

Characterization and performance of Pt-Pd-Rh cordierite monolith catalyst for selectivity catalytic oxidation of ammonia

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ABSTRACT

This work considers the oxidation of ammonia (NH₃) by selective catalytic oxidation (SCO) over a Pt-Pd-Rh cordierite monolith catalyst in a tubular fixed-bed flow quartz reactor (TFBR) at temperatures between 423 and 623 K. A Pt-Pd-Rh cordierite monolith catalyst was prepared by incipient wetness impregnation with aqueous solutions of H₂PtCl₆, Pd(NO₃)₃ and Rh(NO₃)₃ that were coated on cordierite substrates. The catalysts were characterized using XRD, PSA and SEM. The experimental results show that around 99.0% NH₃ removal was achieved during catalytic oxidation over the Pt-Pd-Rh cordierite monolith catalyst at 623 K with oxygen content of 4%. N₂ was the main product in the NH₃-SCO process over the Pt-Pd-Rh cordierite monolith catalyst. These results also verify that the Pt-Pd-Rh metals on cordierite monolith surfaces, resulting in the formation of catalytically active sites at the metal-support interface in the reduction of NH₃ in the process.

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1. Introduction

Extensively adopted in industry, ammonia (NH₃) can be abated in numerous ways. Actually, NH₃ is used in the ammonium nitrate and nitric acid production industry, livestock feedlots, urea manufacturing plants, the nitrogen fertilizer application industry, fossil fuel combustion and petroleum refineries as well as the refrigeration industry. NH₃ is a toxic, corrosive, and highly reactive inorganic gas with a pungent odor under ambient conditions, and is potentially harmful to public health as reported in recent years [1,2]. Moreover, it is known, various technologies have been explored for the typical biological, physical and chemical treatments, including biofilters, stripping, scrubbing with water, post-combustion control, electrochemical oxidation and the use of activated carbon fibers for soot adsorption, only induce a phase transformation and may yield contaminated sludge or adsorbent, both of which require further treatment. The maintenance and operating costs associated with these physical and/or chemical methods are high. Therefore, in an environmental point of view, the removal and control of NH₃ emission from air quality and waste streams are important.

More recently, catalytic oxidation has been proposed to enhance the effectiveness of advanced oxidation processes technology using dedicated catalysts, which potentially shorten the reaction times of oxidation, and allow it to proceed under milder operating con-

ditions. Nevertheless, the selective catalytic oxidation process of ammonia (NH₃-SCO) in a stream to N₂ and H₂O is one method for solving problems of NH₃ pollution [3,4]. The catalytic oxidation of NH₃ has been reported to proceed as follows.



Overall, the SCO process that involves NH₃ should be selective for nitrogen (reaction (1)), and prevent further oxidation of nitrogen (reactions (2)–(4)). Earlier work on NH₃ oxidation was reviewed by Il'chenko [5–7], who focused on the reaction mechanism of NH₃ oxidation, and compared catalytic activities. At current, various catalysts have been used in oxidizing NH₃ in the gaseous phase. For instance, the work of Amblard et al. [8] demonstrated the excellent selective conversion of NH₃ to N₂ (>90%) by γ -Al₂O₃-supported Ni by SCO processes. Moreover, Wang et al. [9], who developed Ni-based catalysts for oxidizing fuel gas generated by gasifying biomass, found that fresh Ni-based catalysts were more active at lower temperatures in decomposing of NH₃, and the partial pressure of hydrogen in the flue gas is a critical factor that governed NH₃ oxidation. Another paper by Liang et al. [10] studied the oxidation of NH₃ in a fixed-bed microreactor in the temperature range 873–1023 K at GHSV = 1800–3600 h⁻¹. They found that the conversion of NH₃ reached 98.7% and 99.8% on nitrated MoNx/ α -Al₂O₃ and NiMoNy/ α -Al₂O₃ catalysts, respectively. Schmidt-Szałowski et al. [11] also developed a hypothetical

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model of the effect of these catalysts and their activity and selectivity in oxidizing NH_3 . Until recently, Hung [12] summarized the catalytic oxidation of NH_3 in gaseous stream by a nanoscale copper-cerium bimetallic catalyst in the temperature range 423–673 K at $\text{GHSV} = 92,000 \text{ h}^{-1}$. There is a synergistic effect of the bimetallic nanoscale structure, which is the material with the highest NH_3 reduction activity and the highest N_2 selectivity.

