Report Title: **DEVELOPMENT OF IMPROVED CATALYSTS FOR THE SELECTIVE CATALYTIC REDUCTION OF NITROGEN OXIDES WITH HYDROCARBONS**

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ABSTRACT

Significant work has been done by the investigators on the cerium oxide-copper oxide based sorbent/catalysts for the combined removal of sulfur and nitrogen oxides from the flue gases of stationary sources. Evaluation of these sorbents as catalysts for the selective reduction of NO_x gave promising results with methane. Since the replacement of ammonia by methane is commercially very attractive, in this project, the effect of promoters on the activity and selectivity of copper oxide/cerium oxide-based catalysts and the reaction mechanism for the SCR with methane was investigated.

Unpromoted and promoted catalysts were investigated for their SCR activity with methane in a microreactor setup and also, by the temperature-programmed desorption (TPD) technique. The results from the SCR experiments indicated that manganese is a more effective promoter than the other metals (Rh, Li, K, Na, Zn, and Sn) for the supported copper oxide-ceria catalysts under study. The effectiveness of the promoter increased with the increase in Ce/Cu ratio. Among the catalysts tested, the Cu1Ce3 catalyst promoted with 1 weight % Mn was found to be the best catalyst for the SCR of NO with methane. This catalyst was subjected to long-term testing at the facilities of our industrial partner TDA Research. TDA report indicated that the performance of this catalyst did not deteriorate during 100 hours of operation and the activity and selectivity of the catalyst was not affected by the presence of SO_2. The conversions obtained by TDA were significantly lower than those obtained at Hampton University due to the transport limitations on the reaction rate in the TDA reactor, in which $1/8^{th}$ inch pellets were used while the Hampton University reactor contained $250 - 425-$ μm catalyst particles.

The selected catalyst was also tested at the TDA facilities with high-sulfur heavy oil as the reducing agent. Depending on the heavy oil flow rate, up to 100 % NO conversions were obtained.

The temperature programmed desorption studies a strong interaction between manganese and cerium. Presence of manganese not only enhanced the reduction rate of NO by methane, but also significantly improved the N_2 selectivity

To increase the activity of the Mn-promoted catalyst, the manganese content of the catalyst need to

be optimized and different methods of catalyst preparation and different reactor types need to be

investigated to lower the transport limitations in the reactor.

TABLE OF CONTENTS

LIST OF FIGURES

I.   EXECUTIVE SUMMARY

Significant work has been done by the investigators on the cerium oxide-copper oxide based sorbent/catalysts for the combined removal of sulfur and nitrogen oxides from the flue gases of stationary sources. A relatively wide temperature window was established for the use of alumina-supported cerium oxide-copper oxide mixtures as regenerable sorbents for SO_2 removal. Evaluation of these sorbents as catalysts for the selective reduction of NO_x gave promising results with methane (DE-FG22-96PC96216). Since the replacement of ammonia by methane is commercially very attractive, in this project, the effect of promoters on the activity and selectivity of copper oxide/cerium oxide-based catalysts and the reaction mechanism for the SCR with methane was investigated.

All sorbents were prepared by the co-impregnation of ALCOA alumina by $Cu(NO_3).2\frac{1}{2}H_2O$, $(NH_4)_2Ce(NO_3)_6$, and a suitable salt of the promoter (such as rhodium(III) chloride hydrate and manganes (II) nitrate hydrate purchased from Sigma-Aldrich Co., Milwaukee, WI) and by subsequent calcination at 923 K for 6.5 hours (heating rate=10ºC/min). In all catalyst samples the total metal (Ce-Cu) loading is 10 %. All the promoters are added at 1% loading except rhodium, which has a loading of 0.1%. In the subsequent sections of this report Cu7.5Ce2.5 is designated by Cu3Ce1 and Cu2.5Ce7.5 is designated by Cu1Ce3.

For NO_x removal experiments, 2 grams of the catalyst/(sorbent) (particle size of 250 - 425 μm) is weighed and placed in the quartz microreactor. The reactant gas mixture is prepared from high purity bottled gases without further purification. Methane is used as the reducing agent. The reactant gas composition for the standard SCR experiments is 650-900 ppm NO, which contains a maximum of 5 ppm NO_2, 1.5% O_2, 7% H_2O, CH_4/NO molar ratio of 1, and balance He. Temperature range is 573 – 798 K. A gas hourly space velocity of 13700 was used for all tests. Gas samples were analyzed using a Varian 3400 Gas Chromatograph for CO, CO_2, N_2, O_2, and CH_4. For the first five components, TCD detector with a 15' Carboxen 1000 column from Supelco was used. The column was temperature-programmed for the optimum resolution of the components and analysis time needed. Good resolution was obtained for O_2, N_2, CO, CO_2, and CH_4. A Thermo Environmental Instruments Model 42 H Chemiluminescence $NO-NO_2-NO_x$ analyzer was employed for the quantitative analysis of NO.

Unpromoted and promoted catalysts were investigated for their selective catalytic reduction (SCR) activity with methane in a microreactor setup and also, by the temperature-programmed desorption (TPD) technique. Rhodium and the oxides of Rh, Li, K, Na, Zn, and Sn were selected as promoters because they were expected to facilitate the SCR of NO by enhancing the creation of oxygen vacancies in ceria, which in turn will facilitate NO adsorption and further reaction to nitrite and nitrate species and by facilitating the activation of methane and formation of surface carboxylates and their interaction with surface nitrites and nitrates. The results from the SCR experiments indicated that manganese is a more effective promoter than the other metals for the supported copper oxide-ceria catalysts under study. The effectiveness of the promoter increased with the increase in Ce/Cu ratio. Among the catalysts tested, the Cu1Ce3 catalyst promoted with 1 weight % Mn was found to be the best catalyst for the SCR of NO with methane. This catalyst was subjected to long-term testing at the facilities of our industrial partner TDA Research. TDA report indicated that the performance of this catalyst did not deteriorate during 100 hours of operation and the activity and selectivity of the catalyst was not affected by the presence of SO_2. The conversions obtained by TDA were significantly lower than those obtained at Hampton University due to the transport limitations on the reaction rate in the TDA reactor, in which 1/8th inch pellets were used while the Hampton University reactor contained 250 – 425- μm catalyst particles.

The selected catalyst was also tested at the TDA facilities with high-sulfur heavy oil as the reducing

agent. Depending on the heavy oil flow rate, up to 100 % NO conversions were obtained.

For temperature-programmed experiments, a Micromeritics Pulse Chemisorb 2705 with TPD/TPR Option is used. A mass spectrometer-gas chromatograph system (SATURN 2000MS/3800GC) from Varian is used for the identification of desorbed species and reaction products. When a suitable temperature program was used, the Carboxen 1000 capillary column from Supelco provided good separation for O_2, N_2, NO, CO, and CH_4. Unfortunately both N_2O and CO_2 resulted in two peaks both at the same times making the identification of N_2O and CO_2 difficult. Therefore, when the identity of the species is not known a priori, the results are reported as N_2O and/or CO_2.

During the TPD studies, no NO desorption was observed for the manganese promoted catalysts and the N_2O desorption was significantly less than those observed with the promoted catalysts especially for the catalyst with Ce/Cu weight ratio of 3. This indicated the presence of a strong interaction between manganese and cerium, which resulted in not only the enhancement of the rate of NO reduction, but also a significant increase in the N_2 selectivity.

It was concluded that in order to increase the activity of the Mn-promoted catalyst, the manganese content of the catalyst need to be optimized and different methods of catalyst preparation and different reactor types need to be investigated to lower the transport limitations in the reactor.

II. INTRODUCTION

The objective of this research is to improve the activity and selectivity of alumina supported cerium oxide-copper oxide-based sorbent catalysts for the reduction of NO_X by methane by the addition of promoters to enhance NO chemisorption, NO oxidation, intermediate stabilization, or methane activation.

II. i. Background Information

Simultaneous removal of SO_2 and NO_X using a regenerable solid sorbent will constitute an important improvement over the use of separate processes for the removal of these two pollutants from stack gases and possibly eliminate some disadvantages of the individual SO_2 and NO_X removal operations. Various sorbents consisting of cerium oxide and copper oxide impregnated on alumina were prepared and characterized during a previous research project funded by DOE (DE-FG22-96PC96216). Their sulfation performance was investigated in a TGA setup, studying mainly the effects of temperature, sorbent composition, metal loading and support type. As a result of the sulfation experiments, a relatively wide temperature window was established for the use of alumina-supported cerium oxide-copper oxide as regenerable sorbents for sulfur dioxide removal. In the 723-823 K temperature range, cerium oxide-copper oxide sorbents have specific sorbent capacities (mass of sulfur removed per unit mass of metal sorbent) and sulfation rates significantly higher than those of cerium oxide and copper oxide sorbents used alone. Best sulfation performance was exhibited by the sorbent containing 1:1 molar ratio of cerium and copper. Specific sulfur capacities decreased as the coverage of the support surface by the metal oxides approached monolayer coverage. Sorbents appeared to be resistant to cycling. No loss of sulfation capacity was observed after the third cycle.

CuO-CeO$_2$ catalysts supported on alumina were also tested in a bench-scale batch reactor for their performance in the SCR of NO with Methane. Catalysts containing both copper and cerium oxides had better activities for NO reduction with methane, regardless of the Cu/Ce metal ratio[1]. The maximum NO conversion at the space velocity used (13700/hr) was about 17 % obtained at 425°C with both SOR10-III (Cu/Ce=3) and SOR10-IV (Cu/Ce=1/3) catalysts, being slightly lower for the former. The properties of these catalysts are summarized in Table 1.

Table 1. Properties of the baseline copper oxide/cerium oxide catalysts

Sorbent	Cerium Loading, mass %		Copper Loading, mass %		Surface Area, m^2/g
	Nominal	Actual	Nominal	Actual	
SOR10-III (Cu3Ce1)	2.5	2.26	7.5	8.42	134
SOR10-IV (Cu1Ce3)	7.5	6.49	2.5	2.77	122

III.   EXPERIMENTAL

III. i. NO$_x$ Removal

III. i. A. Catalysts

New catalysts were prepared by the promotion of the catalysts presented in Table 1 in order to investigate their selective catalytic activity for the reduction of NO by methane. The promoters were selected according to the following observations.

- A noble metal added in small amounts is expected to enhance the creation of oxygen vacancies in ceria, which in turn will facilitate NO adsorption and further reaction to nitrite and nitrate species. The activation of methane and formation of surface carboxylates and their interaction with surface nitrites and nitrates may also be facilitated by the noble metal.

Its ability to create oxygen vacancies in ceria and to suppress N_2O formation makes Rh a good candidate as a promoter.

- Mn_2O_3 is known to catalyze the NO oxidation. Therefore, Mn is expected to facilitate the formation of surface nitrogen species on the catalyst.

- SnO_2 is reported to effectively promote the reaction of alkene with NO in the presence of oxygen. Thus, Sn might have a potential for increasing the NO reduction selectivity and facilitating the removal of oxygen from the surface.

- Zinc-MFI was suggested in the literature as a catalyst for the reduction of NO_2.

- Alkaline earth cations (K, Na, Li) were reported to stabilize nitriles and isocyanates on zeolite catalysts. Since these intermediates were reported to be essential for the N-N pairing, addition of these metals may improve selectivity towards N_2 formation.

All sorbents were prepared by the co-impregnation of ALCOA alumina by $Cu(NO_3).2\frac{1}{2}H_2O$, $(NH_4)_2Ce(NO_3)_6$, and a suitable salt of the promoter (such as rhodium(III) chloride hydrate and manganes (II) nitrate hydrate purchased from Sigma-Aldrich Co., Milwaukee, WI) and by subsequent calcination at 923 K for 6.5 hours (heating rate=$10^oC/min$). In all catalyst samples the total metal (Ce-Cu) loading is 10 %. All the promoters are added at 1% loading except rhodium, which has a loading of 0.1%. In the subsequent sections of this report Cu7.5Ce2.5 is designated by Cu3Ce1 and Cu2.5Ce7.5 is designated by Cu1Ce3.

III. i. B. Experimental Setup and Procedure

The experimental setup used for the selective catalytic reduction of NO is presented in Figure 1. For NO_x removal experiments, 2 grams of the catalyst/(sorbent) (particle size of 250 - 425 μm) is weighed and placed in the quartz microreactor. The reactant gas mixture is prepared from high purity bottled gases without further purification. Methane is used as the reductant.

The reactant gas composition for the standard SCR experiments is 650-900 ppm NO, which contains a maximum of 5 ppm NO_2, 1.5% O_2, 7% H_2O, CH_4/NO molar ratio of 1, and balance He. Temperature range is 573 – 798 K.

Gas samples were analyzed using a Varian 3400 Gas Chromatograph for CO, CO_2, N_2, O_2, and CH_4. For the first five components, TCD detector with a 15' Carboxen 1000 column from Supelco was used. The column was temperature-programmed for the optimum resolution of the components and analysis time needed. Good resolution was obtained for O_2, N_2, CO, CO_2, and CH_4. A Thermo Environmental Instruments Model 42 H Chemiluminescence $NO-NO_2-NO_x$ analyzer was employed for the quantitative analysis of NO_2 and NO. In the presence of a reductant, the high temperature (923 K) converter in the instrument leads to side reactions and gives erroneous NO_2 and NO_x readings. To overcome this shortcoming, the low temperature (623 K) Mo converter is utilized. Even with this converter reliable NO_2 measurements could not be made. Since GC-MS measurements during the TPD and TPReaction runs did not indicate any NO_2 formation, conversions were reported based on NO measurements:

NO conversion (X_{NO}) = [NO in feed – NO in reactor effluent]/[NO in feed]

III. ii. Temperature-Programmed Desorption Experiments

In the investigation of the mechanism of selective catalytic reduction reaction, one approach is to use Temperature-Programmed Desorption (TPD) Experiments in order to evaluate the NO and O_2 chemisorption capacity of the catalysts and to identify the surface species and desorption species. For temperature-programmed experiments, a Micromeritics Pulse Chemisorb 2705 with TPD/TPR Option is used. A mass spectrometer-gas chromatograph system (SATURN 2000MS/3800GC) from Varian is used for the identification of desorbed species and reaction products. When a suitable temperature program was used, the Carboxen 1000 capillary column from Supelco provided good

separation for O_2, N_2, NO, CO, and CH_4. Unfortunately both N_2O and CO_2 resulted in two peaks both at the same times making the identification of N_2O and CO_2 difficult. Therefore, when the identity of the species is not known a priori, the results are reported as N_2O and/or CO_2.

A typical TPD run is described below:

1. Pretreat all the samples in He (20 ml/min) at 323 K for 2 hours. This thermal treatment will prevent any appreciable oxygen uptake.

2. Carry out NO ($NO+O_2$, O_2, CH_4, or CH_4+O_2) adsorption at 323 K by flowing 40 ml/min of He carrier gas through the absorption cell and injecting 1-ml doses of a NO/He mixture containing 1.93 % NO in He, or a similar mixture containing 3.6 % O_2 in He or 2.03 % CH_4 in He. Continue injections until the composition of the gases exiting the adsorption cell remains approximately constant for three injections.

   Flow rate: 40 ml/min

   Temperature range: 35 ^{o}C – 700 ^{o}C

   Temperature ramp: 2 or 3 ^{o}C/min

3. Flush the sample with a stream of dry helium at 323 K to eliminate gaseous NO and weakly adsorbed NO (or any other adsorbent).

4. When no NO (or any other adsorbent) is observed, heat the sample to 973 K in flowing He stream (40 ml/min) at the rate of 2 or 3 K/min. Record the desorbed species.

5. In all the runs performed, the desorbed species were the surface reaction products and/or decomposition products of surface species that were formed. Therefore, the amount of chemisorbed NO was not determined from the TPD results. Instead, the TPD results are used to obtain information on the possible surface reactions.

IV. RESULTS AND DISCUSSION

IV. i. Screening of Promoted Catalysts

To avoid clutter the selective catalytic reduction results are shown in three separate figures. Figure 2 shows the effect of alkali metals as promoters. Figure 3 presents the performance of catalysts promoted with transition metals, namely Sn, Zn, and Mn. Figure 4 shows the effect of rhodium as promoter. The results are summarized in Table 2.

When the catalysts are promoted with alkali metals (Figure 2), the effect on NO conversion is small. The largest improvement is obtained with lithium (about 18% increase in NO conversion) followed by potassium (about 15%). With these promoters, the temperature for the highest NO conversion appears to be the same for both base catalysts Cu3Ce1 and Cu1Ce3. Consequently, the highest NO conversions obtained are also the same for these catalysts.

As can be seen from Figure 3 and Table 2, Zn is ineffective as promoter. Tin added to Cu1Ce3 base catalyst increases the maximum NO conversion slightly, but there is no change in the temperature for maximum conversion. By far the largest improvement in the catalyst performance is obtained for catalysts promoted with manganese. The conversion-temperature behavior of these catalysts are shown separately in Figure 4. The NO conversion on the manganese-promoted Cu1Ce3 catalysts is about 47 % higher than that on unpromoted catalyst. The improvement produced by manganese promotion of Cu3Ce1 is not as high but still quite significant (about 30 %). Another important observation from Table 2 and Figure 4 is that the temperature at which the maximum NO conversion is obtained is lowered by manganese ($15^{o}C$ for Cu3Ce1Mn and $20^{o}C$ for Cu1Ce3Mn). In fact, Figure 4 shows that manganese promotion enlarged the temperature window of operation. Between $335^{o}C$ and $475^{o}C$, NO conversion on the Cu1Ce3Mn is above 15%. Since low temperatures favor reduction of NO over that of O_2, increase in the low temperature activity of the catalyst is expected to be also

favorable for the SCR activity.

Table 2. Maximum NO Conversion and Temperature

Promoter	Maximum NO conversion, % (Temperature, ºC)	
	on Cu3Ce1	on Cu1Ce3
None	16.8 (425)	18.2 (435)
Mn	21.8 (410)	26.8 (415)
Rh	18.7 (425)	18.8 (425)
Sn	17 (425)	19.1 (435)
Zn	16.9 (435)	17.9 (435)
Li	19.1 (435)	20 (435-450)
K	19.5 (450)	19.3 (435)
Na	16.8 (450)	19.4 (450)

Effect of promoter on catalyst activity is more pronounced on catalysts with higher Ce/Cu ratio; this observation implies that the synergy is due to cerium rather than copper. This observation has been supported by information in the literature[2]. The authors used a manganese-cerium composite oxide as a catalyst for the wet oxidation of polyethylene glycol. They observed that as the content of cerium was increased, the catalytic activity reached a maximum at a cerium content of about 40%, which corresponds to a molar ratio of Mn to Ce of one. This has been attributed to the increase of the redox properties of Mn_2O_3 by combination with CeO_2. This may be due to the electron transfer between the Mn/Ce catalyst and the reactant (PEG). Their XRD analysis indicated the presence of only Mn_2O_3 and CeO_2. This fact coupled with the fact that maximum activity is at a Mn/Ce molar ratio of one indicates that the active site is at the interface between the Mn(III) oxide and Ce(IV) oxide. Their ESCA results show a decrease in the binding energy for $Mn(2p_{3/2})$ as the cerium

content increases; in contrast, the binding energy for $Ce(3d_{5/2})$ increases upon addition of Mn. These binding energies suggest the presence of MnO_2. The addition of cerium seems to change the surface manganese species from MnO_2 to Mn_2O_3 or MnO. These observations indicate that the electron transfer from Ce to Mn is an easy process, thus, producing manganese species with lower valence states (Mn^{3+} or Mn^{2+}) at the interface of the two oxides and increase the redox property of the manganese oxide catalyst.

Figure 5 shows that the catalysts promoted by 0.1% Rh, the improvement in catalyst SCR activity is small. The maximum NO conversion and the temperature for maximum conversion are about the same for both Cu1Ce3Rh and Cu3Ce1Rh.

All the results given in this report are for the space velocity of 13700 per hour imposed by the limitations of the experimental setup and NO analysis instrument, which is higher than about 4000 per hour generally used in the commercial SCR operations. To establish the effect of space velocity on NO conversion, a set of runs were made with different catalyst mass while the reactant gas rate was held constant. Figure 6 and Table 3 summarize the results. Although it can be seen that decreasing space velocity increases the NO conversion in general, the variation of the NO conversion is not uniform. This observation could not be explained.

Table 3. The Effect of Space Velocity on the Maximum NO Conversion on Cu1Ce3Mn

Catalyst Amount, g	Space Velocity, hr^{-1}	Maximum NO Conversion	Temperature for Max. NO Conv., ^{o}C
1.5	19,300	26	420
2.0	13,700	26.8	415
2.5	11,000	30	390
3.0	9,100	31	390

The main conclusion from the screening of the promoted catalysts is that only the promotion of the baseline catalysts with manganese produced significant improvements in the activity of the catalyst.

The catalyst Cu1Ce3 promoted by manganese resulted in the highest NO conversions and the widest temperature window for the SCR with methane. For this reason, batches of manganese–promoted catalysts were selected for long-term testing at the TDA facilities. Results also indicated that reducing the space velocity would increase the NO conversion but, using the available information we could not explain the erratic variation of NO conversion with space velocity.

IV. ii. Temperature Programmed Desorption Studies

The results of the temperature programmed desorption (TPD) studies are shown in figures 7 to 30. Both the absorption curves and the TPD curves are presented for NO, O_2, and CH_4. Absorption curves involve more random error because they require the sample injections to the GC-MS at the maximum point of the pulse accounting for the time needed for the pulse to travel to the GC-MS injection valve. The gaps in the absorption graphs represent periods of overnight or longer between the subsequent pulses for which the catalysts are kept under stagnant helium at room temperature.

NO absorption: The nitrous oxide absorption curves are shown in figures 7 to 10. These figures indicate that a significant portion of the injected NO stays and/or reacts on the catalyst surface. Table 4 summarizes the observed results. The number of injections needed to reach steady state and the ratios of the injection peak area to the steady state desorption peak area are obtained from the Micromeritics Pulse Chemisorb 2705 measurements. Since the relative thermal conductivities for NO, O_2, and N_2 are 0.99, 1.02, and 1.00, respectively; the difference in the areas cannot be attributed to the dissociation of NO. Also it cannot completely be due to the formation of N_2O, because the GC-MS results show the formation of only a very small amount of N_2O. Therefore, the difference in the areas, to a large extent, is due to the retention of NO on the catalyst surface and the formation of surface nitrite and nitrate species.

Table 4. Results of NO absorption and TPD on promoted and unpromoted supported copper oxide ceria catalysts. Absorption:1-ml pulses of 1.94 % NO in He. TPD to 700 oC.

Catalyst	Number of pulses to reach steady state	Desorption peak area/ Injection peak area	Ratio of evolved N_2 to N_2O during TPD
Cu3Ce1	13	0.66	1
Cu3Ce1Mn	15	0.65	5
Cu1Ce3	24	0.71	4
Cu1Ce3Mn	15	0.67	7

TPD on Catalysts Treated with NO: Figures 11-14 represent the temperature programmed desorption results for catalysts treated with NO. Figure 13.a is for a replicate run and is included to indicate the reproducibility of the TPD results. These results are summarized below.

- The surface nitrogen is released mainly as N_2O and N_2, except for the catalyst Cu3Ce1 for which NO desorption is observed for a small temperature window around 190 ^{o}C.

- Two N2O peaks are observed, one around 140 ^{o}C for Cu3Ce1, 120 ^{o}C for the others; and the second around 280, 260, 330, 230 ^{o}C for Cu3Ce1, Cu3Ce1Mn, Cu1Ce3, and Cu1Ce3Mn, respectively. Apparently manganese oxide lowers the temperature of the second N2O peak. In addition, manganese significantly reduces the height of the first N2O peak. The effect is much more pronounced for the Cu1Ce3 catalysts indicating the promoting effect of manganese is mainly through its interaction with Ce rather than Cu as discussed above.

