Honeycomb Cordierite-Carriers Pt-Pd-Rh Ternary Composite for Ammonia Removal

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ABSTRACT

This work considers the development of ammonia (NH_3) by selective catalytic oxidation (SCO) over a honeycomb Pt-Pd-Rh ternary composite cordierite catalyst in a tubular fixed-bed flow quartz reactor (TFBR) at temperatures between 423 and 623 K. A honeycomb Pt-Pd-Rh ternary composite cordierite catalyst was prepared by incipient wetness impregnation with aqueous solutions of H_2PtCl_6, $Pd(NO_3)_3$ and $Rh(NO_3)_3$ that were coated on cordierite cellular ceramic materials. The catalysts were characterized using OM, TGA-DTA, SEM/EDX and TEM. Based on the experimental results show that around 99.5% NH_3 removal was achieved during catalytic oxidation over the honeycomb Pt-Pd-Rh ternary composite cordierite catalyst at 623 K with an oxygen content of 4%. N_2 was the main product in the NH_3-SCO process over the honeycomb Pt-Pd-Rh ternary composite cordierite catalyst. Moreover, the present study also shows that contaminants crystal aggregation phases and washcoat loss may be responsible for the deactivation of the catalysts. These results also verify that the high initial concentration of the influent NH_3 decreases the efficiency of removal of ammonia.
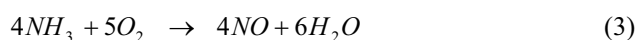
Keywords: Selective catalytic oxidation (SCO); Tubular fixed-bed reactor (TFBR); Ammonia (NH_3); Honeycomb Pt-Pd-Rh ternary composite cordierite catalyst.

INTRODUCTION

Atmospheric ammonia (NH_3) is emission from the ammonium nitrate and nitric acid production industry, livestock feedlots, urea manufacturing plants, the nitrogen fertilizer application industry, biomass combustion and petroleum refineries as well as the refrigeration industry. In this regard, NH_3 is a toxic inorganic gas with a pungent odor under ambient conditions, and is potentially harmful to public health as reported in the literature (Geng *et al.*, 2008). The maintenance and operating costs associated with these physical and chemical methods are high so far. As a result, the removal and control of NH_3 emission from air and waste streams are important because of stricter regulations in Taiwan.

As a rule, catalytic oxidation has been established to increase 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 conditions. The selective catalytic oxidation process of ammonia (NH_3-SCO) in a

stream to N_2 and H_2O is one method for solving problems of NH_3 pollution (Escandón *et al.*, 2002; Dravell *et al.*, 2003). Performance of the catalytic oxidation of NH_3 has been reported to proceed as follows.

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (1)$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad (2)$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (3)$$

Overall, the SCO process that involves NH_3 should be selective for nitrogen (reaction 1), and prevent further oxidation of nitrogen (reactions 2 and 3). Earlier work on NH_3 oxidation was reviewed by Il'chenko (1975), who focused on the reaction mechanism of NH_3 oxidation, and compared catalytic activities. Further catalysts have been used in oxidizing NH_3 in the gaseous phase. For instance, the work of Amblard *et al.* (2000) demonstrated the excellent selective conversion of NH_3 to N_2 by γ-Al_2O_3-supported Ni by SCO processes. Moreover, Wang *et al.* (1999), 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 NH_3, and the partial pressure of H_2 in the flue gas is a critical factor that governed NH_3 oxidation. One of the recent works has

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summarized that the catalytic oxidation of NH_3 in gaseous stream by a nanoscale Cu/Ce bimetallic catalyst in the temperature range 423-673 K at GHSV=92,000 1/hr (Hung, 2008a). 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.

It has been reported that cordierite material is a combination of oxides of a composition crystalline magnesium aluminosilicate ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) with a hexagonal structure, combining a relatively low thermal expansion coefficient with both thermal shock resistance and adequate refractoriness (Radwan *et al.*, 2004; El-Shovaky *et al.*, 2006). The previous works (2008b) showed that platinum, palladium, and rhodium metals exhibited remarkably activity used to elucidate the removal characteristics of NH_3 conversion in a wet oxidation system. In addition, as has been reported (Hung, 2009), the interaction between platinum, palladium oxide and the rhodium is complex, because various Pt-Pd-Rh interactions can result in synergistic effects, enhancing catalytic characteristics. However, little work has been undertaken on the use of honeycomb Pt-Pd-Rh ternary composite cordierite 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 honeycomb Pt-Pd-Rh ternary composite cordierite 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 OM, TGA-DTA, SEM/EDX and TEM.