Nowadays, it has been reported that cordierite material is a crystalline magnesium aluminosilicate ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) with a hexagonal structure, combining a relatively low thermal expansion coefficient (TEC) with both thermal shock resistance and adequate refractoriness [13,14]. For the cordierite material, it has been reported that the cordierite support can promote catalytic activity through noble metal-support sites interaction effects in heterogeneous catalysis [15]. Noble metals as additives in catalysts for enhancing NH_3 conversion have been given great attention. Platinum-based catalytic system has a high melting point and high thermal stability and corrosion resistance that are extensively used for automotive three-way catalysts (TWCs) convert and fuel cell catalyst electrodes application. Recently, the previous works [16,17] showed that platinum, palladium, and rhodium metals' structure exhibited remarkably activity than the monometallic sample used to elucidate the removal characteristics of NH_3 conversion in a wet oxidation system. In addition, as has been reported in literature [18], the interaction between platinum, palladium oxide and the rhodium is complex, because various Pt-Pd-Rh interactions can result in synergistic effects, enhancing catalytic properties. Moreover, combining composite metals with cordierite monolith material also can stabilize the metal against sintering and volatilization reaction with the support [19]. However, little work has been undertaken on the use of Pt-Pd-Rh cordierite monolith material to determining the reactive characteristics of these active metals for catalytic gaseous-phase oxidation of NH_3 . On the basis of this, due to the application of the catalytic oxidation technique, the activity of the Pt-Pd-Rh cordierite monolith catalyst in the oxidation of NH_3 given by various values of parameters and its effect on the removal of NH_3 in SCO processes were studied. To this end, the obtained catalysts were characterized with XRD, PSA and SEM.

2. Materials and methods

2.1. Material and chemicals

The platinum-palladium-rhodium composite oxide catalysts that were used in this study were prepared by the incipient wetness impregnation, which involved aqueous H_2PtCl_6 , $\text{Pd}(\text{NO}_3)_2$ and $\text{Rh}(\text{NO}_3)_3$ (all grade, Merck, Darmstadt, Germany). A platinum-palladium-rhodium catalyst was coated onto cordierite substrate ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, KJ Environmental Technology, Taiwan) with high-surface-area gamma-alumina with platinum, palladium and rhodium in weight ratios of 4:3:1, maintaining the ratio of catalytic active metals at a constant 6.4%. The catalysts were then calcined at 773 K in an air stream for 4 h. Fig. 1 presents the textural characteristics of the Pt-Pd-Rh cordierite monolith catalyst.

2.2. Experimental methods

Experiments were conducted on a tubular fixed-bed flow quartz reactor (TFBR). The typical reactant gas ($\text{GHSV}, 92,000 \text{ h}^{-1}$) composition was as follows: 1000 ppm NH_3 , 4% O_2 , and He as balance, which flowed into the inlet of the reactor. A mass flow regulator was used to control independently the flows of NH_3 and O_2 . Highly pure He was used as a carrier gas at a flow rate from 8 to 13 L/min, controlled using a mass flow meter (830 Series Side-Trak™, Sierra, Monterey, CA, USA). An inert material formed from (hydrophilic

