Selective NO_x Reduction by Urea under Oxidizing Conditions over a Single Step Sol-Gel Prepared Catalysts

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INTRODUCTION

Decomposition and Hydrolysis of Urea

$CO(NH_2)_2$ ===> NH_3 + HNCO

HNCO + H_2O ===> NH_3 + CO_2

NO Reduction

2 $CO(NH_2)_2$ + 6 NO ===> 5 N_2 + 2 CO_2 + 4 H_2O

4 HNCO + 6 NO ===> 5 N_2 + 4 CO_2 + 2 H_2O

4 NH_3 + 4 NO + O_2 ===> 4 N_2 + 6 H_2O

BACKGROUND

Held, W. et al (1990); urea SCR on Cu-ZSM5 for a diesel car.

Hug, H.T. et al (1993); urea SCR for off-highway diesels.

Luders, H. et al (1995); urea SCR on V_2O_5-WO_3-TiO_2.

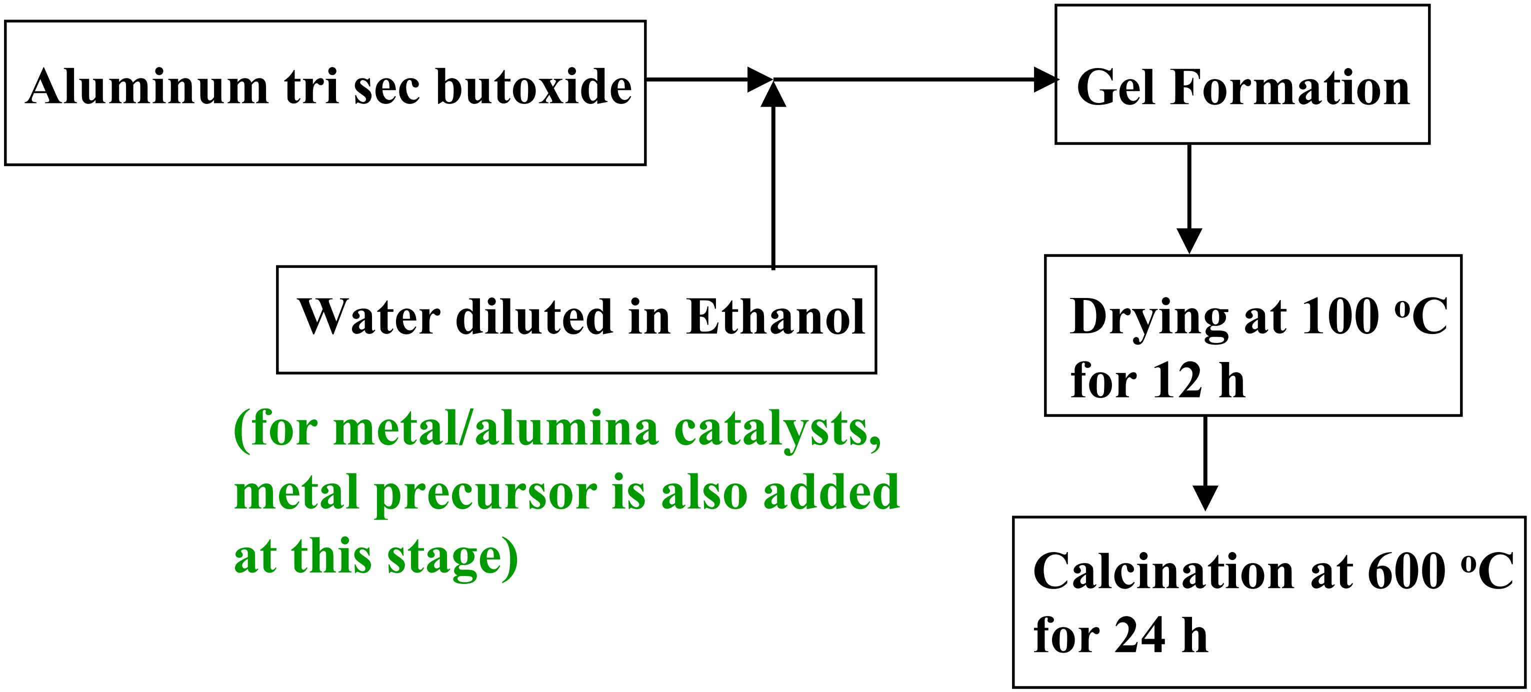
Koebel, M. et al (1996); urea SCR on V_2O_5-WO_3-TiO_2 for MAN diesel engine.

Morimune, T. et al (1998); uera SCR on V_2O_5-TiO_2.

Koebel, M. et al (2000); brief review on urea SCR for automotive diesel engines.

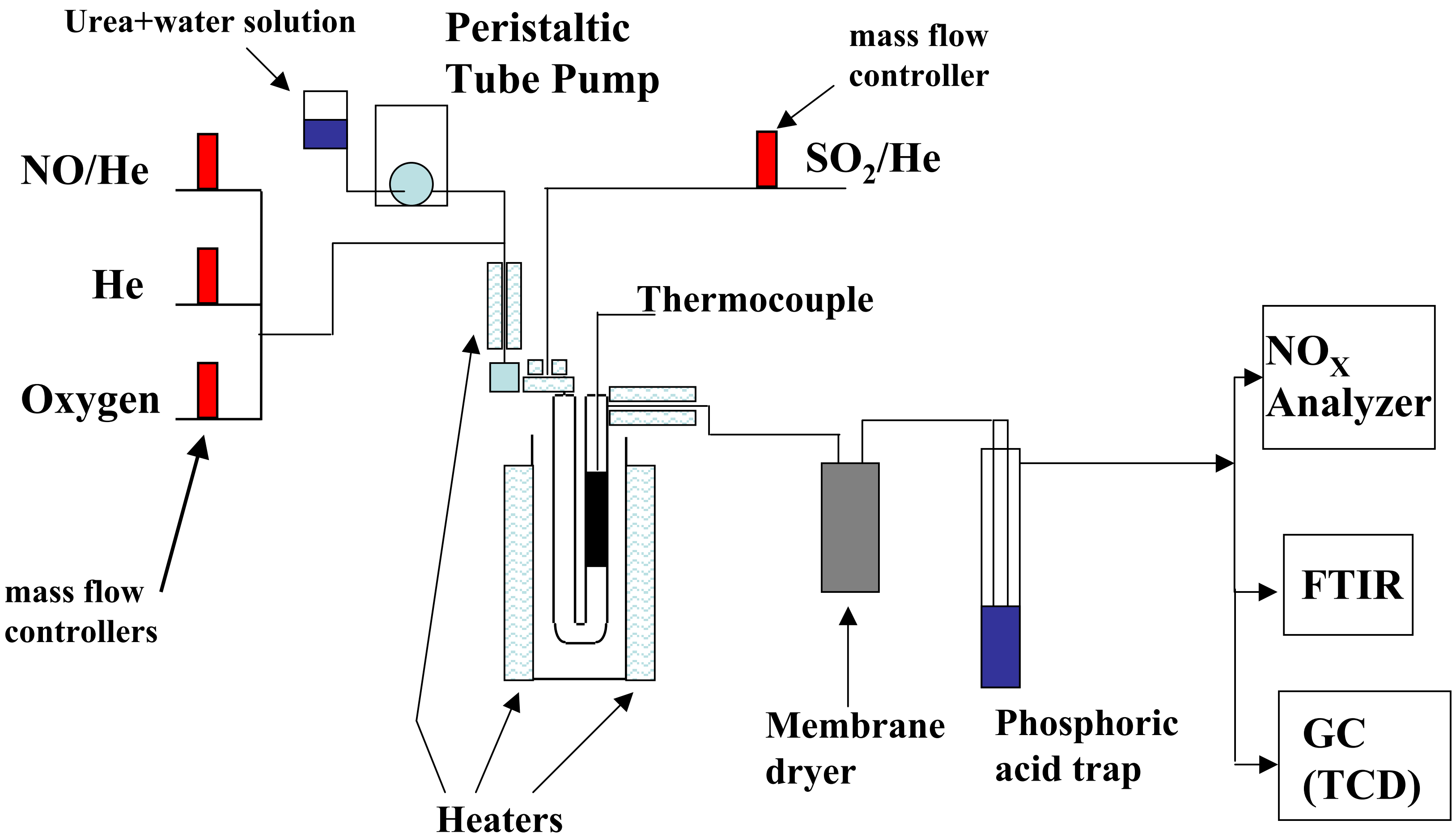
There is no paper on NO SCR by Urea over Cu/Alumina catalyst.

