GAS POLLUTANT CLEANING BY A MEMBRANE REACTOR

by

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An alternative technology for the removal of gas pollutants at the intergrated gasification combined cycle process for power generation is the use of a catalytic membrane reactor. In the present study, ammonia decomposition in a catalytic reactor, with a simultaneous removal of hydrogen through a ceramic membrane, was investigated. A Ni/Al_2O_3 catalyst was prepared by the dry and wet impregnation method and characterized by the inductively coupled plasma method, scanning electron microscopy, X-ray diffraction, and N_2 adsorption before and after activation. Commercially available $\alpha\text{-}Al_2O_3$ membranes were also characterized and the permeabilities and permselectivities of H_2, N_2, and CO_2 were measured by the variable volume method. In parallel with the experimental analysis, the necessary mathematical models were developed to describe the operation of the catalytic membrane reactor and to compare its performance with the conventional reactor.

Key words: *ammonia decomposition, nickel/alumina catalyst, ceramic membrane, hydrogen separation*

Introduction

The development of alternative technologies for the removal of gas pollutants at the integrated gasification combined cycle is considered as an important aspect for the environmental friendliness of energy production. During coal gasification, N_2 contained in coal is converted to NH_3. As much as 50% of the ammonia in the fuel gas can be converted to nitrogen oxides (NO_x) in the gas turbine when the gas is combusted to produce power. The decomposition of NH_3 before it enters to the gas turbine is an acceptable solution. A sulfur tolerant catalyst is needed for ammonia decomposition, as hydrogen sulfide is another component of the gasifier outlet. High concentration of hydrogen is also contained at the gasification gas and inhibits ammonia decomposition.

Separation technology plays an important role in many processes. The use of membrane technology for different kinds of gas separation processes is a strongly expanding field, which showed a major breakthrough in the 1970's due to the development of new polymeric membrane materials. Currently, industrial applications of gas separation polymer membranes are mainly focused to hydrogen recovery from oil refineries,

natural gas purification, and oxygen separation from air. However, many industrially important gas separation problems, like gas cleaning in coal upgrading processes, occur at high temperatures, where polymeric materials are insufficient. So, in the last two decades, there was an important direction in research and development in the inorganic membrane field. Inorganic membranes have the advantage of a broad temperature and pressure operating range [1-3].

Furthermore, the application of inorganic membranes in so-called membrane reactors, using catalytically active or passive membranes, has proven to be very promising and an increasing research effort in this field is observed in the past few years. The idea of simultaneous reaction and separation with a membrane was first brought up by Michaels in 1968. It was thought that higher conversions could be obtained by using a membrane, as it would allow the selective permeation of one of the reaction products, leading to a shift in the equilibrium limited reaction [4]. Gobina *et al.* [5] reported the potential application of inorganic membranes to coal gas clean up processes. Ammonia decomposition was investigated in the literature primarily theoretically [5-7]. The authors concluded that membranes with high hydrogen selectivities are necessary to achieve high NH_3 conversions. Therefore, the researches were mainly focused in metallic membranes, because of their high hydrogen selectivity. Collins and Way [8] used a composite palladium-ceramic membrane reactor and achieved conversions of over 94% at a temperature of 600 °C and pressure of 16 bar. A ceramic membrane reactor, which is investigated in the present study, could be an economic alternative option to palladium based membrane reactors.

Experimental

Ni/Al_2O_3 catalysts were prepared by the dry and wet impregnation method of the γ-alumina support with the appropriate solution volume and concentration of aqueous $Ni(NO_3)_2 \cdot 6H_2O$ so as to prepare catalysts with ~10% Ni. In both cases, catalysts were dried at 110 °C for 15-18 h, calcined in air at 500 °C for 3 h and finally activated by 30 cm^3/min. H_2, at 500 °C for 3 h. A small heating rate of 2.5 °C/min. was used. Atomic Emission Spectroscopy by the Inductively Coupled Plasma method (AES/ICP) was used for the calculation of the metal concentration. Catalysts were characterized before and after their activation by N_2 adsorption (BET), X-Ray Diffraction (XRD), and Scanning Electron Microscopy/Energy Dispersive Spectroscopy (SEM/EDX). Catalytic activity tests were carried out in a ¼" outside diameter stainless steel packed bed. The gas products were analysed on-line by a mass spectrometer. Experimental conditions were: $T = 300$-700 °C, $P = 2$-6 bar, $W = 0.3$ g, $V_{react} = 0.5$ cm^3, $F = 30$ cm^3/min. and 300 cm^3/min. Feed gas contained 3000 ppm NH_3 in He.

The $α$-Al_2O_3 membranes were procured by Eco-Ceramics and they have mean pore diameter of 80 nm. The permeabilities of H_2, N_2, and CO_2 were determined by the variable volume method at pressures 5-20 psig and temperatures 25-70 °C. The permselectivities were calculated as the ratio of permeabilities.

