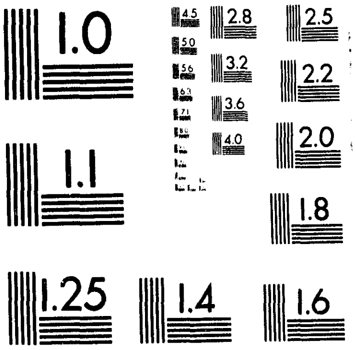
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DIRECT CATALYTIC DECOMPOSITION OF NITRIC OXIDE

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Direct Catalytic Decomposition of Nitric Oxide

This project investigates a suitable catalyst system for the direct nitric oxide decomposition in post-combustion gas streams. This process does not use a reductant, such as the ammonia used in the Selective Catalytic Reduction (SCR) of NO_x to nitrogen. Therefore, it is a greatly simplified process basically involving passing the flue gas through a catalytic converter.

Catalysts are prepared by incorporating metal cations into zeolite supports according to ion exchange procedures widely used in preparation of metal/zeolite catalysts. The catalysts of primary interest include copper, palladium, silver, and nickel exchanged ZSM-5 catalysts. Particular emphasis is given in this work on promoted Cu-exchanged zeolites, especially the catalyst system Mg/Cu-ZSM-5 and a few others, which are promising for NO conversion to nitrogen at typical flue gas O_2 and NO levels and over the temperature range of 723- 873°C. The effect of zeolite modification, copper exchange level and catalyst preparation conditions on the catalytic activity are studied in a packed-bed microreactor. Temperature-programmed desorption (TPD) and reduction (TPR) experiments are carried out in a thermogravimetric analyzer. Kinetic studies of NO and O_2 interaction with catalysts over a wide temperature range as well as catalyst structural investigations are planned.

Progress Summary

A systematic study of water vapor effects on the structure and Cu^{2+} ion exchange capacity of parent ZSM-5 zeolites and on the catalytic activity of the Cu-ZSM-5 and metal ion (Mg^{2+} and Ce^{3+}) modified Cu-ZSM-5 catalysts for NO decomposition has been performed during this quarter. Mg^{2+} and Ce^{3+} cocations in copper ion-exchanged ZSM-5 zeolites display a positive effect on the decomposition of nitric oxide to nitrogen and oxygen. Severe steaming (with 20% water vapor) at 500-750°C deactivates both the Cu-ZSM-5 and metal modified Cu-ZSM-5 catalysts. Under these conditions, dealumination of the parent ZSM-5 zeolites results in the loss of micropore volume and a much reduced uptake capacity for Cu^{2+} cations. X-ray diffraction analysis of the catalysts showed that the unit cell of steamed Cu-ZSM-5 catalysts underwent shrinkage. The catalytic activity of a Cu-ZSM-5 catalyst was examined after it was exposed to different inert and oxygen-containing gas streams. The results show that the steady-state catalyst activity is not sensitive to three treatments.

Catalyst Synthesis and Characterization

Parent ZSM-5 samples (Davison Chemical, SMR 6-2670-1191, Si/Al= 21.5) pretreated in 20 vol% water vapor-containing gas mixture were ion-exchanged with Cu^{2+} cations according to ion exchange procedures described in our earlier reports [1, 2].

During this quarter, a Ce^{3+} ion modified Cu-ZSM-5 material was prepared by incorporating Ce^{3+} and Cu^{2+} cations into the ZSM-5 zeolite supports. The ZSM-5 samples were first ion-exchanged with Ce^{3+} cations from dilute aqueous solutions of cerous nitrate with Ce^{3+} concentration of 0.007M. A triple exchange was made at 85°C for 2 hours. After each exchange, the filtered Ce-ZSM-5 was dried in air at 100°C for 10 hours, then calcined in air at 500°C for two hours. The catalyst was further ion-exchanged with Cu^{2+} in an aqueous solution of cupric acetate of concentration 0.007M at room temperature for 19 hours. This was repeated three times. Finally, the catalyst was washed with deionized water at room temperature and dried in air at 100°C for 19 hours.

Elemental analyses were performed by Inductively Coupled Plasma Emission Spectrometry after the catalyst sample was dissolved in dissolution reagents, purchased from UniSolv, Inc., of New Jersey, since Ce cations in the Ce/Cu-ZSM-5 catalyst are fluoride insoluble. These reagents have three types of solutions. One containing HF dissolves the catalyst, the other two neutralize and stabilize the solution to 1) deactivate the HF by increasing the pH to a value of 7.5 to 8.0, and 2) maintain solubility of the sample. The Ce^{3+} and Cu^{2+} exchange levels in this catalyst are 60% and 138%, respectively, based on the ratios of Ce/Al and Cu/Al measured by ICP.

Experimental

The effects of water vapor on the structure and Cu^{2+} ion exchange capacity of the parent ZSM-5 zeolites and on the catalytic activity of the Cu-ZSM-5 and metal ion modified Cu-ZSM-5 catalysts for NO decomposition were investigated this quarter.

The parent Na-ZSM-5 zeolite was pretreated for 20 hours in a gas mixture containing 20% H_2O- 4% O_2- He at temperatures of 500, 600 and 750°C to examine dealumination. Micropore volumes of the as-received and the steamed Na-ZSM-5 zeolites were measured by nitrogen uptakes in a Micropore Analyzer (ASAP 2000, Micromeritics). The Cu^{2+} uptake capacity of these steamed samples was examined by Cu^{2+} ion exchange, according to procedures described in our earlier reports [1, 2].