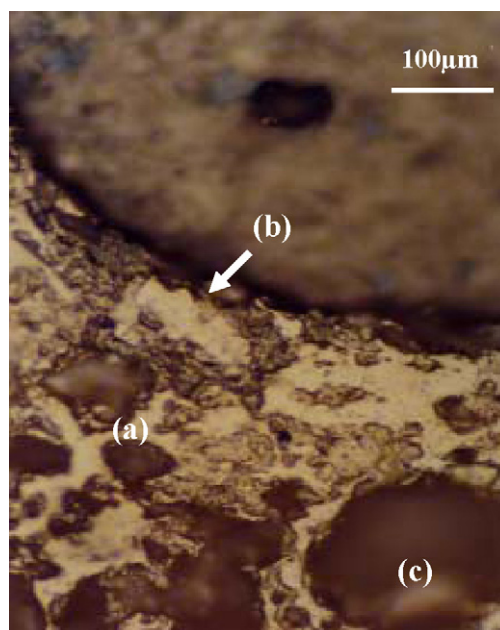


Fig. 1. Morphology of a Pt-Pd-Rh cordierite monolith catalyst showing: (a) cordierite cellular ceramic support material, (b) active metal-catalyzed washcoat layer, and (c) cross-section cut of channel. Images were taken with an optical microscopy.

and inert) $\gamma\text{-Al}_2\text{O}_3$ spheres was used to increase the interfacial area between the solid and the gas phase to increase the mass transfer of NH_3 from gaseous streams. This approach resembled that of Hung [12], who conducted experiments on the catalytic oxidation of NH_3 . A reaction tube with a length of 300 mm and an inner diameter of 28 mm was placed inside a split tube furnace. The tube that contained the catalyst was placed in the same furnace. The temperature was measured using two type-K thermocouples (KT-110, Kirter, Kaohsiung, Taiwan), each with a diameter of 0.5 mm, these were located in front of and behind the catalytic bed. The thermocouples were also connected to a PID controller (FP21, Shimadzu, Tokyo, Japan) to maintain the temperature in the tube within $\pm 0.5\%$.

2.3. Instrumental analyses

Before and after the reaction, samples were automatically injected through a sampling valve into a gas chromatograph (Shimadzu GC-14A), equipped with a thermal conductivity detector. A stainless-steel column (Porapak Q 80/100 mesh) was used to separate and determine the concentrations of N_2O isothermally at 100°C . The areas associated with the signals were electronically measured using a data integrator (CR-6A, Shimadzu, Kyoto, Japan). Dilute sulfuric acid was used to scrub the residual NH_3 in the vapor gas and the amount present was measured using a Merck kit (Merck, Spectroquant Vega 400, Darmstadt, Germany). The concentrations of NO , NO_2 and O_2 in the gas samples were monitored continuously during catalytic at a particular location, using a portable flue gas analyzer (IMR-3000, Neckarsulm, Germany). Data were collected when the SCO reaction was in a steady state, typically after 20 min at each temperature. Each temperature was maintained for 90 min to allow the system to enter a steady state. Most experiments were repeated once to ensure reproducibility, and similar results were always obtained.

X-ray diffractograms (XRD) were obtained using a Diano-8536 diffractometer with $\text{CuK}\alpha$ radiation as the source. During analysis, the sample was scanned from 20 to 80° at a rate of $0.4^\circ/\text{min}$. The changes in the sizes of the catalytic particles were measured using a laser light-scattering particle size analyzer (PSA, Coulter LS100,

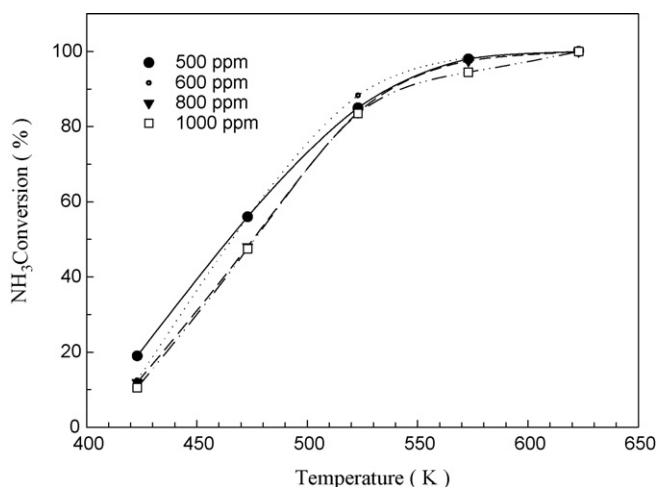


Fig. 2. Effect of NH_3 concentration on the Pt-Pd-Rh cordierite monolith catalyst used in the conversion of NH_3 . Test conditions: $\text{O}_2 = 4\%$, $\text{RH} = 12\%$, temperature = 423–673 K, $\text{GHSV} = 92,000 \text{ h}^{-1}$.