CATALYST PREPARATION



Sol-gel procedure to make supported metal catalysts and pure alumina

EXPERIMENTAL SETUP



CATALYST PROPERTIES

Catalyst	BET (m^2/g)	Particle Size (XRD)
2%Pt-SG	289	16 nm
1%Cu-SG	297	<5 nm
Pure Alumina	314	-

Copper on Alumina Catalysts

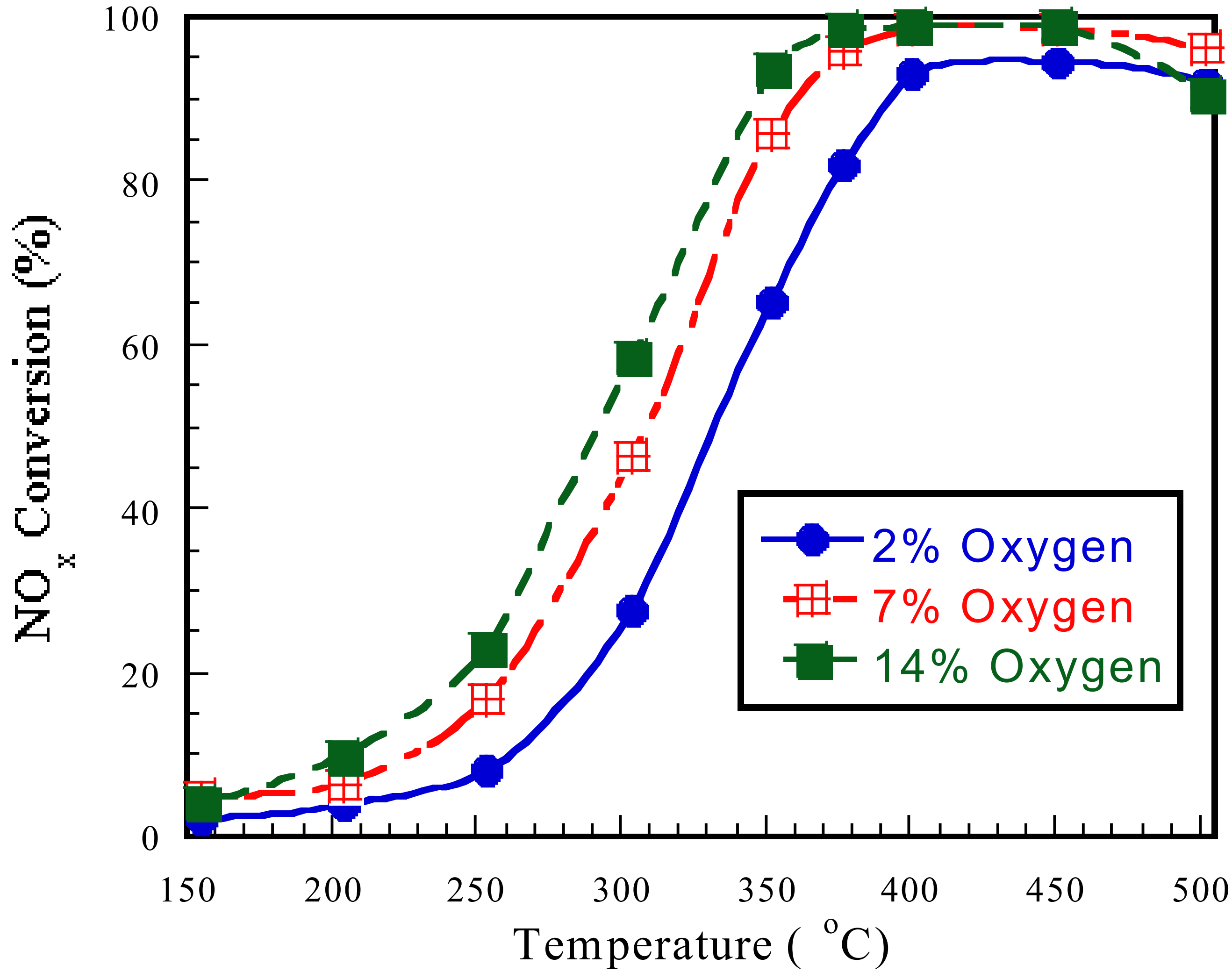


Figure 1: The activity of **1%Cu-SG** as a function of oxygen. Reaction conditions: 300 ppm NO, above oxygen concentrations, 4% water and 300 ppm urea and He as balance. 0.1 g catalyst and 176 ml/min of flow rate.

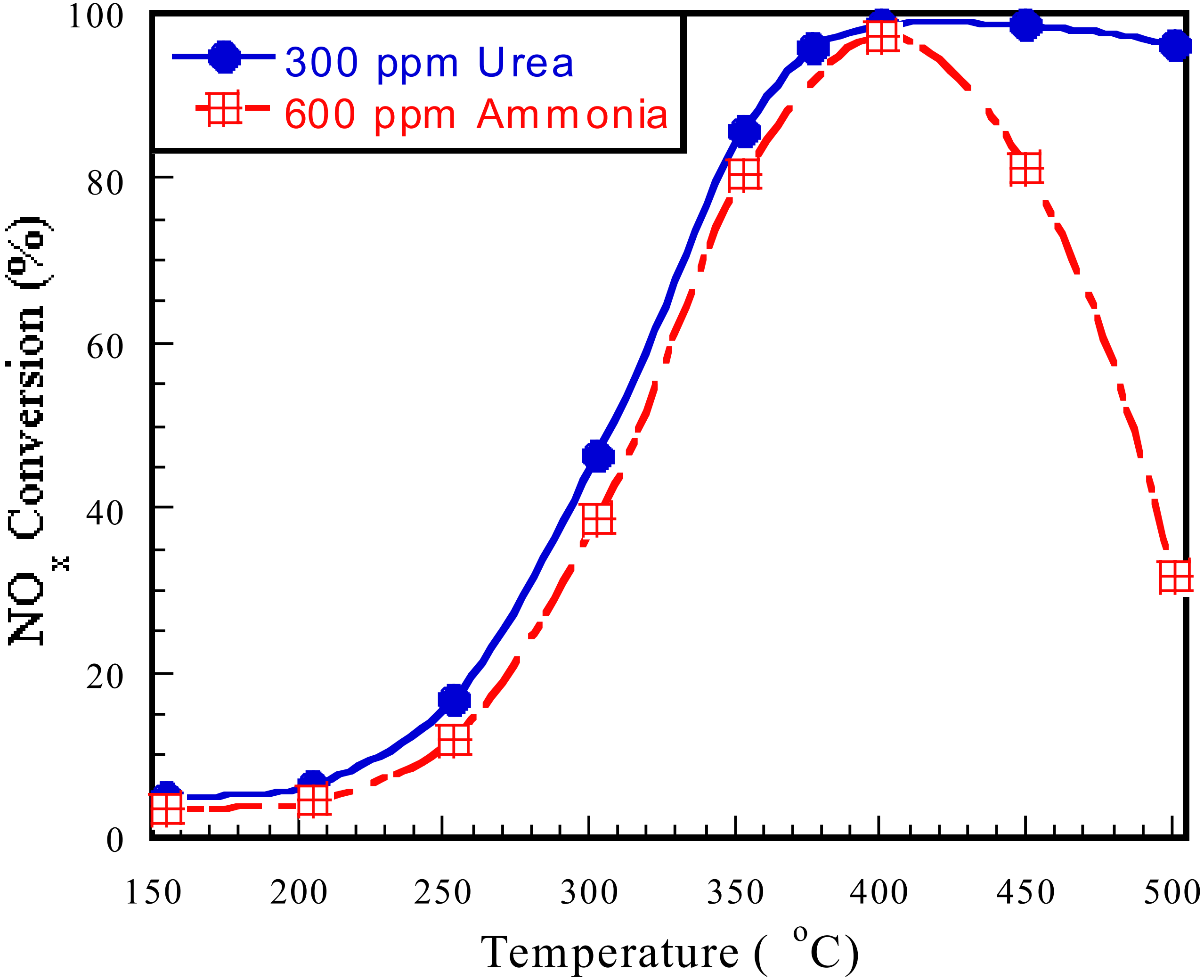


Figure 2: The activity of **1%Cu-SG** as a function of urea and ammonia. Reaction conditions: 300 ppm NO, 7% oxygen, 4% water, above urea and NH_3 concentrations and He as balance. 0.1 g catalyst and 176 ml/min of flow rate.

