Titanium-Promoted Cobalt Sulfide Catalysts for NO Decomposition and Reduction by CO

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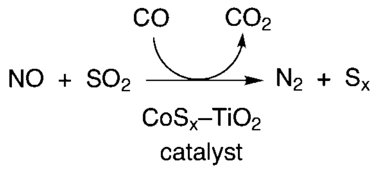
Cobalt sulfide and titanium-promoted cobalt sulfides were reported as catalysts for NO decomposition and reduction by CO. Titanium-promoted cobalt sulfides showed not only nearly complete NO removal but the simultaneous catalytic reduction of NO and SO_2 by CO to N_2 and elemental sulfur, respectively.

Direct decomposition of NO and its reduction with reductants are now two methods for the removal of NO from exhaust streams. Among various catalysts used in this purpose, cobalt oxide has attracted much attention. It is testified that Co_3O_4 is one of the most active single metal oxides for NO decomposition; moreover, its catalytic activity can be improved by other additives, for example, Ag[1] and Na.[2] Catalysts containing cobalt oxides are an important class in the reduction of NO. Bulk Co_3O_4 has been extensively studied for the reduction of NO by CO owing to its simultaneous removal of both NO and CO.[3,4] Co/ZSM-5[5,6] and cobalt supported on ZrO_2,[7] Al_2O_3[8] or SiO_2[9] catalysts are also studied for the selective catalytic reduction (SCR) of NO using hydrocarbons.[5,6] This letter firstly reported the results of NO decomposition over cobalt sulfide as well as NO decomposition and reduction by CO over titanium-promoted cobalt sulfides.



Titanium-promoted cobalt oxides (Co_3O_4 : TiO_2 = 4:1, 1:1, 1:4, weight ratio) were prepared by the coprecipitation method. Stoichiometric mixed solutions of $Co(NO_3)_2{\cdot}6H_2O$ and $Ti(SO_4)_2$ 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. Co_3O_4 was prepared by the precipitation method from $Co(NO_3)_2{\cdot}6H_2O$ and ammonia solutions, as described above. An oxide catalyst was in situ sulfided in a flow of 5 vol% H_2S in H_2 gas at 400 °C for 1 h, and then cooled down to room temperature with an Ar purge to eliminate adsorbed H_2S. The catalytic reaction tests were carried out on a fixed bed reactor. The reaction conditions [2050 ppm NO + Ar and 1025 ppm NO + 2085 ppm CO + Ar at a flow rate of 40 cm^3/min over 0.3 g catalyst (GHSV = 8000 h^{-1})] were employed for NO decomposition and NO + CO reaction, respectively. The products in the effluent stream were analyzed by a quadrupole mass spectrometry (LZL-204, Beijing Analytical Instrument Plant). The NO_x conversion was calculated on the basis of differences between the inlet and outlet NO intensities.

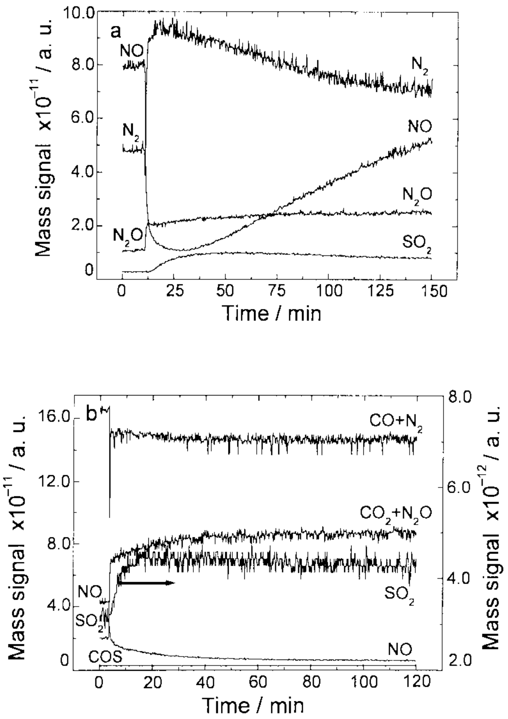


Figure 1. Transient response curves obtained over cobalt sulfide at 350 °C after switching from Ar to (a) NO + Ar, and (b) NO + CO + Ar.

The activity of cobalt sulfide (CoS_x) towards NO decomposition and NO + CO reaction was studied with a transient technique, as shown in Figures 1a and b. The instantaneous N_2 and N_2O response curves showed that cobalt sulfide was active in NO decomposition in the absence of CO in the gas phase (Figure 1a). However the sulfur-containing species, SO_2 (*m/z* 64), was observed. The delayed response of SO_2 indicated that the oxygen from NO decomposition was firstly taken up by the highly reduced catalyst, and then reacted with sulfur species on the catalyst surface. The catalytic activity of NO decomposition into N_2 decreased with time. This may be related to the depletion of lattice sulfur vacancies formed after sulfurization. By introducing the reducing agent, CO, although it cannot completely eliminate the formation of SO_2 (Figure 1b), more than 90% NO conversion at 350 °C was maintained.

