

CHAPTER 1

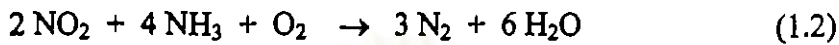
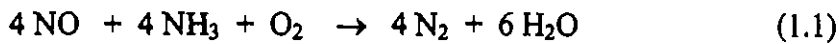
INTRODUCTION



Environmental quality is certainly a worldwide concern. Air pollution knows no boundaries, and reducing it is of the utmost importance. Many countries are now establishing tougher environmental regulations that must be met by mobile as well as stationary pollution sources; more stringent regulations will likely be introduced in the future. Exhausts containing volatile organic compounds (VOCs), carbon monoxide (CO), nitrogen oxides (NO_x), ozone (O₃), and so forth all can be converted to harmless nonpollutants at reasonable temperatures and with cost-effective systems utilizing heterogeneous catalysts. The use of the right catalyst system converts pollutants to nonpollutants with low energy requirements and at higher rate, resulting in cost-effective pollution control. The use of catalytic system for pollution abatement was virtually nonexistent before 1976, but now it is a multibillion-dollar worldwide business that addresses gasoline- and diesel-fueled automobiles and trucks, destruction of volatile organic compounds from stationary sources such as chemical processing plants, reduction of nitric oxides from power plants and stationary engines, decomposition of ozone in high flying commercial aircraft, and so on. The utilization of catalysts for future pollution abatement applications promises to grow at a strong pace well into the next century.

Stationary sources such as power plants contribute roughly half of all of the nitric oxide (NO), major air pollutant which causes photochemical smog and acid rain, emitted into the atmosphere from combustion [1]. Currently much of the NO

emission from these stationary sources is controlled by selective catalytic reduction (SCR). In this process, NO is reduced in the presence of oxygen (O₂) by ammonia (NH₃) over titania-supported vanadia (V₂O₅/TiO₂).



While this technology is effective, high NO conversion, the use of ammonia as the reductant is undesirable for a number of reasons. First, large quantities of ammonia must be transported and stored either as liquid ammonia or ammonium hydroxide (NH₄OH), raising the risk of release of a toxic compound. Second, the introduction of ammonia to the SCR process must be carefully controlled to avoid ammonia slippage into the effluent gases leaving the convertor (another air pollutant). Third, ammonia in the reactor effluent can react with water and sulfur trioxide (SO₃) to produce ammonium sulfate ((NH₄)₂SO₄) which can deposit onto the surface of the heat exchanger thereby causing a reduction in heat transfer efficiency. Forth, ammonia, one of the corrosive gases, is required the non-corrosion system, at the expense of high equipment cost [2-4]. For all of these reasons there is a strong interest in finding alternative means for controlling NO emission from stationary sources.

Hydrocarbons could offer an attractive, alternative reductant to ammonia. The use of hydrocarbons as reducing agents for NO_x in an oxidizing atmosphere is a subject of intense research. Recently, propane (C₃H₈), propylene (C₃H₆) and ethylene (C₂H₄) are the most intensely investigated hydrocarbons for NO reduction [5-7]. In all these early reports, the presence of oxygen is essential for the NO reduction, demonstrating that hydrocarbons can be effective for the selective reduction of NO.

However, the use of methane as a selective reducing agent for NO was never reported. In fact, methane is often regarded as a non-selective reducing agent for NO in the excess of oxygen [8]. Methane is difficult to activate because of the strong C-H bond (101 kcal/mol) which often necessitates high reaction temperatures. It is well known that methane reacts much faster with oxygen than with NO on most catalysts, and to use methane, in place of ammonia, selectively for NO reduction is indeed a great challenge. On the other hand, with the plentiful supply of natural gas in the world and the widespread use of natural gas as a fuel by many utilities, one could use natural gas (methane) already on site to reduce the NO_x in the flue gas.

Li and Armor [2-3] were the first to report that NO can be selectively reduced by methane in the presence of excess oxygen over a cobalt ion-exchanged ZSM-5 zeolite (Co/ZSM-5). This reaction could find an application as a NO_x control method in lean-burn, natural gas fueled vehicles. The catalytic activity of Co/ZSM-5 was found to be low in the absence of oxygen and was significantly enhanced in the presence of excess oxygen. The NO conversion increased with the methane level, although a relatively small amount of methane was needed for complete NO reduction because of the high selectivity of methane towards the NO reduction reaction. Additional screening tests [2-3] revealed that Ni- and Mn-exchanged ZSM-5 zeolites were also active for this reaction, Fe-, Cu- and H-ZSM-5 zeolites exhibited very low activities, while Cr- and the parent Na-ZSM-5 were completely inactive. These results suggested that the nature of the transition metal cation is crucial.

The effect of the zeolite structure was also studied by Li and Armor [2]. Using methane as the reducing agent, the authors compared a number of cobalt-exchanged zeolites and found Co/ZSM-5 to be the most active one. However, it is

generally recognized that the ion-exchanged Al-silicate catalysts (ZSM-5 included) have a disadvantage in thermal and hydrothermal stability, owing to both the sintering of exchanged metal components and the dislocation of the aluminium from the zeolite framework [9-10] and these are the serious problems for the practical application [11]. In order to develop the new catalysts for defeat these problems and investigate such potentials, two catalysts, having MFI structure but different in the position of Co, cobalt aluminosilicate (Co,Al-silicate) which Co is incorporated into the MFI framework and Co ion-exchanged MFI type (Co/ZSM-5) which Co is at cationic position were prepared according to the rapid crystallization method [12] and their performance in the NO removal reaction by methane in the presence of an excess oxygen were examined with comparison of each other.

1.1. The Objectives of this Study

1.1.1. To compared the catalytic activities of Co,Al-silicate, Co ion-exchanged Co,Al-silicate and Co/ZSM-5 for the selective reduction of NO by methane in an oxidizing atmosphere.

1.2. The Scope of this Study

1.2.1. Prepare bimetallosilicate (Co,Al-silicate) catalysts by adding the metal sources at the stage of gel formation and synthesizing the catalysts according to the rapid crystallization method [12]. The sources of metals are aluminium chloride (AlCl_3), and cobalt(II) acetate

($\text{Co}(\text{CH}_3\text{COO})_2$). The metal elements were incorporated in the structure. Co/Co,Al-silicate catalysts were prepared by using an ion-exchange method.

1.2.2. Characterize the prepared catalysts by the following methods:

- Identifying the synthesized crystals by X-ray diffractometer (XRD).
- Analyzing the shape and size of the crystallized catalysts by Scanning Electron Microscope (SEM).
- Analyzing the percentage of metal loading of the catalysts by Atomic Absorption Spectrometer (AAS).

1.2.3. Study the catalytic activities of the prepared catalysts for the selective reduction of NO by methane in the presence of an excess oxygen under the following conditions:

- Reaction feed gas: NO 1000 ppm, CH_4 10000 ppm, O_2 10 %, SO_2 0 or 500 ppm , and He as balance gas
- Reaction temperature: 150-600 °C
- Space velocity: 4000 h^{-1}