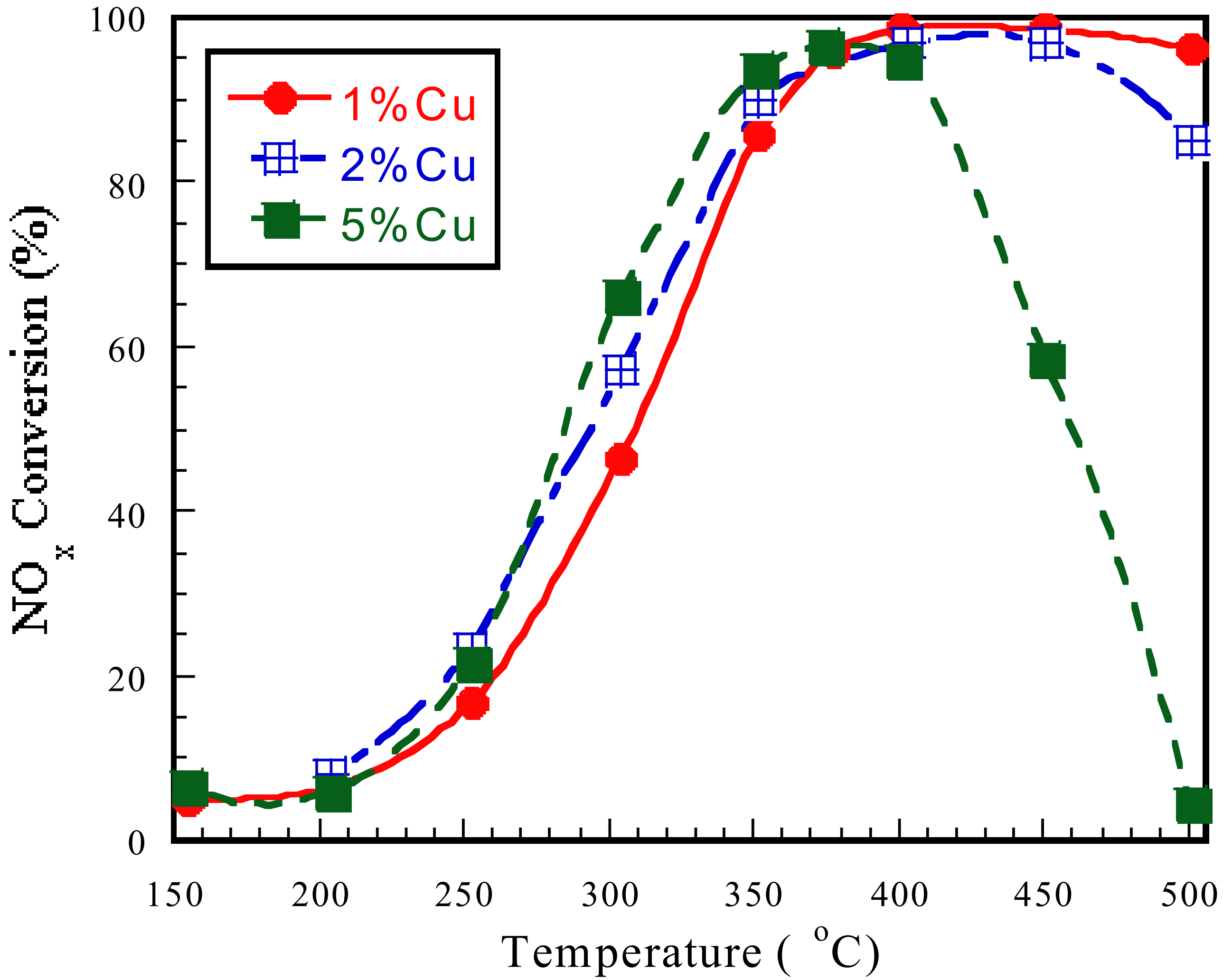


Figure 3: The catalytic activity of our single step sol-gel made Cu on alumina. Reaction conditions : 300 ppm NO and 4% water and 7% oxygen and 300 ppm urea. 0.1 g catalyst and 176 ml/min of flow rate.

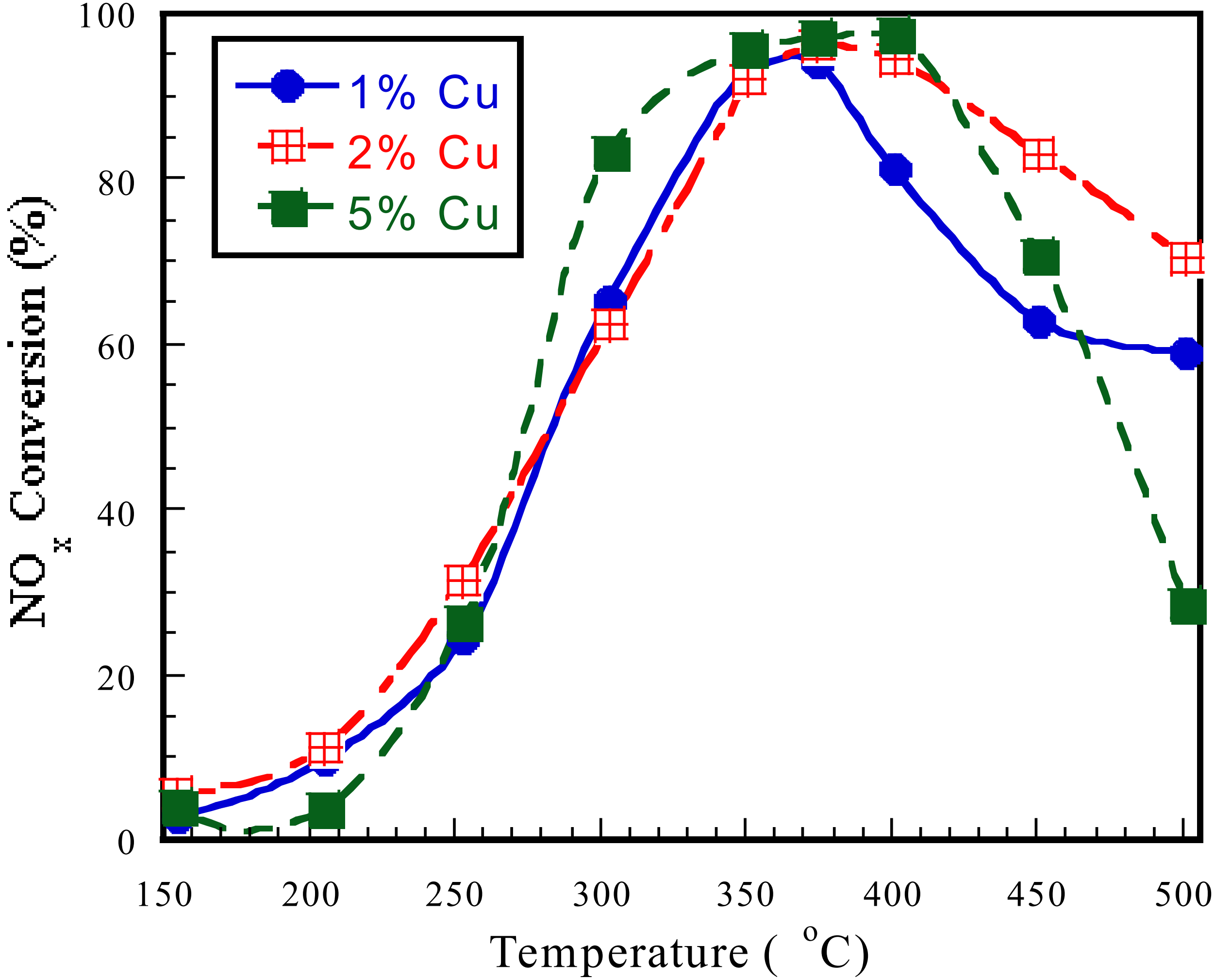


Figure 4: The catalytic activity of classical single step sol-gel made Cu on alumina. Reaction conditions : 300 ppm NO and 4% water and 7% oxygen and 300 ppm urea. 0.1 g catalyst and 176 ml/min of flow rate.

