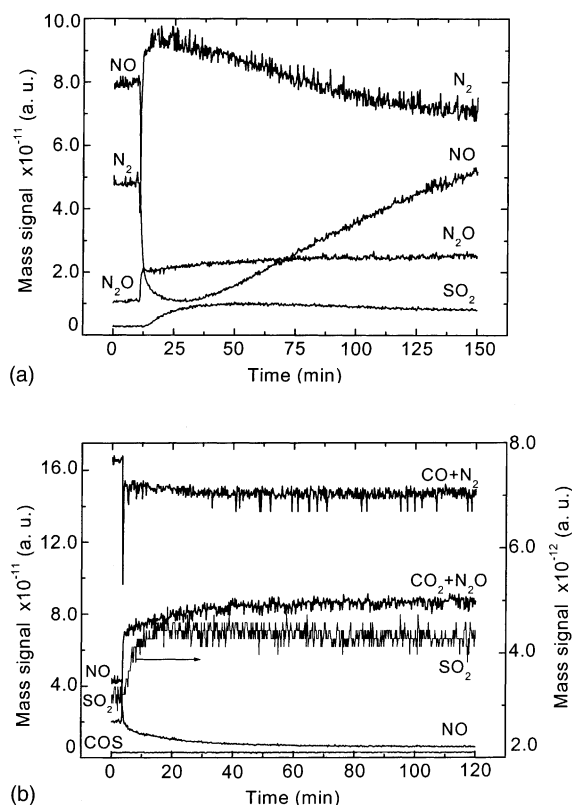


Fig. 3. Transient response curves obtained over cobalt sulfide at 350 °C after switching from Ar to (a) NO+Ar; (b) NO+CO+Ar.

with high conversion of NO was achieved, although SO<sub>2</sub> by-product was formed as in the case of cobalt sulfides (Fig. 3). Compared with single cobalt sulfide, the reduction of NO by CO over TiO<sub>2</sub>-promoted cobalt sulfides was detected with the substitute of SO<sub>2</sub> by COS formation. As shown in Fig. 4b–d, even when the CO/NO molar ratio was one time higher than the stoichiometric value for the NO + CO reaction, the production of COS is nearly negligible for 1:4 sample at the reaction temperature of 400 °C. It is reasonable to deduce that TiO<sub>2</sub>-promoted cobalt sulfide catalysts were comparatively stable at optimum reaction conditions, for example, at the stoichiometric ratio and suitable reaction temperatures. Fig. 5 shows NO conversion towards NO + CO reaction over TiO<sub>2</sub>-promoted cobalt sulfides after SO<sub>2</sub> + CO reaction. It is notable that NO conversions were nearly independent of the TiO<sub>2</sub> content. Therefore, the activity may only be associated with sulfide, while