- With all catalysts there is an inverse relationship between the N_2O and O_2 amounts in the desorbed gas. This could be due to various mechanisms such as some surface nitrogen reacting with gaseous oxygen to form N_2O, surface nitrogen species desorbing as N_2O creating surface oxygen vacancies, which are subsequently filled with gaseous oxygen, or oxygen adsorbing on the surface sites vacated by the release of N_2O. The TPD curves show

that the correlation between the first N_2O peak and the amount of gaseous oxygen is not very strong suggesting that the last mechanism is not significant and at least for the first N_2O peak the second mechanism is more probable with the filling of oxygen vacancies taking place at slightly higher temperatures.

- Gaseous nitrogen amount decreases slowly but at approximately constant rate as the temperature increases.

- The ratios of evolved N_2 to N_2O, based on the estimation of areas under the N_2O and N_2 curves are given in Table 4. The N_2 to N_2O ratios are higher for the manganese containing catalysts and higher for Cu1Ce3 compared to Cu3Ce1 catalysts. This observation suggests that the Cu1Ce3Mn catalyst will have the highest N_2 selectivity. In fact this catalyst produced the least amount of N_2O during TPD after treatment with NO.

Oxygen Absorption on Catalysts Treated with NO: Gaseous species observed during absorption of oxygen on catalysts treated with NO are presented in Figures 15-18. The results are summarized below:

- A small amount of N_2O is produced on the Cu3Ce1 catalyst during all the oxygen pulses. With all other catalysts a small amount of N_2O is observed only for the first few pulses (2 to 4 pulses). It is interesting to note that when the catalyst is stored overnight under helium N_2O is again produced for the first few pulses (Figure 18).

- Very small amount of oxygen is retained on the catalyst surface and/or reacted during the oxygen pulses. Comparison of the desorption peak areas to the injection peak area indicated that the differences between the peak areas were all less than 5%.

TPD on Catalysts Treated with NO and O_2: Figures 19-22 represent the temperature programmed desorption results for catalysts treated with NO and O_2. These results are summarized below.

- The surface nitrogen is released mainly as N_2O and N_2, except for the catalyst Cu3Ce1Mn

for which NO desorption is observed for a small temperature window around 210 ^{o}C.

- Two N_2O peaks are observed, one around 150 ^{o}C for Cu3Ce1 catalysts and 130 ^{o}C for Cu1Ce3 catalysts; and the second around 280 ^{o}C for Cu3Ce1 and around 310 ^{o}C for the others. Apparently for this case, the differences in the second N_2O peak temperatures are not significant. On the other hand, the presence of manganese reduces the first peak height similar to those observed with catalysts treated with NO only. Again the effect is much more pronounced for the Cu1Ce3 catalysts indicating the promoting effect of manganese is through its interaction with Ce rather than Cu.

- The inverse relationship between the N_2O and O_2 amounts in the desorbed gas is again observed. The discussions presented above for the catalysts treated with NO also apply here.

- On all catalysts during TPD, gaseous nitrogen amounts appear to decrease slowly at approximately constant rate as the temperature increases. The different shape of the N_2 curve observed for Cu1Ce3 is possibly due to an error in the first data point.

- The ratios of evolved N_2 to N_2O, based on the estimation of areas under the N_2O and N_2 curves are given in Table 5. The N_2 to N_2O ratios are higher for the manganese containing catalysts and higher for Cu1Ce3 compared to Cu3Ce1 catalysts. This observation suggests that the Cu1Ce3Mn catalyst will have the highest N_2 selectivity. This catalyst produced the least amount of N_2O during TPD after treatment with NO and O_2.

Table 5. Results of O_2 absorption and TPD on catalysts treated with NO. Absorption: 1-ml pulses of 3.6 % O_2 in He after 1-ml pulses of 1.94 % NO in He. TPD to 700 ^{o}C.

Catalyst	Number of pulses to reach steady state	Desorption peak area/ Injection peak area	Ratio of evolved N_2 to N_2O during TPD
Cu3Ce1	1	0.99	1
Cu3Ce1Mn	1	0.99	3
Cu1Ce3	1	0.99	1
Cu1Ce3Mn	1	0.99	7

Methane Absorption on Catalysts Treated with NO and O_2: Gaseous species observed during absorption of oxygen on catalysts treated with NO are presented in Figures 23-26. The results are summarized below:

- A small amount of N_2O and/or CO_2 is produced on all the catalysts during the methane pulses. There seems to be no correlation between the N_2O and/or CO_2 amount and the pulse number or the storage of catalyst overnight under helium.

- A small amount of methane is retained on the catalyst surface and/or reacted during the methane pulses. The desorption peak areas,about 80% of the injection peak area.

TPD on Catalysts Treated with NO, O_2, and CH_4: Figures 27-30 represent the temperature programmed desorption results for catalysts treated with NO, O_2, and. These results are summarized below:

- Since the N2O and CO2 desorption peaks are superimposed, it is difficult to interpret the TPD results. Each catalyst shows a different desorption spectrum.

- The Cu3Ce1 catalyst has a very large N_2O and/or CO_2 peak at about 130 ^{o}C, which may be due to a large extent, to the direct oxidation of methane. After this peak, the N_2O/CO_2 desorption

gradually decreases as the temperature is increased. This decrease seems to be oscillatory, but this appearance may also be due to random errors in determining the small peak areas. The presence of this big low-temperature peak indicates the low-temperature oxidation activity of this catalyst, but the selectivity towards NO reaction with methane appears to be low considering the NO peak observed around 130 ^{o}C.

- On the Cu3Ce1Mn catalyst the NO desorption peak is not observed. The single low-temperature N_2O/CO_2 peak is replaced by a succession of smaller peaks up to 700 ^{o}C, each getting smaller as the temperature is increased. This observation suggests that the addition of manganese increases the selectivity toward NO reduction.

- On Cu1Ce3 catalyst two distinct N_2O/CO_2 desorption peaks are observed, one smaller peak around 170 ^{o}C and a much larger peak around 320 ^{o}C. This indicates that the oxidation activity of the catalysts containing a larger amount of cerium is shifted to higher temperatures. Since no NO desorption is observed, the selectivity of this catalyst towards NO reduction appears to be higher.

- The N2O/CO2 desorption peaks on Cu1Ce3Mn catalyst are much smaller than those observed on the other catalysts. Three small peaks, approximately the same size, are observed at 130, 230, and 310 ^{o}C. No NO desorption is observed. These results suggest that the addition of manganese to the high-ceria catalyst increases the N_2 selectivity of the NO reduction reaction. The direct oxidation of methane appears to be significantly retarded compared to the unpromoted catalysts. These observations are also in line with the arguments presented above on the interaction between manganese and cerium.

- The strong correlation between the decrease in the gaseous oxygen amount and the N_2O

production is also present during TPD after CH_4 absorption. The onset of rapid reduction in the oxygen amount coincides with the second N_2O/CO_2 peak as observed in the previous TPDs.

IV.   iii.   Results of Long-term Testing at the TDA Facilities:

 Basing ion the results discussed above it was decided to subject the Cu1Ce3Mn catalyst to long-term testing to obtain information on its robustness and its ability to resist poisoning by SO_2. Unpromoted Cu1Ce3 catalyst is also tested for comparison. Details of these tests are provided in the TDA report provided in Appendix 1. Main findings are summarized below. A brief discussion of the interpretation of TDA results in the light of our observations at Hampton University is also included.

- The manganese-promoted Cu1Ce3Mn catalyst showed better performance characteristic in comparison to the un-promoted sample. This catalyst achieved approximately 9% NO reduction when methane was used as the reducing agent at 400-450°C temperature range (at a CH_4:NO molar ratio of 9). The NO reaction with methane was very selective consuming very little or no oxygen. The TDA tests, thus, confirm the higher activity and selectivity of the manganese promoted catalyst. The reported temperature for maximum conversion coincides with the results obtained at Hampton University. However, a significantly lower activity is reported by TDA at about one half the space velocity used at Hampton University.

- Higher levels of NO reduction were accomplished when heavy oil was used as the reducing agent. Depending on the molar ratio, up to 100% NO reduction was achieved at a space velocity of 6,000 h^{-1}. These results are also in line with the observations made earlier at Hampton University using a mixture of hexane and CO as the reducing agent, which indicated CO to be a superior reducing agent for NO.

- In each case, the performance tests were carried out in the presence 300 to 3,000 ppm SO_2.

No adverse effect of SO2 on catalyst activity and selectivity was observed. This was also expected since copper and cerium sulfates were also shown to be good catalysts for NO reduction.

- A 100-hr durability tests, demonstrated the stable performance for the catalysts without any sign of degradation or undesirable side reactions.

- A visual inspection of the pellets shows that the mechanical structure of the pellets was intact after the testing. The color of the used catalyst pellets is different than the color of the fresh catalyst. The fresh Cu1Ce3 catalyst has a light grayish green color while the used catalyst was a mixture of pellets ranging in color from almost black (a few) to white (majority of pellets). The observed change in the color of the Cu1Ce3Mn catalyst was very slight. Only a few of the pellets acquired a lighter bluish tint upon usage. Although it is impossible to understand the changes in the catalyst composition without further analysis, several possible causes for the observed color changes may be suggested, such as the sulfation/sulfidation of copper at various levels and the migration of cerium oxide to the surface of the pellets and reverse migration of copper oxide to the inside of the pellets. The slight color change for the Mn-promoted catalyst, in addition to the reasons mentioned for the unpromoted catalyst, may be due to the reduction of MnO_2 to MnO.

The significant difference in the activities of the catalysts observed at the TDA and Hampton University tests need some explanation. Although the conditions of the two sets of tests were kept as close to each other as possible, there still were two significant differences. The CH4/NO ratios used at TDA were significantly larger and due to pressure drop restrictions of the larger reactor, in TDA tests 1/8th –in pellets were used rather than the mixture of 250 - 425 μm particles employed at Hampton University. Both of these results may explain the lower conversions

observed at TDA. Most plausible explanation will be the presence of transport limitations in the TDA reactor, while the sulfidation of copper and reduction of copper and manganese oxides might have also played a role.

V.   CONCLUSIONS AND RECOMMENDATIONS

The results presented in this report show that the catalyst Cu1Ce3Mn has some activity for the reduction of NO with methane and excellent NO-reduction selectivity in the presence of oxygen. This catalyst exhibited very high activity when high-sulfur heavy oil was used as the reducing agent for NO. No deterioration in catalyst performance was observed over 100 hours of operation. The presence of SO_2 did not alter catalyst activity.

These results are very promising, but there is a need for the improvement of the catalyst especially if methane is to be used as the reducing agent. For this purpose it would be informative if catalysts prepared by different methods such as the co-precipitation and sol-gel methods can be tested under similar conditions. In addition, the manganese content of the catalyst should be optimized. The strong interaction between cerium and manganese suggests that a higher manganese content which would produce a catalyst containing about equal moles of the two metals (about 2.5 weight % Mn) needs to be tested.

VI.   DISSEMINATION OF RESULTS

- Akyurtlu, J. F. and Akyurtlu, A.; "Selective Catalytic Reduction of Nitrogen Oxides with Hydrocarbons over Supported Copper Oxide-Cerium Oxide Sorbents;" presented at the AIChE 2000 Spring Meeting; Atlanta, GA; March 5-9, 2000.

- Akyurtlu, J. F. and Akyurtlu, A.; "Investigation of Metal Oxide Catalysts for the Selective Catalytic Reduction of NO by Methane and Propylene;" presented at the AIChE 2001 Annual

Meeting; Reno, NV; Nov. 4-9, 2001.

- Akyurtlu, J. F. and Akyurtlu, A.; "Selective Catalytic Reduction of NOx by Hydrocarbons over Supported Copper Oxide-Cerium Oxide Catalysts;" presented at the 17th North American Catalysis Society Meeting; Toronto, Ontario, CA; June, 2002.

- Akyurtlu, J. F., Bridges, W., Akyurtlu, A.; "Promoted Mixed Metal Oxides for SCR with Methane;" presented at the AIChE 2002 Annual Meeting; Indianapolis, Indiana; November 3-8, 2002.

- Akyurtlu, J. F. and Akyurtlu, A.; "Reaction of NO with Methane on Promoted Mixed Metal Oxide Catalysts;" presented at the 18th North American Catalysis Society Meeting; Cancun, Mexico; June 6, 2003.

Student researcher Wesley Bridges was a co-author for the 2002 AIChE presentation. Another student researcher Anthony Samuels made two presentations entitled "Selective Catalytic Reduction with Hydrocarbons" presented at the AIChEMid-Atlantic Conference at Virginia Tech, Blacksburg, VA on March 15-17, 2002; "An Investigation of the Viability of Using Hydrocarbons as the Reductant in the Selective Catalytic Reduction of NO_x" presented at the Boehringer Ingelheim Pharmaceuticals, Inc. Fellowship Symposium on Oct. 14-15, 2002.

FIGURES
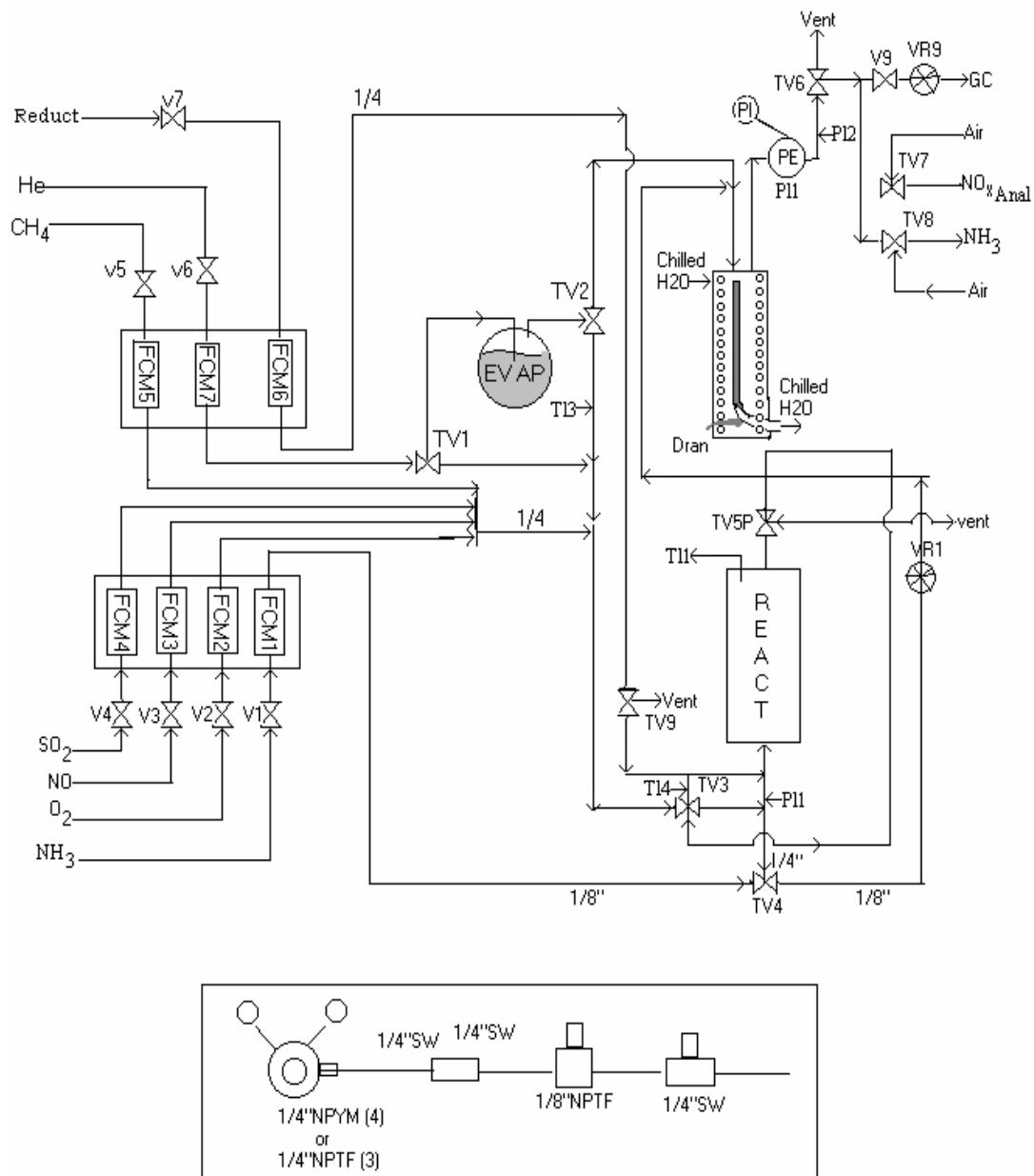
Figure 1. Experimental Setup for NO$_x$ Removal Experiments