USA). Scanning electron microscopy (SEM, JEOL, JSM-6400, Kevex, Deltall) elucidated the morphology of the catalysts.

3. Results and discussions

Fig. 2 plots the effect of the initial concentration of NH_3 during catalytic incineration runs over the Pt-Pd-Rh cordierite monolith catalyst at 423–673 K at an oxygen concentration of 4.0%. The results reveal that the Pt-Pd-Rh cordierite monolith catalyst is very active in the decomposition of NH_3 . Therefore, the extent of removal of NH_3 increased markedly with the temperature of the influent stream. When the initial concentration of the influent NH_3 was set to 500 ppm, around 99.0% NH_3 reduction was obtained at 673 K. The corresponding value at 1000 ppm was 98.3%. Evidently, the effect of temperature on the reduction of NH_3 was also found to be significant at NH_3 concentrations ranging from 500 to 1000 ppm in the influent stream.

Fig. 3 presents the X-ray diffraction (XRD) patterns of fresh and used catalysts for comparison, confirming the PtO_2/Pt^0 , PdO/Pd^0 , and $\text{Rh}_2\text{O}_3/\text{Rh}^0$ states of the Pt-Pd-Rh cordierite monolith catalyst. As indicated, the catalyst changed after exposure to a catalytic oxidation environment. The dominant PtO_2 diffraction peaks were close to $2\theta = 42.5$ and 54.9° for a Pt-Pd-Rh cordierite monolith catalyst [20]. The dominant Pt^0 diffraction peaks were close to $2\theta = 67.4^\circ$ for this catalyst following activity test. This finding agrees with data that were presented by Shin et al. [21] and García-Cortés et al. [22] for this system. The dominant PdO and Pd^0 diffraction peaks were near $2\theta = 41.9$ and 40.4° for a Pt-Pd-Rh cordierite monolith catalyst [23]. However, under oxidation conditions over the Pt-Pd-Rh cordierite monolith catalyst, the platinum and palladium were transformed from the oxide to the metal form.

The dominant Rh_2O_3 diffraction peaks were close to $2\theta = 35.4^\circ$ for an orthorhombic structure with hexagonal symmetry. This result is similar to that of Mulukutla et al. [24]. The dominant Rh^0 diffraction peaks were in the range $2\theta = 40$ – 50° for the catalyst following the activity test [25]. However, under oxidation conditions, over a Pt-Pd-Rh cordierite monolith catalyst, the oxidation state of rhodium may vary between Rh^{3+} and Rh^0 . Particularly, an earlier work established that Rh_2O_3 is the most active phase in the catalytic reaction, because it is a good promoter of oxygen storage, and the selectivity towards dinitrogen, thus enhancing the NH_3 removal, although some noble metals are used as the major catalysts [26]. Moreover, rhodium dioxide in a platinum catalyst may be assumed to promote the formation of the active phase of PtO_2 and PdO under

