**Catalyst for Utilization of Methane in
Selective Catalytic Reduction of NO_x
Task 2.6**

**Topical Report
February 1996**

Edwin S. Olson
Ramesh K. Sharma

November 1995

Work Performed Under Contract No.: DE-FC21-93MC30097

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
University of North Dakota
Grand Forks, North Dakota

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TASK 2.6 – CATALYST FOR UTILIZATION OF METHANE IN SELECTIVE CATALYTIC REDUCTION OF NO_x

EXECUTIVE SUMMARY

Selective catalytic reduction (SCR) of nitrogen oxides (NO_x) in flue gas or engine exhaust gas with hydrocarbons as the reductant has great potential for less expense, less pollution, and easier operation than SCR with ammonia. Methane is the preferred reducing gas because of its low cost and low toxicity. Stable, low-cost catalysts for SCR with methane are required to demonstrate this technology for controlling NO_x emissions. Several cobalt and nickel catalysts on synthetic clay and uranium oxide supports were investigated for their activities in reducing NO_x with methane in the presence of air.

The efficiency of the synthetic clay-supported nickel and cobalt catalysts for nitric oxide (NO) reduction with methane as the reducing gas was poor. The nickel oxide-uranium oxide catalyst, which was chosen for its high stability, was also ineffective.

Results from the two-step experiments conducted at two temperatures produced some interesting information on the reactions of methane with the catalysts and the reactivity of the carbonaceous intermediate. The carbonaceous material formed from methane dissociation at 450°C not only reduces NO to N₂O at lower temperatures, but also prevents oxidation of NO to NO₂. Unfortunately, the carbonaceous forms that reduce the NO are not available for reactions at 400°C in the presence of oxygen. A two-step process employing this chemistry would be difficult because the catalyst would have to be cycled between the two temperatures. Also the desired reduction to nitrogen is not very efficient.

TASK 2.6 - CATALYST FOR UTILIZATION OF METHANE IN SELECTIVE CATALYTIC REDUCTION OF NO_x

1.0 INTRODUCTION

The combustion of fossil and biomass fuels results in the emission of nitrogen oxides (NO_x), which play a damaging role in the environment through smog formation, acidic deposition, depletion of the stratospheric ozone layer, the greenhouse effect, and effects on human health. Nitric oxide (NO) is the main NO_x component (90%-95%) formed in the combustion of fossil fuels and is rapidly converted to NO₂ in the atmosphere. Smaller amounts of N₂O are formed and subsequently converted to NO. The primary nitrogen source can be either air or fuel. Power plants are responsible for 25% of the human-generated NO_x and transportation systems for about 50%, with domestic combustion, biomass burning, and agricultural production accounting for smaller amounts (1). NO_x emissions are increasing at a fast rate, and, consequently, regulations to reduce this emission have been enacted. In order to meet the National Ambient Air Quality Standards (NAAQS) for ozone, urban areas must implement NO_x control regulations (2).

Several options are available for reducing NO_x in combustion plants, but each has disadvantages. Various modifications to the combustion systems have achieved moderate NO_x reductions. However, postcombustion NO_x reduction processes (with a reductant such as ammonia) can give high removal efficiencies, especially those that employ a selective catalyst that gives higher reaction rates with NO_x than with the oxygen present in the flue gas. In order to be more widely applied in the United States, operating costs for the process must be lowered and, at the same time, nonpolluting reducing gases must be developed to replace the ammonia reductant.

The abatement of NO_x emissions from coal-fired and other combustion units has employed several methods for postcombustion NO_x reduction, including selective noncatalytic reduction (SNR) with ammonia or urea injections in a high-temperature zone (> 800°C), nonselective catalytic reduction (NCR) with CO or H₂, and selective catalytic reduction (SCR). In SCR, the reducing gas exhibits selectivity favoring the reaction with NO_x over the reaction with oxygen; therefore, SCR can be used when oxygen is present in the flue gas, which gives SCR a large advantage over NCR. SCR operates at a lower temperature (150°-600°C) than SNR, which means it can be used after an air preheater exchange. In the tail end design, the flue gas is reheated prior to SCR.