Figure 2. Reduction of NO by Methane on Catalysts Promoted by Alkali Metals
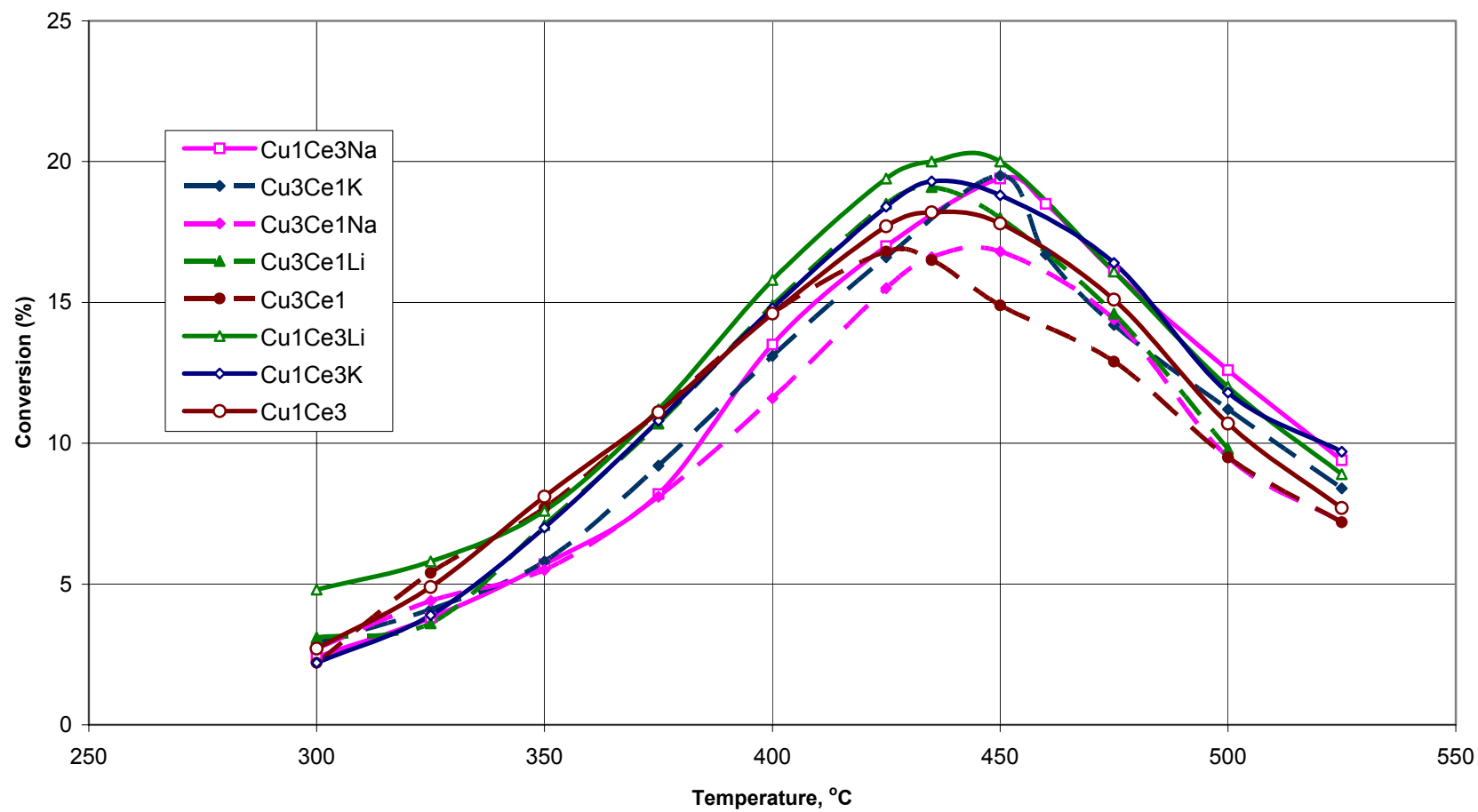
Figure 3. Conversion of NO Over Catalysts Modified with 1% Sn, Zn, or Mn
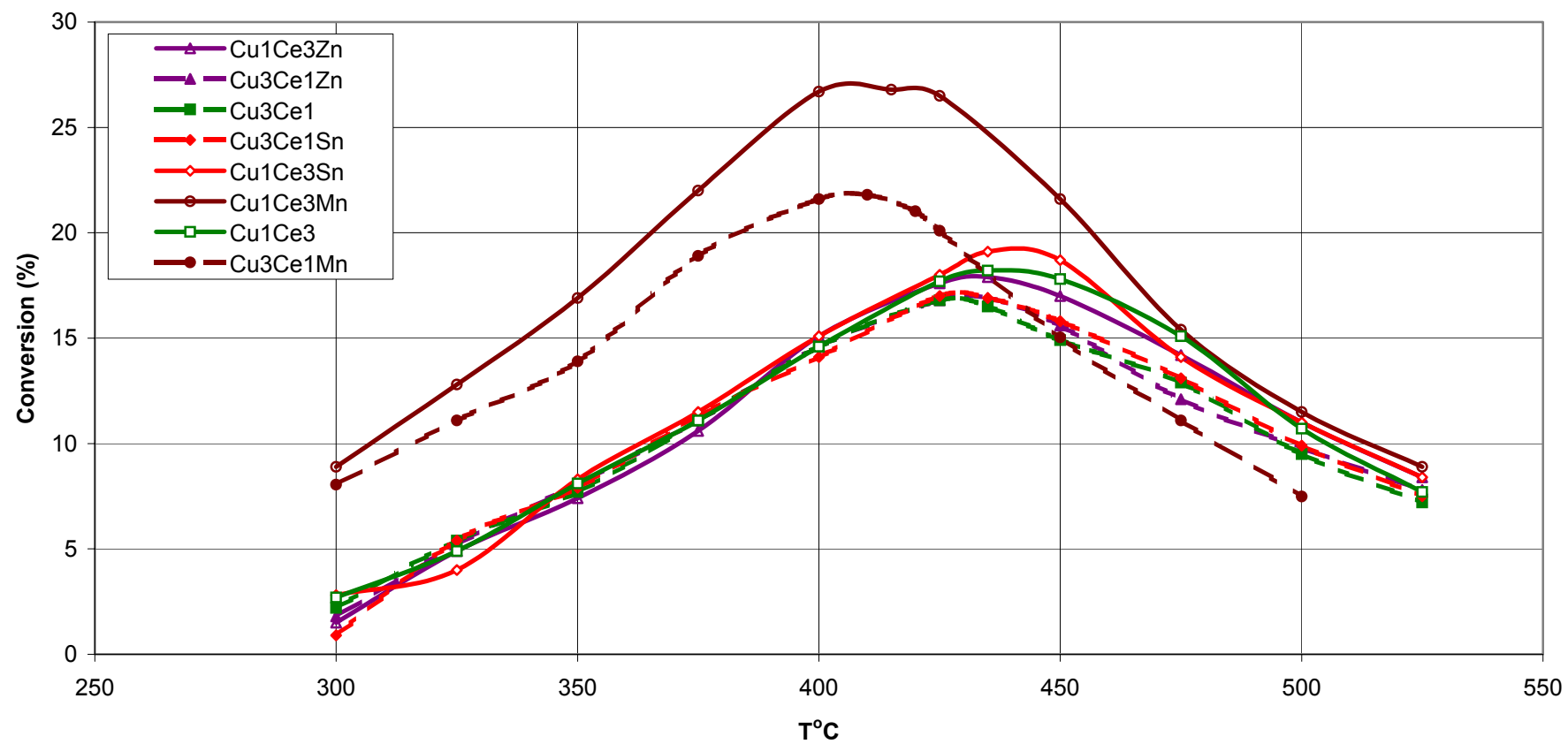
Figure 4. Reduction of NO by Methane on Catalysts Promoted by Mn
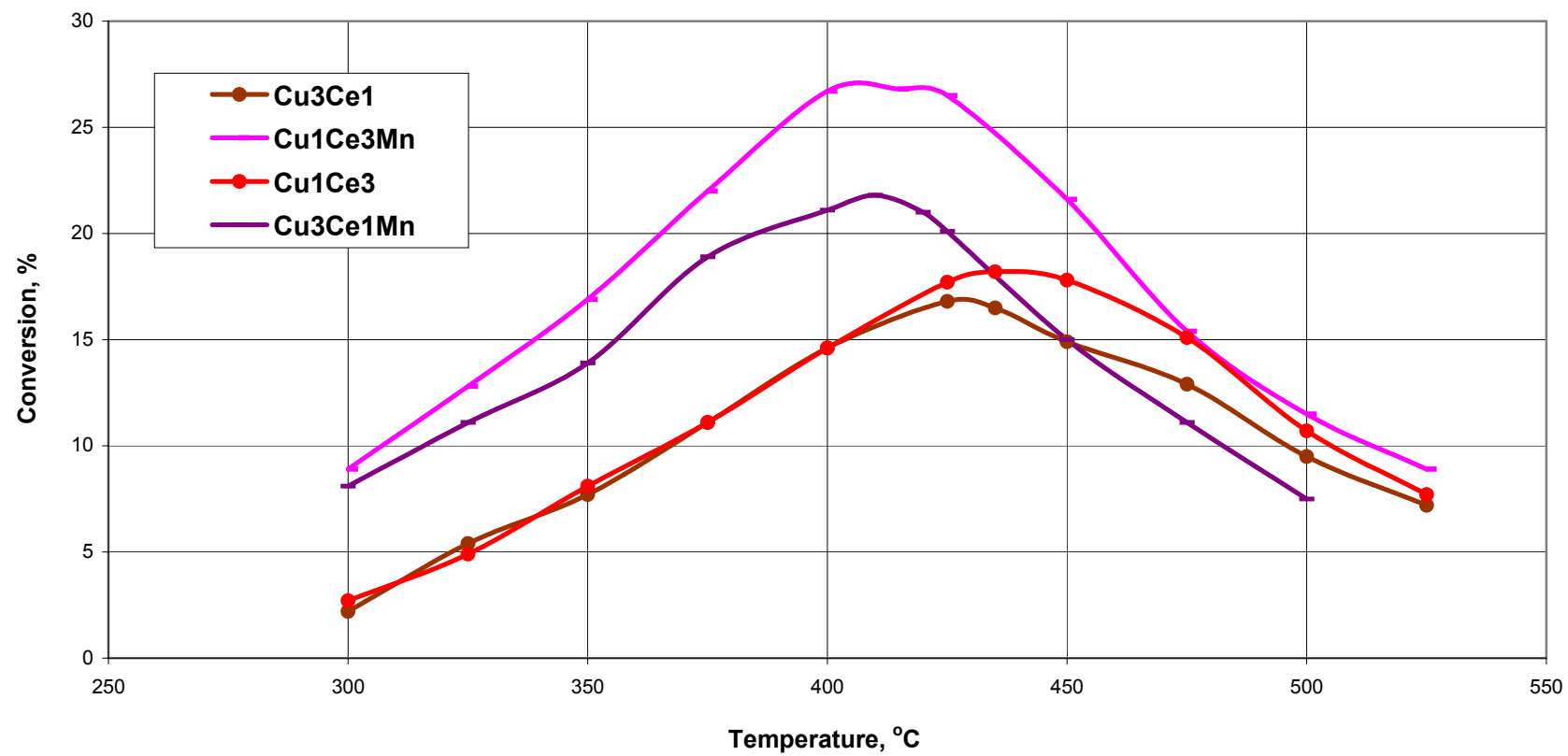
Figure 5. Conversion of NO Over Catalysts Modified with 0.1% Rh
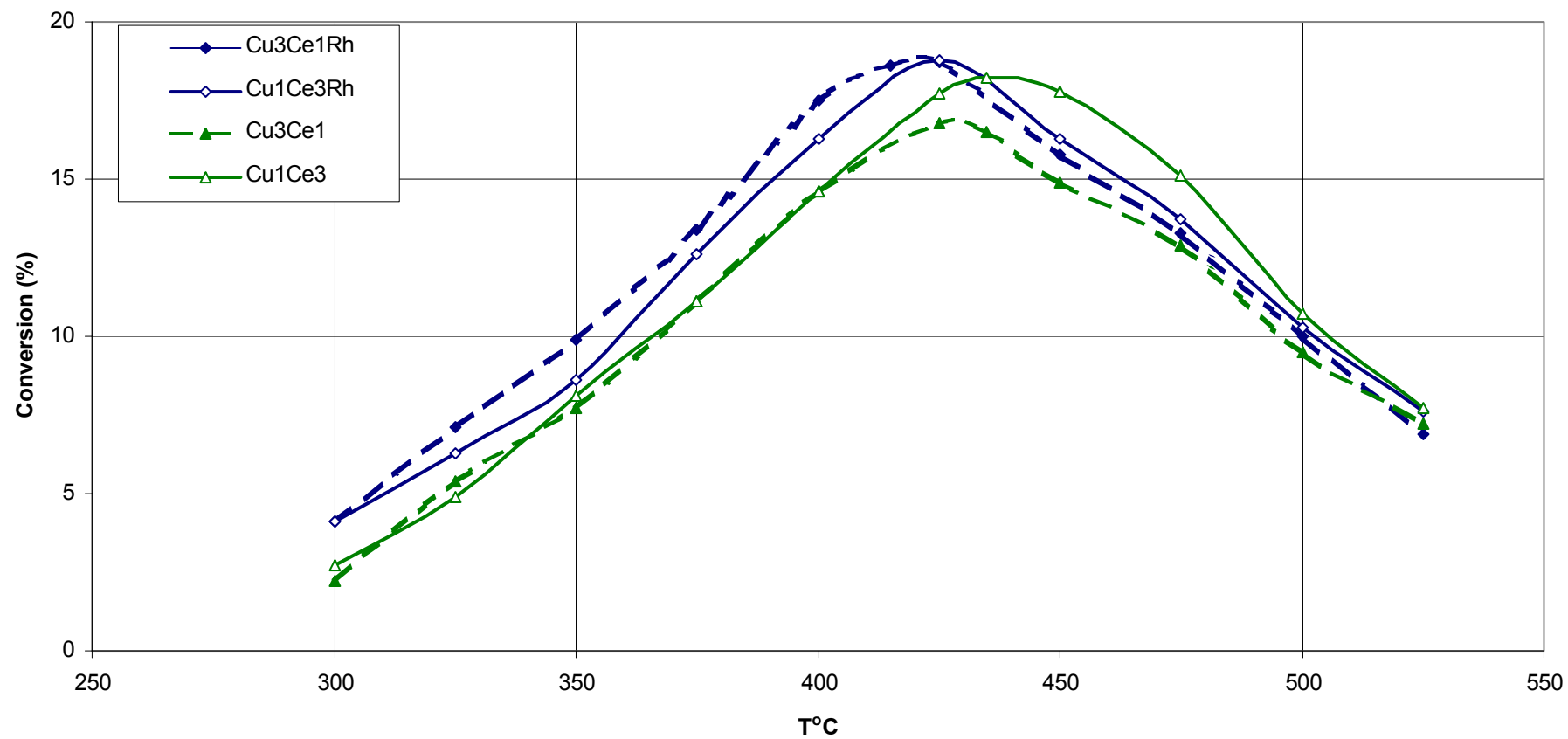
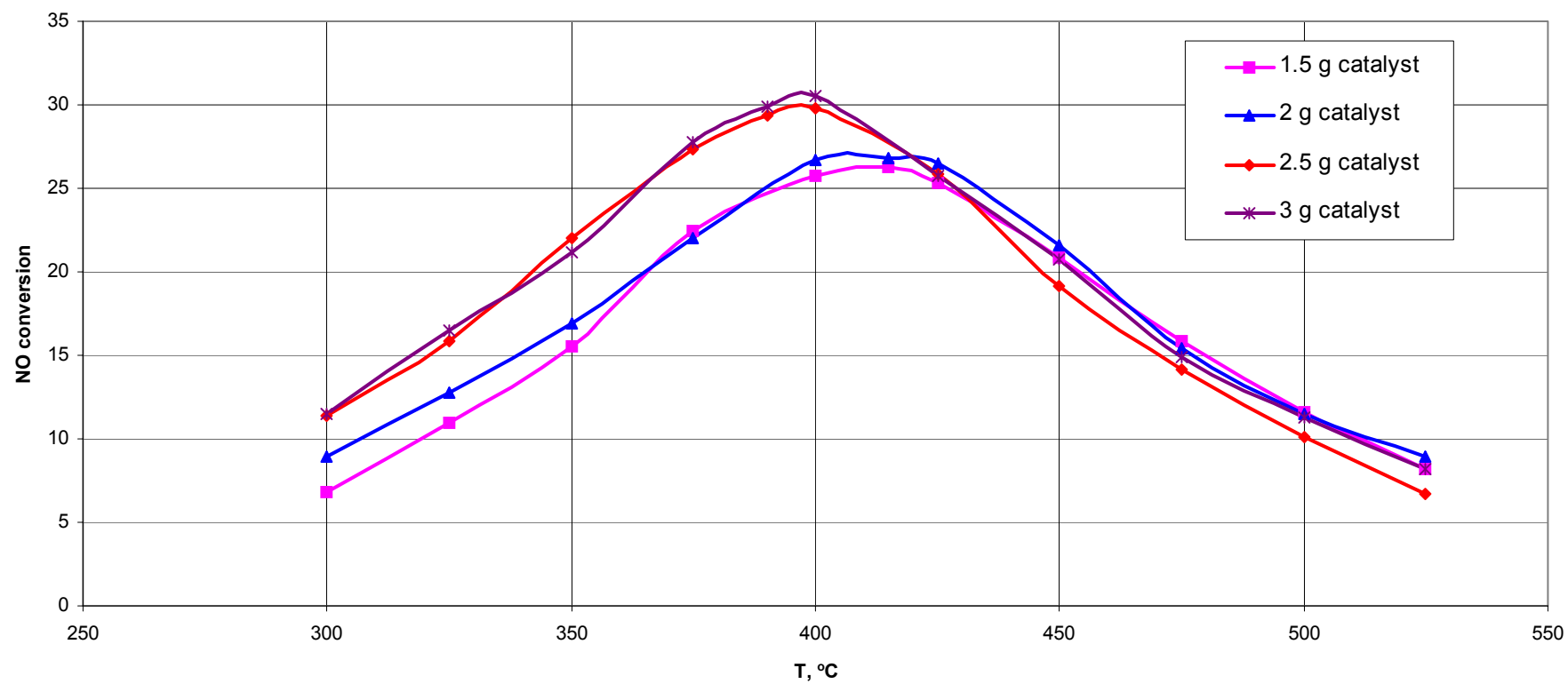**Figure 6. Effect of Space Velocity on the Conversion of NO on Cu1Ce3Mn Catalysts**

