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Catalysis Today 90 (2004) 35–38
CATALYSIS TODAY
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# Reduction of NO by $C_3H_6$ over CuO–MnO/$MgF_2$ in the presence of $H_2O$

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Received 4 September 2003; received in revised form 14 October 2003; accepted 14 October 2003

## Abstract

The effect of the presence of steam on the catalytic activity of $MgF_2$ supported binary copper and manganese oxides in the reaction of $NO + C_3H_6 + O_2$ has been investigated in comparison to that on the activity of single metal systems such as Cu–O/$MgF_2$ and Mn–O/$MgF_2$. The reaction was performed for different compositions of the reaction mixture, i.e. under reducing, stoichiometric and oxidising conditions. The most resistant to steam proved to be the mixed Cu–Mn–O/$MgF_2$ system, with a high conversion of NO to $N_2$. When the inflow of steam was stopped, the catalyst underwent regeneration.

*Keywords:* SCR NO; Copper–manganese oxide catalyst; $MgF_2$; Water tolerance; Catalyst deactivation

## 1. Introduction

Removal of $NO_x$ from exhaust gases is a challenging subject that has been extensively studied in recent years. Selective catalytic reduction of $NO_x$ by hydrocarbons is one of the most effective methods [1]. The performance of zeolite, metallic and oxide systems in this process has also been tested. The activity of zeolite catalysts dropped rapidly in the presence of water, while the metallic catalysts were resistant to water but in their presence $N_2O$ appeared during the conversion of NO to $N_2$. Recently much attention has been paid to oxide systems.

The systems studied included $La_2O_3/Al_2O_3$ promoted by strontium [2], $Ga_2O_3/Al_2O_3$ catalyst [3] and mixed oxide catalysts: Cu, Ni, and Co–$Al_2O_3$ with spinel-type structure [4]. They show a high activity and resistance to the presence of steam in reaction gases. Interesting results have been obtained for transition metal oxides supported on magnesium fluoride in the reduction of NO by $C_3H_6$ of the mixed oxide systems, the best performance was found for copper–manganese catalysts [5].

This paper reports results of a study of the effect of steam on the activity of $MgF_2$ supported binary copper and manganese oxides in the reaction of $NO + C_3H_6 + O_2$ in comparison to single metal systems such as CuO/$MgF_2$ and MnO/$MgF_2$. The study was performed at 370 °C under reducing, oxidising and stoichiometric conditions.

## 2. Experimental

### 2.1. Preparation of catalysts

Magnesium fluoride was obtained by adding small portions of $MgCO_3{\cdot}3H_2O$ into an aqueous solution of hydrofluoric acid until neutralisation, then the mixture was acidified by the introduction of a few additional drops of the acid. The precipitate was aged at room temperature for a couple of days under stirring, followed by calcination at 400 °C for 4 h. After calcination, $MgF_2$ was ground to obtain 0.2–0.5 mm grain size.

The impregnated CuO/$MgF_2$ preparations were obtained by introduction of earlier prepared magnesium fluoride into a water solution of copper nitrate [$Cu(NO_3)_2{\cdot}3H_2O$]. The amount of the copper nitrate solution used was enough to wet the entire surface of magnesium fluoride layer. The preparation was evaporated at continuous stirring then dried at 105 °C for 24 h. Finally the sample was calcined at 400 °C for 4 h.

The preparations were marked with a symbol $MFCu_2$, where “2” stands for the content of metallic copper in wt.%.

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0920-5861/$ – see front matter
doi:10.1016/j.cattod.2004.04.005

The impregnated preparations $MnO/MgF_2$ were prepared by introduction of earlier prepared magnesium fluoride into a water solution of manganese acetate $[Mn(CH_3COO)_2\cdot 4H_2O]$. Further preparation procedure and thermal treatment were as above for the preparation of $CuO/MgF_2$.

The series of samples were marked with a symbol $MFMn_4$, where "4" stands for metallic manganese in wt.%.