Ammonia is used as the reductant gas in several SCR applications in Europe and Japan and can achieve NO_x reductions of greater than 90% (3). Although ammonia is effective for reducing NO in an oxidizing atmosphere, the excess ammonia required (ammonia slip) can contribute to toxic emissions or can form plugs of ammonium bisulfate. This can cause problems with increased pressure, poor heat exchange, and down time for washing out the ammonium salts.

SCR of NO_x in flue gas or engine exhaust gas with hydrocarbons as the reductant has great potential for less expense, less pollution, and easier operation than SCR with ammonia. Attention has focused on the use of light gases such as ethylene, propane, and propylene for SCR in flue gas containing oxygen. The excess oxygen in the flue gas results in an enhancement of the catalyst activity for selective NO_x reduction by the hydrocarbons.

Several catalysts have been tested for SCR with hydrocarbons in the presence of oxygen. The most effective catalysts are the transition metal-exchanged zeolites (4, 5). In a comparison of the activities of a large number of zeolite and other supported metals with ethylene reductant in 2% oxygen, Sato and others (4) found that Fe-ZSM-5, Fe-silicate, and Fe-mordenite were effective catalysts at the lowest temperatures (200°–300°C). Cu-ZSM-5 was also effective at 250°C (5, 6), Co-ZSM-5 at 400°C, Ag-ZSM-5 at 500°C, and Zn-ZSM-5 at 600°C (5). The Ce- and Pr-ZSM-5 catalysts were found to be highly reactive for SCR with propylene at 400°C (7). Ga-ZSM-5 exhibited very high activity and selectivity with propane as the reductant (8). Fe-silicate showed high activity for SCR with propylene and was not affected much by SO₂ (9). The H-form of zeolites and alumina also exhibits some activity (10, 11) at temperatures above 400°C.

The unsaturated hydrocarbons (propylene and ethylene) are more reactive with NO than the saturated gases. The NO conversions with some catalysts, e.g., the Ga-ZSM-5, were 100% (8). Isobutane was shown to be quite active, and the zeolite-catalyzed cracking of the isobutane was demonstrated (12). The light hydrocarbon olefins and alkanes are, of course, petroleum refinery products and are widely used chemical feedstocks. Their cost will increase substantially if oil prices rise. The transportation costs from a refinery to the combustion plant site may be a significant factor in their price. The use of low- or negative-cost hydrocarbon sources that are available universally or at least close to the combustion plants would facilitate the development of SCR with hydrocarbon reductant.

Recently methane has been successfully utilized for SCR. Methane is relatively inexpensive and readily available in most localities via pipeline. The selective catalysis of methane reaction with NO_x is more difficult to achieve, however. Alumina and tin oxide are used at high temperatures, but they are not very selective catalysts. Cobalt-loaded zeolites exhibit the required selectivity for NO (13, 14). Since a methane SCR technology has not yet been commercialized, there are still questions concerning the temperatures required, and the stability of the catalyst to the sulfur acids formed in flue gases may be a problem. Thus stable, low-cost, low-temperature catalysts and reducing gas systems need to be investigated for effective NO_x removal.

2.0 OBJECTIVES

The objective of this work was to demonstrate that catalysts consisting of metal ion impregnated on a clay or pillared clay support or on a highly stable composite support are effective for SCR of NO_x.

3.0 WORK PERFORMED

3.1 Summary

Nickel-substituted mica montmorillonite (NiSMM), cobalt-exchanged NiSMM, cobalt-substituted mica montmorillonite, and nickel/uranium oxide catalysts were prepared and tested in a fixed-bed reactor for NO_x reduction with methane in a 2% oxygen atmosphere over a range of temperatures from ambient to 550°C. Reactions were performed in a Vicor tube reactor heated in a vertical furnace. Product gases were analyzed by direct interface of the column to an infrared

spectrometer cell. Earlier tests that were carried out in a stainless steel reactor were determined to be influenced significantly by reactions occurring on the metal surface.