Figure 7. Species Evolved During Injection of 1-ml pulses of NO on Cu3Ce1 Catalyst at 50 $^{\circ}$C
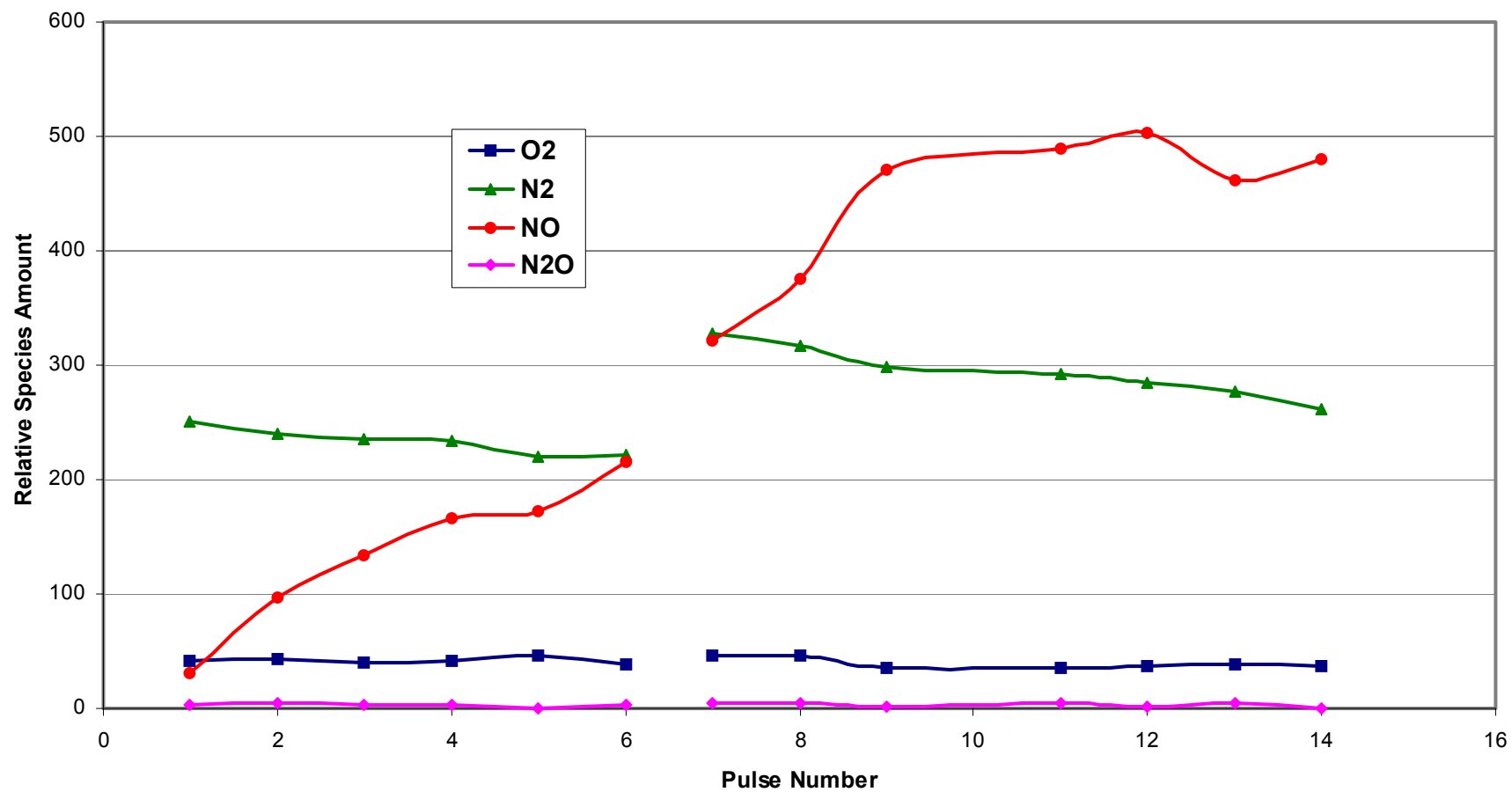
Figure 8. Species evolved during injection of 1-ml pulses of NO on Cu3Ce1Mn Catalyst at 50 ^{o}C
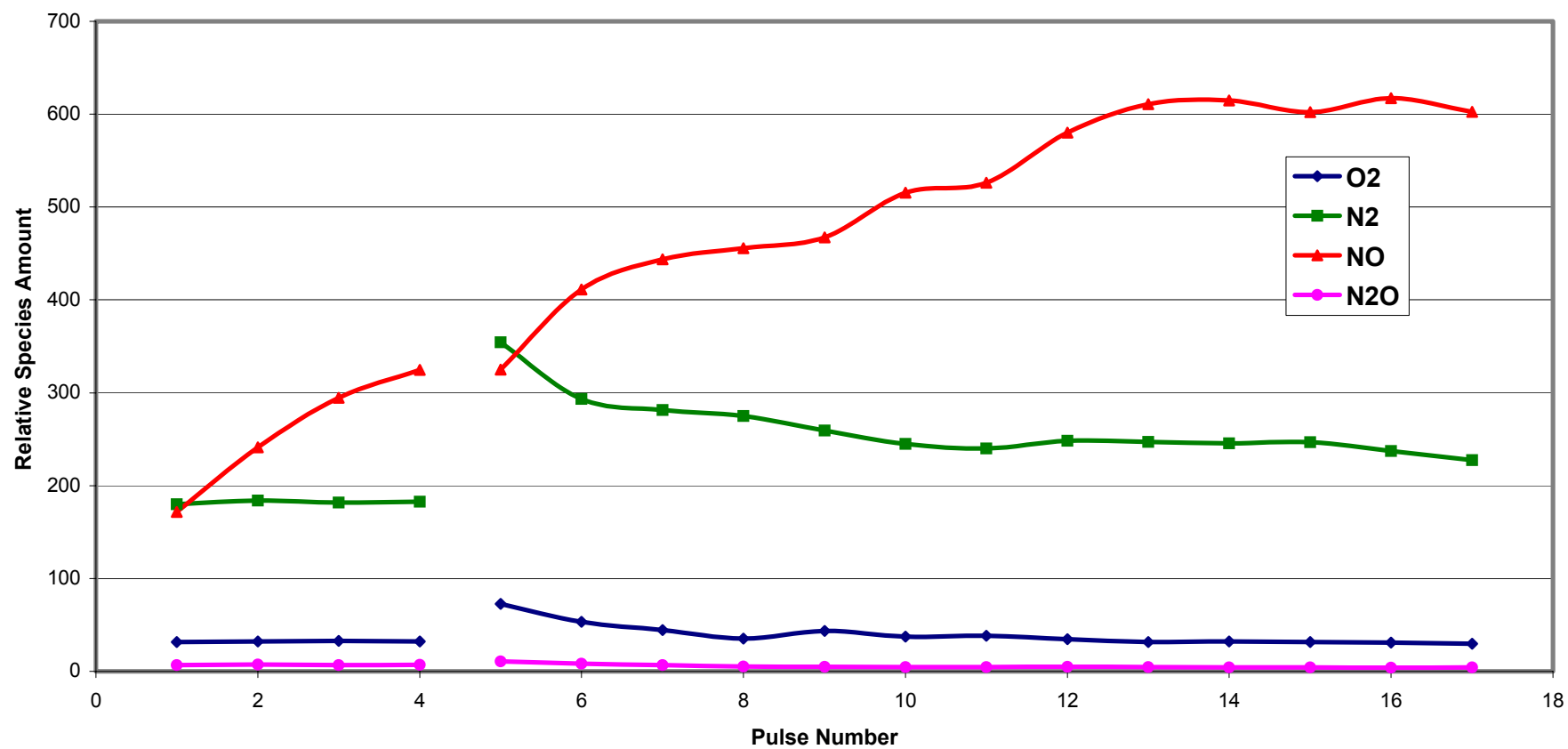
Figure 9. Species Evolved During Injection of 1-ml Pulses of NO on Cu1Ce3 Catalyst at 50 ^{o}C
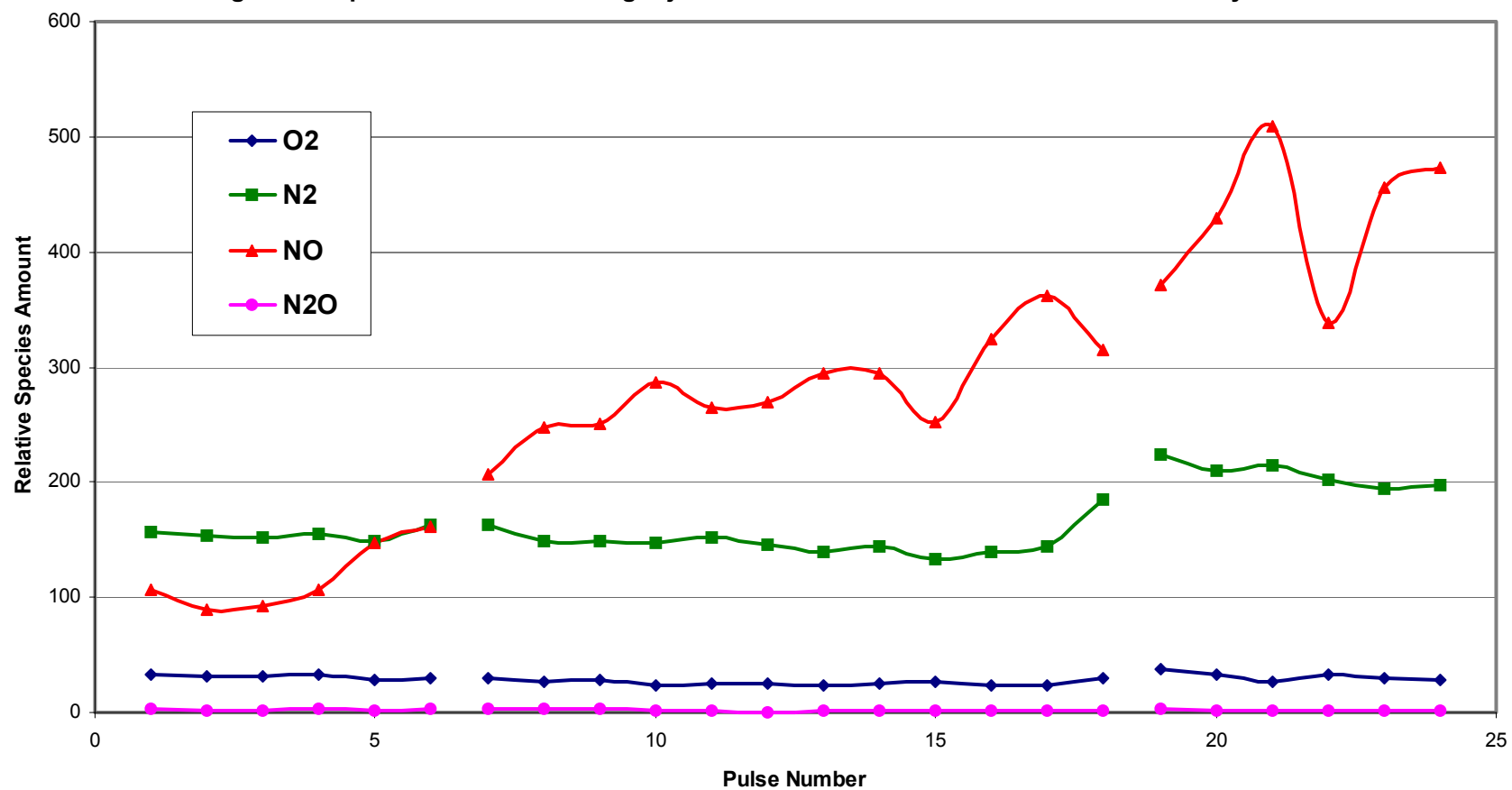
Figure 10. Species Evolved During Injection of 1-ml Pulses of NO on Cu1Ce3Mn Catalyst at 50 ^{o}C
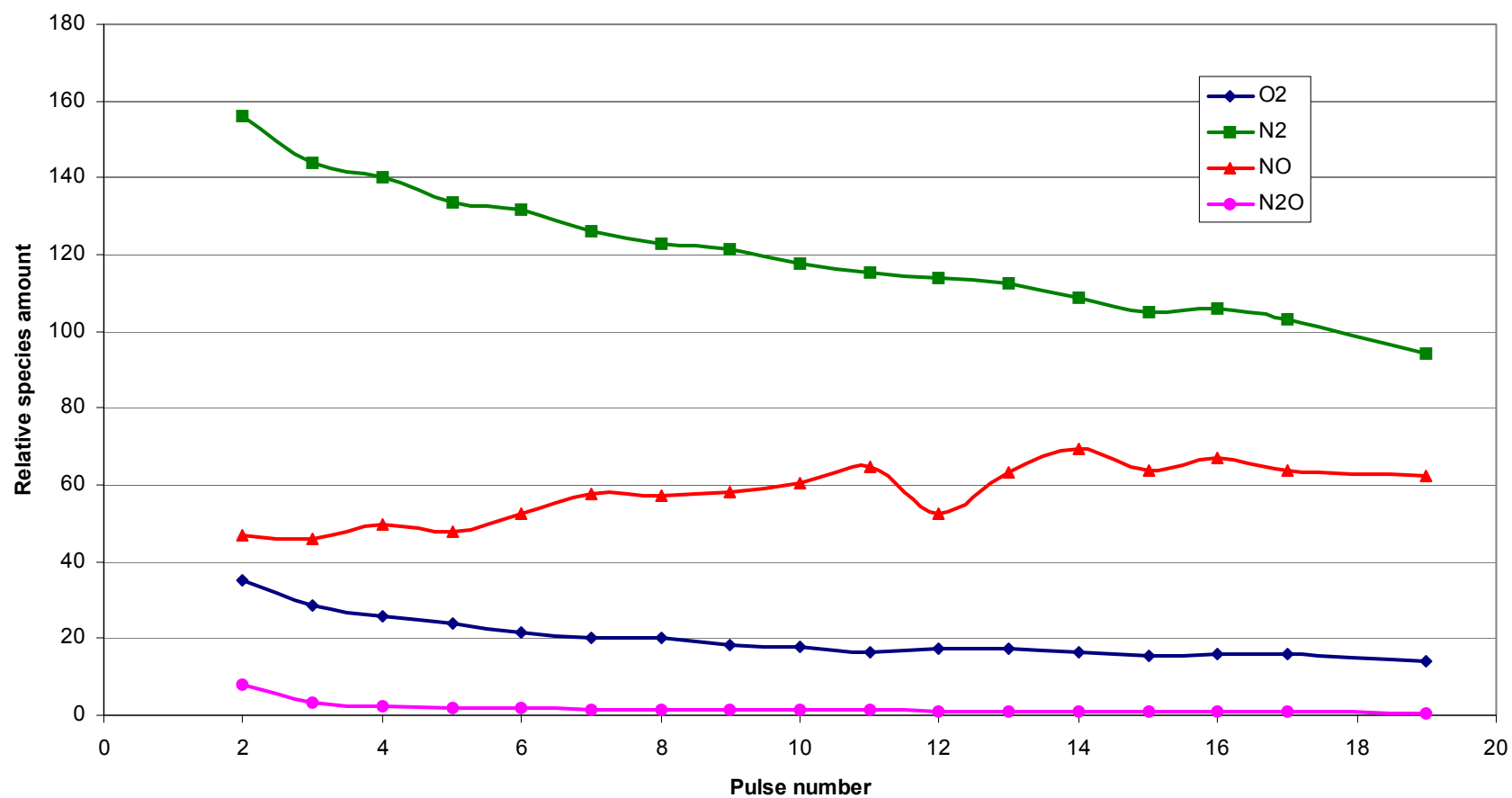
Figure 11. Species Evolved During TPD After the Adsorption of NO on Cu3Ce1 Catalyst at 50 ^{o}C
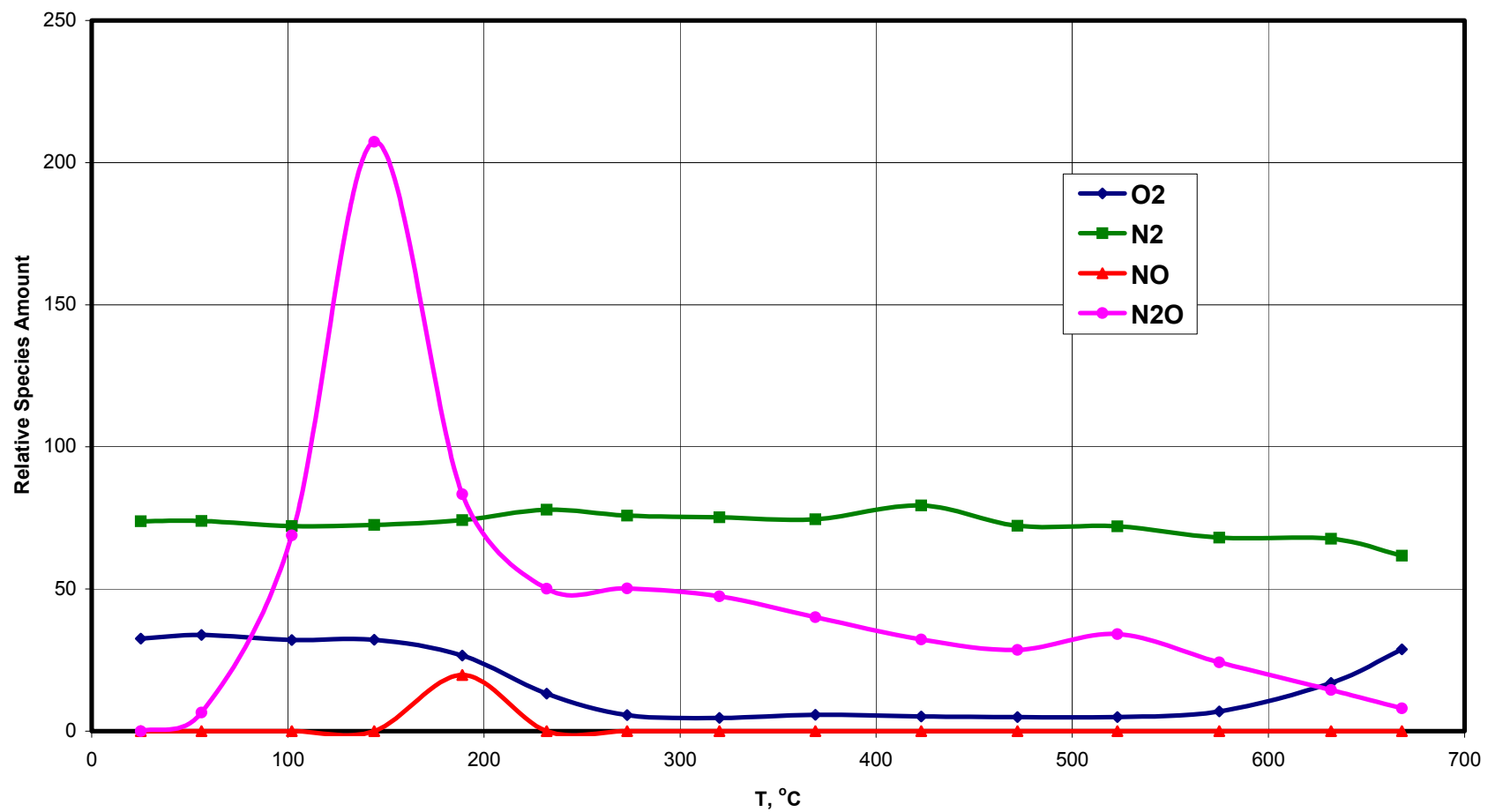
Figure 12. Species Evolved During TPD of Cu3Ce1Mn Catalyst Treated with NO at 50 ^{o}C
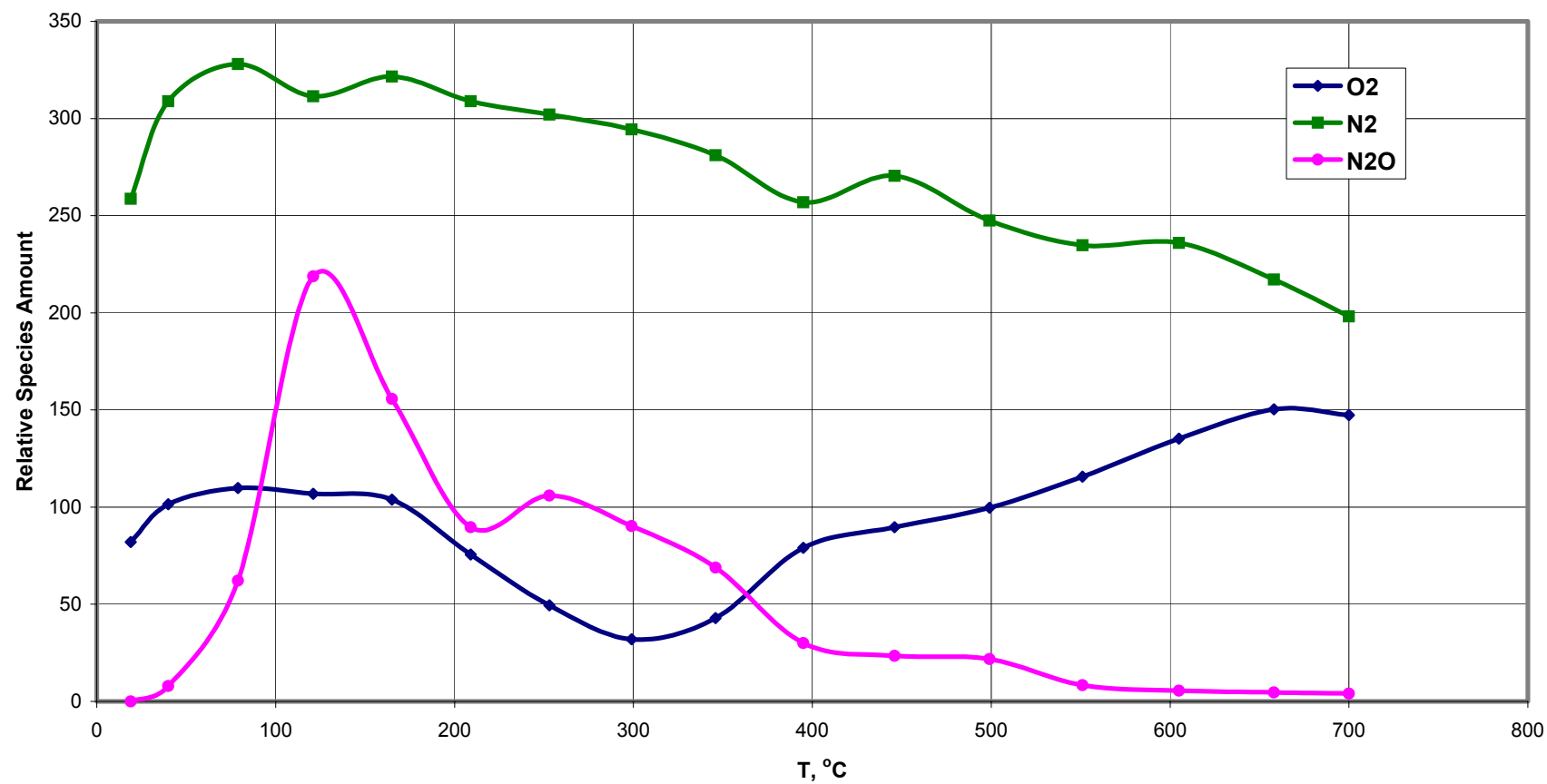
Figure 13. Species Evolved During TPD of Cu1Ce3 Catalyst Treated with NO at 50 ^{o}C
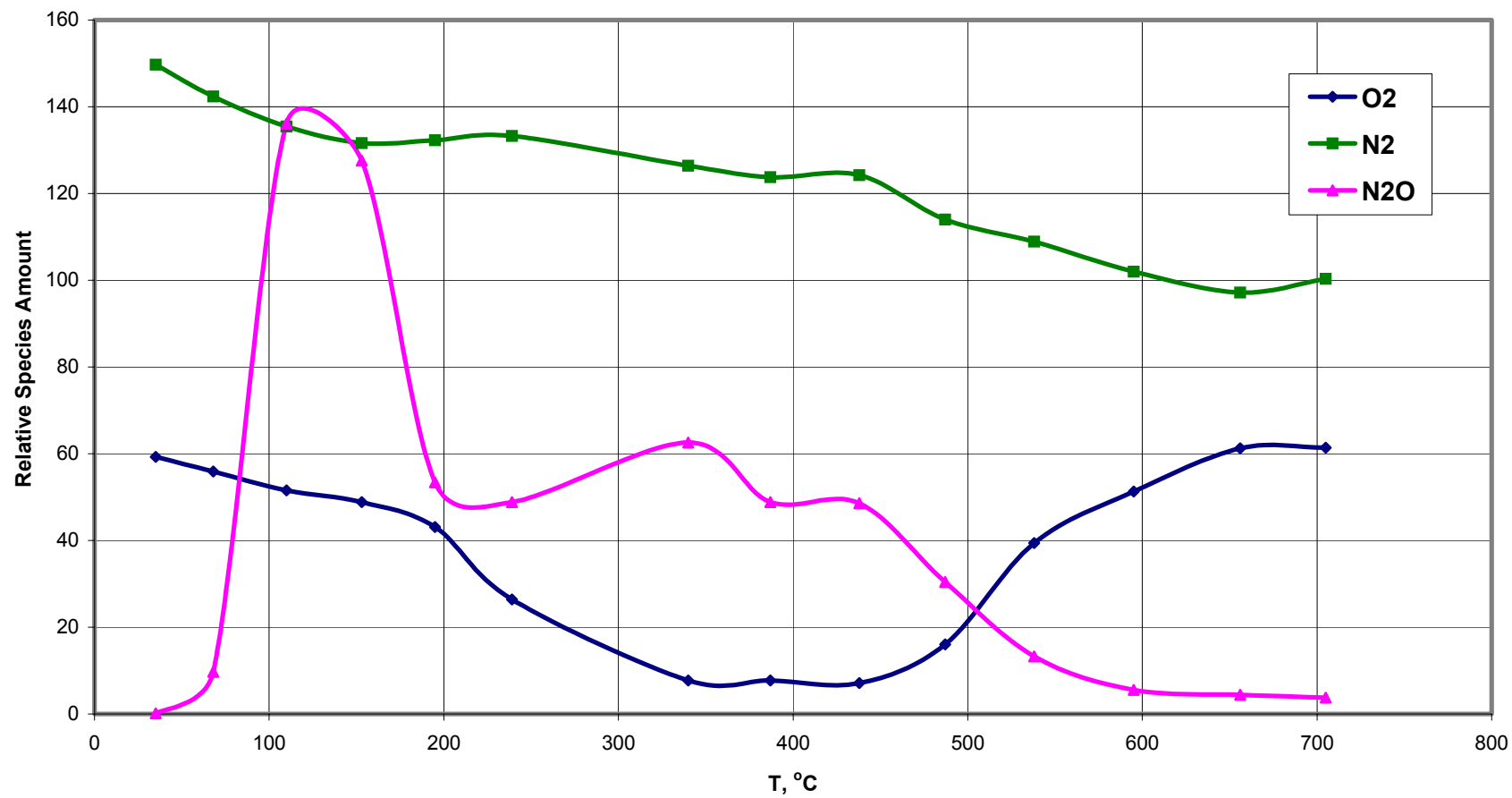
Figure 13-a. Species Evolved During TPD on Cu1Ce3 Catalyst Treated with NO at 50 ^{o}C
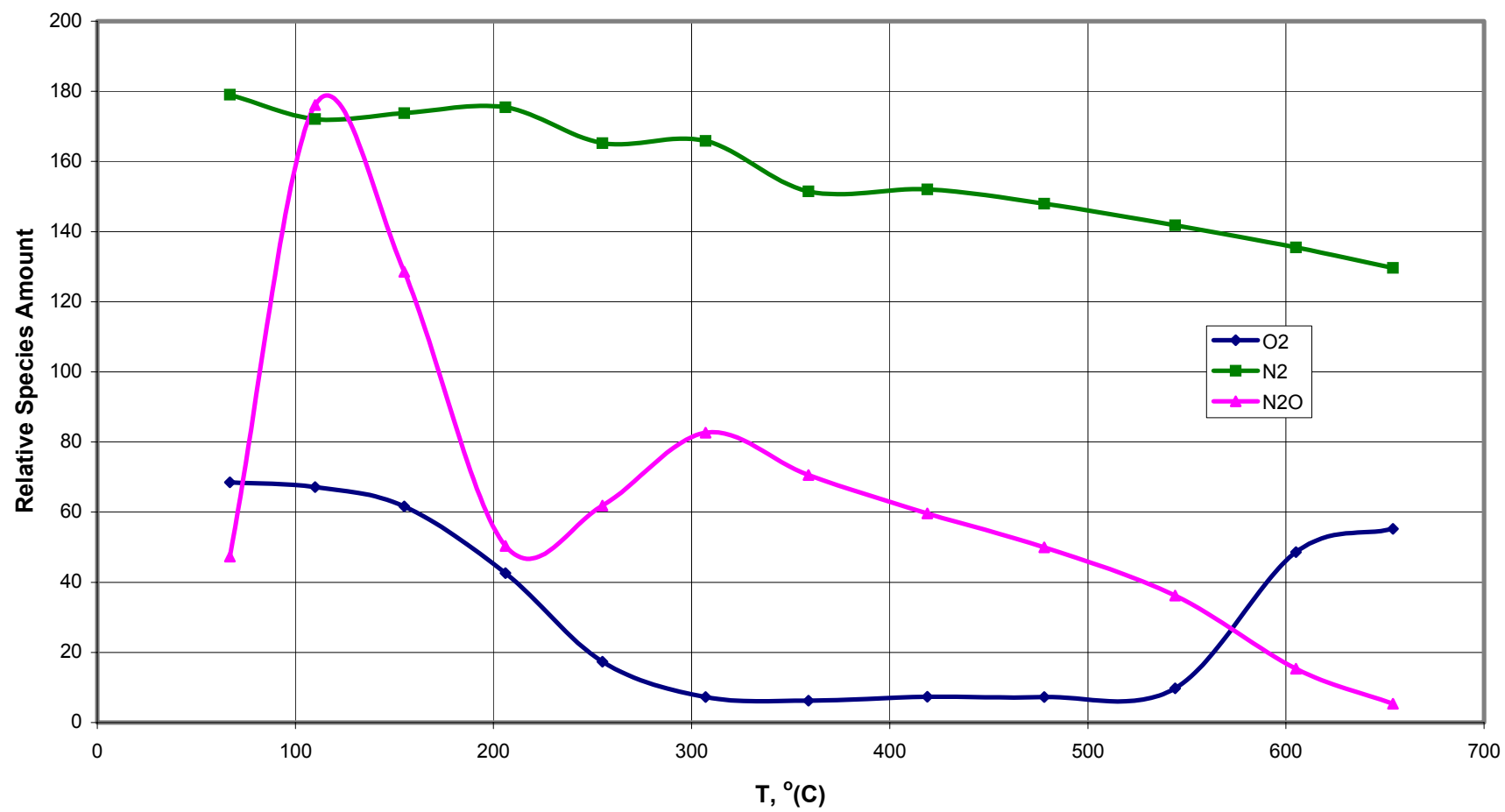Repeated with Fresh Catalyst

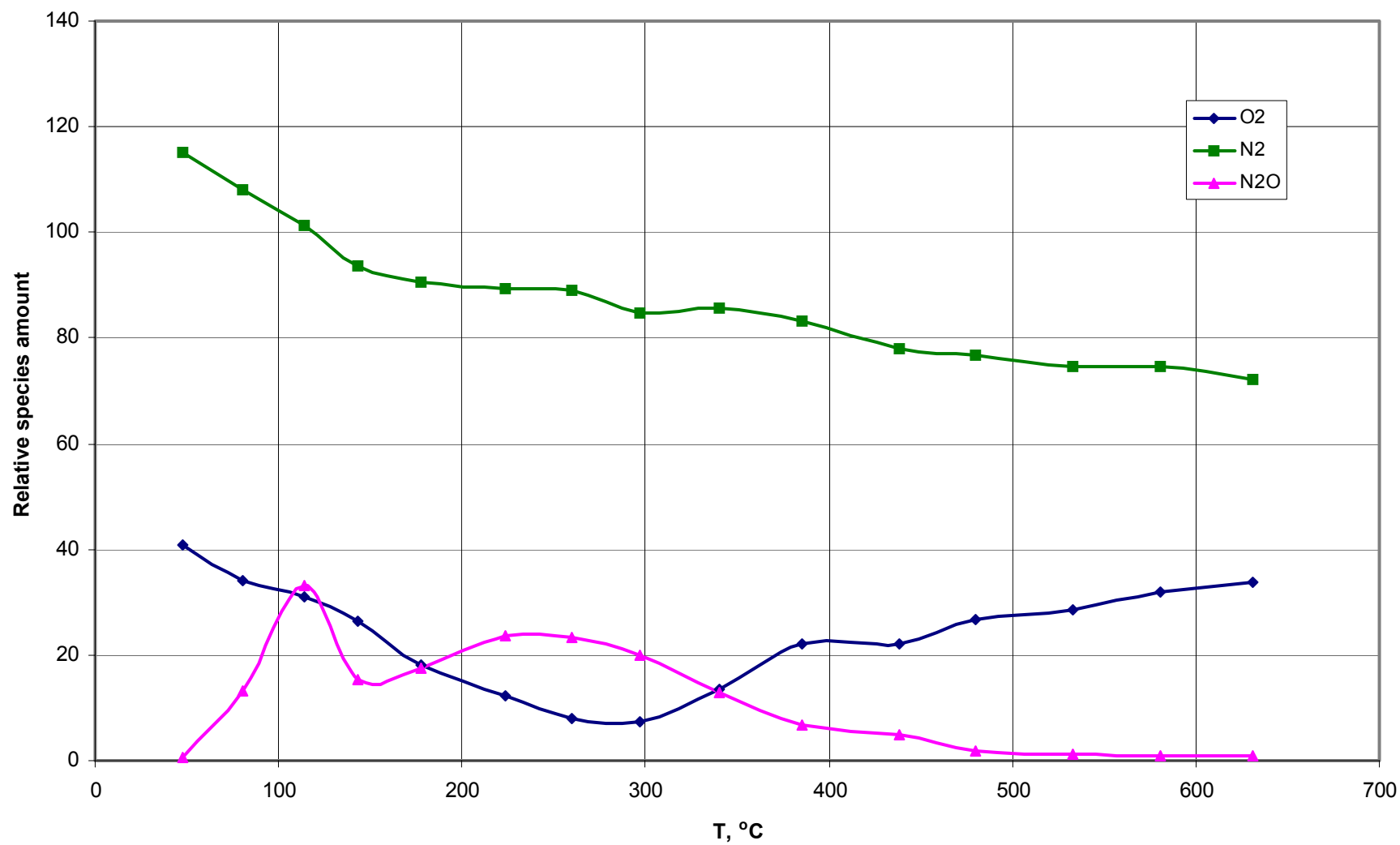**Figure 14. Species Evolved During TPD of Cu1Ce3Mn Catalyst Treated with NO at 50 ^{o}C**
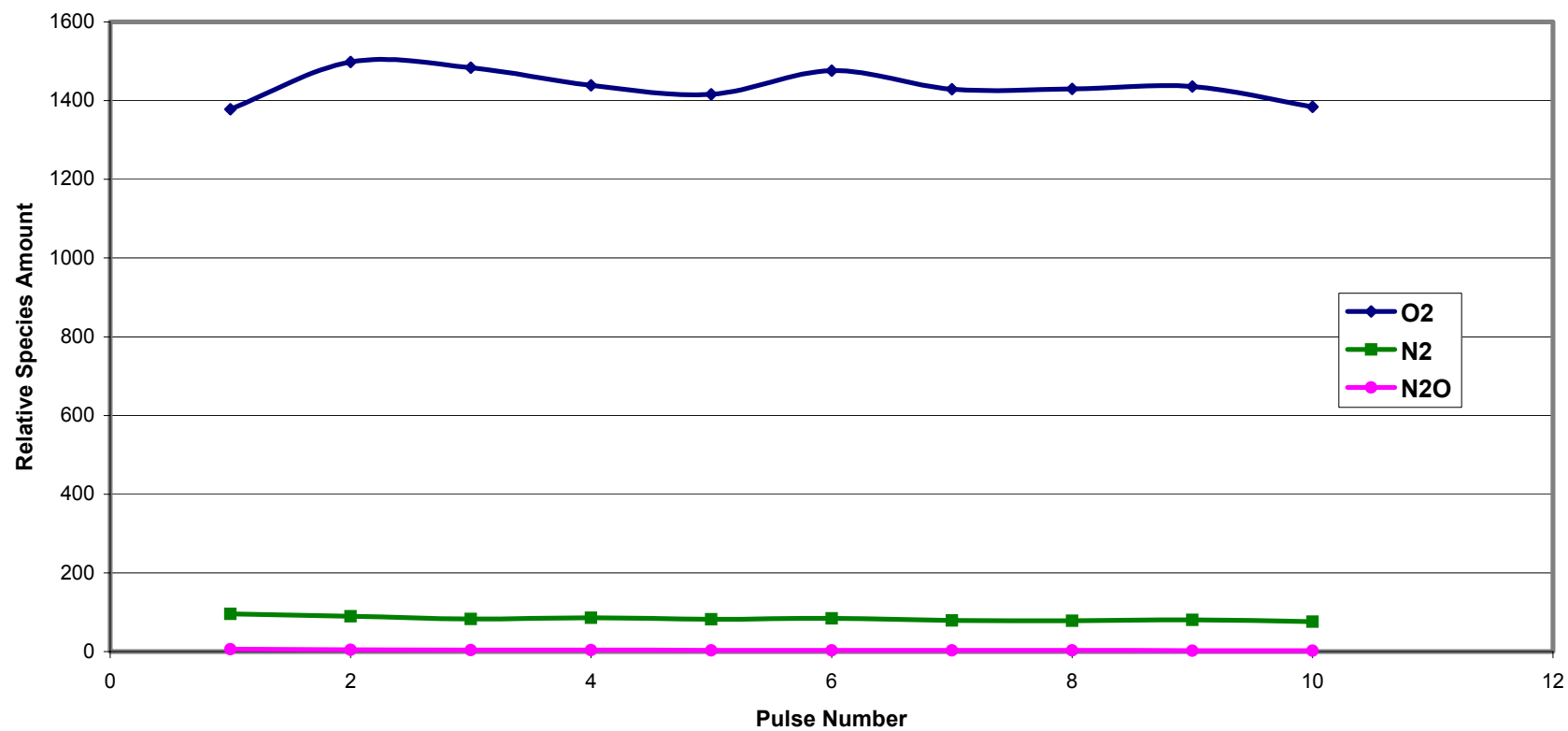
Figure 15. Species Evolved During Injection of 1-ml Pulses of O_2 on Cu3Ce1 Catalyst treated with NO at 50 ^{o}C