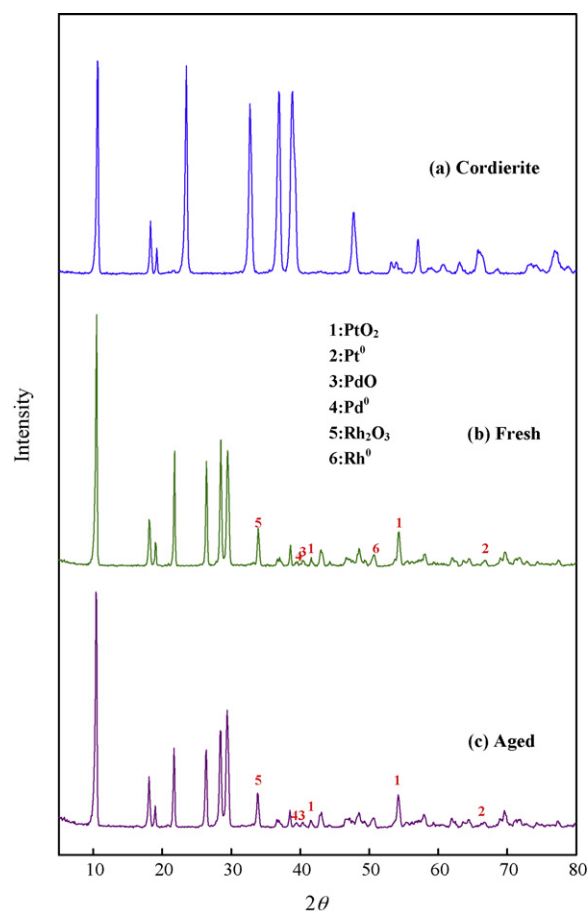


Fig. 3. X-ray diffraction pattern of Pt-Pd-Rh cordierite monolith catalyst. (a) Cordierite, (b) fresh, (c) after activity test. Test conditions: 1000 ppm NH_3 in He , $\text{O}_2 = 4\%$, $\text{RH} = 12\%$, $\text{GHSV} = 92,000 \text{ h}^{-1}$.

ammonia oxidation. Thus, according to the experimental results, the X-ray powder diffraction approach confirmed the formation of platinum (IV), palladium (IV) and rhodium (III) oxide active sites on the Pt-Pd-Rh cordierite monolith catalyst. Hence, it can be supposed that the NH_3 was adsorbed on the surface of cordierite monolith, and then the adsorbed NH_3 was followed the oxidation–reduction mechanism through the platinum, palladium and rhodium oxide active sites.

The change in the sizes of particles of the catalyst was determined using the laser light-scattering method, as depicted in **Fig. 4**. The mean particle size converged to approximately $195.9 \mu\text{m}$ for fresh Pt-Pd-Rh cordierite monolith catalyst. However, the diameters of the catalyst declined after activity test and the mean particle size was around $183.3 \mu\text{m}$, indicating that catalyst particle size effect complicated by particle migration, sintering, coalescence and agglomerate mechanism after catalytic reaction [27]. Hence, such changes in the sizes of particles of the catalyst can be attributed to over-oxidation of the Pt-Pd-Rh cordierite monolith catalyst surface sites during the reaction.

Fig. 5 plots the effect of oxygen concentration on conversion over a Pt-Pd-Rh cordierite monolith catalyst at various temperatures. The figure reveals that the activity gradually rises with the oxygen concentration from 4 to 20%, and that the conversion of NH_3 is maximal at 20% O_2 , since a concentration of O_2 above this value will clearly increase the oxidation of NH_3 . This result is similar to that of Pérez-Ramírez et al. [28]. According to the results, when gaseous oxygen is fed into NH_3 , the oxidation of NH_3 is considered to be an unimportant step in the reaction mechanism. It is noteworthy that the oxidation of NH_3 to N_2 may be the first step in the catalysis of

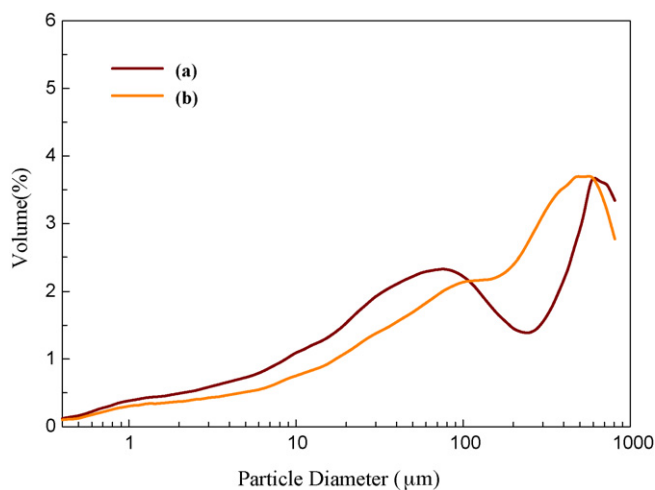


Fig. 4. Changes in particle sizes distribution of the Pt-Pd-Rh cordierite monolith catalyst showing: (a) fresh, (b) after activity test. Test conditions: 1000 ppm NH_3 in He, $\text{O}_2 = 4\%$, GHSV = 92,000 hr^{-1} .