To check the effect of cocations in metal modified Cu-ZSM-5 materials on the resistance to water deactivation, comparisons of the catalytic activities of Cu(72)-ZSM-5 and Cu(141)-ZSM-5, with those of Mg(52)/Cu(66)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 for NO decomposition were made in a feed gas mixture of 20%H_2O-1.6%NO-balance He at 500°C. Nitric oxide conversions to nitrogen were measured before and after introduction of water vapor into the feed stream. An amount of 0.5g of catalyst was placed in the reactor. Contact time was 1g s/cc (STP). The NO concentration was 2% in the feed gas stream.

Results and Discussion

Effect of water on the micropore volume and Cu cation exchange capacity of ZSM-5. The parent ZSM-5 materials were pretreated in a gas mixture containing 20% water vapor at different temperatures for 20 hours. It was found that the micropore volume decreased from 0.11 cm^3/g for the as-received ZSM-5 zeolites to practically zero for the ZSM-5 materials steamed at high temperatures, and the subsequent Cu^{2+} ion exchange capacity was reduced from 141% to 15%. The catalytic activity of the Cu-ZSM-5 materials for NO decomposition also decreased. Results from these tests are shown in Table 1. As can be seen in Table 1, the zeolites steamed at 600 and 700°C have zero micropore volume, and subsequently low Cu^{2+} exchange capacity and low catalytic activity. It appears that excessive dealumination took place by this steaming treatment. The results at 500°C indicate no dealumination. It is at this temperature, then, that the effect of water vapor on the catalytic activity for Cu-ZSM-5 and Mg (or Ce)-ZSM-5 materials was examined to correlate it with the copper alone in the absence of zeolite structural modifications.

Cocation effect on the catalytic activity in dry NO-containing gas streams. Alkaline earth and transition metal cocation effects have been reported for Cu^{2+} ion-exchanged ZSM-5 zeolites used for the direct decomposition of nitric oxide in oxygen-free [1-3] and oxygen-rich gases [1, 2]. The Ce(60)/Cu(138)-ZSM-5 catalyst was slightly better than the over-exchanged Cu(141)-ZSM-5 catalyst in O_2-free gas [1]. However, the Ce^{3+} promotion effect was more pronounced for low Cu exchange levels at low reaction temperatures. Figure 1 shows NO conversions to N_2 for the Ce(60)/Cu(138)-ZSM-5, Ce(10)/Cu(116)-ZSM-5 materials and the Cu(141)-ZSM-5 catalyst. It should be pointed out, here, that alkaline earth and transition metal promotion effect are manifested at high reaction temperatures [1-3].

Cocation effect on the catalytic activity in wet NO-containing gas streams. A pronounced effect of cocation on the NO decomposition conversion was found after prolonged treatment with water vapor at

500°C. The results are shown in Figure 2. In 20% H_2O-containing reactant stream for 20 hours, the catalysts Cu(72)-ZSM-5 and Mg(52)/Cu(66)-ZSM-5 lost most of their dry gas-activity, reaching about 8%. After removal of the water vapor from the feed stream, the catalytic activity of Mg(52)/Cu(66)-ZSM-5 was gradually restored, but only to about 45% of its original value. No recovery was observed for the unpromoted Cu(72)-ZSM-5 catalyst. However, for the over exchanged Cu(141)-ZSM-5, 30% of its original dry gas activity was restored after removal of water vapor. In the presence of Ce^{3+} cocations, the water-resistance was greatly improved. Even during reaction in wet feed gas, the Ce(60)/Cu(138)-ZSM-5 catalyst showed a 20% NO conversion to N_2; after removal of water from the reactant stream, more than 66% of the original activity of the catalyst was gradually restored. Those results show that Mg^{2+} and Ce^{3+} cocations are able to restore the activity of the Cu active sites, probably due to the ability of these cocations to prevent copper ion redistribution or migration to the outer surface and formation of bulk copper oxide, which is not active for NO decomposition.

X-ray diffraction patterns. The crystal structures of the fresh and steamed catalysts were examined by XRD (Model: Rigaku 300). The diffractograms show some loss of crystallinity by the appearance of an amorphous background (halo) compared with the fresh catalysts. Figures 3 and 4 show XRD patterns for the fresh and steamed Cu(72)-ZSM-5 catalyst, and the fresh and steamed Mg(52)/Cu(66)-ZSM-5, respectively. From these results, it is clearly shown that the steamed Cu(72)-ZSM-5 lost its crystallinity more than the Mg(52)/Cu(66)-ZSM-5. Figures 5 and 6 show normalized XRD patterns for the Cu(141)-ZSM-5 and Ce(60)/Cu(138)-ZSM-5 catalysts. No loss of crystallinity is apparent in this case. The XRD measurements for the steamed Cu-ZSM-5 materials show peak shift to higher 2θ. However, the peaks for the steamed cocation modified Cu-ZSM-5 catalysts slightly shift to lower 2θ. Unit cell dimensions were calculated on the Rigaku 300 instrument by using the Least Square Unit Cell Refinement-- a least squares fitting of unit cells with peak positions. The results for the fresh and steamed catalysts are listed in Table 2.