Figure 16. Species Evolved During Injection of 1-ml Pulses of O_2 on Cu3Ce1Mn Catalyst Treated with NO at 50 ^oC
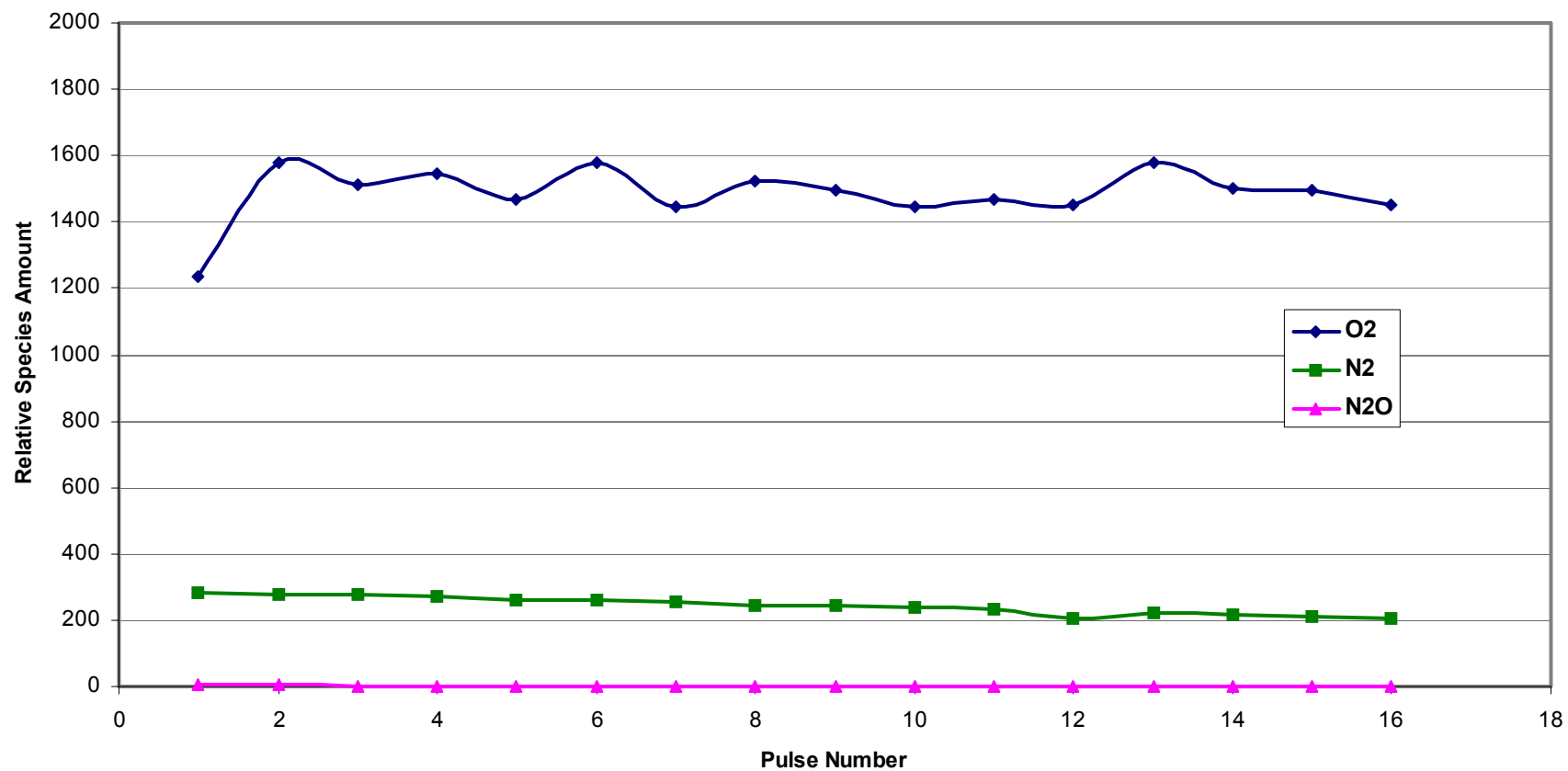
Figure 17. Species Evolved During Injection of 1-ml Pulses of O$_2$ on Cu1Ce3 Catalyst Treated with NO at 50 ^{o}C
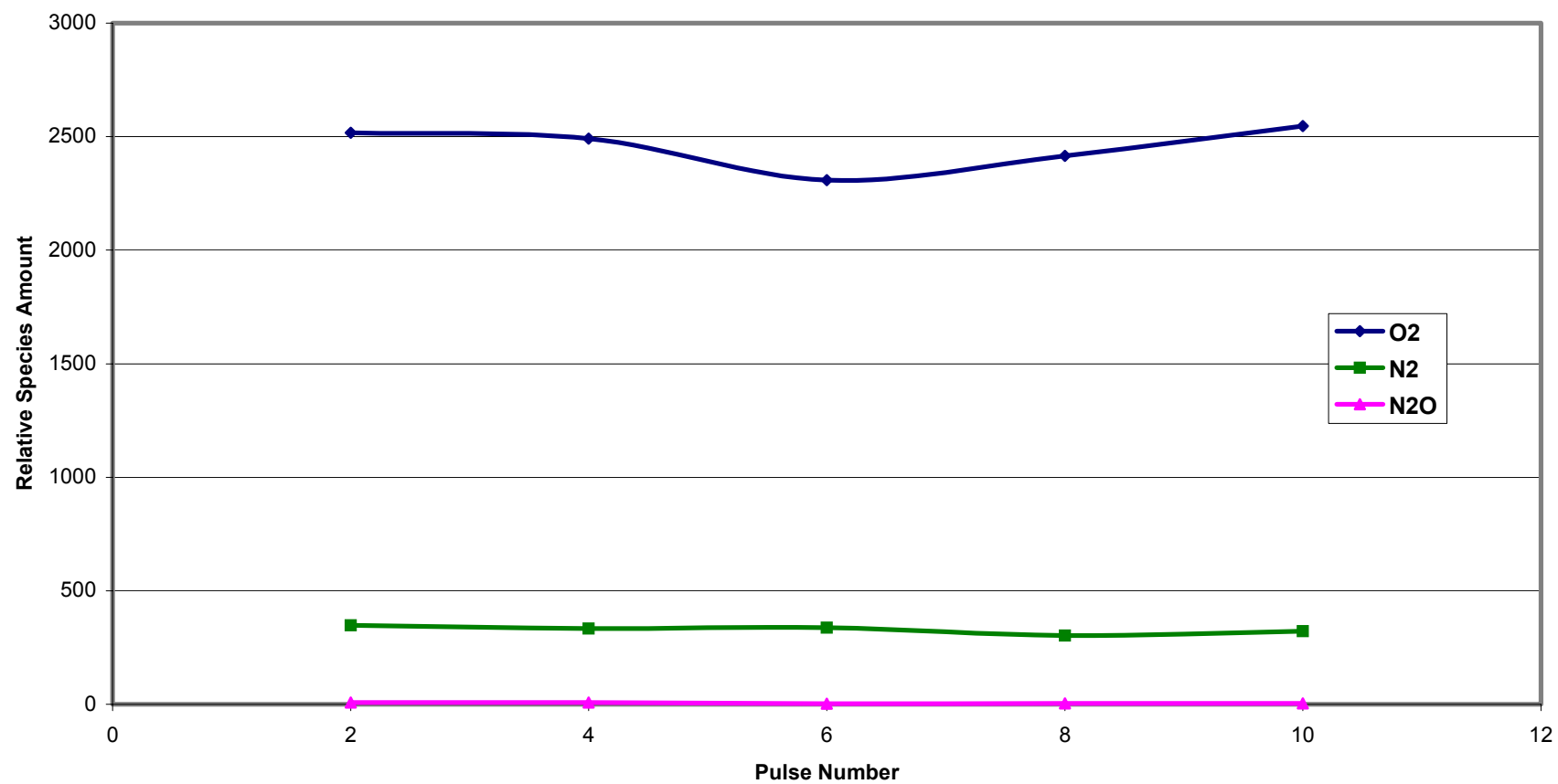
Figure 18. Species Evolved During Injection of 1-ml Pulses of O_2 on Cu1Ce3Mn Catalyst Treated with NO at 50 ^{o}C

Figure 19. Species Evolved During TPD of Cu3Ce1 Catalyst Treated with NO and O_2 at 50 ^{o}C

Figure 20. Species Evolved During TPD of Cu3Ce1Mn Catalyst Treated with NO and O_2 at 50 ^{o}C
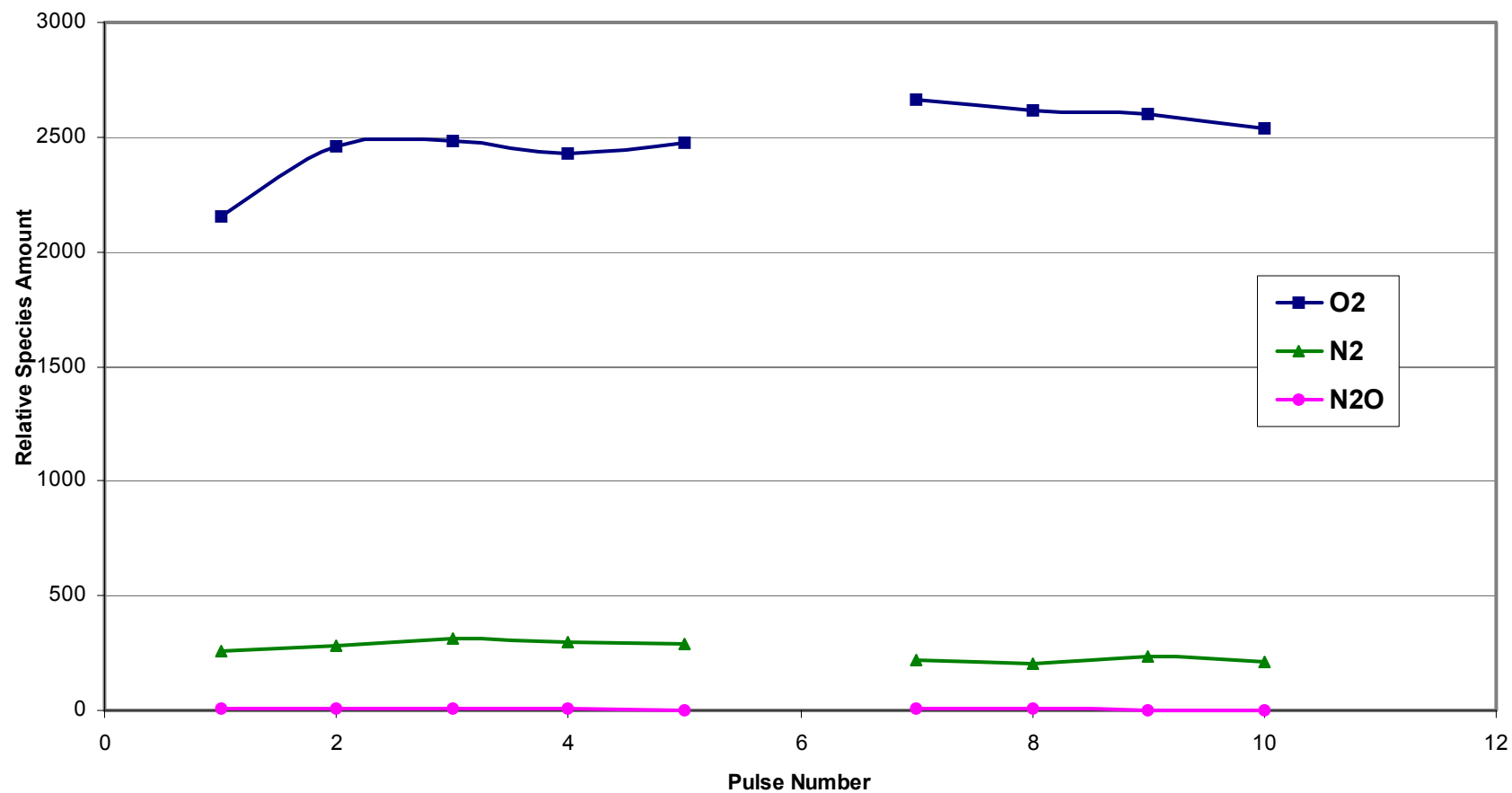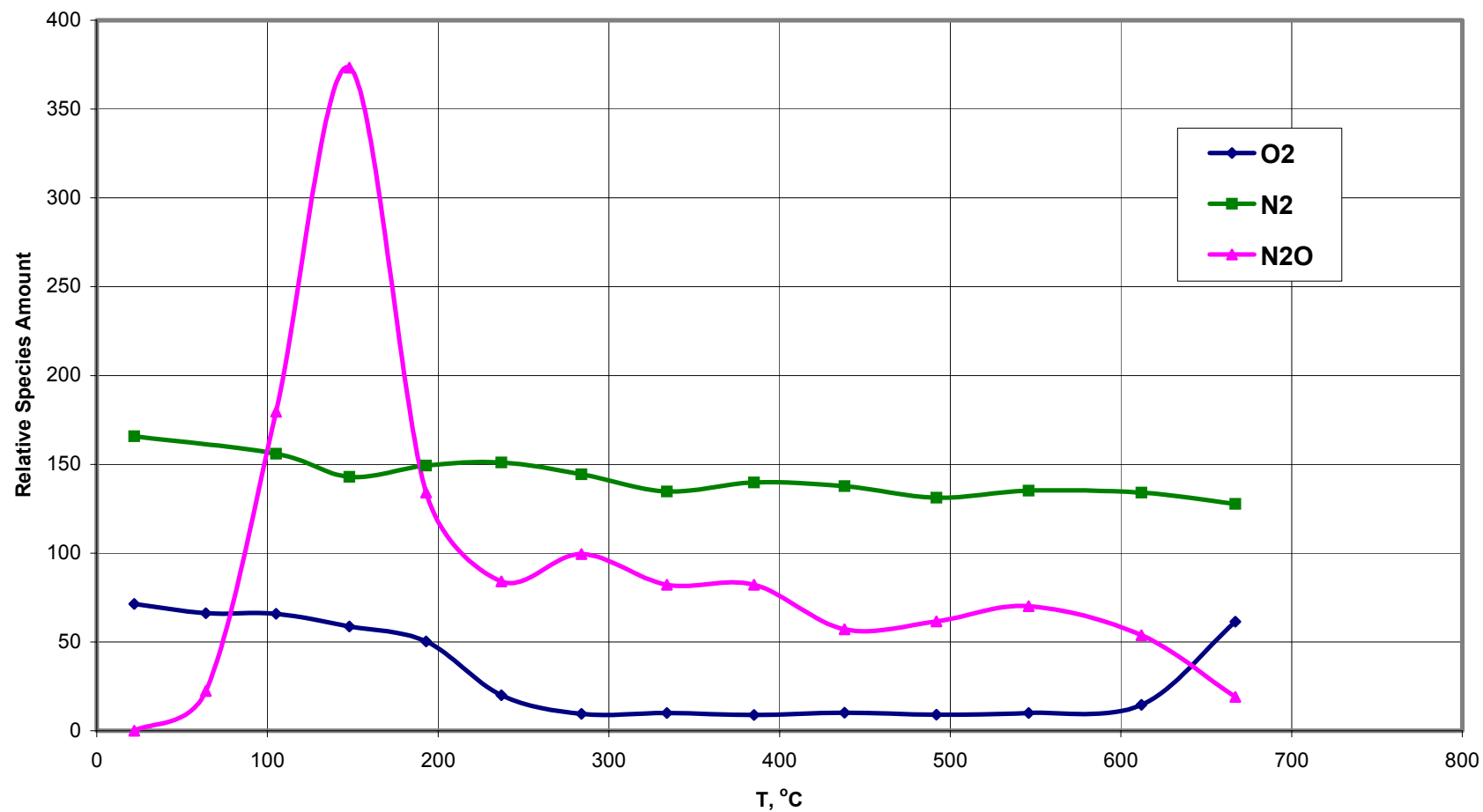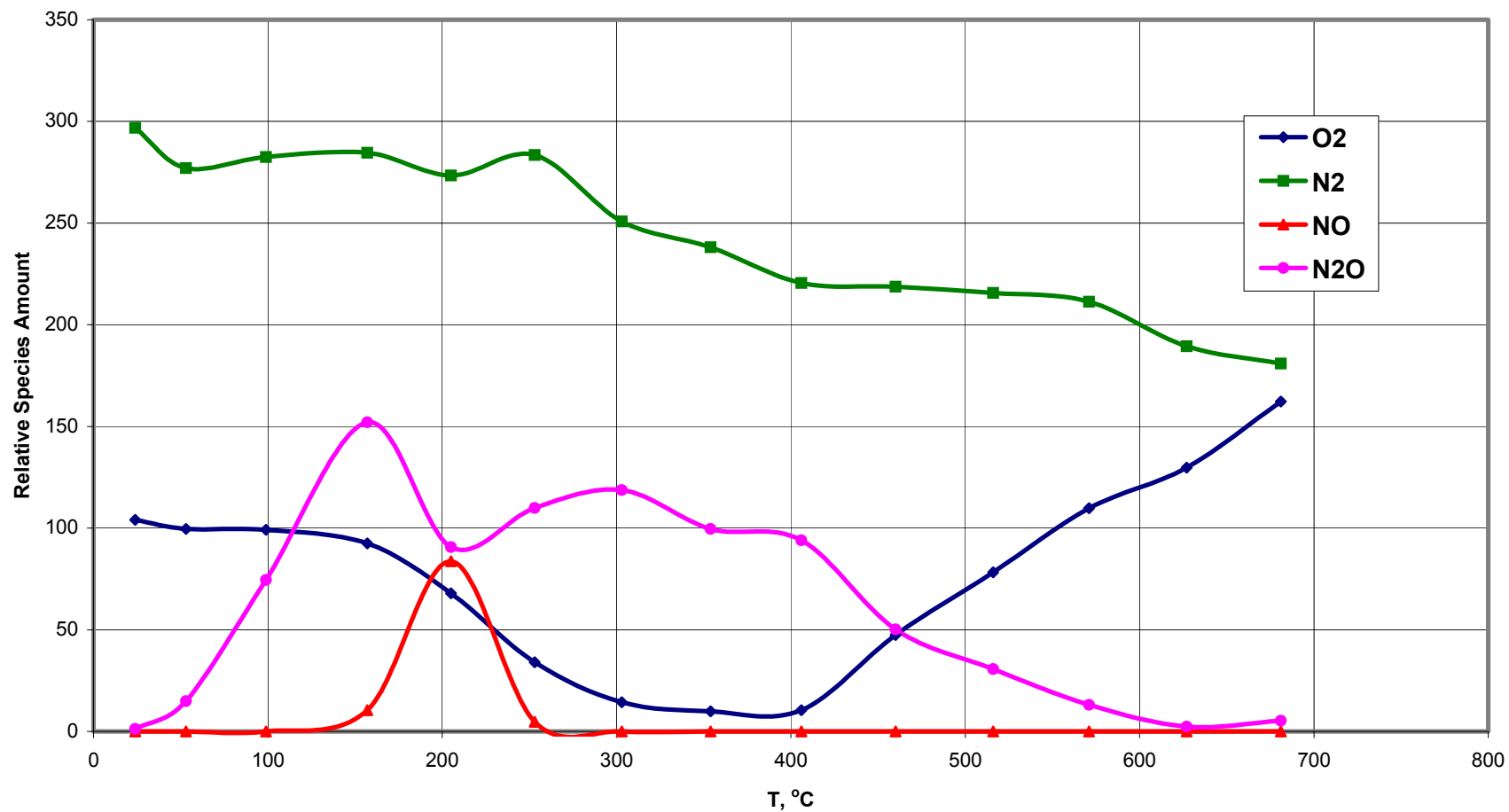
Figure 21. Species Evolved During TPD of Cu1Ce3 Catalyst Treated with NO and O_2 at 50 °C
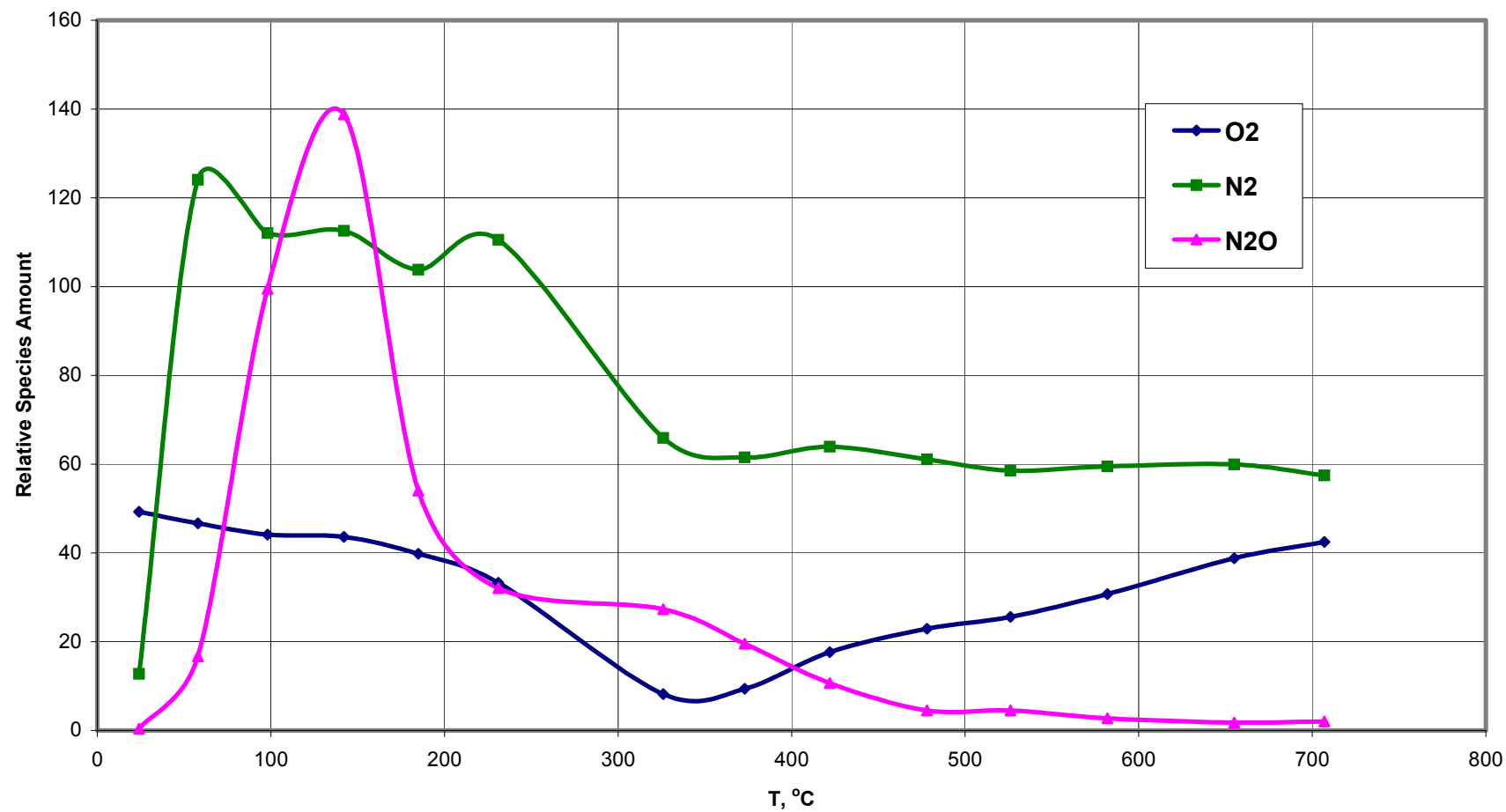
Figure 22. Species Evolved During TPD of Cu1Ce3Mn Catalyst Treated with NO and O_2 at 50 ^{o}C