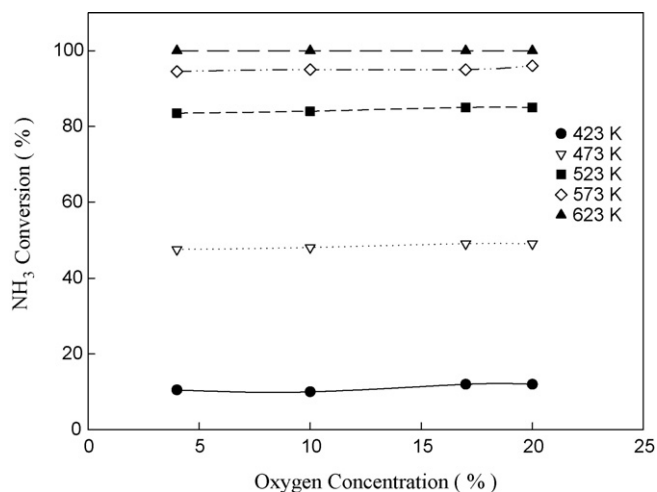


Fig. 5. Effect of the oxygen concentration on the conversion of NH_3 over the Pt-Pd-Rh cordierite monolith catalyst. Test conditions: 1000 ppm NH_3 in He, $\text{O}_2 = 4\text{--}20\%$, RH = 12%, GHSV = 92,000 h^{-1} .

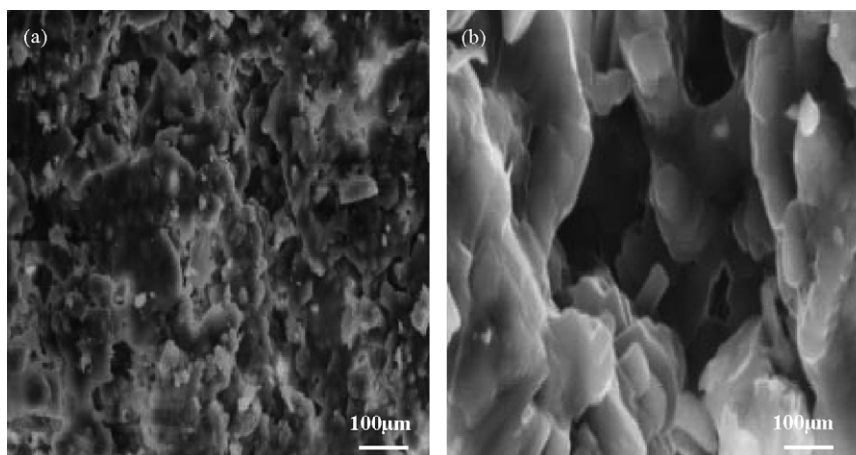


Fig. 7. SEM photograph of (a) fresh and (b) after activity test Pt-Pd-Rh cordierite monolith catalyst. Test conditions: 1000 ppm NH_3 in He, $\text{O}_2 = 4\%$, GHSV = 92,000 h^{-1} .

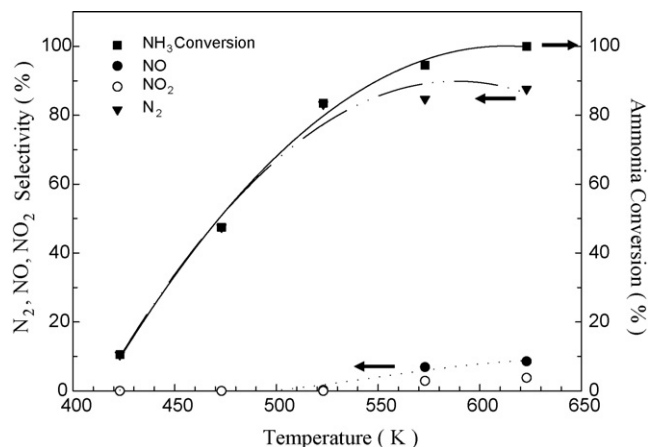


Fig. 6. Relationship among NH_3 conversion, N_2 yield, and NO yield at various temperatures over the Pt-Pd-Rh cordierite monolith catalyst. Test conditions: 1000 ppm NH_3 in He, $\text{O}_2 = 4\%$, RH = 12%, temperature = 423–623 K, GHSV = 92,000 h^{-1} .