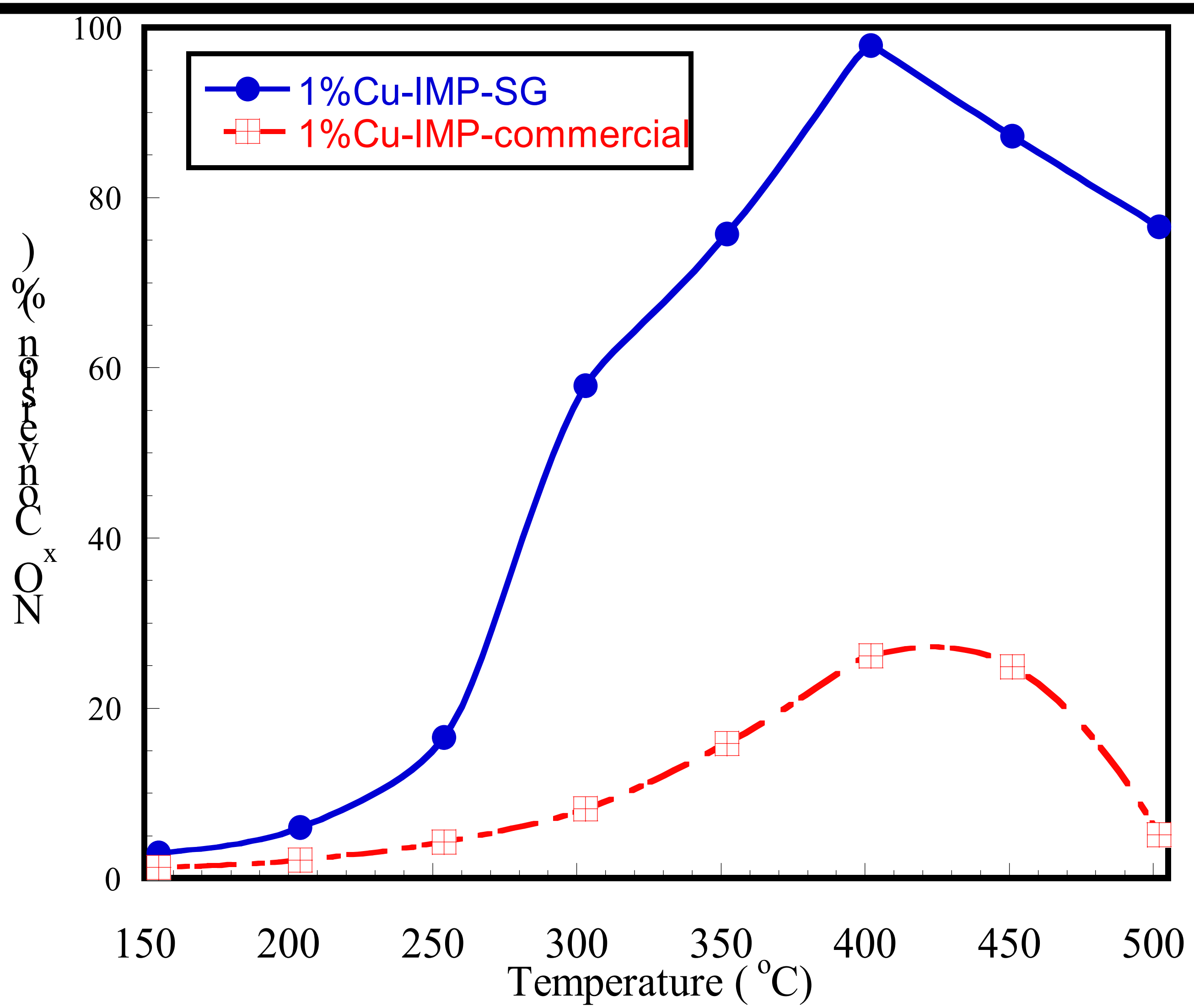


Figure 5: The effect of alumina on the activity of impregnation **1%Cu/Al_2O_3**.
Reaction conditions : 300 ppm NO, 7% oxygen, 4% water, 300 ppm urea and He as balance. 0.1 g catalyst and 176 ml/min of flow rate.

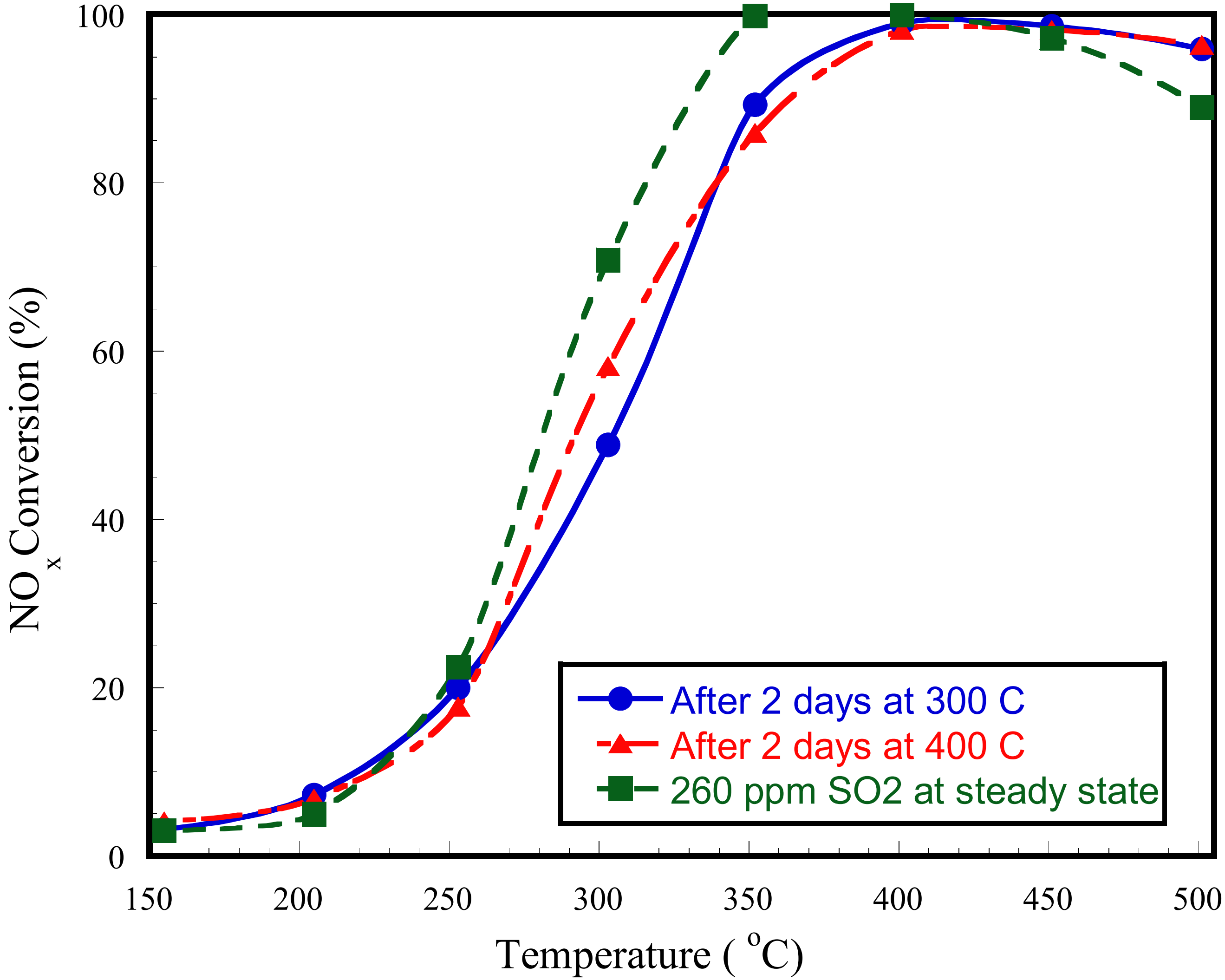


Figure 6: Catalytic activity of **1%Cu-SG** after being exposed to the feed gas mixture containing 35 ppm SO_2 at 300 °C and 400 °C for 2 days or exposed to a feed gas mixture containing 260 ppm SO_2 under steady state. Reaction conditions : the same as in Figure 5.