3.2 Experimental

3.2.1 Catalysts

The catalysts used in this study included the following:

Synthetic clays:

NiSMM (NiSMM was prepared by the method of Heinerman [15])

NiSMM + cobalt (NiSMM was impregnated with cobalt ions [16])

CoSMM (CoSMM was prepared by the method of Heinerman [15])

Oxide-supported metals:

Uranium oxide-nickel oxide (prepared by the method of Berry and coworkers [17])

3.2.2 Equipment

3.2.2.1 FT-IR Spectrometer

The Fourier transform infrared (FT-IR) spectrometer used is a Bomem Instruments MB-100 continuous scan Michelson interferometer, capable of determining wavenumbers with a precision of 0.01 cm^{-1} . The instrument is fitted with a 10-cm path length, heated gas cell and deuterated triglycine sulfate (DTGS) detector. The open-beam sensitivity (peak-to-peak SNR) of the instrument is 1400:1 for a 9-second observation time when equipped with the DTGS detector. All data from the instrument are collected using a 80486-based personal computer (PC) equipped with a digital signal processor board. Locally developed software is used to allow the instrument to collect and display data in real time. This facilitates the use of the instrument for process monitoring and control as well as conventional analytical applications. The PC and software are also capable of monitoring up to 21 analog channels while simultaneously acquiring IR data, allowing time synchronization of other measured parameters with the IR spectroscopic data.

The gas cell used has an optical path length of 10 cm. The cell is equipped with BaF_2 windows allowing a mid-IR passband of 800 cm^{-1} when used with the spectrophotometer described above. The gas cell is fabricated from stainless steel and has closed-loop temperature control. Its internal volume is approximately 50 cc.

3.2.2.2 Gas-Mixing Equipment

The input gas stream to the tube reactor was blended using four compressed gas cylinders, CP-grade methane, certified standard 4.99% nitric oxide in nitrogen, oxygen, and nitrogen. Gas cylinder flow for three of the cylinders was controlled using electronic mass flow controllers

(MFCs). A calibrated floating ball-type meter and metering valve were used to set the nitrogen flow rate. The flow controllers and floating ball meter were calibrated for each gas using a primary flow standard. The linearity of MFC setpoint versus gas flow rate for each was checked using the primary flow standard and the gas for which the MFC was calibrated. The MFCs were used to control the flow of NO, CH₄, and O₂, and the metering valve and floating ball-type meter were used for N₂. The mass flow controllers and metering valve were set to give the gas composition specified for the experiment. The composition used for evaluation of the gas-mixing equipment was 2000 ppm NO, 2000 ppm CH₄, 2.5% O₂, and 97.2% N₂. The repeatability of the gas mixture was verified by monitoring the output of the gas-mixing equipment with FT-IR.

3.2.3 Procedure

A 6" stainless steel or vicor glass tube reactor was packed with the desired catalyst (+25 mesh). The reactor was placed in a vertical furnace. The catalyst was activated by heating in a flow of hydrogen or nitrogen (8–10 mL/min) at desired temperature (350°–400°C) for 2 hours. The tube reactor was attached to a gas supply through metering valves (see gas mixing above). The exit gases were passed through the FT-IR from the bottom of the reactor. The desired gas(es) was passed through the catalyst for desired length of time. After the desired reaction time, the flow of reactant gas(es) was stopped, but the flow of purge nitrogen was maintained for an additional period of 15 minutes to flush the products out of the reactor. A flow diagram for the reaction assembly is shown in Figure 1.

3.3 Results

3.3.1 Selective Catalytic NO Reduction with Methane in Air

Blank reactions were carried out in the Vicor tube inserted in the stainless steel reactor at 400°C with no catalyst present. The methane/nitrogen mixture was passed through the tube at 400°C, and oxygen was then introduced. The reaction of methane with oxygen in the absence of NO resulted in the formation of a small amount of carbon dioxide and water, as expected for a nonselective noncatalytic oxidation of methane. In the blank (noncatalytic) reaction of NO with methane in the presence of oxygen, an equilibrium mixture of NO and NO₂ formed, and no methane reacted with the NO_x.