Effect of the pretreatment stream on catalytic activity. Fresh Cu(97)-ZSM-5 catalyst was pretreated in four gas streams, i. e. pure He, 10%O_2-He, 10%H_2O-He, and 2%NO-He, at 500°C for 4 hours (2 hours in pure He). Immediately after each treatment, the catalyst activity was examined in a gas mixture containing 2%NO-He at 500°C and 1g s/cc of contact time (STP). Test results showed that the steady state catalytic activity is not sensitive to pretreatment, except when water vapor was used, as shown in Figure 7. The initial activity, 63% NO conversion to N_2, after the oxygen-containing gas pretreatment was lower than the 75% conversion measured immediately after exposure to pure He or to 2%NO-He gases.

Plans for Next Quarter

We plan to investigate the effect of water on the structure of parent ZSM-5 materials and the copper activity in Cu-ZSM-5 and cocation modified Cu ion-exchanged ZSM-5 materials. Other work will focus on characterizing the copper states in Cu-ZSM-5 catalysts by XPS and EPR. Characterization of the "excess copper" on samples prepared by various techniques will be performed by activity tests and electron microscopy.

References

[1] M. Flytzani-Stephanopoulos, A. F. Sarofim, Y. P. Zhang, Quarterly Technical Progress report No. 6, Grant No. DE-FG22-91PC91923 (1993).

[2] M. Flytzani-Stephanopoulos, A. F. Sarofim, Y. P. Zhang, Quarterly Technical Progress report No. 7, Grant No. DE-FG22-91PC91923 (1993).

[3] S. Kagawa, H. Ogawa, H. Furukawa, Y. Teraoka, *Chem. Lett.* (1991) 407.

Table 1. Hydrothermal Effects

Catalysts	as-received ZSM-5	Steamed Parent ZSM-5		
Steaming Temp.,°C		500	600	750
Micropore Volume, cm^3/g	0.11	0.11	0.0002	0.0000
Cu Exchange Capacity*, %	141	140	20	15
NO Conversion to N_2, %	91	89	8	8

* a triple Cu^{2+} ion exchange from 0.007 M $Cu(ac)_2$ aqueous solution at room temperature for 20 hours.

Table 2. X-Ray Diffraction Results

Materials	Unit Cell (Å)		
	a	b	c
Fresh Cu(72)-ZSM-5	20.0708±0.0247	19.9360±0.0000	13.5537±0.0568
Steamed Cu(72)-ZSM-5 in 20%H_2O @500°C for 19 hours	20.3586±0.0101	19.9041±0.0000	13.2217±0.0214
Fresh Mg(52)/Cu(66)-ZSM-5	20.0236±0.0121	19.8433±0.0000	13.5017±0.0399
Steamed Mg(52)/Cu(66)-ZSM-5 in 20% H_2O @500°C for 19 hours	20.0793±0.0143	19.9287±0.0000	13.5148±0.0487
Fresh Cu(141)-ZSM-5	20.0709±0.0445	19.9028±0.0000	13.4824±0.1105
Steamed Cu(141)-ZSM-5 in 20% H_2O @ 500°C for 10 hours	20.0845±0.0100	19.8933±0.0000	13.4791±0.0452
Fresh Ce(60)/Cu(138)-ZSM-5	20.0732±0.0040	19.9503±0.0000	13.4485±0.0130
Steamed Ce(60)/Cu(138)-ZSM-5 in 20% H_2O @500°C for 10 hours	20.0840±0.0083	19.9301±0.0000	13.4902±0.0236