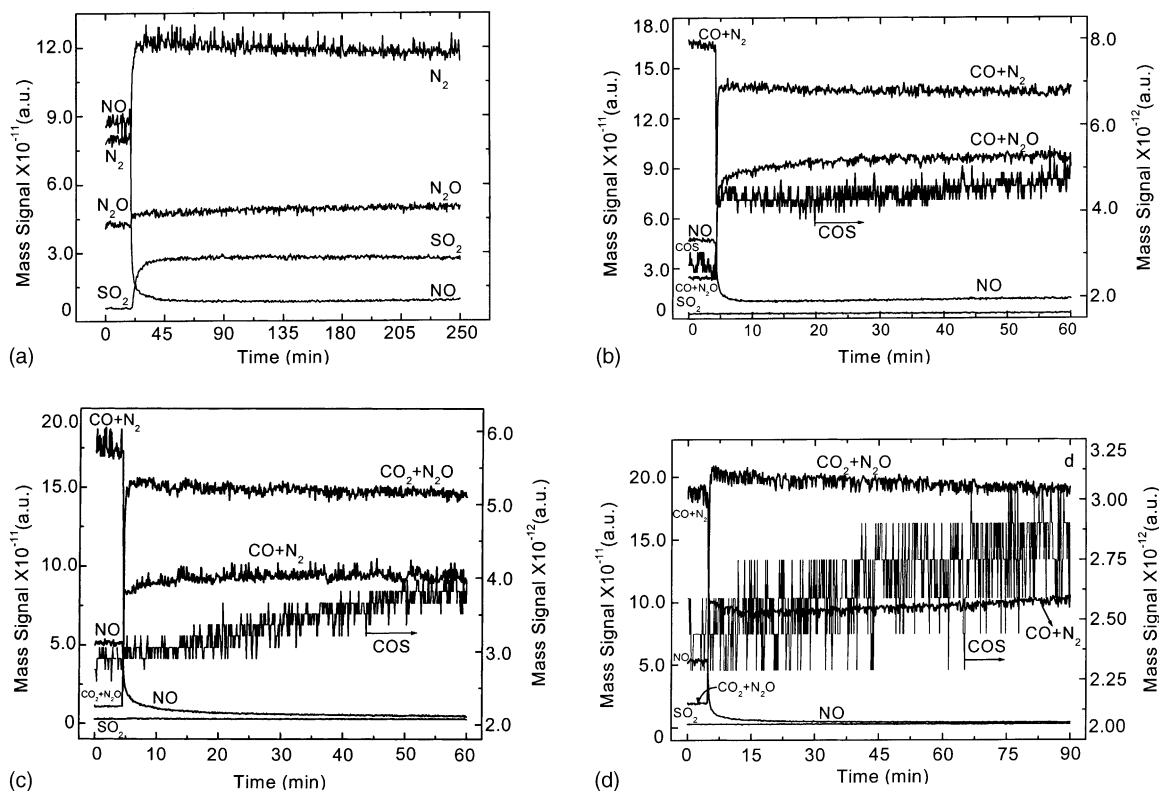


Fig. 4. Transient response curves obtained over 1:1 sample (after  $\text{SO}_2 + \text{CO}$  reaction) at 350 °C after switching from Ar to (a)  $\text{NO} + \text{Ar}$ ; (b)  $\text{NO} + \text{CO} + \text{Ar}$  over samples after  $\text{SO}_2 + \text{CO}$  reaction: 4:1 sample at 250 °C; (c) 1:1 sample at 350 °C; (d) 1:4 sample at 400 °C.

considering the absence of  $\text{SO}_2$  formation on these  $\text{TiO}_2$ -promoted sulfides,  $\text{TiO}_2$  is supported to play an important role in the removal of  $\text{SO}_2$ .

#### 3.2.4. Simultaneous reduction of $\text{SO}_2$ and $\text{NO}$ by $\text{CO}$

According to the observations on the separate  $\text{SO}_2 + \text{CO}$  and  $\text{NO} + \text{CO}$  reactions, at first, 1:1 sample was chosen for further  $\text{SO}_2 + \text{NO} + \text{CO}$  reactions. Fig. 6a shows the  $\text{SO}_2$  and  $\text{NO}$  conversions and  $\text{SO}_2$  selectivity towards elemental sulfur versus temperature. Even at 250 °C, 71%  $\text{NO}$  conversion and 84%  $\text{SO}_2$  conversion with a selectivity to sulfur of 98% were achieved. However, because the amount of labile lattice sulfur that is available for the reaction with  $\text{CO}$  increased in proportion to the temperature increase, and  $\text{CO}$  is more than the stoichiometric value for the reduction of both  $\text{SO}_2$  and  $\text{NO}$  ( $\text{SO}_2 + 2\text{CO} = \text{S} + 2\text{CO}_2$ ;  $2\text{NO} + 2\text{CO} = \text{N}_2 + 2\text{CO}_2$ ), much  $\text{COS}$  formed at higher temperature, as shown in Fig. 6b,

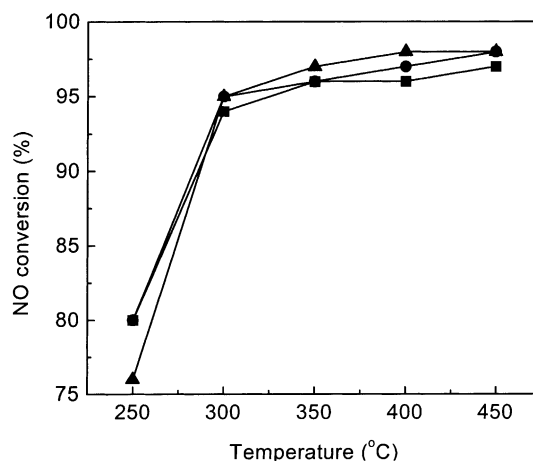


Fig. 5.  $\text{NO}$  conversion towards  $\text{NO} + \text{CO}$  reaction over  $\text{TiO}_2$ -promoted cobalt sulfides after  $\text{SO}_2 + \text{CO}$  reaction as a function of temperature ( $\text{NO}$ , 1025 ppm;  $\text{CO}$ , 2085 ppm; Ar,  $\text{GHSV} = 8000 \text{ h}^{-1}$ ). (■) 4:1; (●) 1:1; (▲) 1:4.

