

COMPETITION OF NO AND H₂O DURING ADSORPTION OVER Cu-ZSM5 De-NOX CATALYST

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Abstract

The adsorption of NO was investigated in the temperature range 50-150°C on Cu-ZSM-5 and La-Cu-ZSM-5 in the presence of water and O₂. TPD experiments were performed after each adsorption test monitoring all desorbed NO_x species. Water displaces NO from copper sites strongly reducing its adsorption except for nitrate-like species partially preserved under wet adsorption conditions. O₂ addition limits the negative effect of water by improving the nitrate-like formation. Lanthanum co-exchange improves the NO adsorption capacity of the catalyst both in the absence and in the presence of water.

Introduction

Cu-ZSM-5 has been extensively studied as DeNO_x catalyst for different applications such as SCR of NO with hydrocarbons [1], ammonia or urea [2-4] and the decomposition of nitrous and nitric oxide [5-8], not only for stationary sources but also for lean Diesel engines [9-11].

In all the mentioned processes the formation and evolution of nitrate species adsorbed onto copper sites seem key-steps [12, 13]; many evidences are reported in the literature about nitrates formation during the NO adsorption over Cu-ZSM-5 [14-18].

One of the main drawbacks is the deactivation of the catalyst under wet operating conditions, generally associated to copper shifting to inactive positions [19]. The negative effect of water has been also associated to a reduced NO adsorption on Cu-ZSM-5, while a positive effect of the presence of O₂ on the adsorption capacity of the Cu-ZSM-5 was found [20]. It has been reported that rare earth ions addition is effective to partially prevent Cu-ZSM-5 deactivation in NO decomposition under wet environments [19], lanthanum providing the most significant improvement of performance under both dry and wet conditions. The addition of lanthanum increased the number of copper reducible sites involved in the redox mechanism of NO decomposition and inhibited the copper mobility responsible for the catalyst deactivation [19].

In this study the effect of water vapour on the adsorption of NO was studied at low

temperature. NO adsorption and TPD tests have been performed in the presence of water and oxygen in order to determine which species are affected by O₂ and H₂O at different temperatures. The effect of lanthanum doping on the adsorption of NO under wet environments and in presence of oxygen has been also studied.

Materials and Methods

The Cu-ZSM5 was prepared by ion-exchange of a commercial H-ZSM5 zeolite (Zeolyst CBU-5020, Si/Al = 25, BET surface area=350 m²/g) in aqueous solution of 20 mM copper(II) acetate monohydrate (Aldrich purity 99.8%) at 50°C for 2h. The exchanged zeolite was calcined 2 h at 550°C (10°C min⁻¹) under helium flow. The La-Cu-ZSM-5 was prepared by a double exchange procedure. Lanthanum was firstly exchanged in a 20 mM lanthanum nitrate (Aldrich purity 99%) aqueous solution at 95°C for 5h. After calcination the sample was then exchanged with copper as described before and calcined again.

The copper and lanthanum concentration, determined with an Agilent 7500 ICP-MS, was 1.8 and 0.16 wt% respectively.

NO adsorption experiment were carried out in the temperature range 50-150°C on both pre-reduced Cu-ZSM-5 and LaCu-ZSM-5 according to the procedure described below consisting of 4 test types, each cycle was followed by a TPD up to 500°C and a new pre-reducing treatment of the zeolite:

Test A: the catalyst was contacted with a 800 ppm NO/He mixture up to initial NO concentration level is restored;

Test B: the catalyst was contacted with a 800 ppm NO/2% H₂O/He mixture up to initial NO concentration level is restored;

Test C: the catalyst was contacted with a 800ppm NO/1% O₂/He mixture adding 2% H₂O after 80 min;

Test D: the catalyst was contacted with a 800ppm NO/1% O₂/2% H₂O/He mixture up to initial NO concentration level is restored.

The quantitative analysis of both adsorption and TPD was carried out by continuously monitoring NO, NO₂ and N₂O concentration using ABB AO2020 specific analyzers and N₂ and O₂ concentration with a Varian micro-GC.

A TPD analysis, performed after each adsorption experiment, was conducted substituting the mixture with pure He flow. After a purging phase at constant temperature (i.e. the adsorption temperature) to remove the reversibly adsorbed NO_x species, the zeolite was heated at 10°C/min up to 500°C analyzing the gaseous species.

Results and Discussion

In Figure 1 the NO adsorption at 125°C in the absence of both H₂O and O₂ (test A) and the following TPD are reported as an example for Cu-ZSM-5. The concentration profiles of NO, NO₂ and N₂O show the same trend at the other temperatures and for LaCu-ZSM-5 as well. NO concentration is zero for some minutes and then starts to approach the initial value when the sample is saturated.

A transient production of N_2O is detected, as expected [8]. Purging with He causes the detection of the reversibly adsorbed NO (peak at constant temperature) and then, when the temperature is raised, two main NO peaks are observed at about 200 and 380°C respectively. In phase with the last NO emission an about equimolar amount of O_2 (not reported) and a lower NO_2 quantity are detected.