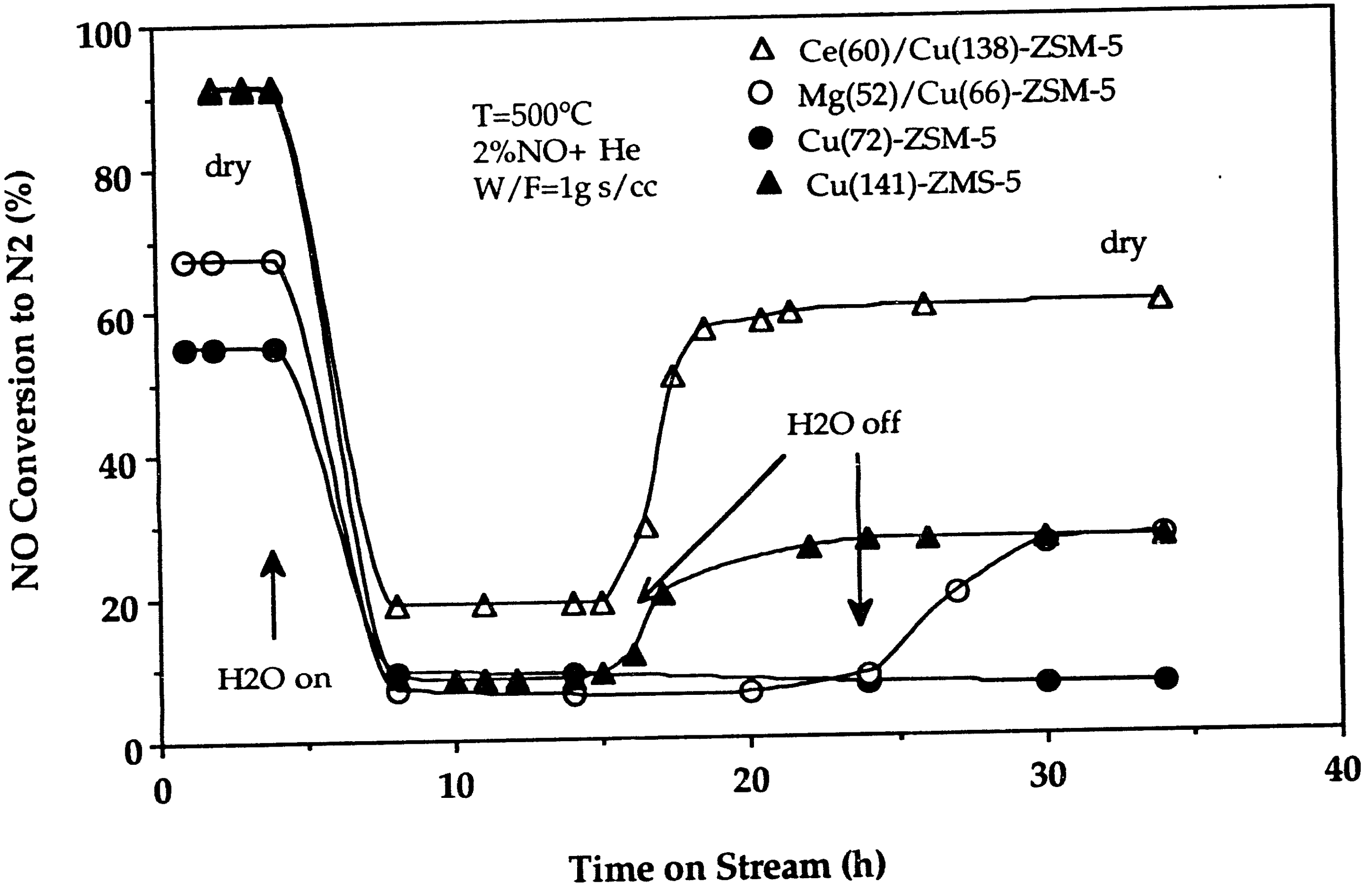

Figure 2. Cocation effect on the NO decomposition over Cu-ZSM-5 in dry and wet (20% H_2O) stream.