MATERIALS AND METHODS

Material and Chemicals

The honeycomb platinum-palladium-rhodium ternary composite cordierite catalysts that were used in this study were prepared by the incipient wetness impregnation, which involved aqueous H_2PtCl_6, $Pd(NO_3)_3$ and $Rh(NO_3)_3$ (all grade, Merck, Darmstadt, Germany). A platinum-palladium-rhodium ternary composite was coated on a honeycomb cordierite cellular ceramic substrate (commercial grade) 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 973 K in an air stream for 5 hours. Fig. 1 presents the textural characteristics of the honeycomb Pt-Pd-Rh ternary composite cordierite catalyst.

Experimental Methods

Experiments were conducted on a tubular fixed-bed flow quartz reactor (TFBR). The typical reactant gas (GHSV, 92,000 1/hr) composition was as follows: 600 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,
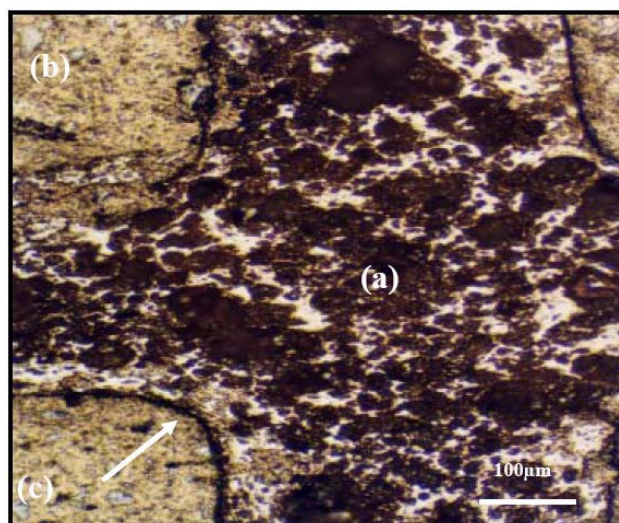

Fig. 1. Optical photograph of a honeycomb Pt-Pd-Rh ternary composite cordierite catalyst showing: (a) cordierite cellular ceramic support material, (b) cross-section of channel, and (c) metal-catalyzed alumina washcoat layer.

controlled using a mass flow meter (830 Series Side-Trak[TM], Sierra, Monterey, CA, USA). The mass of each catalyst was 1g and the empty bed volume was approximately 1.2 cm^3. An inert material formed from (hydrophilic and inert) γ-Al_2O_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 (2008a), 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, Shimaden, Tokyo, Japan) to maintain the temperature in the tube within ±0.5%.

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 373 K. 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.

The surface of the catalyst was characterized using optical microscopy (OM) (Olympus BHM PH-10AK3, Japan). The composition of the catalyst's surface was determined using an energy-dispersive x-ray spectrometer (SEM/EDX, JEOL, JSM-6400, Kevex, DeltaII). Thermogravimetric and differential thermal analysis (TGA-DTA) experiments were conducted in a TGA-DTA unit (Seiko SSC-5000, Japan) at a heating rate of 283 K/min. Transmission electron microscopy (TEM) (Philips CM-200 Twin, Netherlands) elucidated the morphology of the catalysts and yielded information on the distribution of honeycomb Pt-Pd-Rh ternary composite on the catalyst surface.

RESULTS AND DISCUSSIONS

Fig. 2 plots the results of TGA-DTA thermal decomposition of the honeycomb cordierite monolith precursor to determine the calcinations temperature. The catalyst does not lose mass until a temperature of about 973 K is reached. Above this temperature, a significant loss of mass may contribute to the decomposition and desorption of metal salts, oxygen and water. Moreover, the DTA curve reveals whether the reaction that involved the honeycomb cordierite monolith was exothermic or endothermic.

Fig. 3 depicts the surface morphological of fresh honeycomb Pt-Pd-Rh ternary composite cordierite catalyst, identified by scanning electron microscopy (SEM) with

elemental dot mapping photographs, for honeycomb Pt-Pd-Rh ternary composite cordierite catalyst with various metal contents. These figures thus provide information on the surface structures of fresh catalysts. The observations of agglomerates by SEM reveal that the composite catalyst particles are shaped into fine sheet-like. Based on the above results, the findings confirm that the dispersion phenomena of the catalyst increased the efficiency of the removal of NH_3. The elemental distribution proportional onto these particles was homogeneous, as shown by the electron backscattering in SEM micrographs.