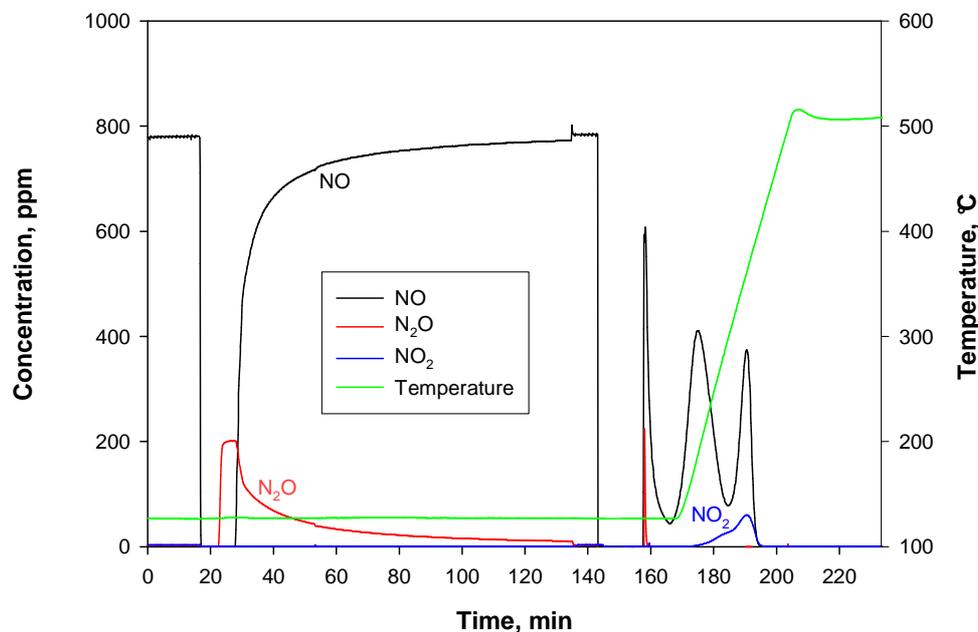


Figure 1. NO_x species detected during NO adsorption at 125°C in the absence of both H_2O and O_2 (Test A) on pre-reduced Cu-ZSM-5 and the following TPD.

The presence of water in the feed (Test B) strongly reduces NO adsorption and moreover, after a given time, promotes a sharp desorption of a fraction of NO previously adsorbed (not reported). At the same time, also N_2O is released, thus suggesting a displacement of both NO and N_2O by water. This phenomenon is associated to a temperature increase of about 10°C, due to a higher exothermicity of water adsorption compared to NO_x species. When O_2 is co-fed, NO and NO_2 emissions are detected when water is added after 80 min; the temperature peak already observed in the Test B is detected again, suggesting that some NO adsorbed under dry conditions, also as NO_2 , is substituted by water on the same copper sites. Finally, when both water and O_2 are fed since from the beginning of the experiment (Test D) the catalyst shows the same qualitative behaviour observed during the Test B; however, the presence of oxygen reduces the amount of adsorbed NO displaced by water.

The results shows that also in the presence of water the copper re-oxidation by NO takes place, as in the absence of H₂O, and that only after this reaction occurred the N₂O produced by copper oxidation is replaced by water [20].

The nature of the adsorbed NO not replaced by water has been investigated by TPD carried out after each test. The presence of either water or oxygen or both strongly reduces the physical NO adsorption. The reversibly adsorbed NO is practically the only species detected during TPD after wet adsorption in the absence of O₂, suggesting that copper sites mostly adsorb water which totally inhibits NO chemisorption. However, in the presence of oxygen NO and NO₂ desorption peaks at high temperature (TPD after Tests C and D) are detected. The attribution of this peak to nitrate-like species [20] is in agreement with a larger formation of nitrates promoted by the presence of O₂ in the feed. As a consequence, adsorbed nitrates cannot be displaced by water.

The amount of NO_x desorbed in the TPD analyses following each test is reported in Table 1 for both catalysts and for each adsorption temperature investigated. A value of about 200 μmol/g is desorbed from the Cu-ZSM-5 following an adsorption at 50°C. This amount decreases by increasing the temperature, as expected for adsorption phenomena. Nevertheless, a very low quantity of NO is adsorbed in the Tests B at the same temperature due to the competition of water adsorption with NO on the same copper sites. O₂ addition to the gas feed partially restores the adsorption capacity of the Cu-ZSM-5. Feeding water from the beginning (Test D) or after 80 min (Test C) only slightly affects the amount of NO that can be adsorbed onto the catalyst surface.

The effect of doping the catalyst by lanthanum is to increase the amount of adsorbed NO_x at each temperature, in accordance to Palella et al. [19]. The loss of NO adsorption capacity in the presence of a wet feed is proportionally less intense both in the presence and in the absence of O₂, confirming that the rare earth cation partially inhibits the NO displacement by H₂O and/or promotes the nitrates formation. The reduction of NO_x adsorption by water could be then the main cause of the loss of activity in NO decomposition.

Table1. Total amount of NO_x desorbed during the TPD carried out after NO adsorption on pre-reduced Cu-ZSM-5 and LaCu-ZSM-5 at each adsorption temperature in the 4 cycles.

T, °C	Cu-ZSM5				LaCu-ZSM5			
	50	80	125	150	50	80	125	150
Test A	204,2	177,6	159,7	119,6	229,9	208,9	164,9	99,1
Test B	4,1	3,3	2,5	3,2	16,6	6,7	3,1	7,0
Test C	114,2	29,3	11,0	14,2	142,7	62,9	39,9	20,8
Test D	94,9	29,6	11,4	7,4	104,8	46,6	24,7	16,8

Conclusions

NO adsorption on Cu-ZSM-5 is negatively affected by water addition at low temperature. Water almost totally replaces NO pre-adsorbed on copper sites. On the other hand, nitrate-like species seem resistant to water displacement. As a consequence, oxygen co-feeding, promoting oxidation of NO to NO₂ and consequently nitrates formation, partially preserves NO adsorption capacity of Cu-ZSM-5 in the presence of water. Lanthanum co-exchange improves the copper adsorption capacity both in the absence and in the presence of water and O₂.

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