For the mathematical modeling of the catalytic membrane reactor (CMR), the rate of the diffusion of gases through the membrane was included in the differential equa-

tions that describe the mass transfer phenomena in a conventional plug flow reactor (PFR). The generally accepted Temkin-Pyzhev mechanism and the corresponding rate equation [6] were chosen to describe the NH_3 decomposition rate.

Results and discussion

Metal concentrations and N_2 adsorption measurements are shown in tab. 1.

Table 1. Ni/Al_2O_3 catalysts metal concentration and physical characteristics before (BA) and after (AA) their activation

Catalyst	Ni [%]	Specific surface area [m²/g]		Pore volume [cm³/g]		Mean pore size [nm]	
		BA	AA	BA	AA	BA	AA
Ni/Al_2O_3 dry	8.20	129.0	124.1	0.298	0.302	4.62	4.86
Ni/Al_2O_3 wet	8.25	133.8	129.9	0.320	0.326	4.78	5.00

XRD measurements showed that no crystallite phases of NiO or Ni existed. The metal concentration distribution was calculated by SEM/EDS and found to be 7-10% in all samples. That distribution didn't change after catalysts activation.

Catalytic activity tests are shown in figs. 1 and 2. Wet impregnated catalyst showed better activity than the dry impregnated catalyst at lower temperatures (300-500 °C). In both cases, the conversion reached at 98% (~60 ppm NH_3) at temperatures higher than 500 °C.
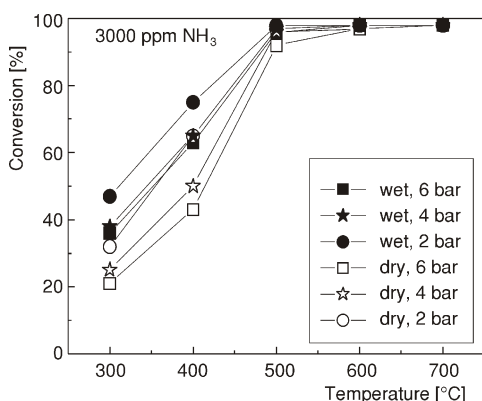

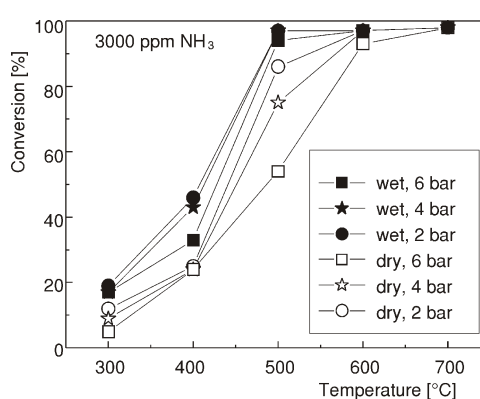**Figure 1. NH_3 conversion with temperature for 0.1 s residence time**

Figure 2. NH_3 conversion with temperature for 1 s residence time

Permeance and permselectivity measurements of the α-Al_2O_3 membranes were done for three gases, H_2, CO_2, and N_2 and are shown in figs. 3, 4, and 5. The permeances are in the range of 10^{-7}-10^{-6} mol/m²sPa and the permselectivities are almost identical with the theoretical Knudsen values.
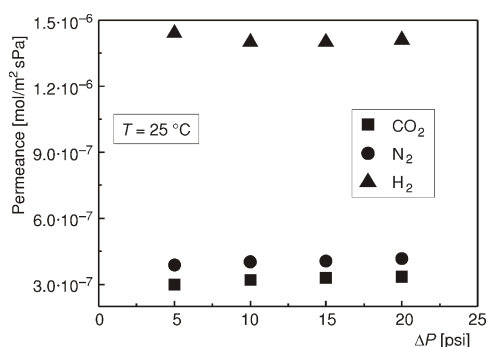

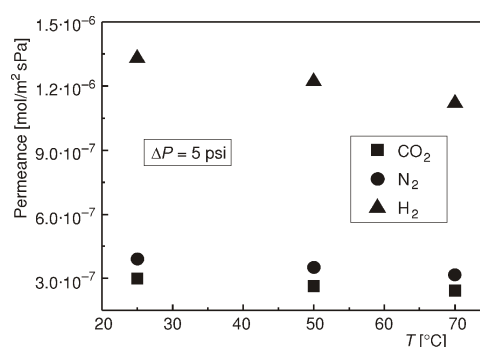**Figure 3. Permeance of H_2, CO_2, and N_2 with pressure for the α-Al_2O_3 membranes**