Fig. 4 plots the NH_3 conversion as a function of temperature exhibits a maximum at 623 K. The overall selectivity of N_2 production varied from 8 to 50% and that of NO production varied from 0 to 8% over the range of 12–99.5% NH_3 conversion at NH_3 concentrations of 600 ppm (Fig. 4). It is known from the literature that nitrogen gas thought to be formed primarily by the dissociation of NO produced by oxidation of adsorbed NH_3 (Bradley *et al.*, 1995). Therefore, we hypothesis that NH_3 and oxygen may be adsorbed onto specific sites on the honeycomb Pt-Pd-Rh ternary composite cordierite catalyst, promoting the rapid conversion of NH_3 to nitrogen and water. As a consequence, nitrogen was the dominant gaseous, and a small amount of NO was detected in the resultant stream, which is similar to that previous finding obtained by Curtin (2000).

To further understand the reactive property of catalyst in this work, Fig. 5 presents the surface morphological changes of honeycomb Pt-Pd-Rh ternary composite cordierite catalyst, which were elucidated using OM to provide information NH_3 concentration at 600 ppm on the catalyst surface structure. Fig. 5b shows that the catalyst exhibits surface degradation and wascoat loss. One other finding in this study was that Fig. 5b shows that the
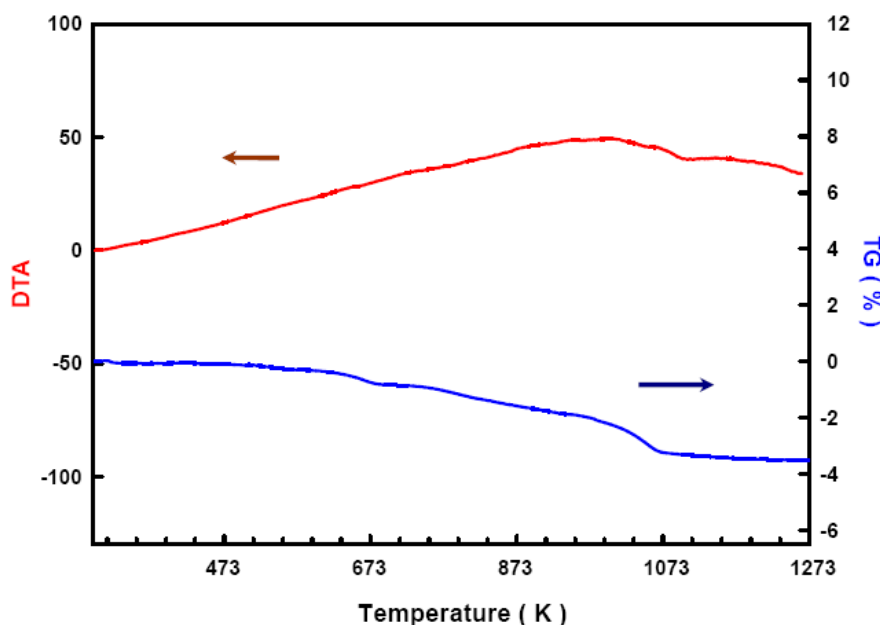