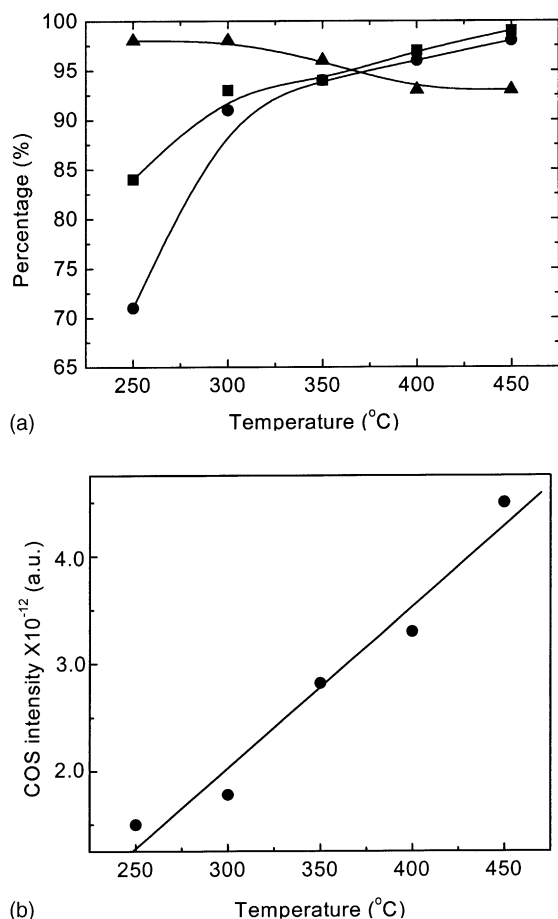


Fig. 6. SO<sub>2</sub> conversion, selectivity to elemental sulfur and NO conversion (a), COS formation (b) as a function of temperature for 1:1 catalyst after SO<sub>2</sub> + CO reaction (SO<sub>2</sub> 525 ppm; NO 520 ppm; CO 2085 ppm; Ar, GHSV = 8000 h<sup>-1</sup>). (■) SO<sub>2</sub> conversion; (▲) SO<sub>2</sub> selectivity to elemental sulfur; (●) NO conversion.

which resulted in a decrease of SO<sub>2</sub> selectivity to sulfur.

By balancing the conversion and selectivity of 1:1 sample, we evaluate the other two samples towards SO<sub>2</sub> + NO + CO reactions at 350 and 400 °C. Results were summarized in Table 3. The data was collected after 12 h-long test, indicating the excellent activity and stability of these catalysts in the present reaction conditions. Fig. 7 shows the activation process of 1:4 sample at 350 °C in SO<sub>2</sub> + NO + CO reaction. Since there are already plenty of atomic sulfur on the catalyst [37], COS was observed to form through the re-

Table 3  
SO<sub>2</sub> and NO conversions and SO<sub>2</sub> selectivity to elemental sulfur for 1:4 and 4:1 catalysts

Samples	Temperature (°C)	SO <sub>2</sub> conversion (%)	NO conversion (%)	SO <sub>2</sub> selectivity to S
1:4	350	93	95	100
4:1	350	91	94	99
4:1	400	96	95	85

SO<sub>2</sub>, 525 ppm; NO, 520 ppm; CO, 2085 ppm; Ar, GHSV = 8000 h<sup>-1</sup>.

action of S and CO, which increased gradually after a delay response. About 40 min later, the accumulated atomic sulfur was nearly used up. A steady state with the balance of COS formation and COS consumption through SO<sub>2</sub> + COS reaction was constructed, COS decreased nearly to zero.

### 3.3. CO<sub>2</sub> effect

CO<sub>2</sub> is produced by the present reaction and often present in the feed gas stream as main combustion product. Thus, its effect on catalysts activity and selectivity was briefly checked. As show in Table 4, addition of about 20 vol.% CO<sub>2</sub> into the reactant gas mixture at 400 °C cannot cause a significant decrease in both SO<sub>2</sub> and NO conversions, while SO<sub>2</sub> selectivity to sulfur decreased dramatically from 93 to 16%. This is because CO<sub>2</sub> has a tendency to lower the SO<sub>2</sub> conversion and promote the production of COS (Table 4). The conversion and selectivity were restored by decreasing CO<sub>2</sub> concentration to 0.1 vol.%.