Figure 23. Species Evolved During Injection of 1-ml Pulses of CH_4 on Cu3Ce1 Catalyst Treated with NO and O_2 at 50 ^oC
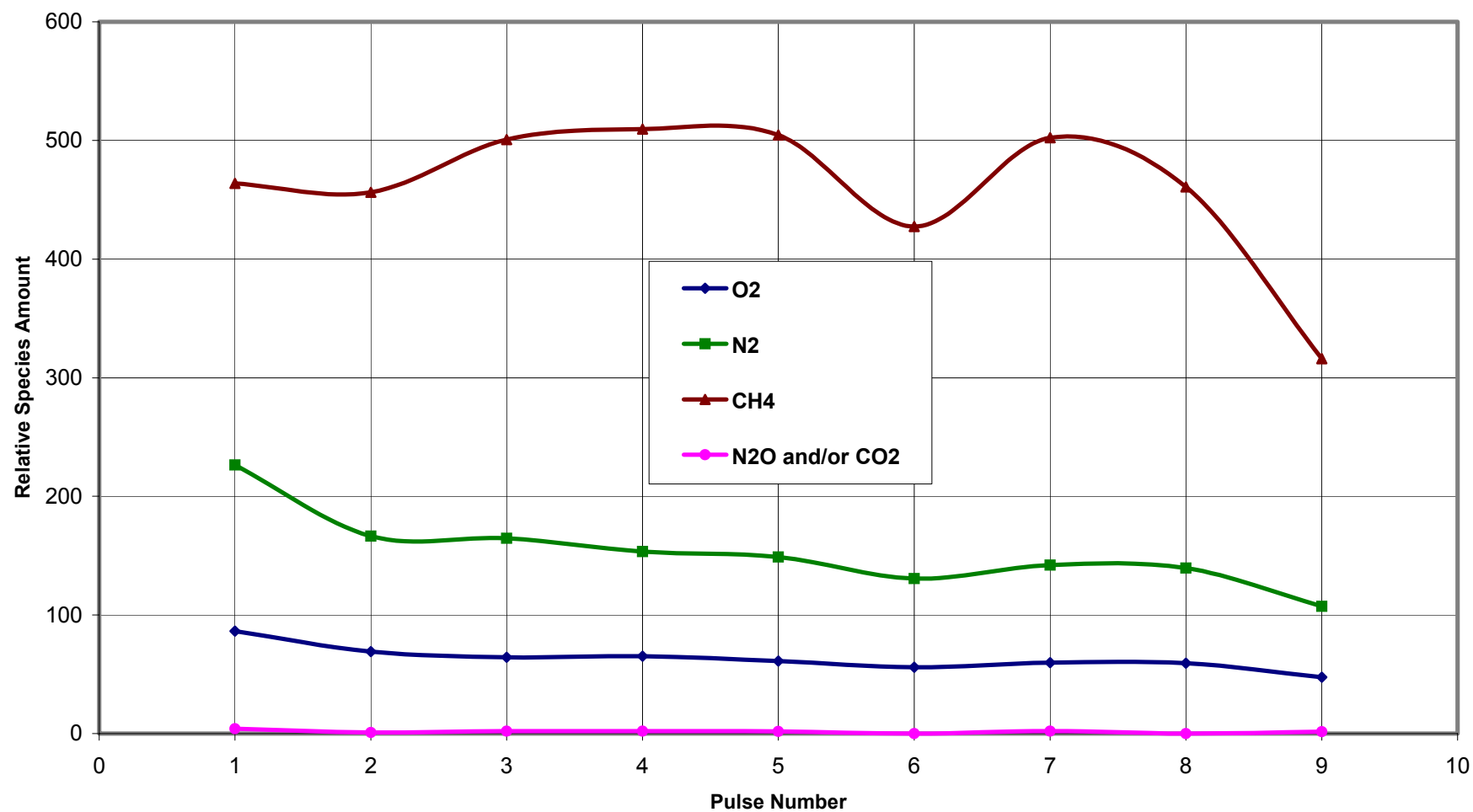
Figure 24. Species Evolved During Injection of 1-ml Pulses of CH_4 on Cu3Ce1Mn Catalyst Treated with NO and O_2 at 50 ^{o}C
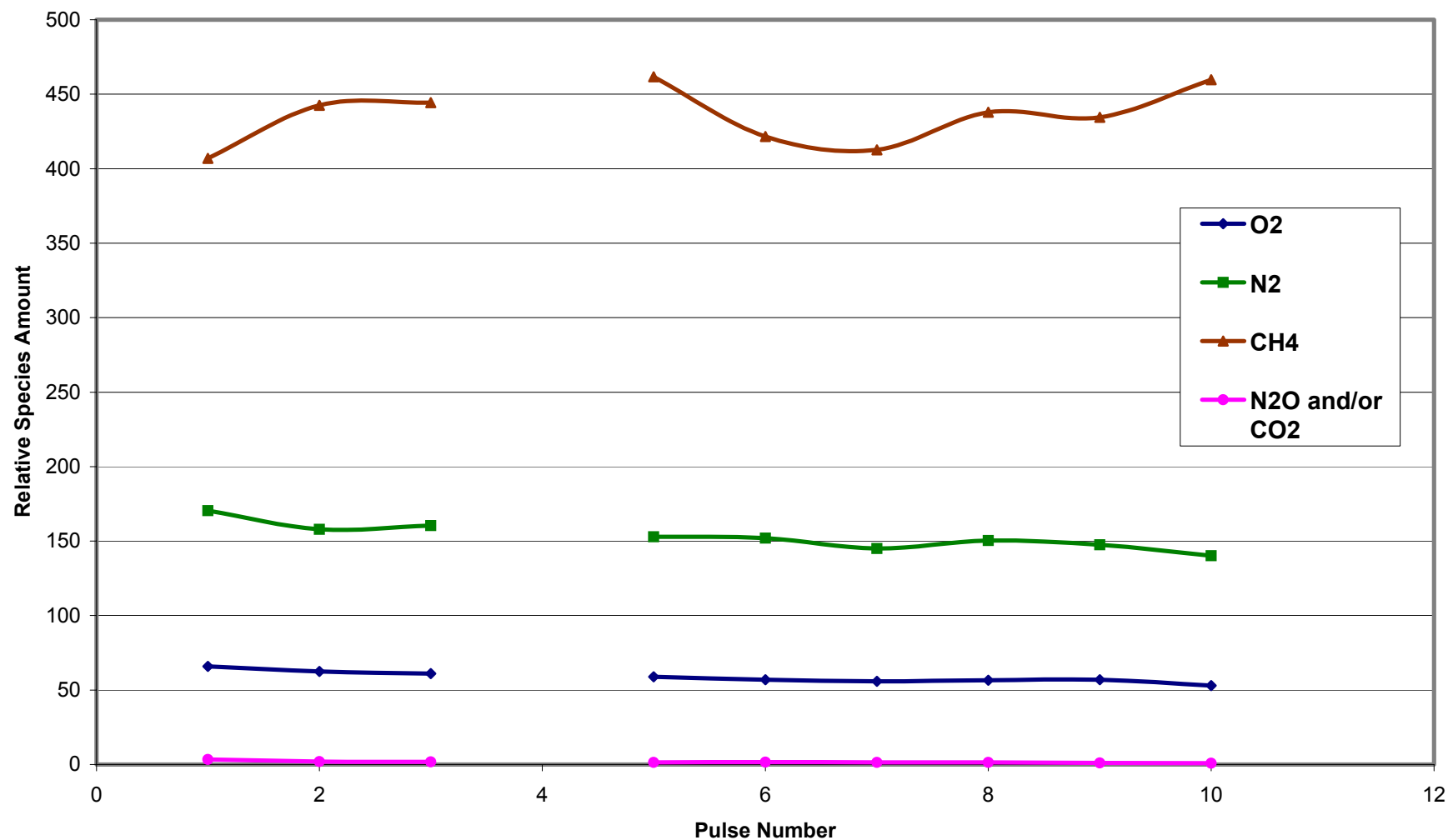
Figure 25. Species Evolved During Injection of 1-ml Pulses of CH$_4$ on Cu1Ce3 Catalyst Treated with NO and O$_2$ at 50 ^{o}C
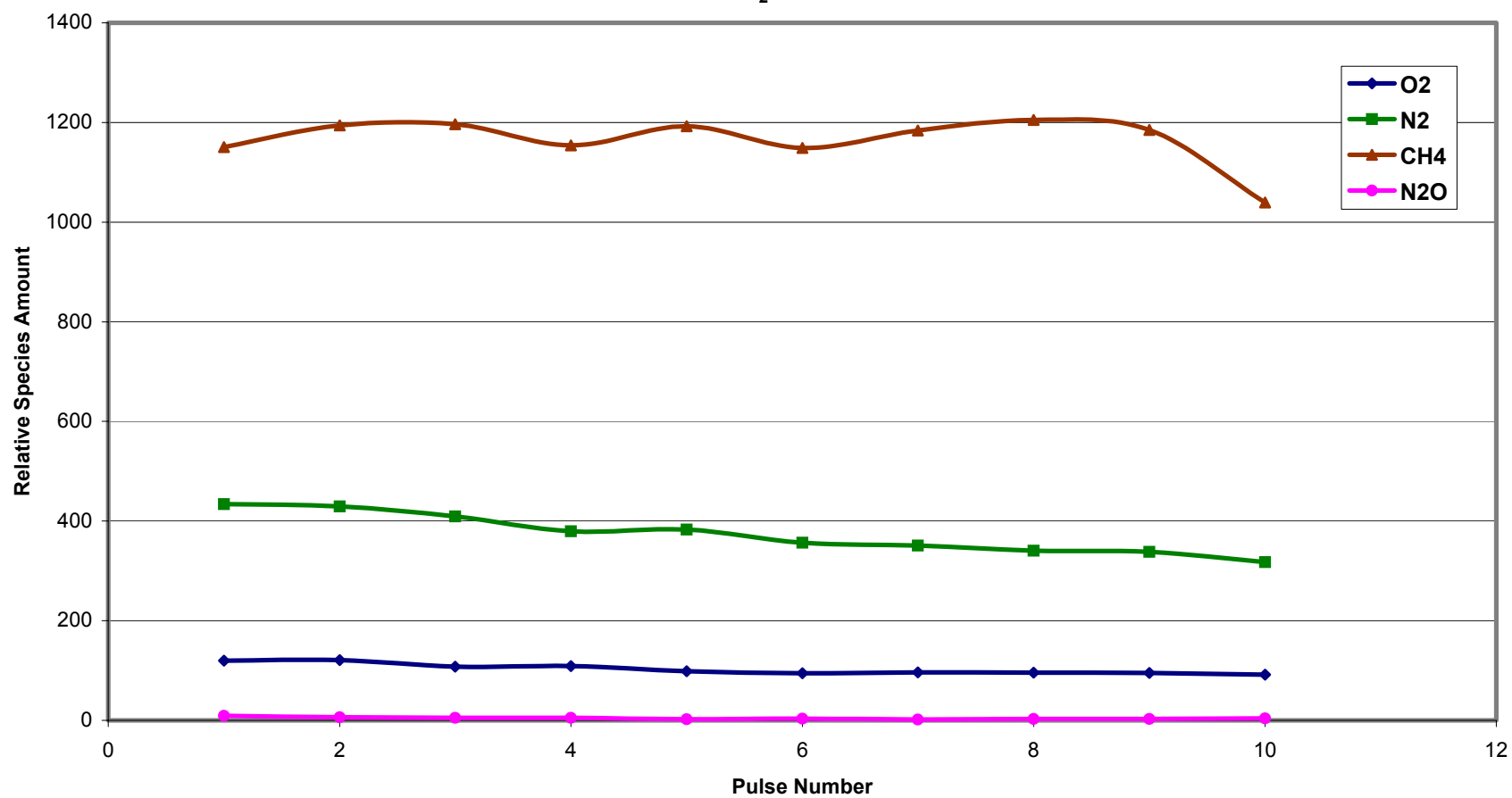
Figure 26. Species Evolved During Injection of 1-ml Pulses of CH_4 on Cu1Ce3Mn Catalyst Treated with NO and O_2 at 50 ^oC