NH_3 interacted with excess oxygen. The availability of oxygen in the surface lattice is generally considered to be an essential property of oxide catalysts used in selective oxidation [29]. Therefore, the NH_3 -SCO process reaction mechanism that involves NH_3 should be selective for nitrogen, and prevent further oxidation of nitrogen. The oxygen flux overwhelms the NH_3 flux, and the reaction is mass-limited (at low GHSV) [30]. However, the oxygen in the stream, provided by the oxygen flow, may suffice for the catalytic process, which proceed at NH_3 concentrations below 1000 ppm in the influent stream; in such a case the reaction is gas-limited (at high GHSV). The NH_3 -SCO process can be generally described by a Langmuir–Hinshelwood type scheme as previously suggested [12], in which ammonia reacts from gas phase with adsorption oxygen atomic and molecular oxygen at the surface leading to nitrogen formation. However, the further kinetic studies of catalytic oxidation of NH_3 on Pt-Pd-Rh cordierite monolith catalyst have not been thoroughly investigated.

The overall selectivity of N_2 production varied from 10 to 80% and that of NO production varied from 0 to 8% over the range of 11.0–99.0% NH_3 conversion at NH_3 concentrations of 1000 ppm (Fig. 6). Nitrogen gas thought to be formed primarily by the dissociation of NO produced by oxidation of adsorbed NH_3 [31]. Therefore, the research results hypothesize that NH_3 and oxygen may be adsorbed onto specific sites on the Pt-Pd-Rh cordierite monolith

catalyst, promoting the rapid conversion of NH_3 to nitrogen and water, and the recombination of nitrogen atoms forming nitrogen. As a consequence, nitrogen was the dominant gaseous, and a small amount of NO was detected in the resultant stream. This result is similar to that obtained by Curtin et al. [29] and Pérez-Ramírez and Kondratenko [32].

Fig. 7 presents the surface morphological changes of Pt-Pd-Rh cordierite monolith catalyst elucidating using SEM to provide information on the fresh/aged catalyst surface structure. Fig. 7a shows that the surface of the catalyst is more aggregated and crystalline than observed in Fig. 7b. Fig. 7b indicates that disaggregated and dispersed phases were formed when the surface of the catalyst was aged or when poisoning occurred because of plugging, implying that the porosity of the particles had changed. Generally, these crystal phases may be responsible for the high activity of the catalysts. These results also confirm that the dispersion phenomena of the catalyst increase the efficiency of removal of NH_3 .

4. Conclusions

Based upon the above results, the present study has shown that selective catalytic oxidation for ammonia (NH_3 -SCO) by a Pt-Pd-Rh cordierite monolith catalyst was found to promote the oxidation of NH_3 . The SCO process was found to be more effective at 623 K. The process altered the oxidation state and the crystalline composition of the catalyst. Moreover, the contaminants crystal aggregation phases and washout loss may be responsible for the deactivation of the catalysts. The overall by-product selectivity of the production of NO varied from 0 to 8% and that of N_2 production varied from 10 to 80% at 11.0 to 99.0% NH_3 conversion, when a Pt-Pd-Rh cordierite monolith catalyst was used. Also, experimental results indicate a reasonable mechanism for the NH_3 -SCO process that involves NH_3 should be selective for nitrogen, and prevent further oxidation of nitrogen. Further studies on the reaction kinetics will be carried out in the future. Overall, with regard to features of the Pt-Pd-Rh cordierite monolith catalyst, this material advance application for the NH_3 -SCO process has the remarkable performance to treat highly concentrated streams of NH_3 , helping industrial plants to meet more stringent air quality discharge regulations in the future.

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