Fig. 2. TGA-DTA curve of the cordierite monolith.
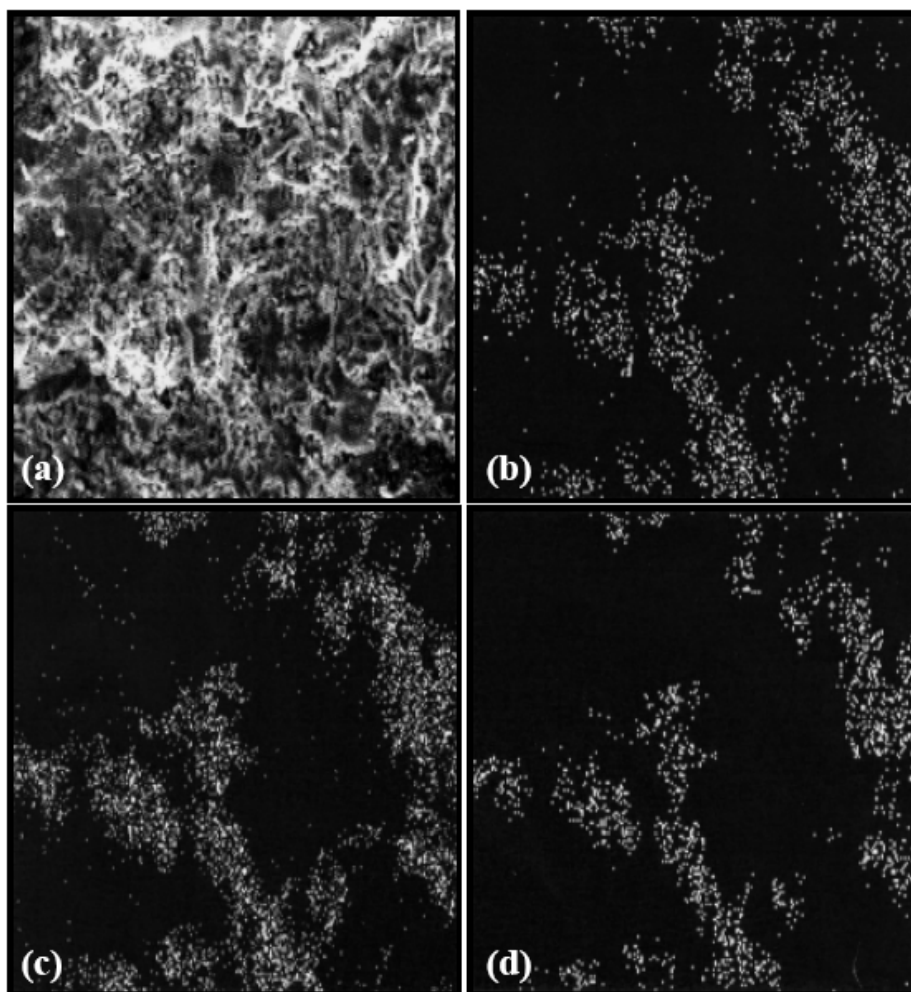
Fig. 3. SEM with dot mapping photographs result of various contents on the fresh honeycomb Pt-Pd-Rh ternary composite cordierite catalyst. (a) top view of surface, (b) Pt, (c) Pd and (d) Rh.
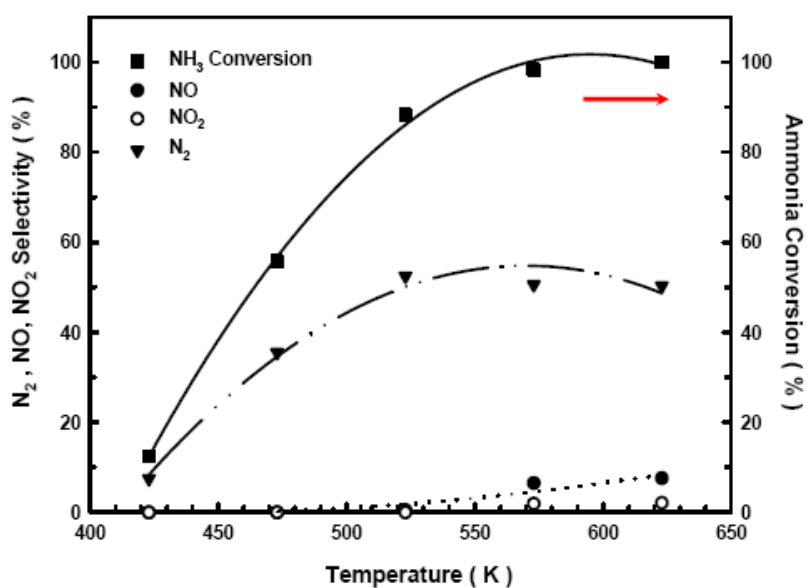

Fig. 4. Relationship of the ammonia conversion, N_2, NO and NO_2 yield at various temperatures over the honeycomb Pt-Pd-Rh ternary composite cordierite catalyst. Test conditions: 600 ppm NH_3 in He, O_2 = 4%, RH = 12%, Temp = 443–623 K, GHSV = 92000 1/hr.

surface of the catalyst exhibits more contaminants aggregation and crystalline than shown in Fig. 5a. It is interesting to see that the crystal phases growth may be responsible for the thermal effects of the catalysts. In addition, Fig. 5 also indicated the presence of deep cracks between the Pt-Pd-Rh ternary composite active phase and the cordierite monolith surface. Notable, these results also verify that the high initial concentration of the influent NH_3 decreases the efficiency of removal of ammonia.