Figure 2 shows the catalytic activity of titanium-promoted cobalt sulfides towards NO decomposition (a) and NO + CO reaction (b). In Figure 2a, a stable high activity was achieved, although SO_2 by-product was formed as in the case of cobalt sulfide. Compared with single cobalt sulfide, the reduction of NO by CO over titanium-promoted cobalt sulfides was detected with no SO_2 formation except traces of COS. It is also notable that NO conversions were nearly independent of the TiO_2 content, but TiO_2 is supposed to play an important role in the removal of SO_2.

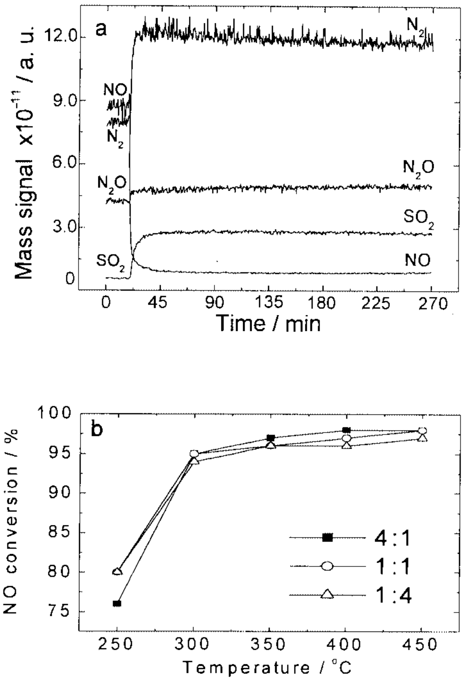


Figure 2. (a) Transient response curves obtained over 1:1 sample at 350 °C after switching from Ar to NO + Ar; (b) NO conversion towards NO + CO reaction over titanium-promoted cobalt sulfides.

For this reason a separate SO_2 + CO reaction was studied over titanium-promoted cobalt sulfide catalysts. Figure 3 shows the SO_2 conversions and selectivity towards elemental S as a function of temperature. As expected high SO_2 conversion and selectivity to S were achieved over them. This behavior is markedly different from that of single cobalt sulfide or oxide, which had negligible activity for the reduction of SO_2 by CO to elemental sulfur.[10] However, COS intermediate generated from the reaction of CO with the lattice sulfur, can not be substantially removed on 4:1 and 1:4 samples at 250 °C. Here we preliminarily suggest a decomposition mechanism and a synergistic effect between cobalt sulfide and TiO_2. First NO decomposed into N_2 and a small part of N_2O, while oxygen reacted with the lattice sulfur in cobalt sulfide to form SO_2. At the same time, over TiO_2 the produced SO_2 was catalytically reduced to sulfur, which may migrate onto cobalt sites to regenerate cobalt sulfide.

In order to determine the above mechanism, transient responses for the 4:1 sample, after a flue of NO + SO_2 + CO + Ar mixture was introduced at 350 °C, were measured, which are shown in Figure 4. A steady state with NO and SO_2 conversions, 93% and 95% (taken after 600 min), respectively, was reached, while COS was only formed at the beginning period. Similar results were also observed on other two samples. In conclusion simultaneous catalytic reduction of NO and SO_2 by CO was carried out over titanium-promoted cobalt sulfides. Further mechanistic studies will be reported.

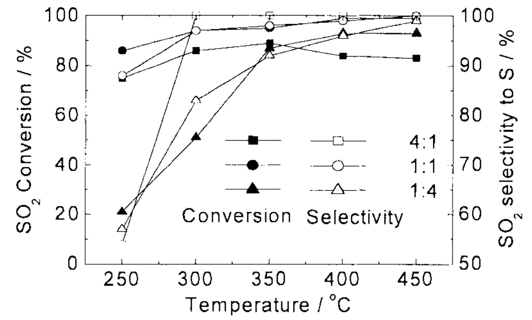


Figure 3. SO_2 conversion and selectivity to elemental S over titanium-promoted cobalt sulfides. (SO_2 1050 ppm, CO 2085 ppm, Ar, 0.3 g catalyst, GHSV = 8000 h^{-1}).

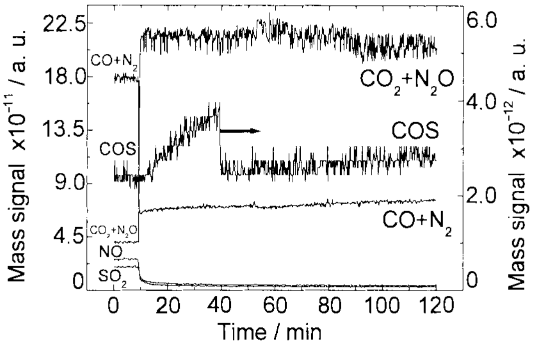


Figure 4. Transient response curves obtained over 4:1 sample at 350 °C after switching from Ar to 520 ppm NO + 525 ppm SO_2 + 2085 ppm CO + Ar.

References and Notes

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