

Removal of Ammonia and Hydrogen Sulfide in a Simulated Coke Oven Gas with Limonite

Yuuki Mochizuki, Ayumu Ogawa, and Naoto Tsubouchi*

Center for Advanced Research of Energy and Materials, Hokkaido University, Sapporo, Japan

*E-mail: tsubon@eng.hokudai.ac.jp

To develop a novel hot gas cleanup method to efficiently remove NH₃ or H₂S in coke oven gas (COG) produced in coke making process is important to save the energy consumption in ironmaking process. Our research group has recently found that α -Fe produced by reduction of an Australian limonite ore containing a large amount of goethite (α -FeOOH), achieves the almost complete decomposition of NH₃ or pyridine (as a model tar-N compound) in simulated fuel gas from air blown coal gasification and exhibits very stable performance [1,2]. In this work, therefore, we investigated the effect of the presence of COG components on NH₃ catalytic decomposition and H₂S removal performance using an Australian limonite to develop a novel gas cleaning method.

An Australian limonite (Fe, 44; Si, 9.4; Al, 7.2; Mg, 0.15; Ca, 0.07 mass%-dry) with about 70 mass% of α -FeOOH was used. The BET surface area and particle size are 40 m²/g and 250–500 μ m, respectively.

NH₃ catalytic decomposition and H₂S removal runs were carried out with a cylindrical quartz reactor. The limonite was first reduced with pure H₂ at 500 °C for 2 h, then the sample was held at a temperature of 300–850 °C under flowing pure He, and finally feed gas (mixture of 1% NH₃ or 3000 ppm H₂S/He and 50% H₂, 30% CH₄, 5% CO, 5% CO₂ and 5% H₂O) was introduced into the reactor, space velocity being 51000 h⁻¹. The amount of N₂ or H₂S in the reactor effluent was measured with a micro-GC or Gastec detector tube, respectively. Conversion of NH₃ to N₂ and removal extent of H₂S was calculated based on N₂ and H₂S amounts detected at the reactor outlet.

Table 1 shows the results of NH₃ catalytic decomposition under various feed gases at 850 °C until 120 min. The almost complete decomposition of NH₃ was maintained beyond 240 min in He, whereas the performance dramatically decreased after 90 min in 50% H₂/30% CH₄/He. A similar tendency was observed in 5% CO coexisted to 50% H₂/30% CH₄/He. A significant amount of C deposition was observed on the catalyst surface after experimental runs in the presence of 50% CH₄ and 50% CH₄/5% CO. Therefore, catalytic deactivation may occur by C deposition derived from CH₄ decomposition. When 5% CO₂, 5% H₂O or 5% CO₂/5% H₂O was coexisted to 50% H₂/30% CH₄/5% CO/He, the NH₃ catalytic

decomposition performance was improved, and > 99 % conversion of NH₃ to N₂ was observed beyond 240 min. Moreover, no significant C deposition was found on the catalyst surface after experimental runs. These results show that C deposition on active sites of catalyst surface is inhibited by 5% CO₂, 5% H₂O or 5% CO₂/5% H₂O addition to 50% H₂/30% CH₄/5% CO.

Table 2 presents the effect of coexisting gas on the removal extent of H₂S at 400 °C until 20 min, as an example. The H₂S removal of 100 % was observed up to 20 min in 50% H₂/He or 50% H₂/30% CH₄/He, whereas the performance decreased from 5 min in 50% H₂/30% CH₄/5% CO/He. Similar decreasing was observed at 5% CO/5% CO₂ added to 50% H₂/30% CH₄/He and other temperatures (300–600 °C). On the other hand, the removal performance of H₂S was improved at 5% H₂O coexisted to 50% H₂/30% CH₄/5% CO/He or 50% H₂/30% CH₄/5% CO/5% CO₂/He (simulated COG). At temperature-programmed-oxidation in 10% O₂/He of samples recovered after experimental runs, formation amounts of CO and CO₂ from solid products recovered after 50% H₂/30% CH₄/5% CO/He and 50% H₂/30% CH₄/5% CO/5% CO₂/He run were greater than those of 50% H₂/30% CH₄/He and 5% H₂O addition. These results show that H₂S removal ability decreases by C deposition derived from CO via disproportionation reaction, and these performance is improved by H₂O addition.

Table 1 Effect of coexisting gas on NH₃ conversion to N₂ at 850 °C until 120 min

Atmosphere	NH ₃ conversion, %
50%H ₂ /30%CH ₄ /He	0
5%CO addition	0
5%CO/5%CO ₂ addition	>99
5%CO/5%H ₂ O addition	>99
5%CO/5%CO ₂ /5%H ₂ O addition	>99

Table 2 Effect of coexisting gas on the removal extent of H₂S at 400 °C until 20 min

Atmosphere	H ₂ S removal, %
50%H ₂ /30%CH ₄ /He	100
5%CO addition	40
5%CO/5%CO ₂ addition	45
5%CO/5%H ₂ O addition	95
5%CO/5%CO ₂ /5%H ₂ O addition	95

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