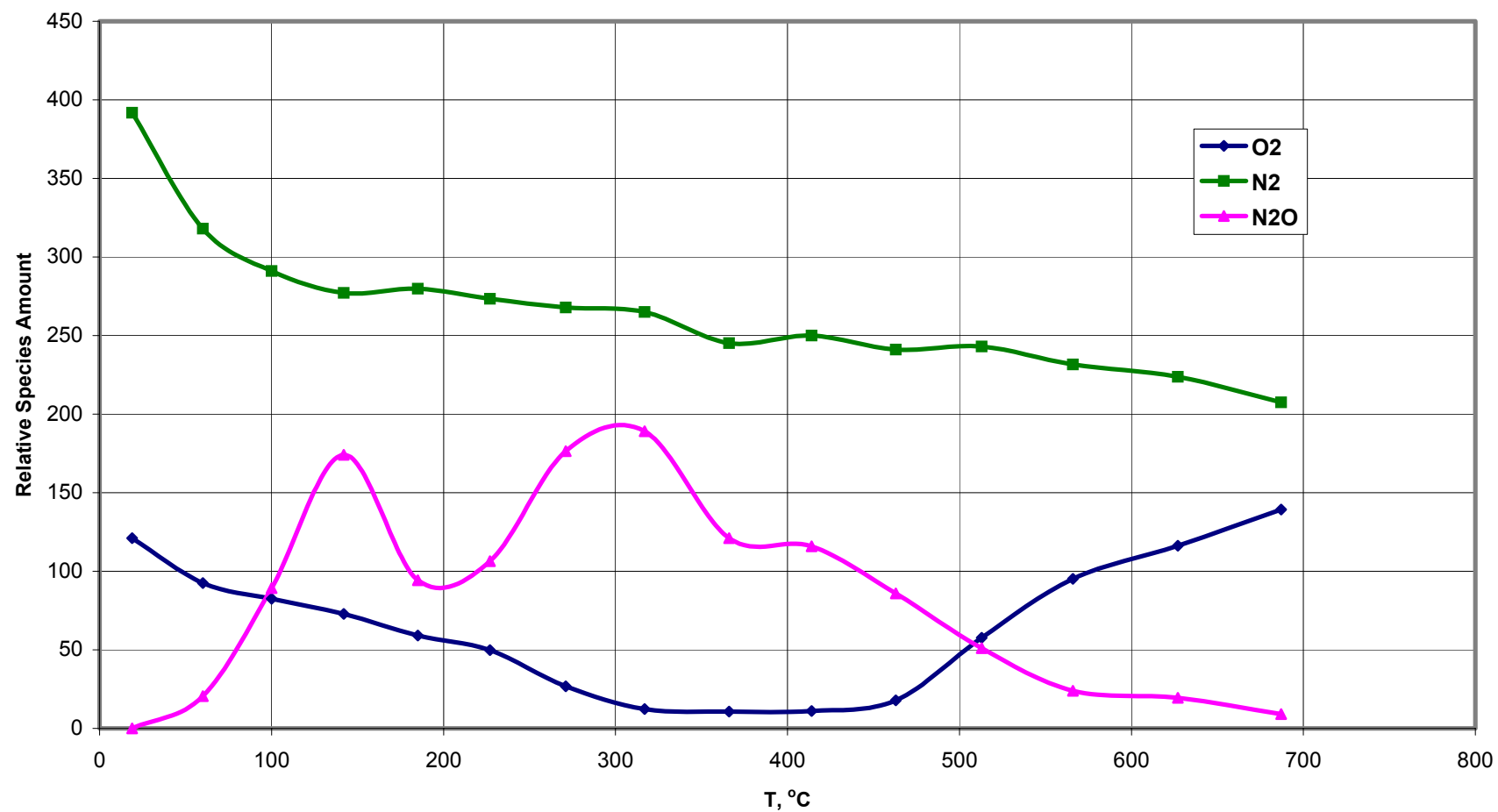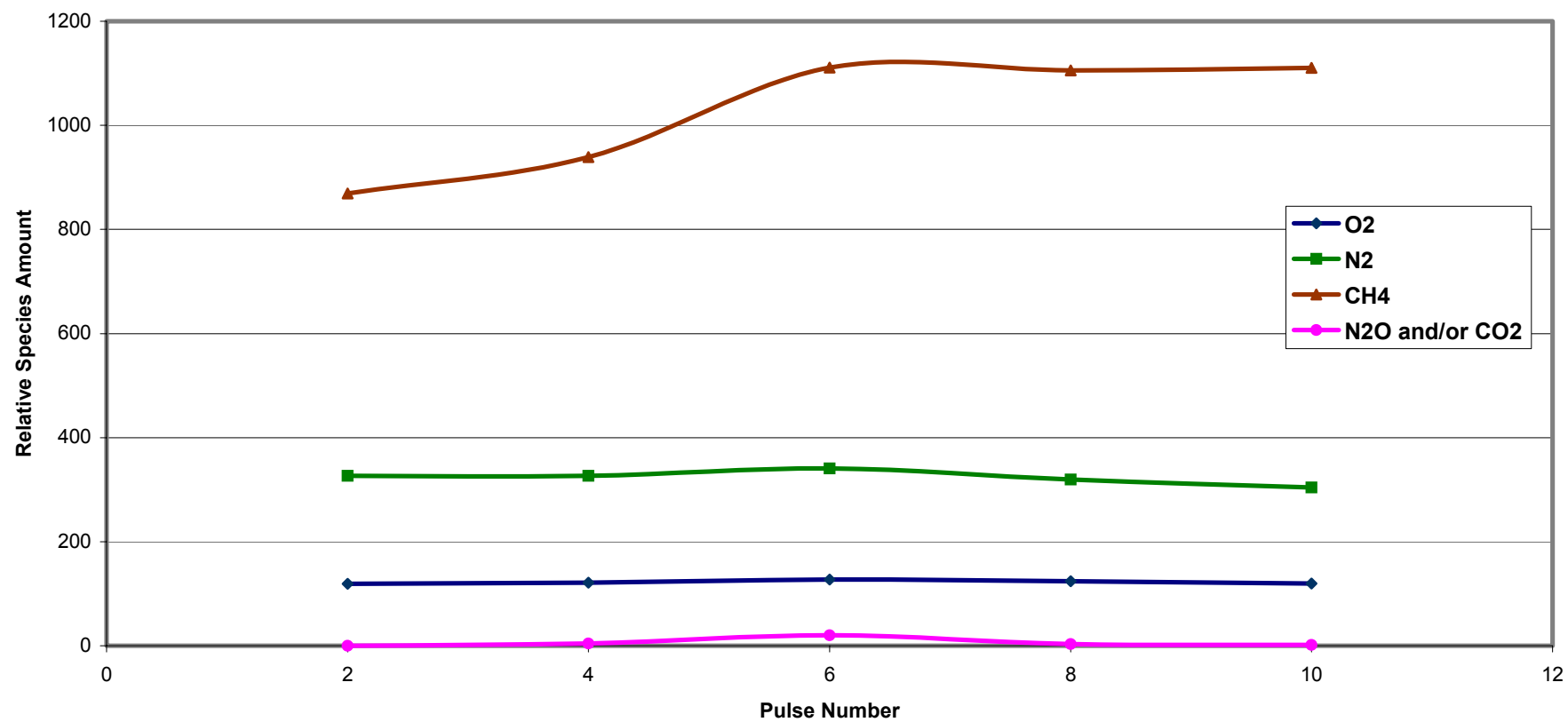Figure 27. Species Evolved During TPD of Cu3Ce1 Catalyst Treated with NO, O_2, and CH_4 at 50 ^{o}C
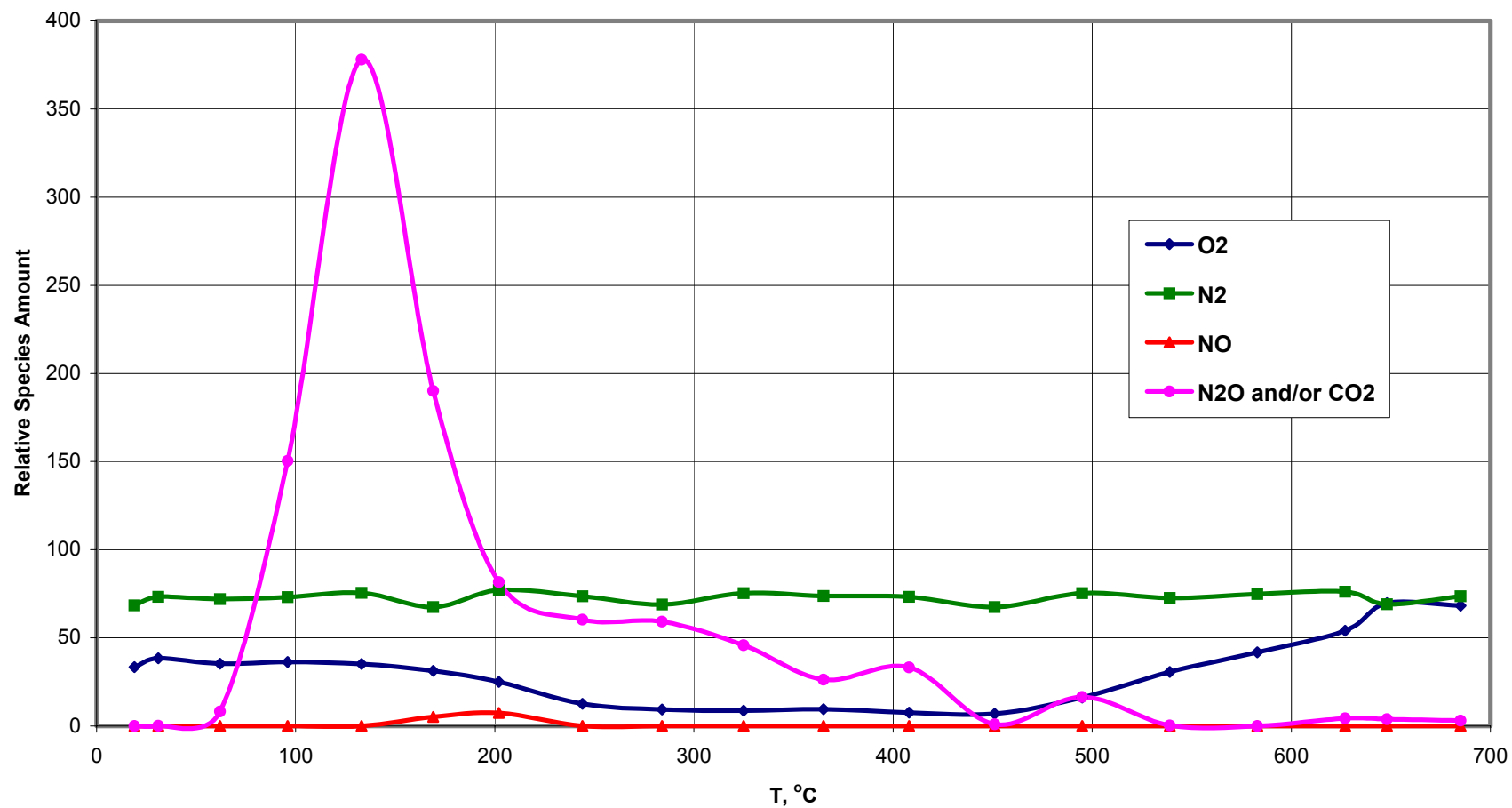
Figure 28. Species Evolved During TPD of Cu3Ce1Mn Catalyst Treated with NO, O_2, and CH_4 at 50 ^{o}C
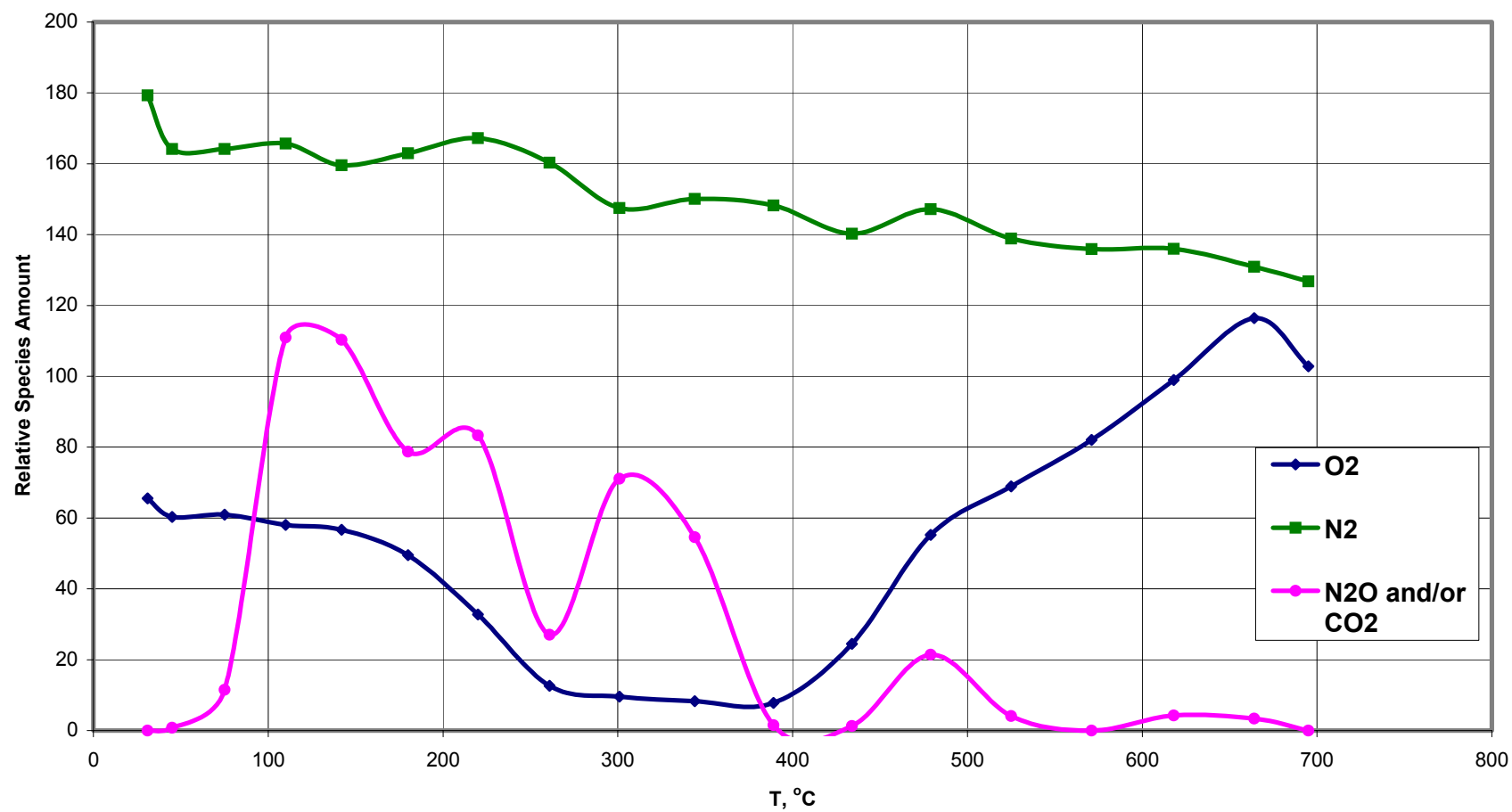
Figure 29. Species Evolved During TPD of Cu1Ce3 Catalyst Treated with NO, O_2, and CH_4 at 50 ^{o}C
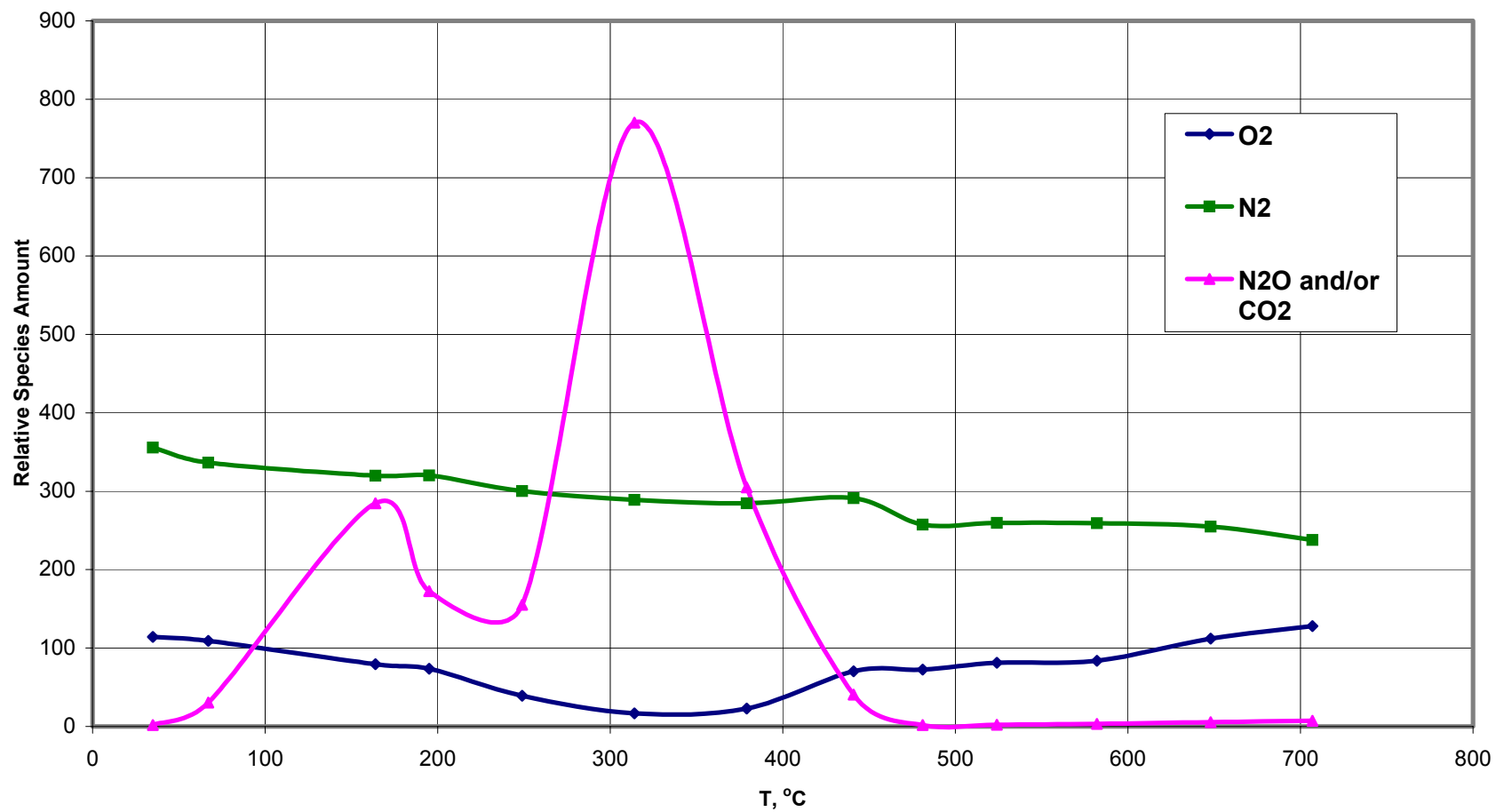
Figure 30. Species Evolved During TPD of Cu1Ce3Mn Catalyst Treated with NO, O_2, and CH_4 at 50 $^{\circ}$C
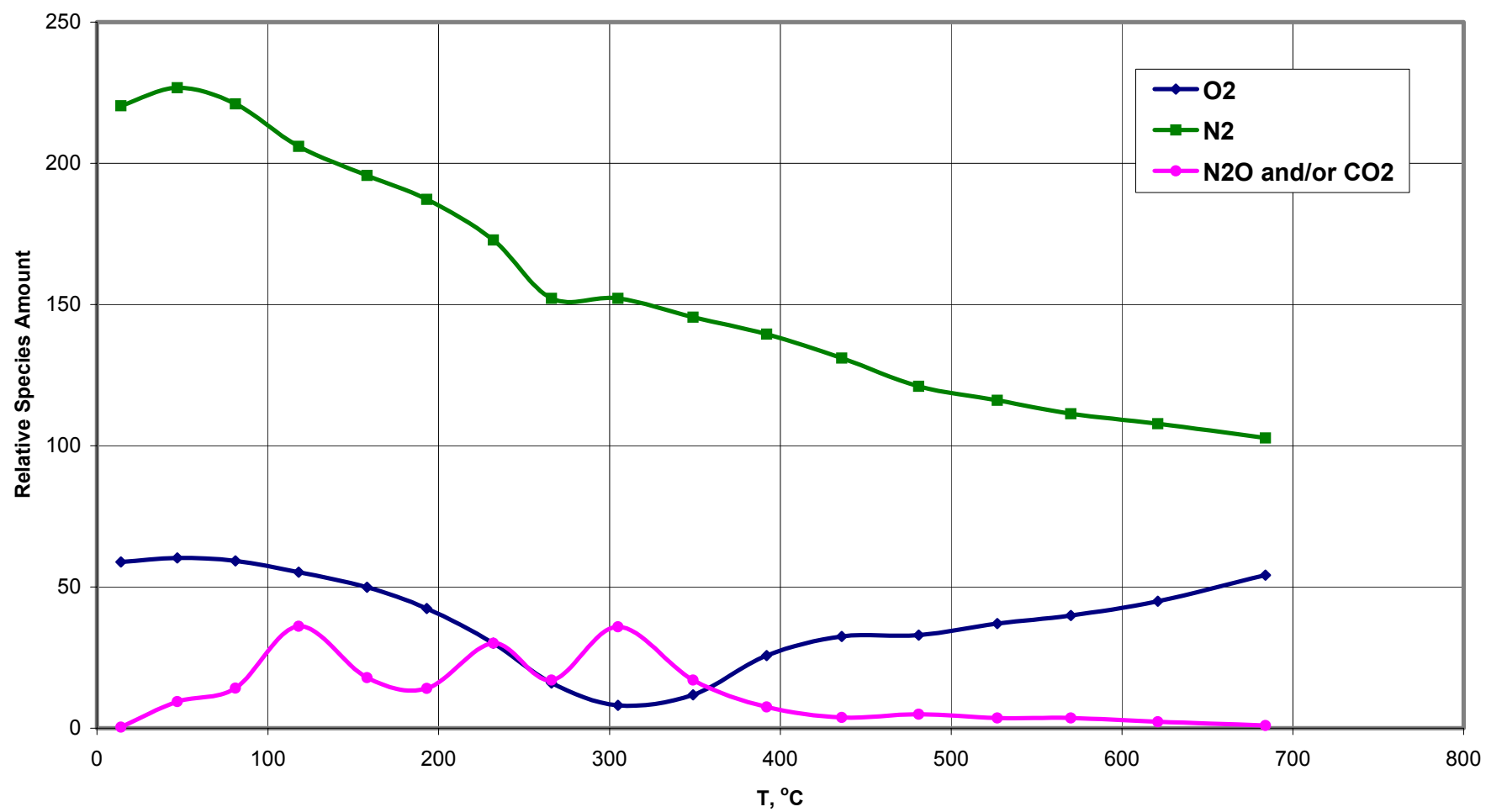
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2. Imamura, S., Nakamura, M., Kawabata, N., and Yoshida, J.;"Wet Oxidation of Poly(ethylene glycol) Catalyzed by Manganese-Cerium Composite Oxide;" *Ind. Eng. Chem. Prod. Res. Dev.,* **25**, 34-37, 1986.

APPENDIX I

TDA Report on the Long-term Testing of the Cu1Ce3 and Cu1Ce3Mn Catalysts

TEST RESULTS FOR HAMPTON UNIVERSITY SUBCONTRACT

LARGE-SCALE TESTING OF NEW CATALYSTS FOR SELECTIVE
CATALYTIC REDUCTION OF NITROGEN OXIDE

BY

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November 26, 2003

1. EXECUTIVE SUMMARY

TDA Research, Inc. (TDA), as a subcontractor to the Hampton University, evaluated the performance of copper-ceria catalysts for selective reduction of NO using unconventional reducing agents (i.e., methane and high sulfur heavy oil). The primary objective of the work was to carry out a large-scale demonstration of NO reduction potential of two copper/ceria catalysts under simulated power plant stack gases and to provide long-term life data at the operating conditions of interest.

The catalyst samples used in the experiments were provided by the Hampton University. They were tested as received without any pre-activation or conditioning prior to experiments. In the initial stages of the project, Hampton University prepared several catalyst samples and screened their performance through temperature-programmed desorption (TPD) and temperature-programmed reaction (TPR) experiments. Some limited bench-scale packed-bed reactor experiments were also performed to identify two candidate formulations for large-scale testing at TDA. The optimum operating conditions for the catalysts were also pre-determined during the initial screening tests. TDA received about 200 g batch of each formulation (un-promoted copper/ceria catalyst and 1% manganese-promoted copper/ceria catalyst) for further evaluations.

Prior to the experiments, TDA modified an existing test apparatus to simulate the operating conditions provided by Hampton University. In these tests, power plant flue gas concentrations (i.e., coal-boiler effluents) were closely simulated. Methane and high sulfur diesel fuel (1% sulfur by weight) have been used as reducing agents to selectively reduce NO. We generated life-data in steady-state experiments tests up to 100 hours long to demonstrate long-term stability of the catalysts. TDA tests also addressed the effects of sulfur dioxide on catalytic activity.

The manganese-promoted catalyst showed better performance characteristic in comparison to the un-promoted sample. This catalyst achieved approximately 9% NO reduction when methane was used as the reducing agent at 400-450°C temperature range (at a CH_4:NO molar ratio was 9). The NO reaction with methane was very selective consuming very little or no oxygen. Higher levels of NO reduction were accomplished when heavy oil was used as the reducing agent. Depending on the molar ratio, up to 100% NO reduction was achieved at a space velocity of 6,000 h^{-1}. In each case, the performance tests were carried out in the presence 300 to 3,000 ppm SO_2.

In a 100 hr durability test, we also demonstrated that a stable performance for the catalyst without any signs of degradation or undesirable side reactions. A visual inspection of the pellets shows that the mechanical structure of the pellets

was intact after the testing. The samples used in these experiments were recovered and sent to Hampton University for detailed characterization.

The subcontract testing at TDA have been completed as of November 24, 2003 within the proposed budget $17,000. The testing facilities, supporting personnel and related research in TDA are described in detail in the following sections.

2. RESULTS

2.1 Test Equipment

The NO_x removal efficiency of the catalysts provided by the Hampton University were measured in an existing, automated testing apparatus. However, the apparatus needed modifications for the specific purpose of measuring activity for NO_x reduction catalysis using methane and heavy oil as reducing agents.

Figure 1 is a photograph of the experimental apparatus. The apparatus uses several electronic mass flow controllers for the introduction of the gases. It contains is a 3.0" (O.D.) stainless steel tube that is designed for 300 psig and $1292°F$ ($700°C$). A 2.0″ diameter glass insert is used to prevent interference of the reaction gases (e.g., NO_x, SO_2) with the stainless steel surface in the hot zone. The isothermal zone of the reactor is 10" (254 mm) high. Without channeling in the bed, pellets up to 0.25" (63.5 mm) can be tested. Figure 2 illustrates the overall layout of the apparatus. A series of mass flow controllers meters the desired gas composition into the reactor. Cylinders of N_2, CO_2, CH_4, CO, NO and SO_2 are stored in the room. NO_x and SO_2 were stored in separate hoods to supply the gases to the reactor that are inside a third hood. Water (or other liquid components) is stored in a drum and pumped into the vent hood where it is boiled and mixed with the bottle gas supply. With this setup, it is possible to generate feed streams of simulated engine exhaust and pass them over sorbent/catalyst formulations at the desired rates. A number of safety devices are installed; the computer monitors them and shuts down all gas supplies, heaters, etc., if any parameter goes out of range. Two computers control the experiments and record the data. One computer controls the temperatures and flow rates, and sequences automatically between absorption and regeneration. The computer also monitors the alarms and high temperatures and shuts the experiment down if any factor

Figure 1. TDA's HTHP Reactors.

(*e.g.,* high SO_2 levels) exceeds preset limits. The second computer controls the gas chromatograph and records the data from the detectors.

The preheated feed mixture is then directed into the reactor. A valve assembly was used to allow the gases bypass the reactor and flow directly to the analytical system for accurate measurement of the feed gas composition. the reactor is used to control the temperature. After exiting the reactor, the NO (and NO_2) content of the stream is monitored by an on-line ThermoEnvironmental (TE) Model 10S chemiluminescence analyzer with 0-10,000 ppm detection range. The system also has a more sensitive low concentration NO_x analyzer (TE Model 42C). This analyzer has a lower detection range (less than 100 ppm) and will be used to analyze low NO_x levels. On-line SO_2 monitoring is provided with a TE Model 43CHL analyzer. We also used a $CO/CO_2/CH_4$ analyzer by the California Analytical for continuous monitoring of these gases.
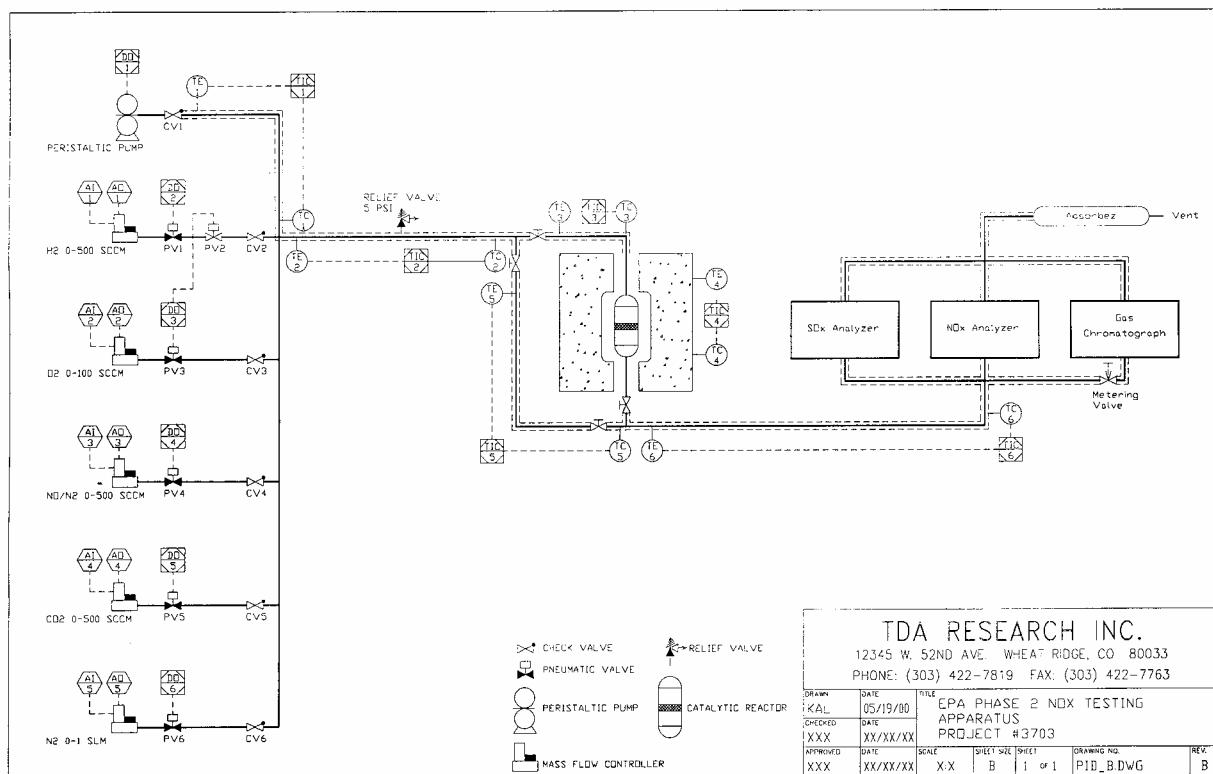
Figure 2. Schematic of the testing apparatus (not all modifications included).