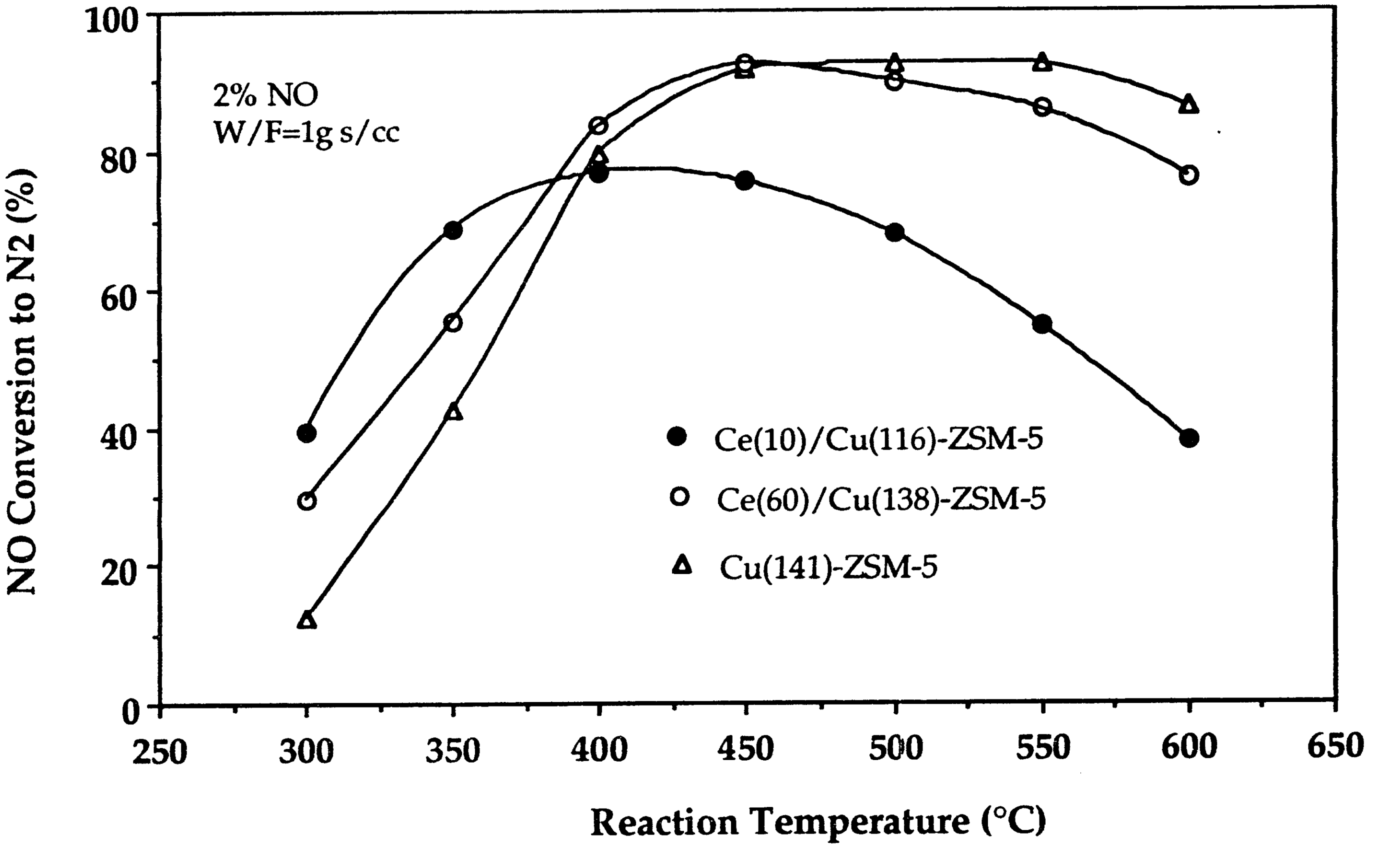

Figure 1. Ce effect on catalytic activity of Cu ion exchanged ZSM-5 zeolites.

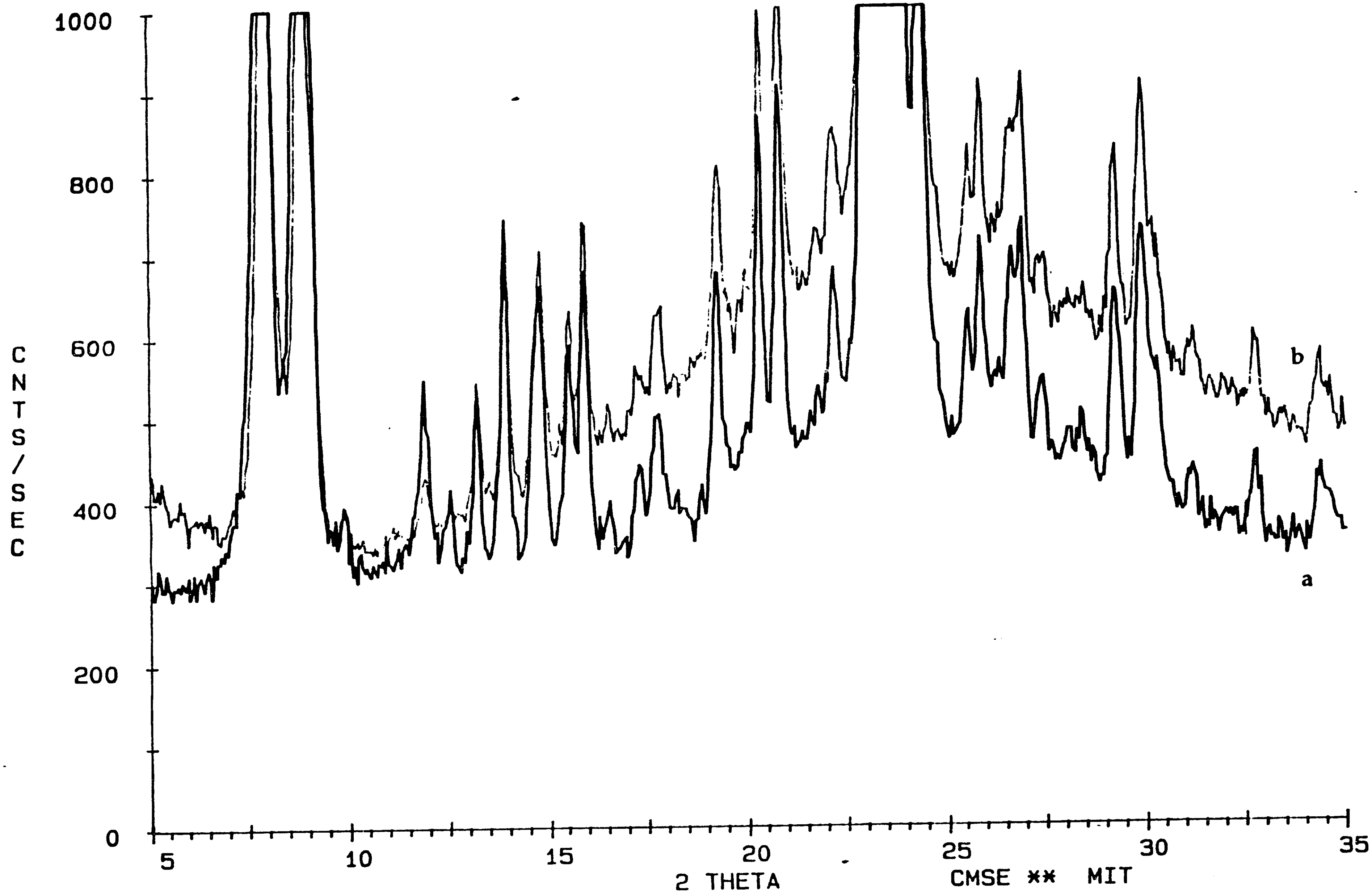

Figure 3. X-ray diffraction patterns of the a) fresh and b) steamed Cu(72)-ZSM-5.

