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

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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. 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. Since the replacement of ammonia by methane is commercially very attractive, in this project, it was planned to investigate the effect of promoters on the activity and selectivity of copper oxide/cerium oxide-based catalysts and to obtain data on the reaction mechanism for the SCR with methane.

The investigation of the reaction mechanism will help in the selection of promoters to improve the catalytic activity and selectivity of the sorbents in the SCR with methane. This will result in new catalyst formulations. The last component of the project involves our industrial partner TDA Research, and the objective is to evaluate long- term stability and durability of the prepared sorbent/catalysts.

In the second year of the project, the 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 rhodium on the supported copper oxide-ceria catalysts under study; the effectiveness of the promoter increases with the increase in Ce/Cu ratio. The TPD profiles of the unpromoted catalyst (Cu/Ce=3) is different than those promoted with 0.1% rhodium.

In the current reporting period, the screening of the promoted catalysts were completed, sufficient amount of the selected catalysts were prepared and delivered to TDA for long term deactivation testing.

WORK DONE

I. Background Information

Catalysts 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). Catalysts containing both copper and cerium oxides had better activities for NO reduction with methane, regardless of the Cu/Ce metal ratio. The maximum NO conversion at the space velocity used 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

The objective of the current research is to enhance the activity and selectivity of copper oxide/cerium oxide catalysts by using various promoters.

II. Experimental

The catalyst preparation method and the experimental setup used for the selective catalytic reduction of NO were presented in the previous reports.

III. Accomplishments

In this reporting period experimental runs for the selective catalytic reduction of NO on the promoted catalysts were completed. The best catalyst composition was selected and sufficient amount of this catalyst was prepared and sent to TDA for long term testing of the catalyst activity with various simulated flue gas compositions.

To obtain more information about the reaction mechanism, a program for a set of temperature programmed desorption and temperature programmed reaction runs were prepared. These runs are currently underway.

IV. Results and Discussion

To avoid clutter the selective catalytic reduction results are shown in three separate figures. Figure 1 shows the effect of alkali metals as promoters. Figure 2 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 1), 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 2 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 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 2 is that the temperature at which the maximum NO conversion is obtained is lowered by manganese (15°C for Cu3Ce1Mn and 20°C for Cu1Ce3Mn). In fact, Figure 2 shows that manganese promotion enlarged the temperature window of operation. Between 335°C and 475°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 1. Maximum NO Conversion and Temperature

Promoter	Maximum NO conversion, % (Temperature, °C)	
	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(1). In this study, a manganese-cerium composite oxide has been employed in the wet oxidation of polyethylene glycol. It was observed that as the content of cerium was increased, the 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 3 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 4 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 cannot be explained at the present. These runs will be repeated.

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., ^oC
1.5	19300	26	420
2.0	13,700	26.8	415
2.5	11,000	30	390
3.0	9,100	31	390

IV. Conclusions

The main conclusion 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. For this reason, batches of manganese–promoted catalysts were prepared and sent to TDA for long-term testing. These tests are currently undergoing. Results indicated that reducing the space velocity would increase the NO conversion but we could not yet explain the erratic variation of NO conversion with space velocity. These runs will be repeated.

This report presents the results of catalyst screening experiments. A more detailed analysis and interpretation of the results will be provided after the completion of the temperature programmed desorption and temperature programmed reaction studies.

V. Additional Activities

Two students (Randolph Ashton, and Anthony Samuels) were employed as undergraduate research students. They were trained in the laboratory to use the TPR/TPD equipment and the reactor setup for the

SCR experiments. They have learnt how to use the gas chromatograph and the NO_x Chemiluminescence equipment. 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.

A paper entitled "Promoted Mixed Metal Oxides for SCR with Methane" has been presented at the AIChE 2002 Annual Meeting at Indianapolis, Indiana on November 3-8, 2002.