Figure 4. Permeance of H_2, CO_2, and N_2 with temperature for the α-Al_2O_3 membranes
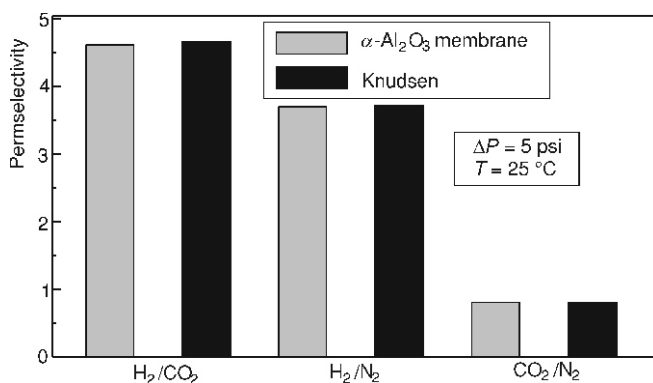

Figure 5. Permselectivities of the α-Al_2O_3 membrane compared with theoretical Knudsen values

A comparison of NH_3 conversion in a conventional PFR and in a CMR with a membrane that has Knudsen diffusion characteristics is shown in fig. 6. NH_3 conversion increases to more than 65% with the use of a CMR at 900 K and 15 bar feed pressure as compared with 39% for the conventional PFR.

The results of the present study indicate that physical and chemical characteristics of the prepared catalysts were fated. N_2 absorption measurements (tab.1) showed slight differences at the physical characteristics of the prepared catalysts that were almost unchanged after activation. Also, the N_2 adsorption diagrams showed a mesoporous structure of the prepared catalysts.
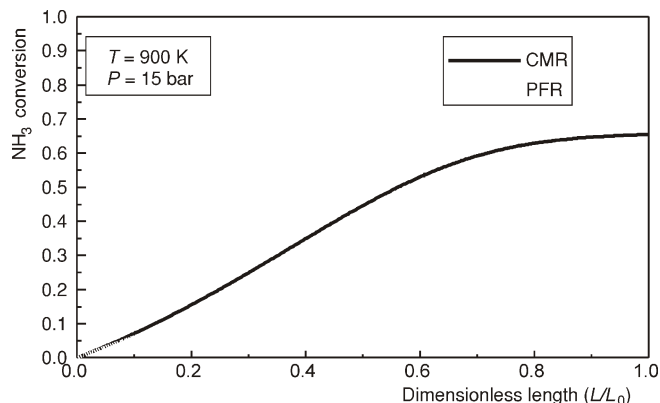
Figure 6. NH$_3$ conversion with dimensionless length for a PFR and a CMR

XRD and SEM/EDS characterization resulted to the assumption that metal or metal oxide were very well dispersed, forming an amorphous spinel-like NiAl$_2$O$_4$ structure on the surface of the catalyst. This phase is accommodated by tetrahedral coordinated nickel ions that are hard to reduce. That formation requires high temperatures (>600 °C) for the complete reduction because of the very strong interaction between the metal and the support [9].

Catalytic activity tests showed that reaction favored by higher temperature and residence time and lower pressure (figs. 1 and 2). Wet impregnated catalyst showed better activity than the dry impregnated catalyst, probably due to smaller interaction between the metal and the support. The use of catalysts with higher metal loading is estimated that will improve catalysts activity. Furthermore, catalytic activity tests with a simulated gasification gas will help to determine the catalyst performance and stability at realistic operating conditions.

The membranes tested presented high tolerance and repeatability. The mass transport through the membrane seems to be governed by Knudsen diffusion as expected for porous materials with 80 nm mean pore diameter. Permeance of the gases is independent of pressure (fig. 3) and decreases with temperature (fig. 4). In addition, the permeance of a gas decreases as the molecular weight of the gas increases. The permselectivities are identical with the theoretical Knudsen ones and equal to the square root of their inverse molecular weight ratio (fig. 5). This indicates that the membranes are crack free and in combination with their smooth surface (surface irregularities <0.1 µm, as provided by the manufacturer) they seem to be appropriate for further deposition of selective silica layers. α-Al$_2$O$_3$ membranes seem to be appropriate for further deposition of selective silica layers which will lead to a significant increase in hydrogen selectivity of the membrane.

Catalytic membrane reactor modeling indicates that ammonia decomposition increases at any case. The increase in NH_3 conversion is caused by the diffusion of hydrogen through the membrane, which shifts the equilibrium of the decomposition reaction. However, NH_3 is not converted completely because of some NH_3 permeation through the membrane.

By using all the information obtained by catalytic activity and membrane selectivity tests, the optimal reaction conditions should be investigated.

Conclusions

Wet impregnated Ni/Al_2O_3 catalysts with low metal loading led to 98% conversion of diluted concentrations of ammonia at temperatures higher than 500 ºC.

α-Al_2O_3 permeabilities and permselectivities were according to Knudsen diffusion as expected for porous materials with 80 nm mean pore diameter.

NH_3 conversion increases to more than 65% with the use of a CMR at 627 °C and 15 bar feed pressure as compared with 39% for the conventional PFR.

For the achievement of higher conversions, membranes with greater H_2 selectivity are necessary.

Acknowlegment

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