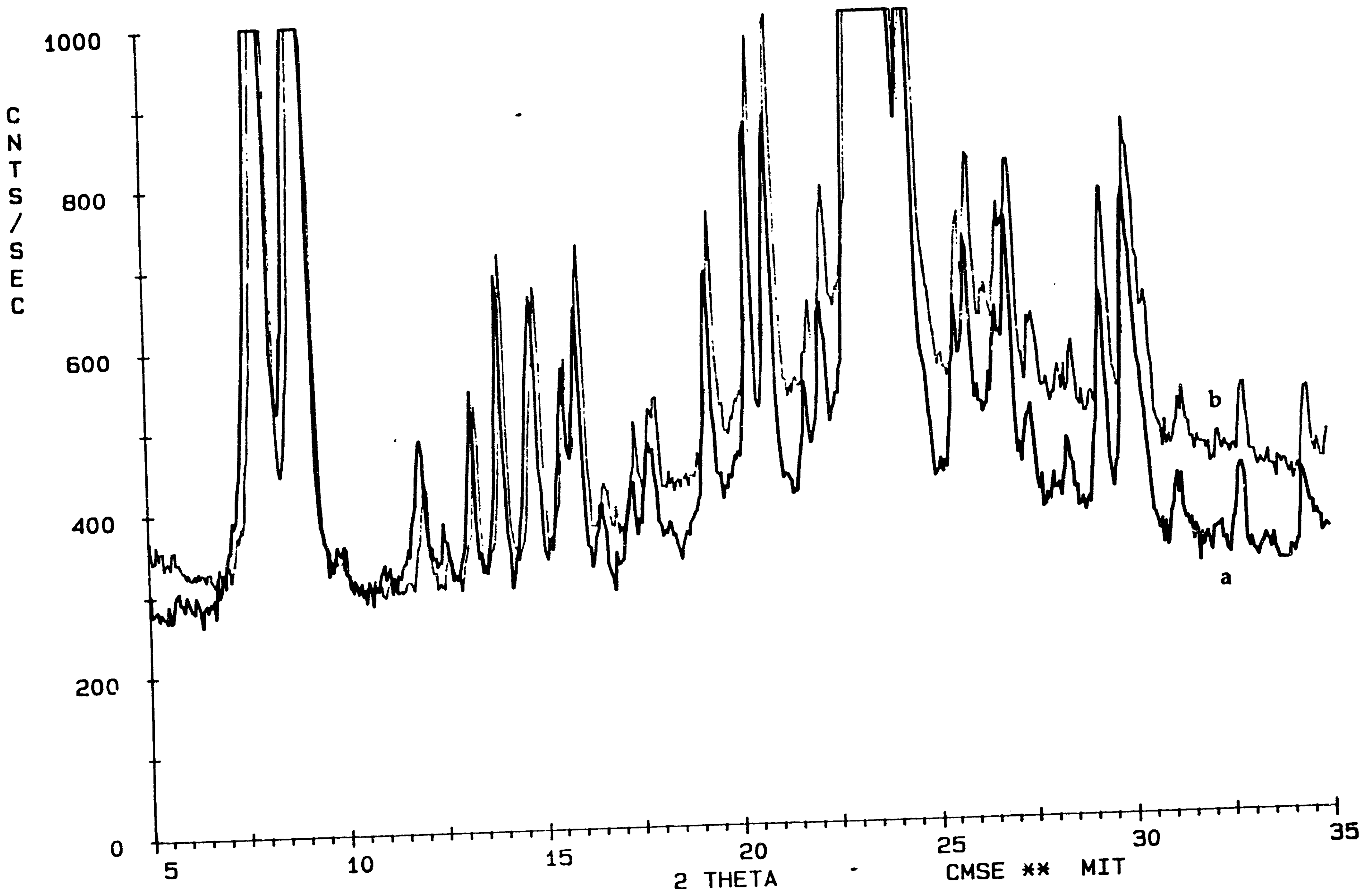

Figure 4. X-ray diffraction patterns of the a) fresh and b) steamed Mg(52)/Cu(66)-ZSM-5.