FUTURE PLANS

During next year, it is planned:

1. to complete TPD and TPRxN experiments with Mn-promoted catalysts;
2. TDA will continue evaluating long-term stability and durability of the Cu1Ce3 and Cu3Ce1-1%Mn sorbent/catalysts and perform SCR tests with fuel oil as reductant.
3. to complete the analysis of data and write the final report.

Figure 1. Reduction of NO by Methane on Catalysts Promoted by Alkali Metals

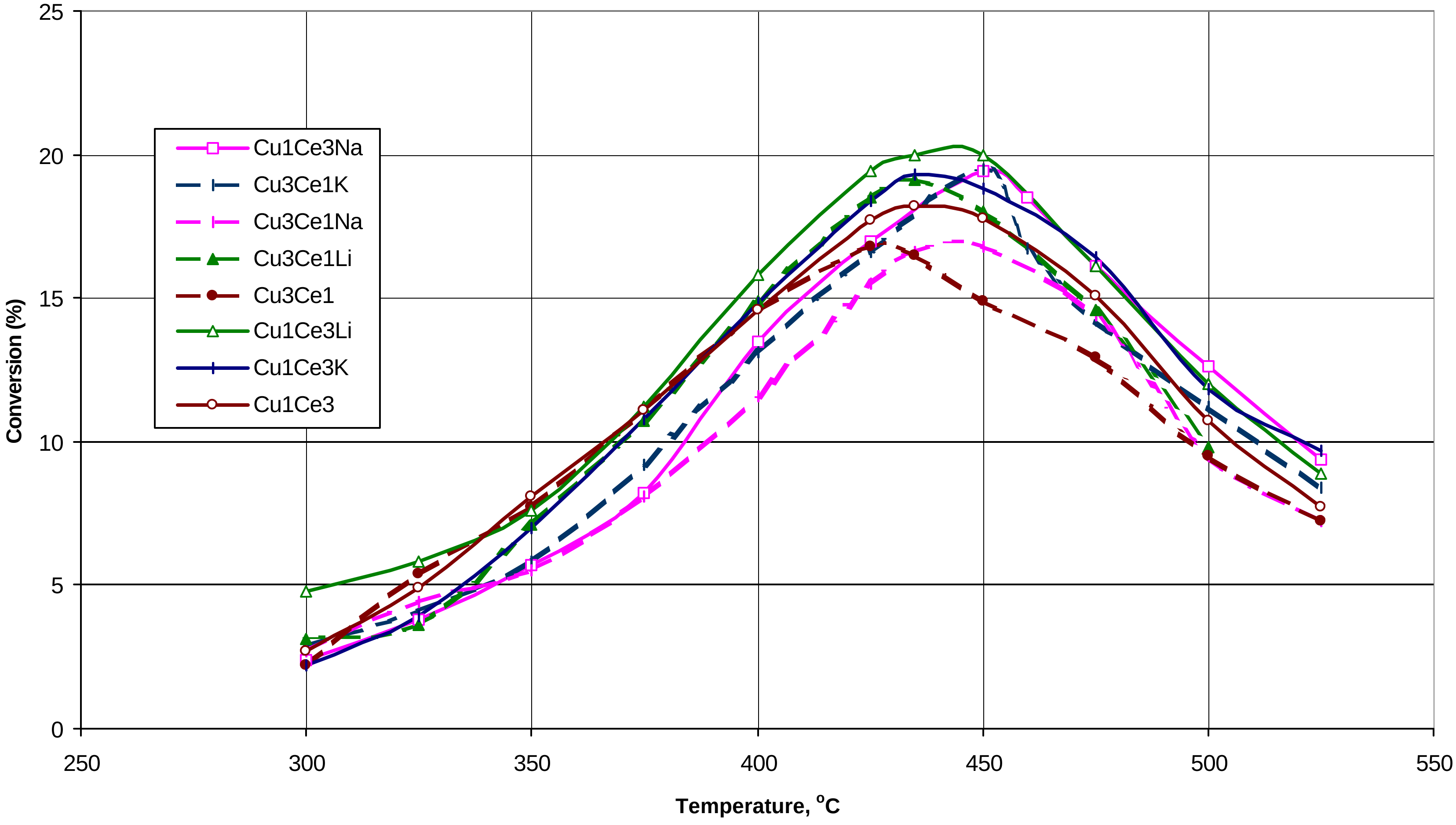

Figure 2. Conversion of NO Over Catalysts Modified with 1% Sn, Zn, or Mn