Platinum on Alumina Catalysts

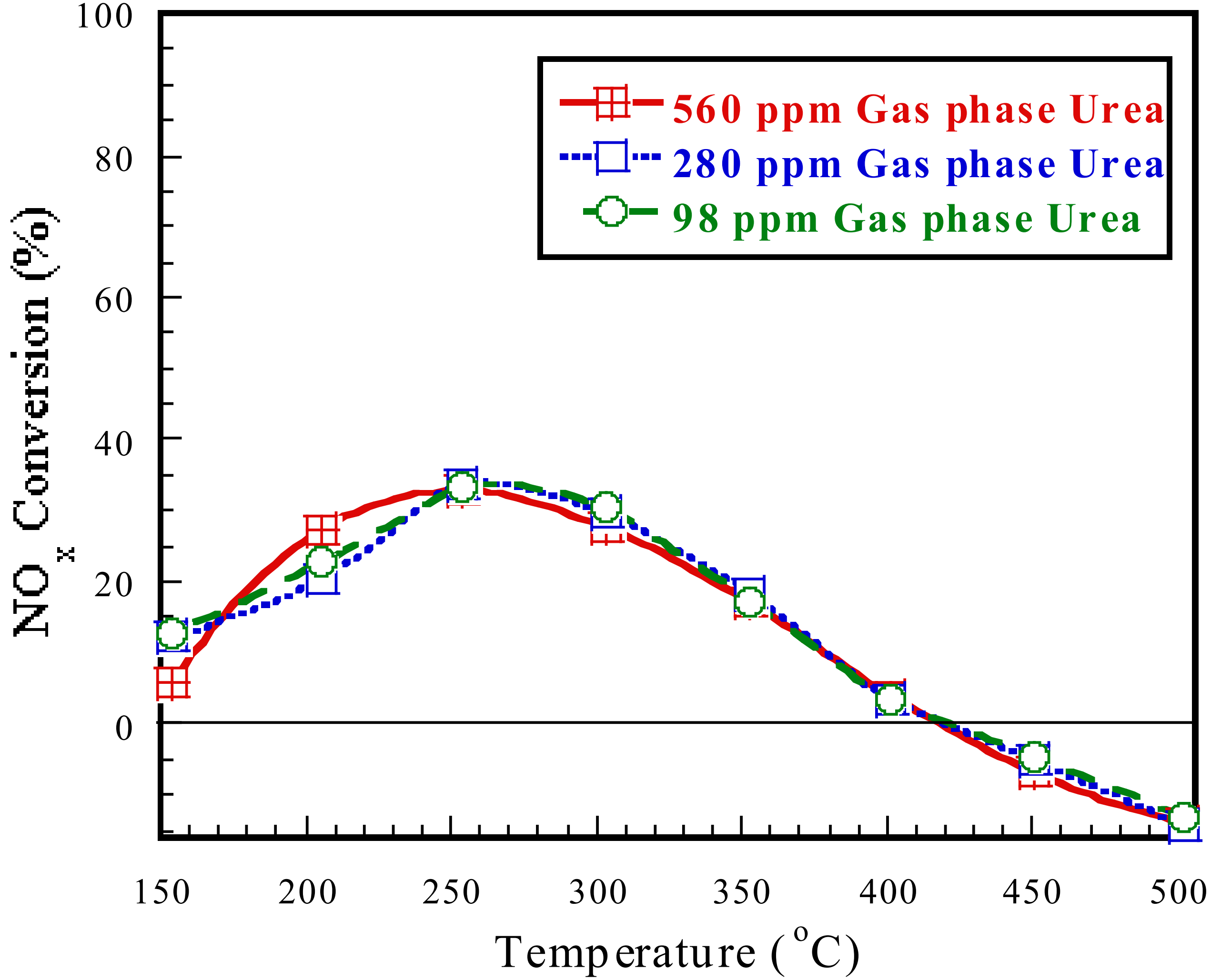


Figure 7: The NO reduction activity of **2%Pt-SG** as a function of urea concentration. Reaction condition: 665 ppm NO, 7% oxygen, 2% water and He as balance. 0.1 g catalyst and 176 ml/min of flow rate.

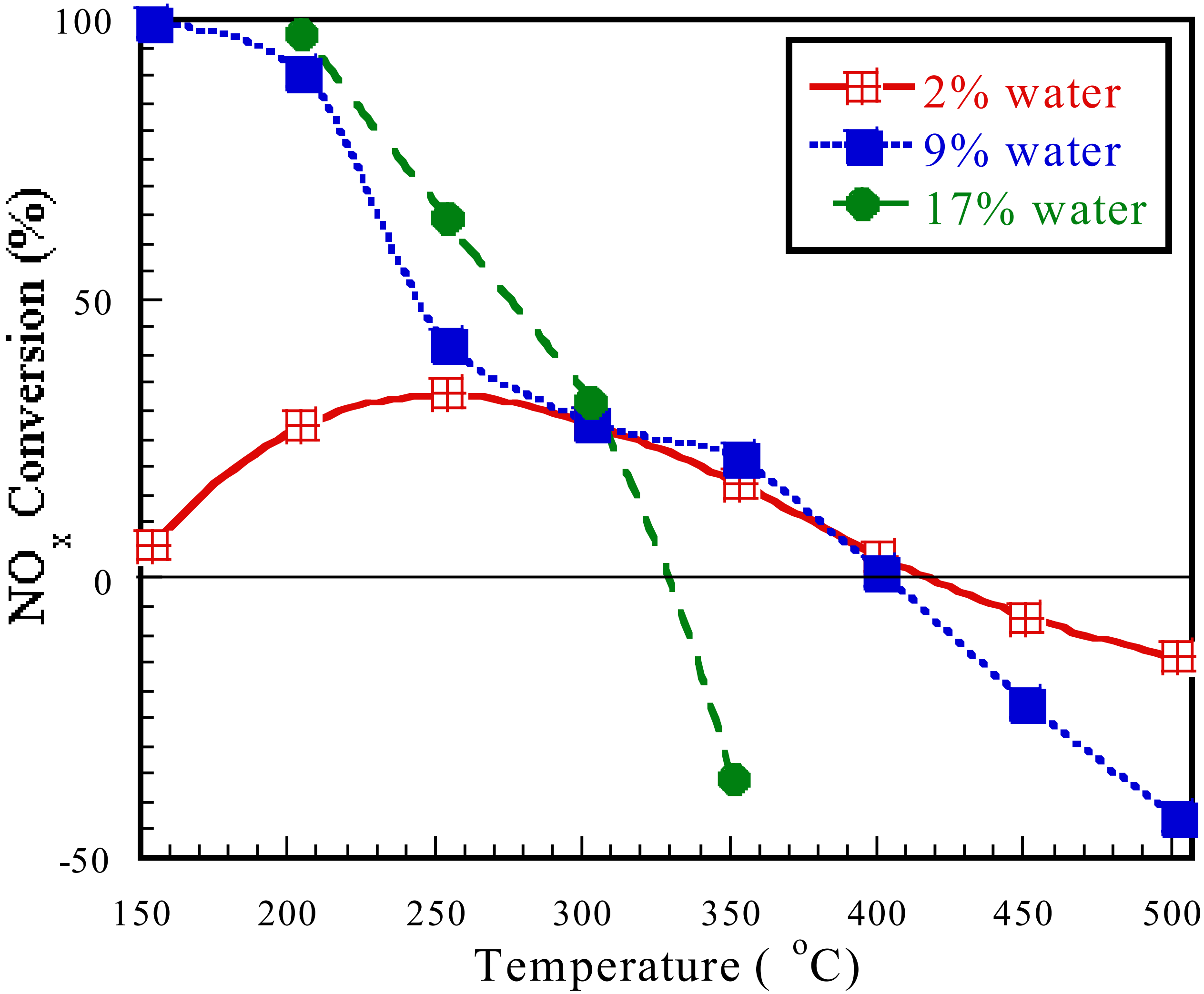


Figure 8: The NO reduction activity of **2%Pt-SG** as a function of water vapor concentration. Reaction condition: 665 ppm NO, 7% oxygen, 560 ppm urea and He as balance. 0.1 g catalyst and 176 ml/min of flow rate.