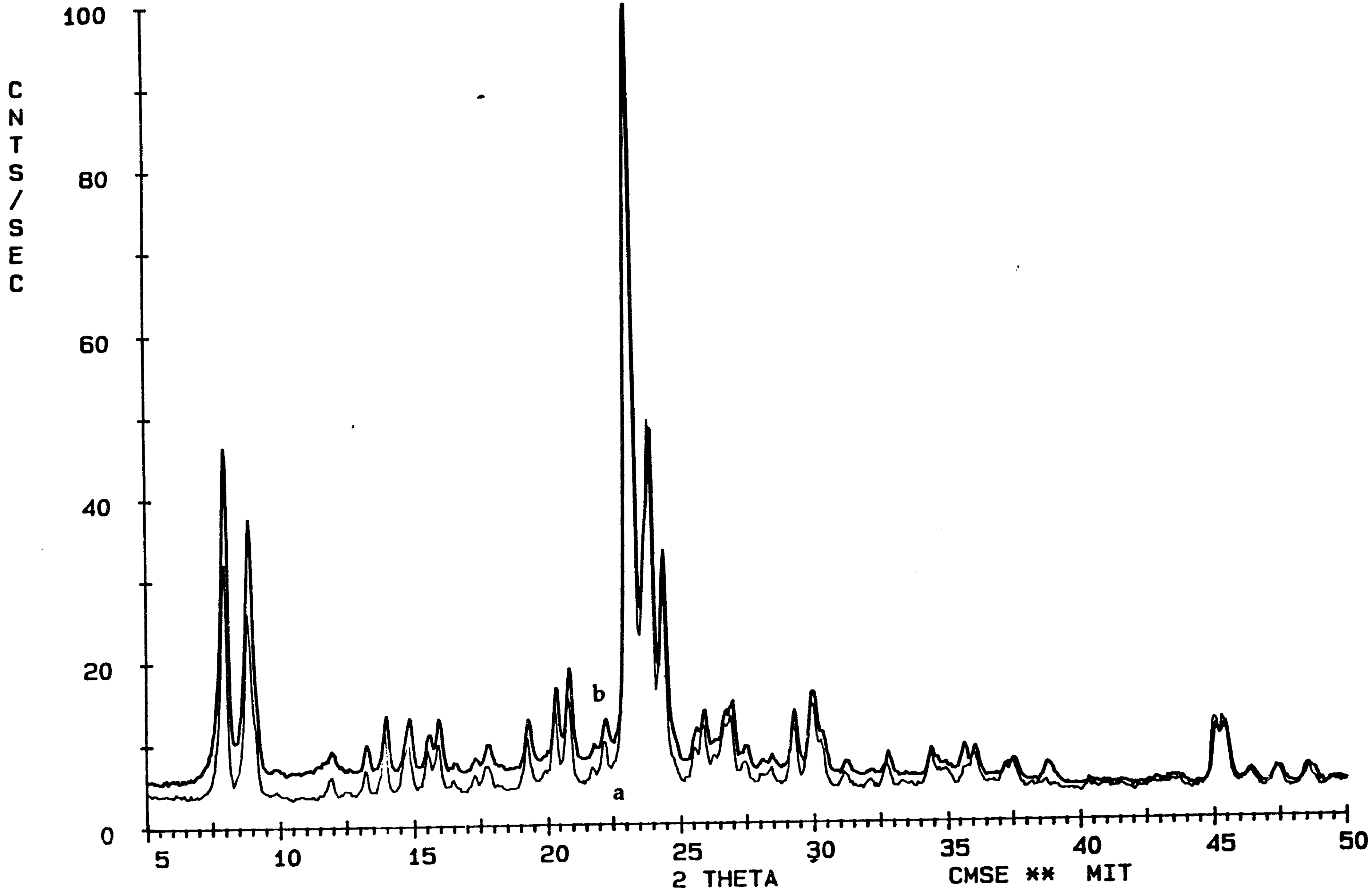

Figure 5. Normalized X-ray diffraction patterns of the a) fresh and b) steamed Cu(141)-ZSM-5.