### 3.4. XRD analysis of used catalysts

Fig. 8 shows the XRD patterns of the catalysts after pre-sulfiding or reactions. It is known that after pre-sulfiding in a flow of H<sub>2</sub>S/H<sub>2</sub> gas, the oxide catalysts will turn into low-sulfur-containing sulfides [14], as the XRD pattern of pre-sulfided Co<sub>3</sub>O<sub>4</sub>, which showed a mixture of Co<sub>9</sub>S<sub>8</sub>, Co<sub>6</sub>S<sub>5</sub>, and Co<sub>4</sub>S<sub>3</sub> (Fig. 8a). The low-sulfur-containing sulfides were then transformed into CoS<sub>2</sub> after the SO<sub>2</sub> + CO or SO<sub>2</sub> + NO + CO reactions. This was confirmed by Fig. 8b and c. For 1:1 sample, a small amount of CoS<sub>2-x</sub> (e.g. Co<sub>3</sub>S<sub>4</sub>) in addition to the major phases CoS<sub>2</sub> and TiO<sub>2</sub> were detected. It is also found that

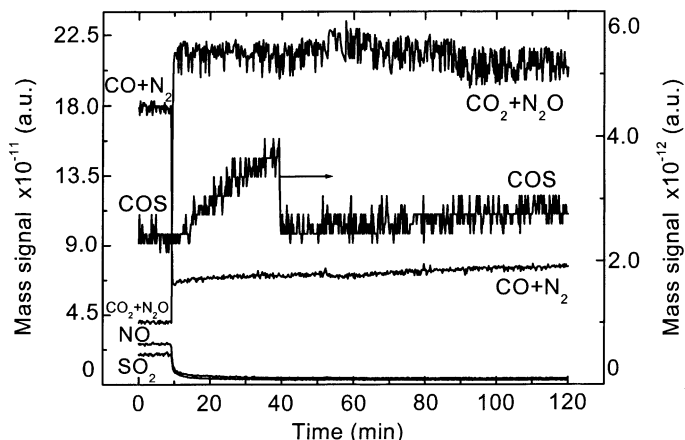


Fig. 7. Transient response curves obtained over 1:4 catalyst (after  $\text{SO}_2 + \text{CO}$  reaction) at  $350^\circ\text{C}$  after switching from Ar to 525 ppm  $\text{SO}_2 + 520$  ppm NO + 2085 ppm CO + Ar.

Table 4  
 $\text{CO}_2$  effects on activity and  $\text{SO}_2$  selectivity to sulfur for 1:1 catalyst at  $400^\circ\text{C}$

$\text{CO}_2$ content (vol.%)	$\text{SO}_2$ conversion (%)	NO conversion (%)	$\text{SO}_2$ selectivity to sulfur (%)	COS intensity (a.u.)
0	97	96	93	$0.1\text{E} - 12$
0.1	97	94	93	$0.1\text{E} - 12$
10	88	80	23	$3.0\text{E} - 12$
20	80	73	16	$5.7\text{E} - 12$

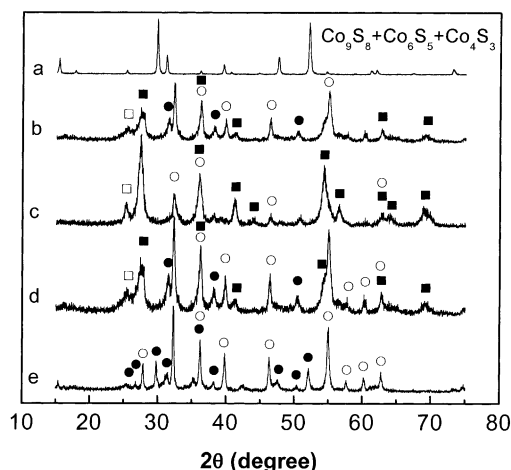


Fig. 8. XRD patterns of used catalysts. (a) Pre-sulfided  $\text{Co}_3\text{O}_4$ ; (b) 1:1 sample after  $\text{SO}_2 + \text{CO}$  reaction; (c) 4:1 sample after  $\text{SO}_2 + \text{NO} + \text{CO}$  reaction; (d) 1:1 sample after  $\text{SO}_2 + \text{NO} + \text{CO}$  reaction; (e) 1:4 sample after  $\text{SO}_2 + \text{NO} + \text{CO}$  reaction. (○)  $\text{CoS}_2$ ; (■) rutile; (●)  $\text{CoS}_{2-x}$ ; (□) anatase.

a small fraction of anatase  $\text{TiO}_2$  was present in the used 1:1 sample (Fig. 8b and d), suggesting the  $\text{CoTiO}_3$  phase dissociation into anatase rather than rutile during pre-sulfiding by comparing Fig. 1c and Fig. 8b and d. As in Fig. 1b, no  $\text{TiO}_2$  phase was detected in the used 1:4 sample (Fig. 8e) except that  $\text{Co}_3\text{O}_4$  has transformed to  $\text{CoS}_2$  and a small amount of low-sulfur-containing cobalt sulfide,  $\text{CoS}_{2-x}$ .