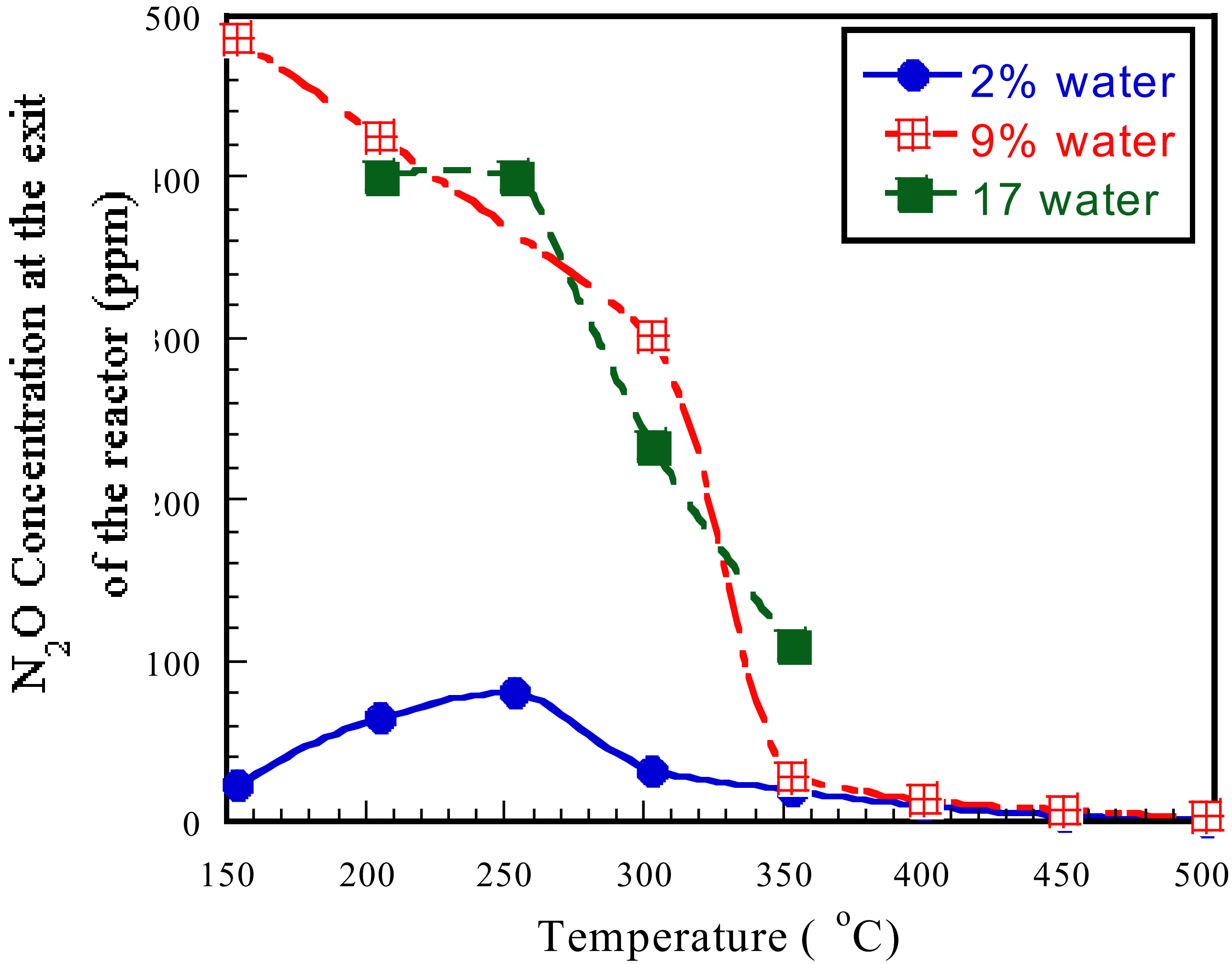


Figure 9: N_2O production over **2%Pt-SG** catalyst as a function of water vapor concentration. Reaction condition: 685 ppm NOx, 7% oxygen, 560 ppm urea and He as balance. 0.1 g catalyst and 176 ml/min of flow rate.

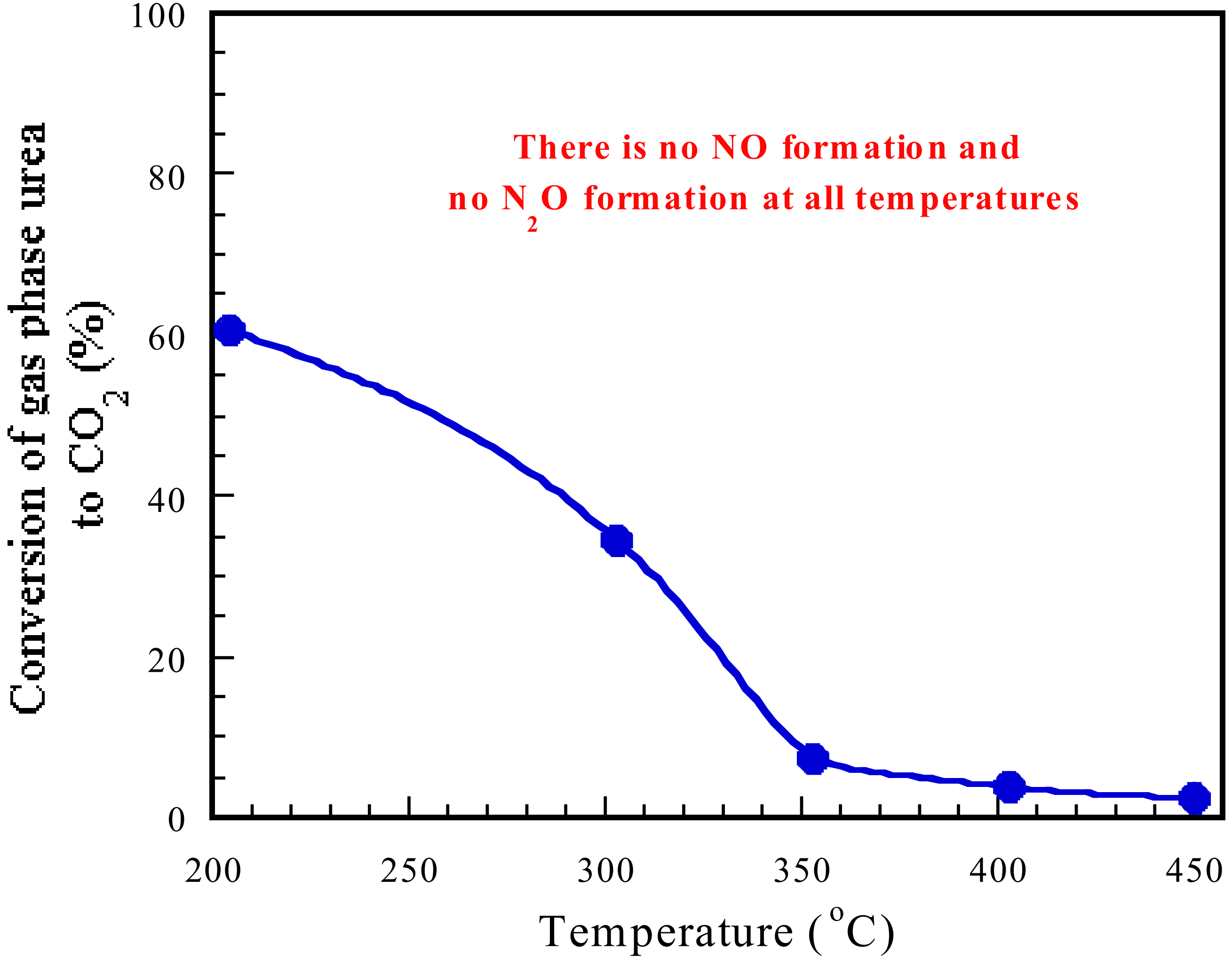


Figure 10: Urea hydrolysis/decomposition activity of **2%Pt-SG** in absence of O_2 and NO in the feed gas. Reaction condition: 560 ppm urea, 17% water and He as balance. 0.1 g catalyst and 176 ml/min of flow rate.