The apparatus was fully automated and can run without an operator for long periods of time, including overnight. We use Control CB software on this apparatus to control test conditions, log analytical data, and to safely shut down the apparatus in case of a malfunction. The high degree of automation allows continuous operation, and we operate the system 24 hours per day.

2.2 Testing Procedure

We tested each sorbent formulation using gas concentrations representative of flue gas conditions. We used certified mixtures of NO in N_2, SO_2 in N_2, CO in N_2, CO_2, O_2 and N_2 obtained from Air Gas, Inc. (Colorado Springs, CO) and Scott Specialty Gas (Longmont, CO) as listed in Table 1.

In each test, about 35 g of the catalyst sample was placed in the reactor. The catalysts were not pre-treated and used as received. We mixed the catalyst pellets with inert magnesium aluminate pellets. These inert pellets were fired at $1500^{\circ}C$ to minimize their surface area and thereby their catalytic activity for any potential side reactions. We loaded the pellets into the reactor sequentially, where the inert pellets stayed on top of the catalyst pellets. The hot inert pellet surface was used to evaporate any liquid water or fuel mixed into the gas stream.

We heated the pellets to the desired temperature by under nitrogen flow. Once the reactor temperature is stabilized, we mix the reaction gas mixture in a gas manifold and send it to the analytical instruments while by passing the reactor to get an inlet measurement. After reading stable inlet concentrations, the gas stream is diverted through the reactor. In the experiments where methane is used as the reducing agent, we premix methane into the feed mixture. When the heavy oil is used as the reducing mixture, the feed analysis was carried out in the

Table 1. Specifications of the gas cylinders used in the experiments.

Certified gas cylinders used to blend reaction gases:

O_2 UHP (Air Gas)
N_2 Industrial grade (Air Gas)
CO_2 Industrial grade (Air Gas)
2% CH_4/N_2 Mixture (Scott Specialty Gas)
18% SO_2/N_2 (Air Gas)
4.5% NO/N_2 (Air Gas)

Certified gas cylinders used for the calibration of the analytical instruments:

50 ppm NO/N_2 (Air Gas)
800 ppm NO/N_2 (Air Gas)
9,072 ppm CH_4/N_2 (Air Gas)
300 ppm SO_2/N_2 (Scott Specialty Gas)
908 ppm CO/H_2 (Air Gas)
4% CO_2/N_2 (Air Gas)

absence of the heavy oil. During the parametric tests, we maintained at each condition at least 1 hr or until we observe stable readings from each gas monitor.

We selected a sample size that ensures minimum gas channeling from the bed. The gas flows were determined based upon the comfortable operating ranges of the mass flow controllers (Table 2).

Table 2. The catalyst bed volume and gas-solid
contact time used in the tests.

Reactor Diameter	1.2 in
Bed Length	2.4 in
Bed Volume -sorbent	2.71 in3
sorbent	50 cc
inerts	30 cc

|	
GHSV	7,200 h-1
Total Gas Flow	6000 sccm

2.3. Test Results

2.3.1. NO Reduction with Methane

Due to the inherent simplicity, we first tested the NO reduction performance each catalyst using methane as the reducing agent. The gas compositions used in these tests are provided in Table 3.

Table 3. Nominal gas concentration for selective catalytic reduction with methane.

300 ppm SO2/ 2,400ppm CH4		3,000 ppm SO2/ 2,400 ppm CH4	
CO2	6.0%	CO2	6.0%
H2O	7.0%	H2O	7.0%
O2	1.5%	O2	1.5%
NO	800 ppm	NO	800 ppm
SO2	300 ppm	SO2	3000 ppm
CH4	2404 ppm	CH4	2404 ppm
N2	86%	N2	86%
Total	100%		100%

We started each test with a CH_4:NO molar ratio slightly above stoichiometric (i.e., CH_4:NO molar ratio from 1 to 3 times reaction stoichiometry) based on the following reaction:

$$CH_4 + 3\,NO = CO + 2\,H_2O + 3/2\,N_2$$
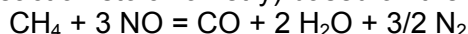
For a 800 ppm NO inlet, we first set the methane concentration in the feed gas to 2,400 ppm (Figure 3). We then flowed higher methane concentrations to see the effect of reducing gas
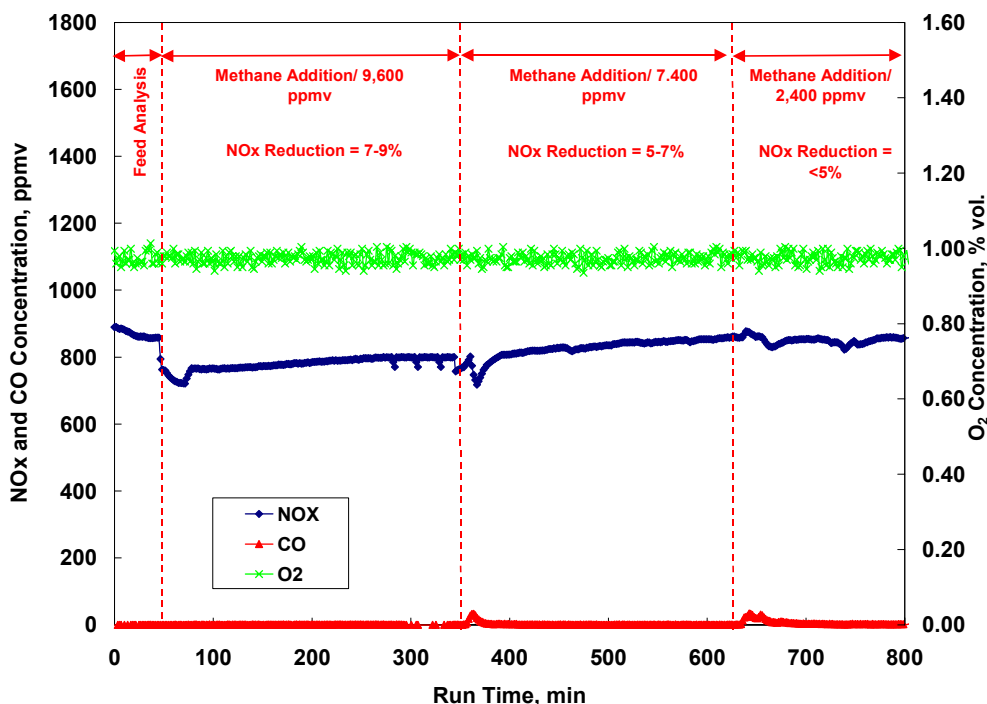

Figure 3. NO reduction with CH_4 over 1% Mn-promoted catalyst. T= 465°C, Inlet SO_2 = 300 ppm, GHSV = 7,200 h^{-1}.

concentration on NO conversion. At a gas hourly space velocity of 7,200 h^{-1}, we did not observe

any catalytic reduction activity with the un-promoted catalyst in 400-550°C with CH_4 inlet concentration as high as 9,600 ppmv in the feed gas.

The unpromoted catalyst, however, showed some limited activity at 450°-550°C range. At a GHSV of 7,200 h^{-1}, we observed that about 7 to 9% of the NO can be reduced. We measured an average CO concentration of 28 ppm, while 7-9% of the NO being reduced at 465°C. The lower than stoichiometric CO concentration in the gas stream is indicative of the presence of other reduction mechanism, such as:

$$CH_4 + 4 \ NO = CO_2 + 2 \ H_2O + 2 \ N_2$$

We did not observe any measurable changes promoted by the reaction above most likely due to the limited sensitivity of the CO_2 analyzer (the CO_2 analyzer has a range from 0-20% vol.), where we observed stable readings of 6.1 ± 0.1 % vol. In either case, we tested the catalytic performance under conditions where the amount of the CH_4 provided was higher than required by the reaction stoichiometry. We did not observe any changes in the oxygen concentration (the O_2 analyzer's sensitivity is 0.05% vol.) between by-pass and reaction measurements. This indicates that catalyst is selective for NO reduction, while not active for CH_4 oxidation with oxygen. Based upon the trend, we anticipate that the NO conversion increases at increased methane concentrations. However, due to the cost concerns of associated with the use of a large excess of methane, we limited these tests to methane inlet concentrations in the proximity of reaction stoichiometric requirement.

It is important to note that the analytical approach only focused on NO removal, not measuring by-products of the reaction such as N_2O. However, the analyzer had the capability of measuring NO_2. In select experiments, we measured NO and total NO_x ($NO+NO_2$) to observe the potential of the catalyst (and/or reactor components) oxidizing NO into NO_2 (Figure 4). We
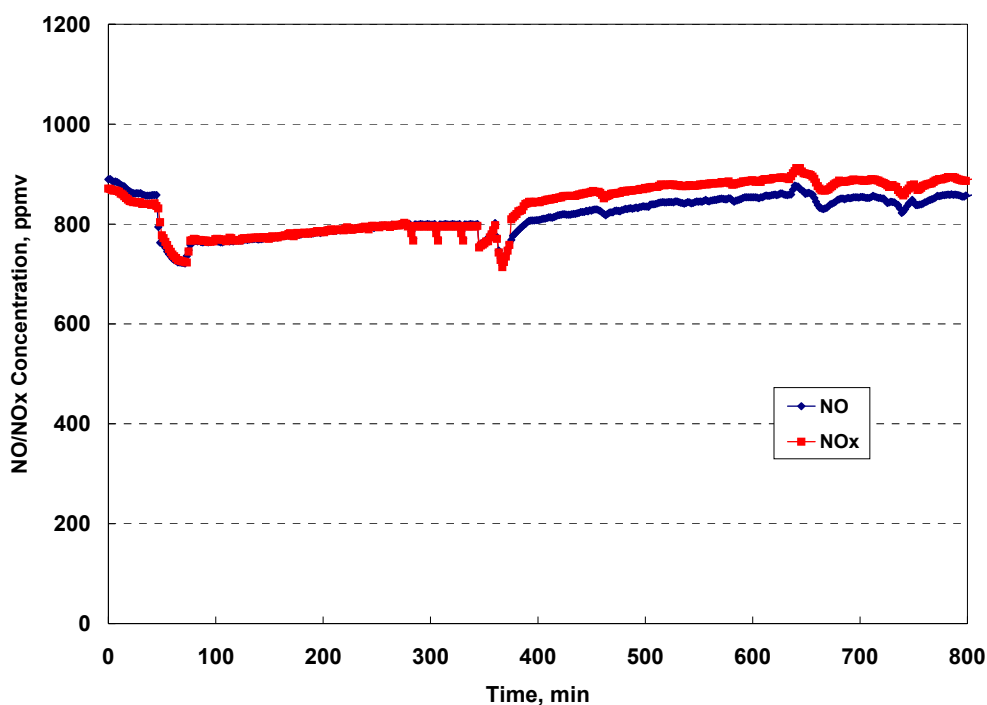

Figure 4. NO reduction with CH_4 over 1% Mn promoted catalyst. T= 465°C, Inlet SO_2 = 300 ppm, GHSV = 7,200 h^{-1}.

observed that the extent of the oxidation is minimal, particularly when an excess of methane (i.e., reducing agent) was present. We carried out the methane reduction tests in the presence of at 0, 300 and 3,000 ppm SO_2, and observed no change in the NO reduction potential of the catalyst.

2.3.2 NO Reduction with the Heavy Oil

In a second set of experiments, we tested the NO_x reduction potential of the catalyst using a simulated heavy oil with high sulfur content. The fuel oil selected was a Navy distillate fuel, similar to a high sulfur diesel fuel, which contains 1% sulfur on a weight basis. Based on a chemical formulae of $C_{16}H_{34}$, we estimated that 0.15 µl/min fuel flow is needed. We flowed the following gas composition through the sorbent bed (Table 4).

Table 4. Nominal gas concentration for selective catalytic reduction with heavy oil.

300 ppm SO2/ 24 ppm Fuel Oil		3,000 ppm SO2/ 24 ppm Fuel	
CO2	6.0%	CO2	6.0%
H2O	7.0%	H2O	7.0%
O2	1.5%	O2	1.5%
NO	800 ppm	NO	800 ppm
SO2	300 ppm	SO2	3000 ppm
Fuel Oil	24 ppm	Fuel Oil	24 ppm
N2 Total	85%		85%
Total	100%		100%

Each test started with an inlet gas analysis. We fed a total of 800 ppm NO and ~24 ppm of the fuel. The un-promoted copper/ceria catalyst showed some potential for reducing NO using heavy oil as the reducing agent. Figure 5 shows the inlet NO concentration and its reduction with
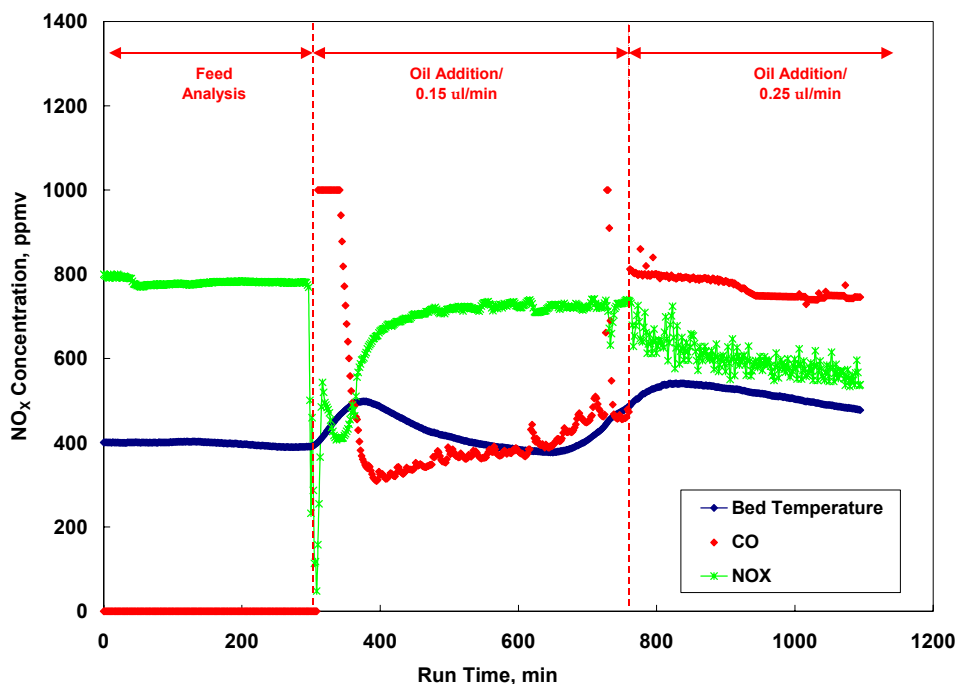

Figure 5. Performance of the un-promoted copper/ceria catalyst. GHSV= 6,000 h^{-1}, T=400°C, nominal gas composition.

the addition of 0.15 and 0.25 µl/min heavy oil. In this experiment, we started the test at 400°C, however, addition of heavy oil caused a small temperature excursion most likely due to the oxidation of the fuel. The response time of the heaters (due to the large mass associated with the furnace and reactor bodies) were slow and it took about 3 hrs for the about the temperature stabilize back at 400°C. We observed about 10% NO reduction when the heavy oil was fed at the stoichiometric ratio. When an excess of oil is provided (60% above the stoichiometric ratio), NO_x

reduction increased to 35%. We also noted two other trends. One is the formation of CO. At the stoichiometric NO:Oil ratio, CO concentration at the exit stabilized at 400 ppm indicating some level of unselective oxidation (assuming that the reduction of NO produced CO only, about 300 ppm CO was formed by non-selective oxidation of the oil). As the oil input increased, the CO level increased to 800 ppm.

We then tested the manganese-promoted copper/ceria catalyst under the same conditions. Table 5 presents a comparison of NO reduction performance of these the samples.

Table 5. Comparison of the catalytic performance.

	NO Reduction Unpromoted Copper/Ceria	NO Reduction Mn-Promoted Copper/Ceria
Oil Addition: 0.15 ul/min	10%	18%
Oil Addition: 0.25 ul/min	35%	47%

Based on its better performance, we used Mn-promoted sample for further evaluations. In select tests, we investigated the effects of SO_2 concentration on the NO reduction capability of the catalyst. We ran experiments with 0, 300 and 3,000 ppm SO_2. We did not observe any major changes in the catalyst performance due to the changes in the SO_2 concentration. We also increased the heavy oil concentration to improve the NO reduction. At 0.5 μl/min oil flow (3.3 times the stoichiometric), the catalyst had the potential to reduce all NO at 400°C in the presence of both 300 and 3,000 ppm SO_2 (Figure 6).
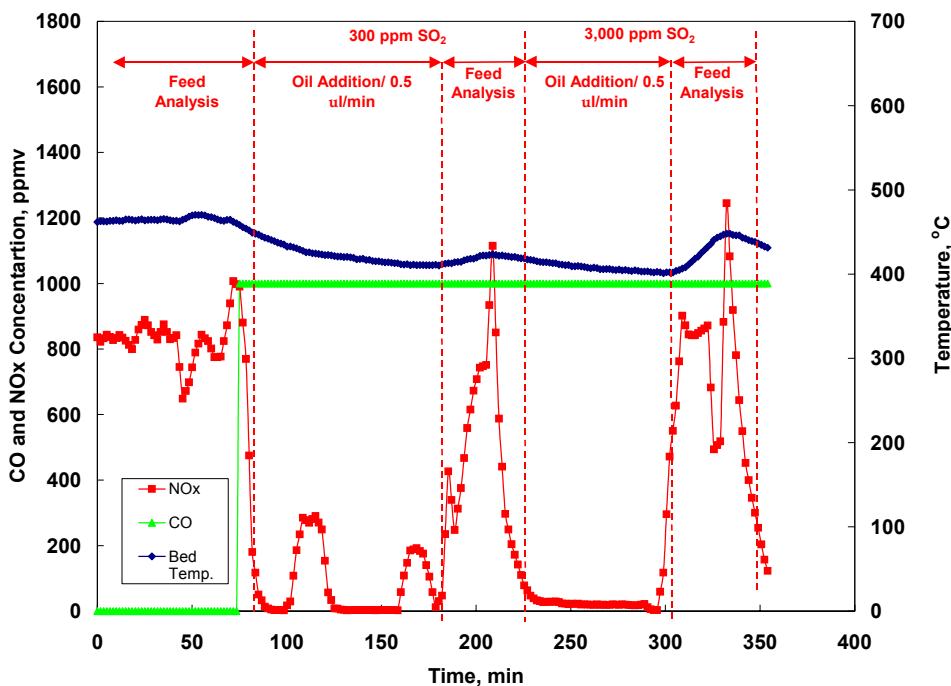

Figure 6. Performance of the Mn-promoted copper/ceria catalyst. GHSV= 6,000 h^{-1}, T=400°C, nominal gas composition.

Finally, we tested the long-term durability of the catalyst in a 100 hr test. We used 0.15 μl/min heavy oil and 300 ppm SO_2 in the gas feed under nominal conditions at 400°C. Figure 7 shows that a stable catalytic activity can be achieved.
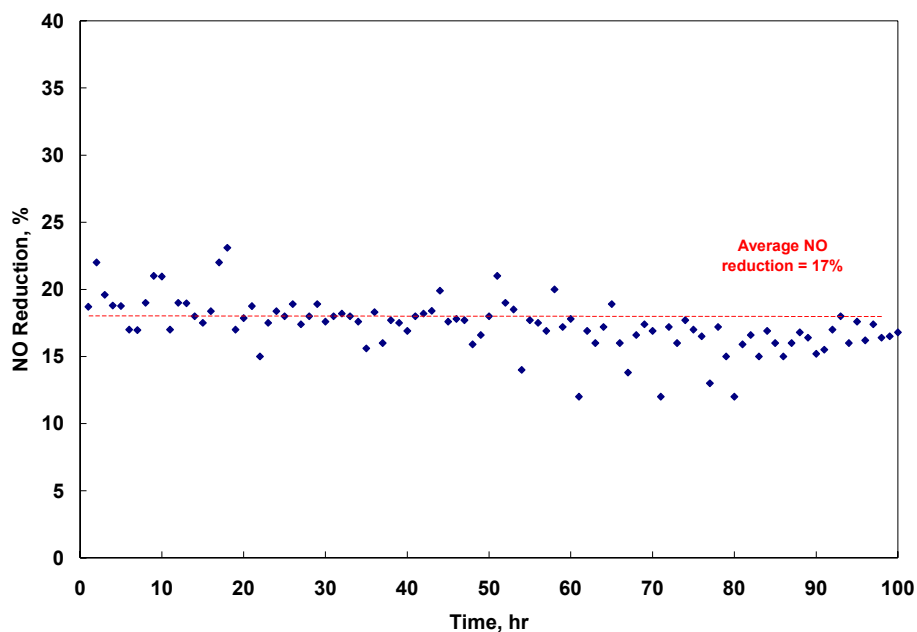
Figure 7. Durability test for the Mn-promoted copper/ceria catalyst. GHSV= 6,000 h^{-1}, T=400°C, 0.15 μl/min oil flow, nominal gas composition.

2.4. Visual Inspection

At the end of the long-term testing, we carried out a visual inspection of the pellets. We observed no signs of degradation in pellet integrity. A slight color change, however, was observed on few pellets (Figure 8). The tested samples were shipped to Hampton University for detailed characterization.
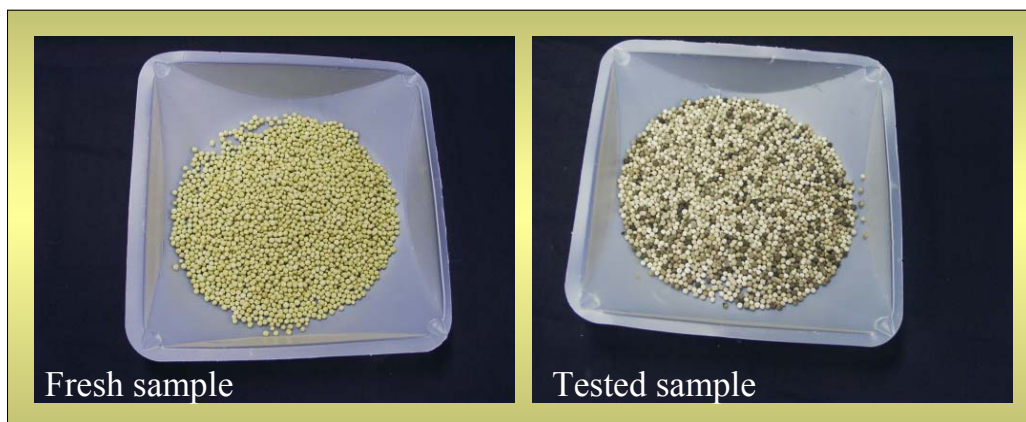

Figure 8. Photographs of the Mn-promoted catalyst before and after testing.