### 3.5. XPS analysis

The qualitative surface compositional analysis of the 1:4 sample by XPS is given in Table 5. The atomic

Table 5  
 Surface compositional analysis of 1:4 catalyst by XPS

Atomic ratio	Ti/Co	Ti/O	Co/S
Bulk <sup>a</sup>	0.25	0.14	–
Fresh	0.43	0.081	–
Used	0.70	0.091	0.507

<sup>a</sup> Based on stoichiometry.



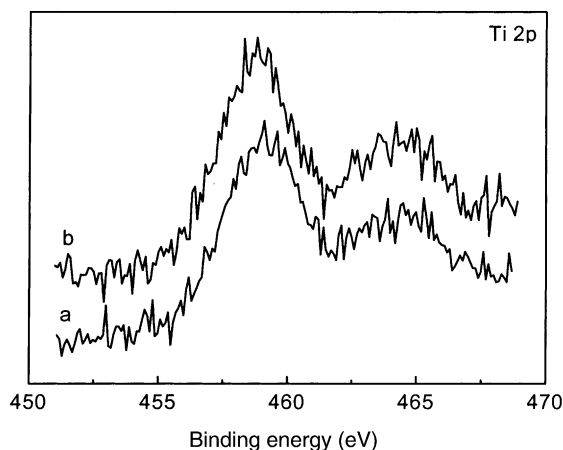


Fig. 9. XPS spectra (Ti 2p) of 1:4 sample. (a) Fresh; (b) after  $\text{SO}_2 + \text{NO} + \text{CO}$  reaction.

ratio of Ti/Co on fresh catalyst was about 0.43, almost double than the stoichiometric one. This suggests that the catalyst surface is segregated of titanium. However, after use further segregation took place, as indicated by the ratio of 0.7. The Ti/O and Co/S ratios after  $\text{SO}_2 + \text{NO} + \text{CO}$  reaction were also shown in Table 5. Based on the value of Co/S, it is calculated that the cobalt sulfide on the catalyst surface can be expressed as  $\text{CoS}_{1.97}$ , which is coincided with the XRD result of the used 1:4 sample (Fig. 8e).

Fig. 9 shows the XPS spectra of Ti 2p of the fresh and used 1:4 sample. The binding energies agree well with  $\text{TiO}_2$  [38].

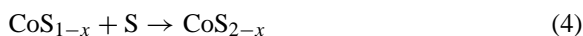
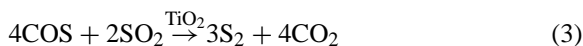
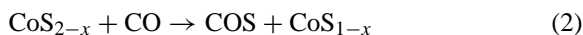
## 4. Discussion

### 4.1. Separate reduction of $\text{SO}_2$ by CO

According to the above results on catalytic activity, it is evident that there exists synergism for the reduction of  $\text{SO}_2$  by CO on  $\text{TiO}_2$ -promoted cobalt sulfides. On the one hand, the XRD patterns of fresh catalysts show that pure  $\text{TiO}_2$  calcined at  $500^\circ\text{C}$  was anatase, but the addition of small proportions of cobalt promoted most of  $\text{TiO}_2$  transformation from anatase to rutile, in conformity with the previous results [33]. Combined with the evidence of titanium segregation on the 1:4 catalyst surface after use, it is easy to think that rutile  $\text{TiO}_2$  plays an important role in the  $\text{SO}_2 + \text{CO}$  reaction. On the other hand, the 1:1 and

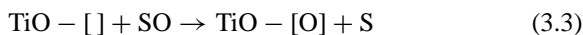
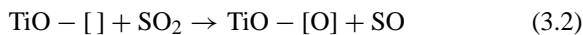
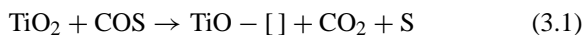
4:1 samples shows negligible catalytic activity below  $400^\circ\text{C}$  before pre-sulfiding, which suggests that the coexistence of cobalt sulfides is a necessary condition for the reduction reaction to be effective.