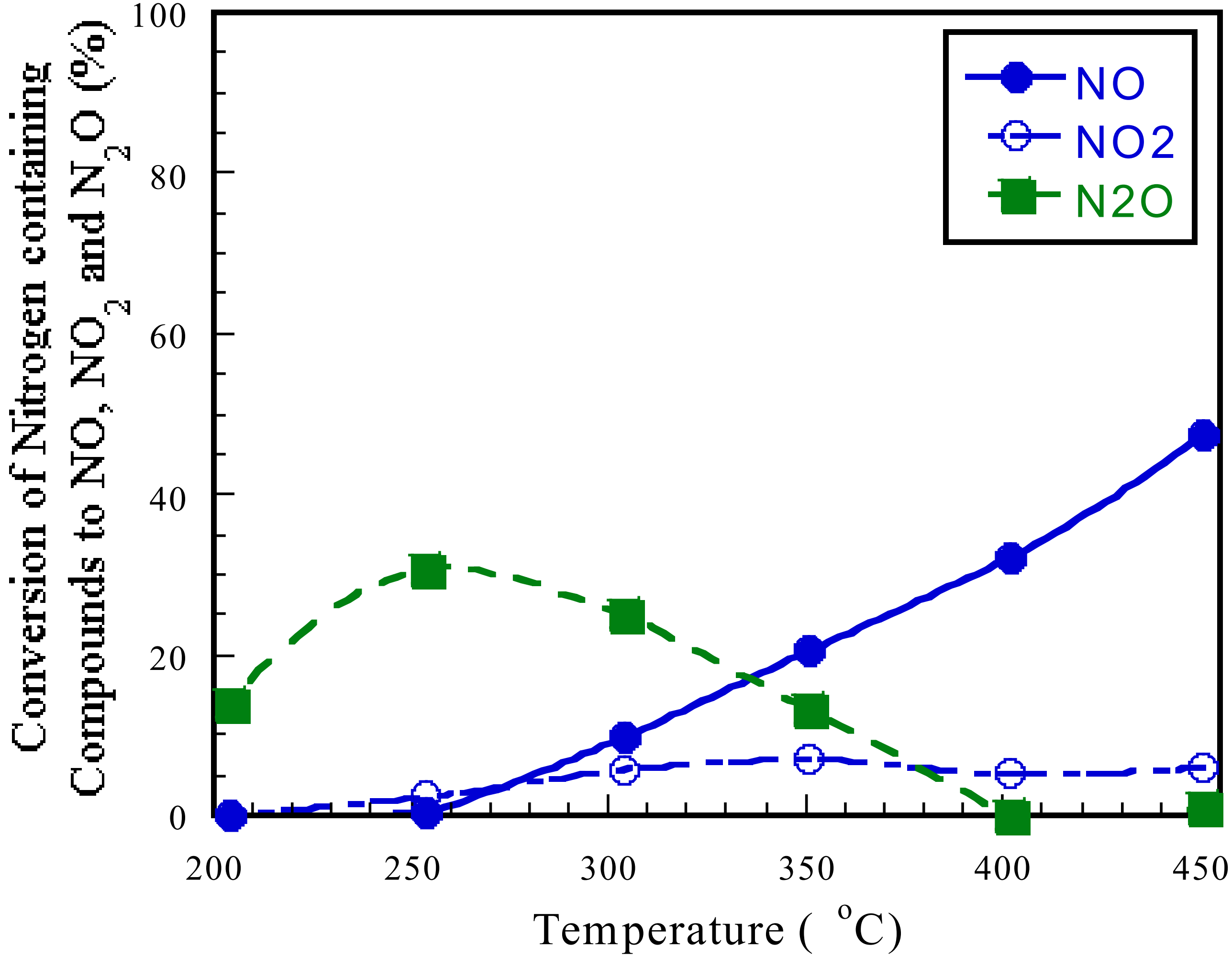


Figure 11: Nitrogen containing compounds oxidation activity of **2%Pt-SG** in the absence of NO in the feed gas. Reaction condition: 560 ppm urea, 7% O_2, 17% water and He as balance. 0.1 g catalyst and 176 ml/min of flow rate.

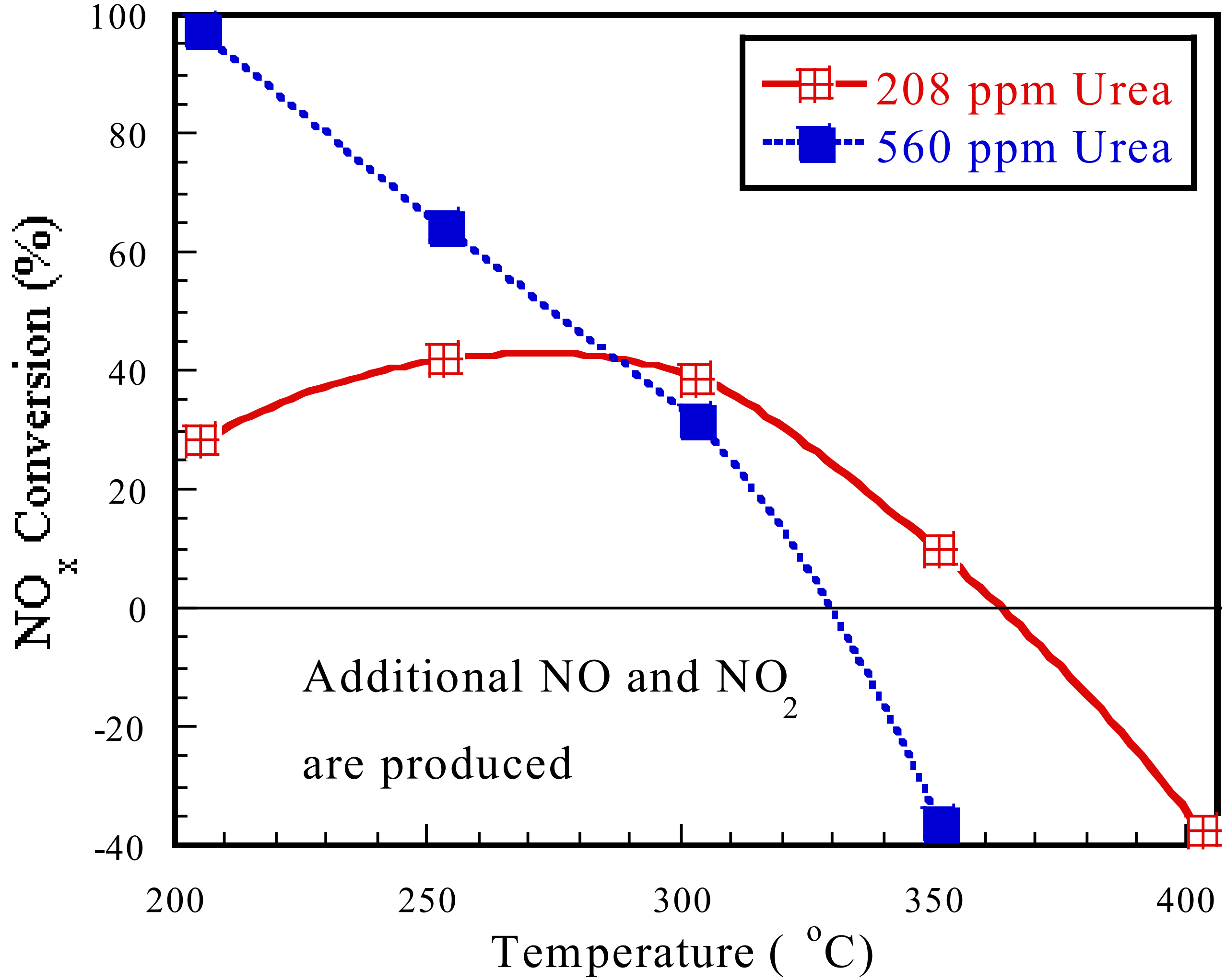


Figure 12: The NO_x reduction activity of **2%Pt-SG** as a function of urea concentration. Reaction condition: 685 ppm NO_x, 7% oxygen, 17% water and He as balance. 0.1 g catalyst and 176 ml/min of flow rate.