The co-impregnated preparations $CuO–MnO_x/MgF_2$ were obtained by introduction of earlier calcined magnesium fluoride into a water solution of a mixture of copper nitrate $[Cu(NO_3)_2\cdot 3H_2O]$ and manganese acetate $[Mn(CH_3COO)_2\cdot 4H_2O]$, adding some diluted ammonia to get pH from the range 8.3–9.0. The preparations were dried at 105 °C for 24 h and finally calcined at 400 °C for 4 h.

This series of samples were marked with a symbol $MFCu_2Mn_4$, where "2" is the content of Cu and "4" is the content of Mn in wt.%.

### 2.2. Catalytic activity

The reaction of NO + propene was performed by a continuous method. The reacting gases (1% of NO in He, 1% of propene in He and 5% of $O_2$ in He) were flown through a quartz reactor filled with 0.1 g of the catalyst. Steam was added to the reaction mixture at amounts up to 10 vol.% $H_2O$. The activities of the catalysts were determined under different reaction conditions described by the parameter $R$:$R < 1$ reducing conditions, $R = 1$ stoichiometric and $R > 1$ oxidising. The parameter $R$ was defined by Tanaka et al. [6] by the following expression:

$$R = \frac{[NO] + 2[O_2]}{9[C_3H_6]}$$

The total flow rate of the gases was 35 ml/min. The products were analysed using Carlo Erba 6000 GC equipped with 2 m long column filled with 13X molecular sieves (2/3) and chromosorb 104 (1/3). The reaction was run at 370 °C.

## 3. Results and discussion

Fig. 1 presents results of measurements illustrating the effect of steam on the activity of $MgF_2$ supported copper and manganese oxides in the reaction $NO + C_3H_6 + O_2$. The measurements were performed at reducing ($R < 1$), stoichiometric ($R = 1$) and oxidising ($R > 1$) conditions. The degree of propene conversion was measured in parallel. For the sake of comparison, similar measurements were performed for the systems containing the single oxides of copper or manganese supported on $MgF_2$ (Figs. 2 and 3).

The most resistant to the effect of steam with a simultaneous high NO conversion to $N_2$ was the catalysts $MFCu_2Mn_4$. The conversion of NO to $N_2$ depended on the conditions of the process and at reducing conditions decreased from 100 to 90%, at stoichiometric conditions to 70% and at oxidising conditions from 80 to 60%. The activity of the copper catalyst did not change in the presence of steam at oxidising conditions, but under these conditions the $NO \rightarrow N_2$ conversion was only 40%. At reducing and stoichiometric conditions the catalyst activity decreased (Fig. 2). The effect of steam on the manganese catalyst activity is illustrated in Fig. 3. As shown it was not resistant to steam and the decrease in $NO \rightarrow N_2$ conversion was almost linearly dependent on the amount of the introduced steam. The degree of $NO \rightarrow N_2$ conversion also rapidly decreased at stoichiometric and oxidising conditions. After introduction of 10 vol.% of steam at oxidising conditions the propene conversion decreased from 100 to ~30%, and at stoichiometric conditions from 75 to ~10%. Much smaller changes in propene conversion were noted for the copper catalyst. A significant decrease from 95 to 70% was obtained for $R > 1$. For the catalyst $MFCu_2Mn_4$, a significant decrease in propene conversion was found at $R = 0.33$, and less at $R = 1$. At oxidising conditions the decrease in conversion was small approximately 10% after introduction of 10 vol.% $H_2O$.