As mentioned in the XRD patterns of used catalysts, low-sulfur-containing cobalt sulfides after pre-sulfiding will be resulfidized in the process of  $\text{SO}_2 + \text{CO}$  reaction, so all or most cobalt sulfides after use were present in  $\text{CoS}_2$  phase. Furthermore, on the basis of COS formation and a small amount of  $\text{CoS}_{2-x}$  involving in  $\text{CoS}_2$ , it is reasonable to believe that the reduction of  $\text{CoS}_2$  by CO to the products of COS and  $\text{CoS}_{2-x}$  has established an equilibrium with the foregoing resulfidization process. The 4:1 sample, containing 20 wt.% of  $\text{Co}_3\text{O}_4$  before pre-sulfiding, only showed patterns of  $\text{TiO}_2$  and  $\text{CoS}_2$ , which is because the concentration of low-sulfur-containing sulfides was too low to be detected by XRD analysis. Hence, the  $\text{SO}_2 + \text{CO}$  reaction was converted to the  $\text{SO}_2 + \text{COS}$  reaction. The COS in turn is better than CO as a reductant for the reduction of  $\text{SO}_2$  to sulfur with  $\text{TiO}_2$  serving as the catalyst [12]. Therefore, the overall reaction follows the COS intermediate mechanism as proposed by [9,39]



$$(0 \leq x < 2)$$

Reactions (4) and (5) are resulfidization processes. For reaction (3), Kim et al. [12] proved that it proceeded via a redox mechanism:



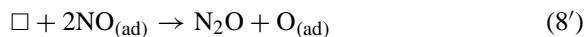
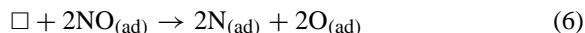
Overall, CO first reacts with  $\text{CoS}_{2-x}$  to form an intermediate, COS, which reduces  $\text{SO}_2$  to  $\text{CO}_2$  and elemental sulfur over  $\text{TiO}_2$  via a redox mechanism, and the formed sulfur then resulfidizes CO reduced cobalt sulfides. We call it COS intermediate enhanced redox mechanism. The important aspect of this mechanism lies in the fact that  $\text{SO}_2$  can easily react with COS

at very low temperatures over  $\text{TiO}_2$  to produce sulfur, which is otherwise impossible for CO. The mechanism is different from that of some mechanical mixture catalysts [8,12]. The produced intermediate COS and product sulfur need not migrate a long distance from  $\text{CoS}_{2-x}$  to  $\text{TiO}_2$  to react with  $\text{SO}_2$  and from  $\text{TiO}_2$  to  $\text{CoS}_{2-x}$  to regenerate  $\text{CoS}_{2-x}$ , respectively, due to an intimate contact between them brought by coprecipitation.

In Ref. [10], Zhuang et al. reported that ca. 90%  $\text{SO}_2$  conversion was achieved at 250 °C over pre-sulfided  $\text{CoMo}/\text{Al}_2\text{O}_3$  catalyst. Although they did not give a definite mechanism, as COS intermediate was suggested to involve in the  $\text{SO}_2 + \text{CO}$  reaction, it is rational to deduce that it proceeds via a COS intermediate mechanism, as indicated by reaction (1). Conversely, a recent paper [11] has shown that  $\text{Al}_2\text{O}_3$  was nearly inactive to the  $\text{SO}_2 + \text{COS}$  reaction at 250 °C. In contrast,  $\text{TiO}_2$  showed a good activity at the same reaction conditions, though COS conversion from an initial value of 90 to 60% after a reaction of 4 h. The above result was another evidence for our proposed mechanism.

#### 4.2. NO decomposition and reduction by CO on cobalt sulfide and $\text{TiO}_2$ -promoted cobalt sulfides

From Figs. 3a and 4a, it is observed that the products of NO decomposition on cobalt sulfide catalysts were  $\text{N}_2$ ,  $\text{N}_2\text{O}$  intermediate and  $\text{SO}_2$  by-product, while  $\text{NO}_2$  and  $\text{O}_2$  were not detected. Accordingly, a  $\text{N}_2\text{O}$  intermediate mechanism may be suggested:



where  $\square$  is sulfur vacancy and  $*\text{S}$  is a sulfide ion in the lattice. Sulfur vacant sites will induce the dissociation of NO, whose function is analogous to the oxygen vacancies in transition oxides. The activity of NO decomposition decreased with the decrease of the  $\text{SO}_2$  signal with time-on-stream, suggesting the consumption of lattice sulfur or the oxidation of the catalyst.