In the catalytic reaction over a fixed bed of NiSMM, the addition of O₂ to the methane in nitrogen stream gave carbon dioxide from combustion of the surface-bound carbon formed from the methane dissociation. When NO was added to the feed gas, NO₂ appeared, and the NO/NO₂ mixture was obtained as in the noncatalytic blank run. The NO concentration was identical to the blank run, and the NO₂ concentration was diminished by only 15%. Very little of the methane reacted at 400°C. Thus the synthetic clay-supported nickel was a poor catalyst for the reduction of NO_x with methane in air. Similar negative results were obtained for the cobalt-exchanged NiSMM and the nickel/uranium oxide catalyst.

In the work reported by Li and Armor (13, 14), Co, Mn, and Ni supported on ZSM-5 and mordenite were active for NO reduction with methane, but Y-zeolite was ineffective as the metal support. The results in both this and Li's report are consistent with the theory that traditional zeolite properties, such as high acidity and shape selectivity, are not important for this reaction,

Figure 1. Catalyst test apparatus.

but some interaction between the metal cation and the support determines the reactivity of the catalyst. Thus the type of support is critical, and the synthetic clays and uranium oxide do not have the proper geometry for binding NO and catalyzing its reduction by methane.

3.3.2 Catalytic Reduction of NO with Methane-Derived Intermediates

The reaction of methane with the clay-supported nickel and cobalt was further investigated to determine if some chemistry could be utilized for NO_x reduction under some conditions. The reaction of methane in nitrogen with the NiSMM at 450°C was performed in the absence of oxygen or NO (30 min). The pretreated catalyst was then cooled rapidly to 150°C, and the NO/N₂ was passed through the reactor. The NO concentration was lowered somewhat by the carbonaceous forms deposited on the catalyst, and N₂O began to form along with some CO₂. When oxygen was introduced at 150°C, a small amount of NO₂ appeared and the N₂O decreased, but in this case only 15% of the NO₂ concentration formed, compared with the earlier experiments.

Further examination of the details of methane reaction with the NiSMM showed that the methane was completely reacted with the catalyst bed at 450°C. The second experiment also showed that no reduction of the NO occurred when introduced after cooling to 150°C, and negligible amounts of NO₂ were produced.

The Co-exchanged NiSMM was also heated with methane at 450°C for 30 min. After cooling rapidly to 150°C, the NO was added. Some initial reduction in the NO concentration was observed, but the concentration increased to the equilibrium level. Subsequent use of these methane-reduced catalysts at higher temperatures for NO reduction in air did not produce positive results.

Earlier work has examined the chemisorption of methane and the reactivity of the surface-bound carbon. Van Santen and coworkers (18) reported that CH₄ is decomposed by a reduced Group VIII metal catalyst at 450–800 K into hydrogen and adsorbed surface carbonaceous species, which can be converted into hydrocarbons by hydrogenation with hydrogen at 300–400 K in a second step. Yang and coworkers (19) decomposed preabsorbed methane on a Ni(III) single-crystal surface by a krypton bombardment at 47 K under ultrahigh vacuum condition ($P = 5 \times 10^{-6}$ Torr). Tanaka and coworkers (20) created surface CH_x fragments by dissociative methane adsorption around 700 K on a cobalt catalyst. None of these studies utilized NO as a substrate, however.

In order to determine the decomposition products of CH₄ over NiSMM catalyst, CH₄/N₂ was passed over the NiSMM catalyst, which was prereduced by heating in a gentle flow of hydrogen at 450°C for 30 minutes. The effluent gas was analyzed by FT-IR. The data indicate almost quantitative decomposition of the CH₄. The reactor was cooled to 150°C, and a gentle flow of H₂ was passed through the catalyst for several minutes. IR data for the effluent gas did not indicate the formation of hydrocarbons. It is thus possible that the carbonaceous material formed on the surface of the catalyst is not active for the hydrogen reaction, although it did have activity for NO₂, as discussed above. van Santen reported that only the C-alpha form of the surface-bound carbon is active for reaction with hydrogen. Upon aging C-alpha was converted into C-beta and C-gamma,

which are inactive carbon forms for hydrogenation. It is likely that these forms are present on the NiSMM surfaces, and they are only partly reactive with NO_2 .