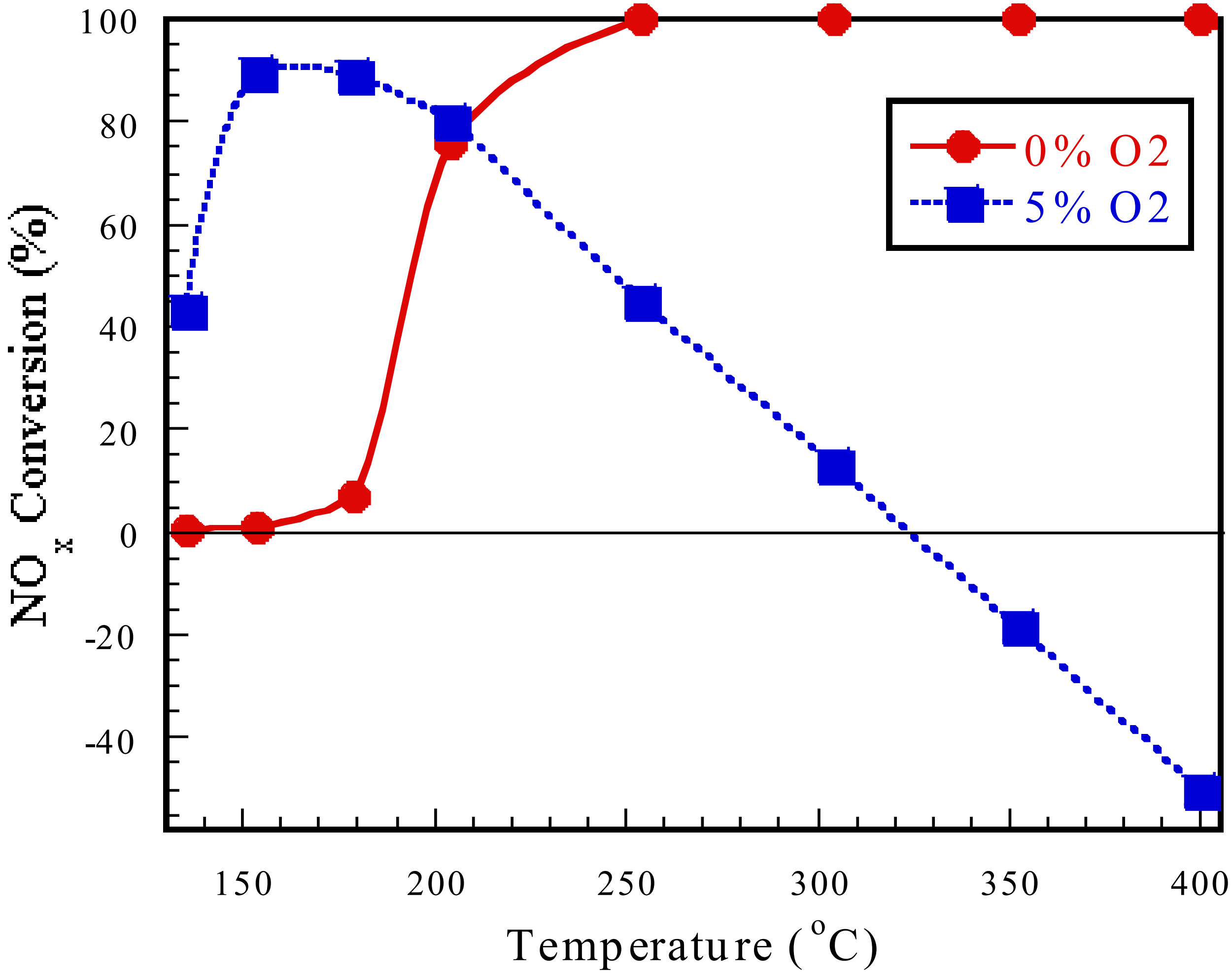


Figure 13: The NO_x reduction activity of **2%Pt-SG** as a function O_2 concentration. Reaction condition: 685 ppm NO_x, 658 ppm NH_3, 2% water and He as balance. 0.1 g catalyst and 176 ml/min of flow rate.

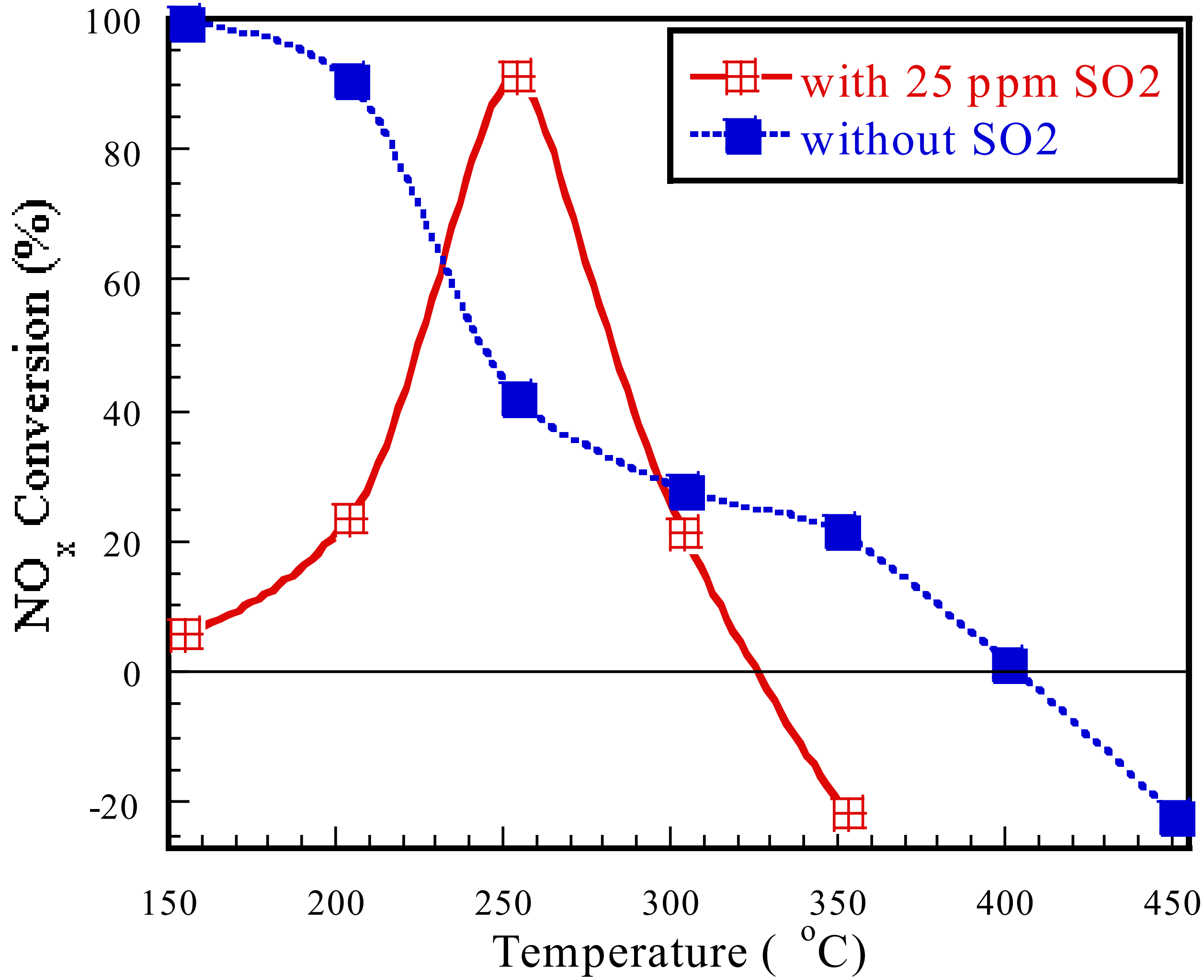


Figure 14: The NO reduction activity of **2%Pt-SG** as a function of SO_2 concentration. Reaction condition: 665 ppm NO, 7% oxygen, 9% water, 25 ppm SO_2 (when used) and He as balance. 0.1 g catalyst and 176 ml/min of flow rate.

CONCLUSIONS

Cu on Al_2O_3 Catalysts

- **Urea is more efficient reducing agent than ammonia.**
- **N_2 selectivity during SCR over 1%Cu-SG is 100% (based on N_2 and N_2O measurements).**
- **NO_x conversion strongly depends on oxygen concentration in the feed.**
- **Regardless of oxygen concentration in the feed, an S shape conversion versus temperature curve is observed over our 1%Cu-SG.**
- **Under steady state conditions, the presence of 35 ppm or 260 ppm SO_2 in the feed does not hinder the activity of 1%Cu-SG catalyst.**

CONCLUSIONS

- Long term exposure to a gas mixture containing 35 ppm SO_2 at 300 ^oC or 400 ^oC does not change the activity.
- The oxidation of NH_3 in the absence of NO in the feed is highly selective to N_2 (>98%) and only by-product was NO.

Pt on Al_2O_3 Catalysts

- High amount of water does not hinder the activity of the sol-gel Pt/alumina catalyst.
- Above 300 ^oC, the rate of oxidation of N containing compounds, e.g. HNCO, to NO or NO_2 increases; hence resulting in negative conversions.

CONCLUSIONS

Pt on Al_2O_3 Catalysts

- N_2O over 2%Pt-SG under our reaction conditions is produced as low as at 200 ^oC during the decomposition and/or hydrolysis of urea in the presence of oxygen (in the absence of NO). The amount of N_2O is strongly dependent on the temperature.
- 25 ppm SO_2 in the feed hinders the activity of 2%Pt-SG catalyst under steady state condition.

ACKNOWLEDGEMENTS

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