$\text{N}_2\text{O}$  can be formed by the reaction of NO with N dissociated from NO (Eq. (8)) or by decomposition of an NO dimer (Eq. (8')), however the later can be excluded on the basis of the fact that  $\text{N}_2\text{O}$  yield did not decrease with the depletion of sulfur vacancies. As shown in Fig. 3b, introducing CO retards the oxidation of the catalyst by the reaction of CO and  $\text{O}_{(\text{ad})}$  to produce  $\text{CO}_2$ . Finally, the sulfide will lose its structure and turn into corresponding oxides.

Because cobalt sulfide ( $\text{CoS}_x$ ) was completely inactive towards the  $\text{SO}_2 + \text{CO}$  reaction [12,40], the measurement of NO decomposition was performed directly on the in situ sulfided  $\text{Co}_3\text{O}_4$ . However,  $\text{TiO}_2$ -promoted cobalt sulfides were measured after the  $\text{SO}_2 + \text{CO}$  reaction (Fig. 4a). As seen in Fig. 8a and b, pre-sulfided  $\text{Co}_3\text{O}_4$  showed a mixture of low-sulfur-containing sulfides, while 1:1 sample after the  $\text{SO}_2 + \text{CO}$  reaction was transformed into  $\text{CoS}_2$  and  $\text{TiO}_2$  in addition to a small concentration of  $\text{CoS}_{2-x}$ . Since more amounts of sulfur in  $\text{TiO}_2$ -promoted cobalt sulfides than in pure cobalt-sulfide can be obtained, NO decomposition thus sustained more time.  $\text{TiO}_2$  is proposed to promote the extent of sulfurization by the transformation from the low-sulfur-containing sulfides such as  $\text{Co}_9\text{O}_8$ ,  $\text{Co}_6\text{O}_5$  and  $\text{Co}_4\text{O}_3$  (Fig. 8a) to  $\text{CoS}_2$  (Fig. 8b) during  $\text{SO}_2 + \text{CO}$  reaction.

Comparing Figs. 3 and 4, it is understood that NO reduction by CO over  $\text{TiO}_2$ -promoted cobalt sulfides proceed via a decomposition mechanism on sulfides. But this is different from pure cobalt sulfide, because no  $\text{SO}_2$  was detected and COS was formed instead. The absence of  $\text{SO}_2$  indicates that adsorbed oxygen from NO dissociation predominantly react with CO to produce  $\text{CO}_2$ . On the other hand, as shown in Fig. 3b, not all of the oxygen adsorbed on cobalt sulfide reacted with CO to produce  $\text{CO}_2$ . Some of them still combined with lattice sulfur to give off  $\text{SO}_2$ . From Ref. [12], we also know that rutile  $\text{TiO}_2$  was not active towards the  $\text{CO} + \text{O}_2$  reaction below 400 °C. On the basis of both observations, it is deduced that at least some oxygen from NO decomposition was supposed to react first with lattice sulfur to produce  $\text{SO}_2$  rather than react with CO reductant in inlet gas to produce  $\text{CO}_2$ , as suggested by Zhuang et al. [41]. Considering the high activity for  $\text{TiO}_2$ -promoted cobalt sulfides in the reduction of  $\text{SO}_2$  by CO, the produced  $\text{SO}_2$  can easily be catalytically reduced to sulfur, which may spill over to cobalt sites to regenerate cobalt sulfide. This has

been confirmed by the XRD patterns of catalysts after reaction (Fig. 8). If there were not TiO<sub>2</sub> added, as in Fig. 3b, the catalyst would eventually lose its activity due to the depletion of lattice sulfur. Thus, there also exists synergism between cobalt sulfides and TiO<sub>2</sub> for the reduction of NO by CO.

As evidence of above mechanism, TiO<sub>2</sub>-promoted cobalt sulfides were tested to be very effective catalysts for simultaneous catalytic reduction of NO and SO<sub>2</sub> by CO at especially low concentrations of them (Fig. 6 and Table 3).

In comparison of SO<sub>2</sub> and NO conversion in SO<sub>2</sub> + CO, NO + CO, and SO<sub>2</sub> + NO + CO reactions, it is found that the SO<sub>2</sub> conversion was not affected by the addition of NO in the measurement error range, while the NO conversion was lowered slightly by the addition of SO<sub>2</sub>. Because SO<sub>2</sub> is one of the products of NO decomposition, the addition of SO<sub>2</sub> into NO + CO reaction thus caused a little suppression of the reaction. This is also evidence for the production of SO<sub>2</sub> intermediate in NO + CO reaction mechanism. However, as traces of COS may form in some cases in the NO + CO reaction, the existence of SO<sub>2</sub> in flue gas will be beneficial to the catalyst's stability. Therefore, the SO<sub>2</sub> + NO + CO reaction can be thought to consist of two fundamental reactions of SO<sub>2</sub> + CO and NO decomposition. However, as discussed above, the two reactions are interrelated. SO<sub>2</sub>, a product of NO decomposition, should be further reduced to sulfur by SO<sub>2</sub> + CO reaction.