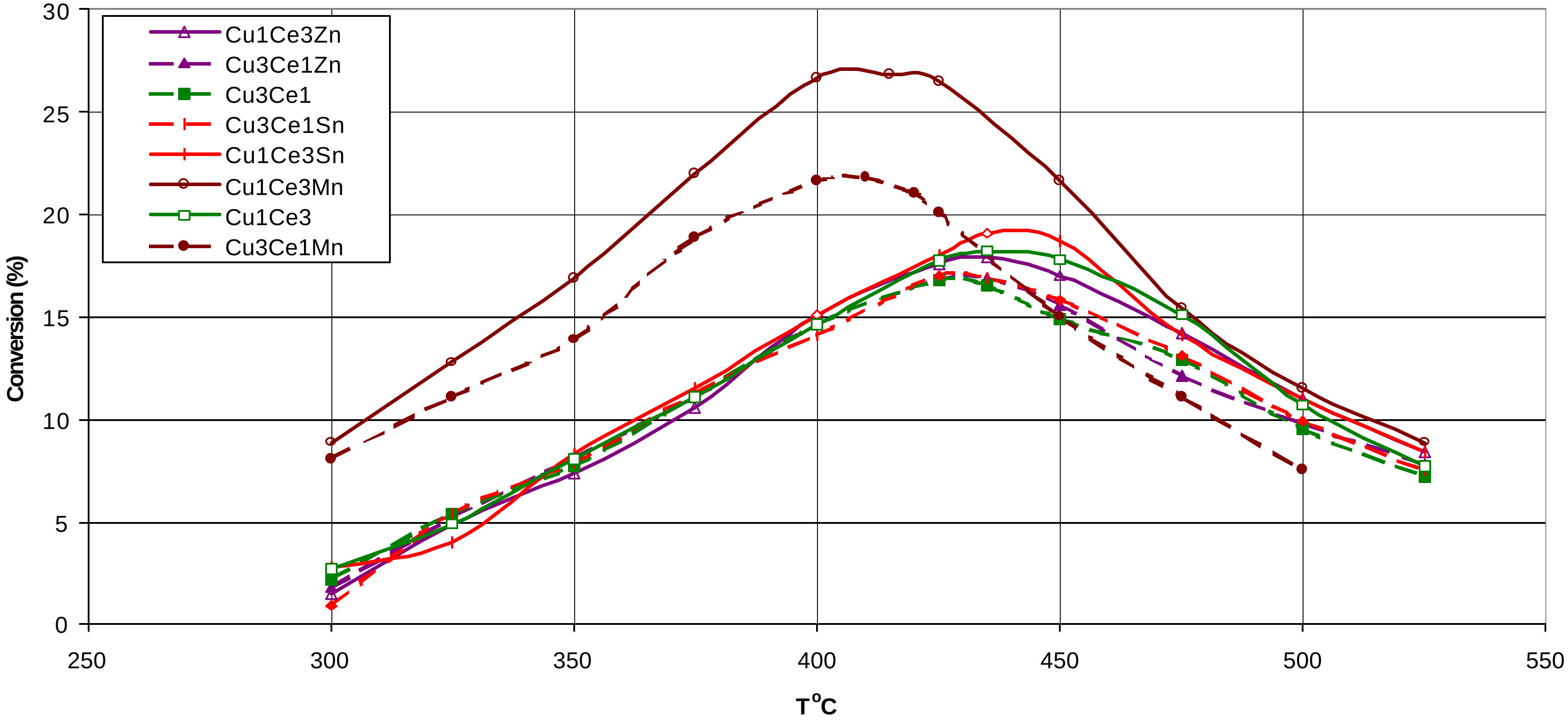

Figure 3. Conversion of NO Over Catalysts Modified with 0.1% Rh

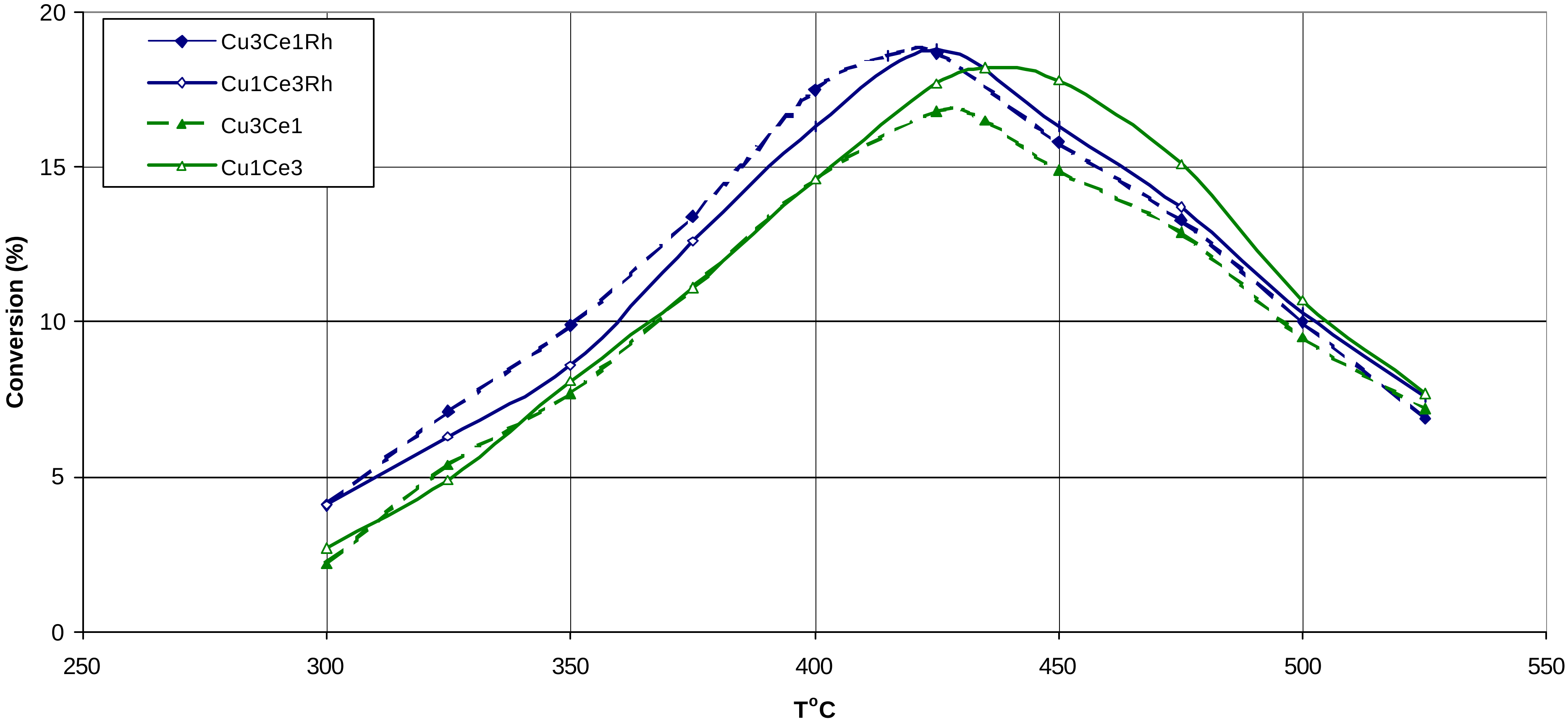

Figure 4. Effect of Space Velocity on the Conversion of NO on Cu1Ce3 Catalysts containing 1 % Mn