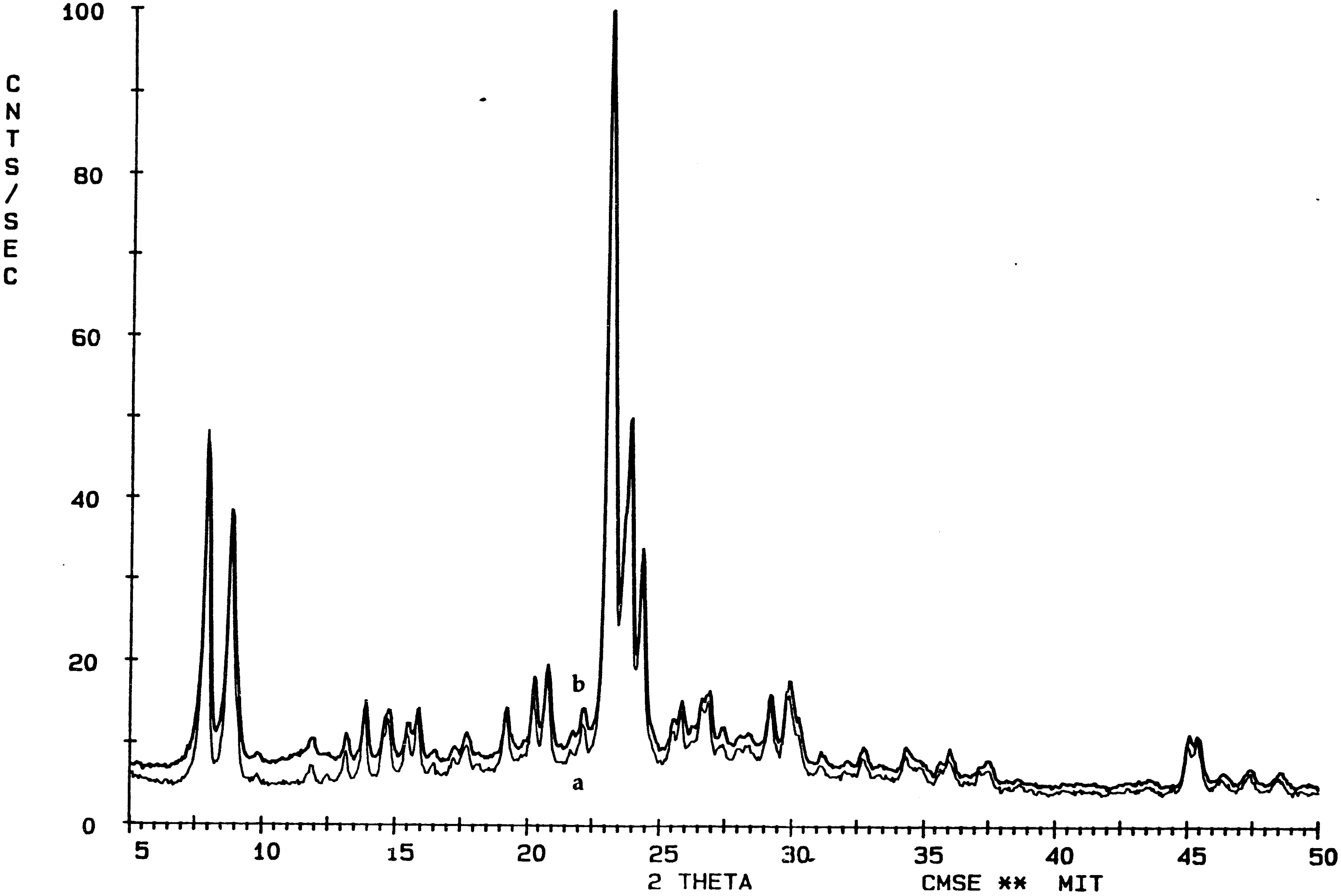

Figure 6. Normalized X-ray diffraction patterns of the a) fresh and b) steamed Ce(60)/Cu(138)-ZSM-5.

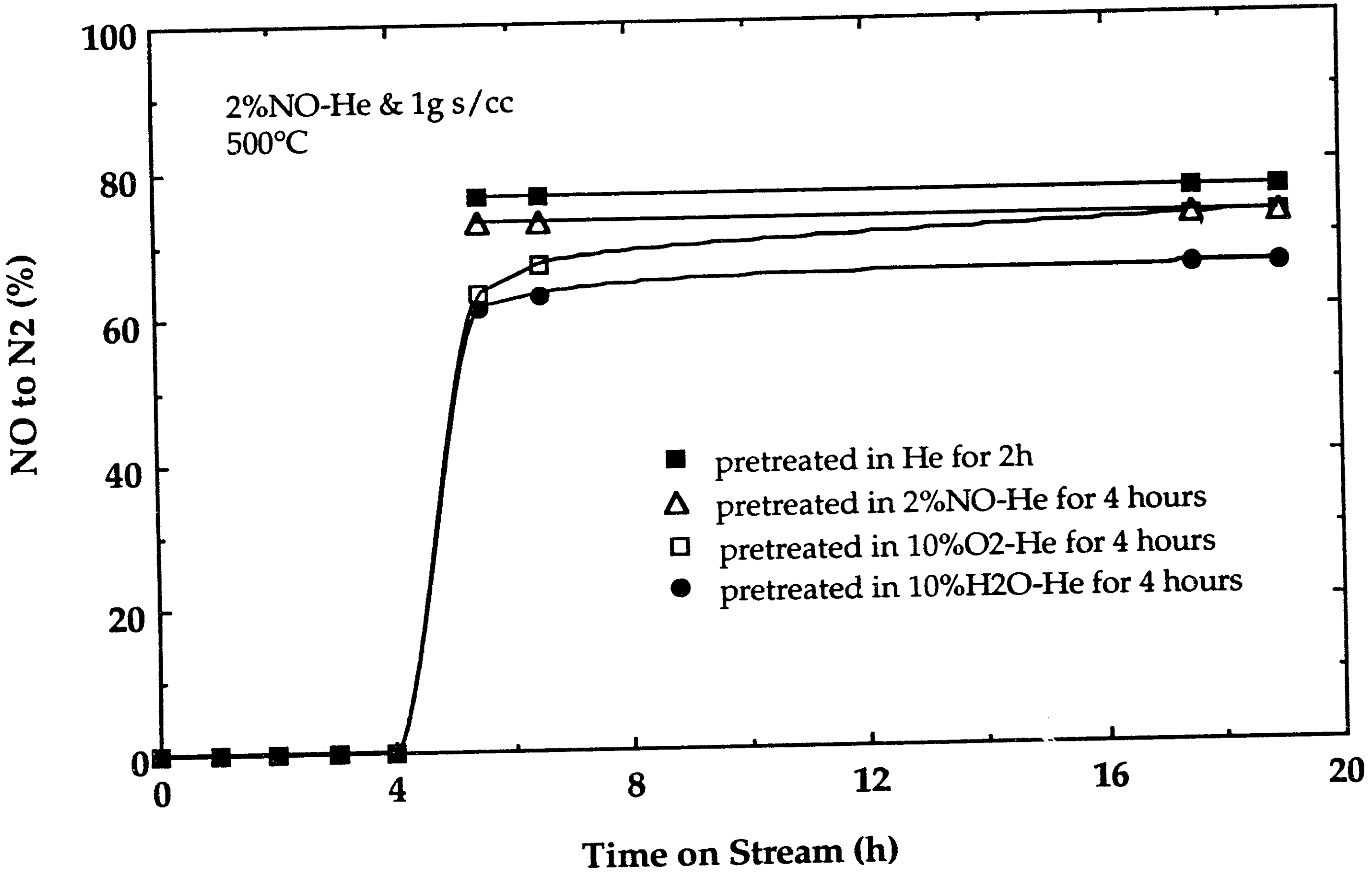

Figure 7. NO decomposition over Cu(97)-ZSM-5 after pretreatment of the fresh catalyst in different environments at 500°C.

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