On summary, both TiO<sub>2</sub> and CoS<sub>2-x</sub> take part in the separate or simultaneous reduction reactions of SO<sub>2</sub> and/or NO by CO. Although the catalytic active sites are on TiO<sub>2</sub> for SO<sub>2</sub> + CO reaction, the reaction between CO and cobalt sulfide is a necessity. The same situation is for NO + CO reaction. NO decomposed into N<sub>2</sub> on cobalt sulfide, but the produced SO<sub>2</sub> should be further reduced to sulfur over TiO<sub>2</sub>. The qualitative surface compositional analysis by XPS showed that titanium is segregated on CoS<sub>2-x</sub> surface of 1:4 sample after use, which testified that TiO<sub>2</sub> played an important role in the reaction.

## 5. Conclusion

In the present study, it is revealed that the addition of TiO<sub>2</sub>-promoted the otherwise inactive cobalt

sulfide to be an effective catalyst not only for separate but also for simultaneous reduction of SO<sub>2</sub> and/or NO by CO. Combined with the results of XRD, BET, XPS and transient MS techniques, the following conclusions can be drawn:

1. TiO<sub>2</sub>-promoted cobalt sulfides exhibit outstanding activity and selectivity for the catalytic reduction of SO<sub>2</sub> to elemental sulfur by CO. The 1:1 sample shows 95% SO<sub>2</sub> conversion and 98% SO<sub>2</sub> selectivity to sulfur at 300 °C. This was lowered ca. 100 °C compared with the temperature at which nearly complete SO<sub>2</sub> removal was achieved on the mechanical mixture catalysts of the components, because the produced COS intermediate and S product need not migrate a long distance from CoS<sub>2-x</sub> to TiO<sub>2</sub> to react with SO<sub>2</sub> and from TiO<sub>2</sub> to CoS<sub>2-x</sub> to regenerate CoS<sub>2-x</sub>, respectively, brought by coprecipitation. The synergism between CoS<sub>2-x</sub> and TiO<sub>2</sub> is elucidated by a COS enhanced redox mechanism.
2. Cobalt sulfide catalyzes NO decomposition into N<sub>2</sub> and N<sub>2</sub>O through formation of the by-product, SO<sub>2</sub>. It lost the catalytic activity with the depletion of lattice sulfur or the oxidation of the catalyst. Adding reducing agent, CO, can suppress SO<sub>2</sub> formation greatly and thus promote NO decomposition, but this is not enough. The addition of TiO<sub>2</sub> prolonged the activity of cobalt sulfide for NO decomposition through that TiO<sub>2</sub> promoted the sulfurization extent of TiO<sub>2</sub>-promoted cobalt sulfides in the process of SO<sub>2</sub> + CO reaction.  
In the reduction of NO by CO over TiO<sub>2</sub>-promoted cobalt sulfides, the first step is NO decomposition on cobalt sulfide. The product oxygen might react with CO to give off CO<sub>2</sub>, or react with active sulfur species to produce SO<sub>2</sub>, which can further be reduced to elemental sulfur through the reaction of SO<sub>2</sub> + CO over TiO<sub>2</sub>. The produced sulfur spills over to cobalt sites to regenerate cobalt sulfide. Thus, cobalt sulfide and TiO<sub>2</sub> had synergistic effect for the reduction of NO by CO.
3. The SO<sub>2</sub> and NO conversions and SO<sub>2</sub> selectivity to elemental sulfur were examined on the three different composition samples. Although the SO<sub>2</sub> + NO + CO reaction can be explained by two separate reactions of SO<sub>2</sub> + CO and NO decomposition, which proceed mainly on TiO<sub>2</sub> and cobalt

sulfide, respectively, the two reactions are interrelated. The reaction between CO and cobalt sulfide to produce COS intermediate is a necessity for the further reduction reaction of SO<sub>2</sub> on TiO<sub>2</sub>, while SO<sub>2</sub>, one of the products of NO decomposition on cobalt sulfide, is recovered to sulfur on TiO<sub>2</sub> by SO<sub>2</sub> + CO reaction.

4. CO<sub>2</sub> in flue gas promoted the production of COS, but it has little effect at levels around 1000 ppm on the simultaneous catalytic reduction of SO<sub>2</sub> and NO by CO.

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