4.0 CONCLUSIONS

The efficiency of the clay-supported nickel and cobalt catalysts for NO reduction with methane as the reducing gas is poor. The only catalysts that evidently can effect this reaction are those reported by Li and Armor (13, 14), who claim that only two zeolite-supported catalysts will activate methane for the NO reduction.

Results from the two-step experiments conducted at two temperatures are much more interesting. The carbonaceous material formed from methane dissociation at 450°C not only reduces NO to N_2O at lower temperatures, but also prevents oxidation of NO to NO_2 . Unfortunately, the carbonaceous forms that reduce the NO are not available for reactions at 400°C in the presence of oxygen. A two-step process employing this chemistry would be difficult because the catalyst would have to be cycled between the two temperatures. Also the desired reduction to nitrogen is not very efficient.

5.0 REFERENCES

1. Sloss, L.L. *NO_x Emissions from Coal Combustion*, IEA Coal Research: London, 1991.
2. Wood, S.C. *Chem. Engineer. Prog.* **1994**, 32-38.
3. Hjalmarsson, A.-K. *NO_x Control Technologies for Coal Combustion*, IEA Coal Research: London, 1990.
4. Sato, S.; Hirabayashi, H.; Yahiro, H.; Mizuno, N.; Iwamoto, M. *Catal. Lett.* **1992**, 12, 193-200.
5. Sato, S.; Yu-u, Y.; Yahiro, H.; Mizuno, N.; Iwamoto, M. *Appl. Catal.* **1991**, 70, L1.
6. Iwamoto, M.; Yahiro, H.; Shundo, S.; Yu-u, Y.; Mizuno, N. *Appl. Catal.* **1991**, 69, L15.
7. Misono, M.; Kondo, K. *Chem.Lett.* **1991**, 1001-1002.
8. Yogo, K.; Tanaka, S.; Ihara, M.; Hishiki, T.; Kikuchi, E. *Chem.Lett.* **1992**, 1025-1028.
9. Kikuchi, E.; Yogo, K.; Tanaka, S.; Abe, M. *Chem. Lett.* **1991**, 1063-1066.
10. Hamada, H.; Kintaichi, Y.; Sasaki, M.; Ito, T.; Tabata, M. *Appl. Catal.* **1990**, 64, L1-L4.
11. Hamada, H.; Kintaichi, Y.; Sasaki, M.; Ito, T.; Tabata, M. *Appl. Catal.* **1991**, 70, L15-L20.

12. Petunchi, J.O.; Sill, G.; Hall, W.K. *Appl. Catal. B: Environ.* **1993**, *2*, 303-321.
13. Li, Y.; Armor, J.N. *Appl. Catal. B: Environ.* **1993**, *2*, 239-256.
14. Li, Y.; Armor, J.N. *Appl. Catal. B: Environ.* **1992**, *1*, L31-L40.
15. Heinerman, J.J.L.; Freriks, I.L.C.; Graaf, J.; Pott, G.T.; Coglegem, J.G.F. *J. of Catal.* **1983**, *80*, 145.
16. Olson, E.S.; Sharma, R.K. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1994**, *39* (3), 706.
17. Berry, F.J.; Murray, A.; Parkyns, N.D. *Appl. Catal. A* **1993**, *100*, 131.
18. Koerts, T.; Deelen, Marc J.G.A.G.; van Santen, R.A. *Journal of Catalysis*, **1992**, *138*, 101-114.
19. Yang, Q.Y.; Johnson, A.D.; Maynard, K.J.; Ceyer, S.T. *J. Am. Chem. Soc.* **1989**, *111*, 8748.
20. Tanaka, K.I.; Yaegashi, I.; Aomura, K. *J. Chem. Soc. Chem. Commun.* **1982**, 938.