Fig. 6 presents the surface morphological changes of honeycomb Pt-Pd-Rh ternary composite cordierite catalyst elucidating using TEM to provide information on the fresh/aged catalyst surface structure. Fig. 6a shows that the surface of the catalyst is more aggregation and crystalline than observed in Fig. 6b. Fig. 6b 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. Obviously, these results also confirm that the dispersion phenomena of the catalyst increase the efficiency of removal of NH_3.

CONCLUSIONS

On the basis of the present study has shown that selective catalytic oxidation for ammonia (NH_3-SCO) by a honeycomb Pt-Pd-Rh ternary composite cordierite catalyst was found to promote the oxidation of NH_3. The process altered 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 NH_3 conversion as a function of temperature exhibits a maximum at 623 K. The overall by-product selectivity of the production of NO varied from 0–8% and that of N_2 production varied from 8–50% at 12–99.5% NH_3 conversion, when a honeycomb Pt-Pd-Rh ternary
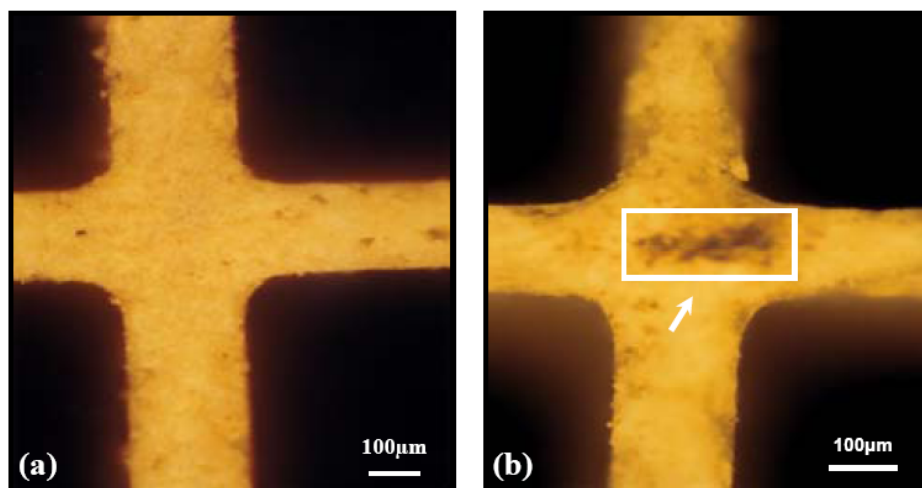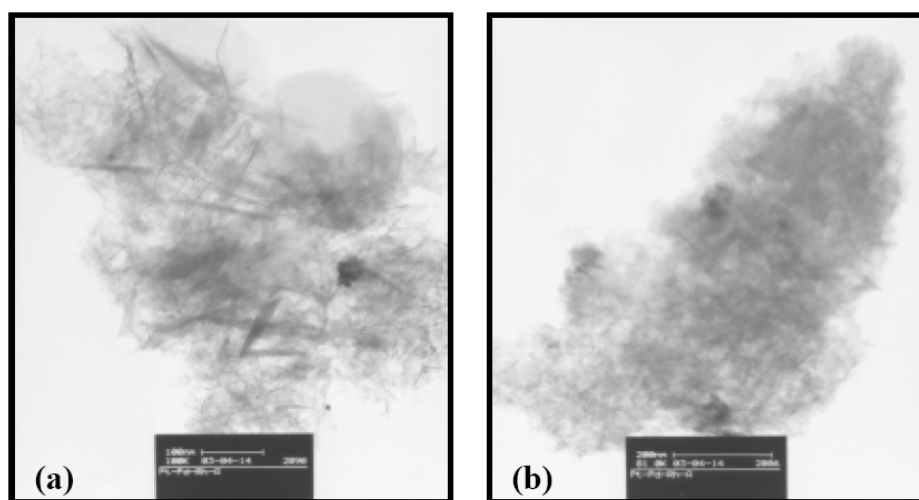

Fig. 5. OM photograph of (a) fresh and (b) after activity test honeycomb Pt-Pd-Rh ternary composite cordierite catalyst. Test conditions: 600 ppm NH_3 in He, O_2 = 4%, GHSV = 92000 1/hr.

Fig. 6. TEM photograph of (a) fresh and (b) after activity test honeycomb Pt-Pd-Rh ternary composite cordierite catalyst. Test conditions: 600 ppm NH_3 in He, O_2 = 4%, GHSV = 92000 1/hr.

composite cordierite catalyst was used. According the results, this work shows that the SCO process has the potential to treat highly concentrated streams of NH_3, helping industrial plants to meet useful information for the concerns of public health and governmental discharge regulations.

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