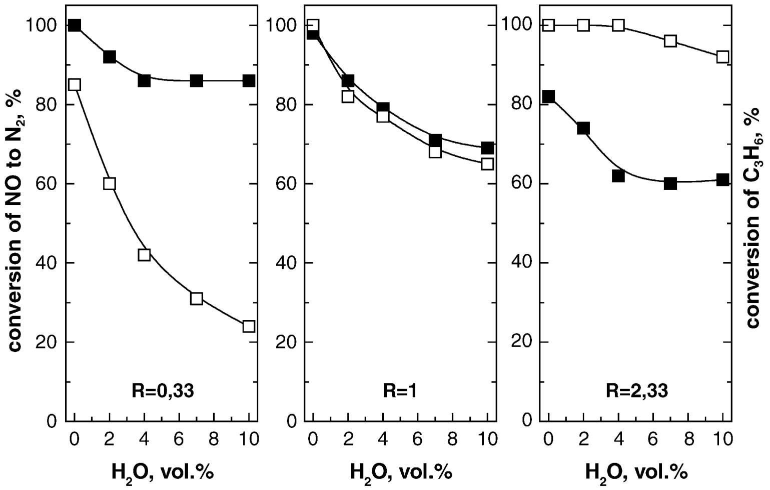

Fig. 1. The effect of steam on the activity of the $MFCu_2$ catalyst for different redox ratios at 370 °C, after 2 h of the reaction. Conversion of NO to $N_2$ (filled symbols), conversion of propene (empty symbols).

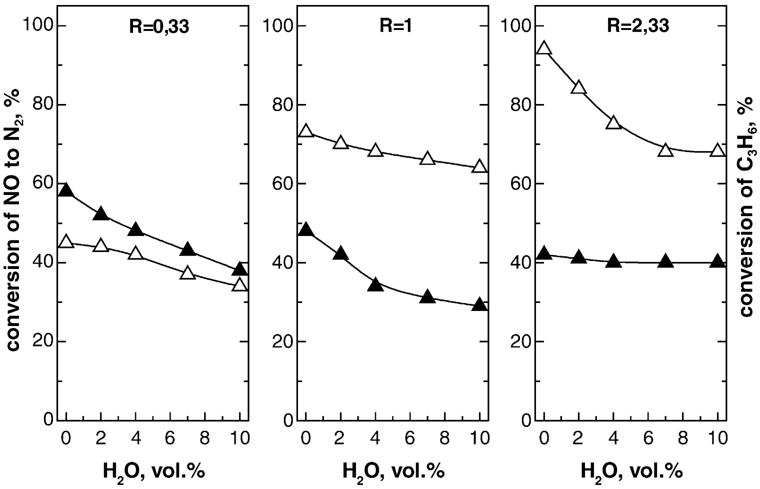

Fig. 2. The effect of steam on the activity of the $MFMn_4$ catalyst for different redox ratios at 370 °C, after 2 h of the reaction. Conversion of NO to $N_2$ (filled symbols), conversion of propene (empty symbols).

As follows from the above presented results, the activity of the catalysts (the degree of conversion of NO and propene) decreased with increasing amount of the introduced steam for all the preparations used. Only for the copper–manganese catalyst under reducing conditions the conversion of NO was at the same level but the propene conversion rapidly decreased. Supposedly, in parallel with NO reduction to $N_2$ by propene decomposition of NO to molecular nitrogen takes place.

In order to determine the character of the catalyst deactivation on exposure to steam, the preparation $MFCu_2Mn_4$ was subjected to an additional study. During the process $NO + C_3H_6 + O_2$ steam was introduced for some time, then its inflow was stopped and the reaction was continued, measuring the changes in the NO and propene conversion, see Fig. 4. The introduction of steam after 3 h of the process caused a gradual decrease in the NO conversion, irrespective of the composition of the reaction gases. The decrease in activity was close to the values obtained when steam was introduced in the beginning of the process. When the inflow of steam was stopped, the catalyst gradually regenerated and its activity was restored to the initial level. Only when the process was conducted at oxidising conditions, the catalyst was permanently deactivated by ~20% with respect to the initial value.

A decrease in the catalyst activity as a result of introduction of steam into the system is a well-known phenomenon. The molecules of $H_2O$ can be bound by not fully coordinated surface cations such as, for example, $Cu^{2+}$ ions being the active centres in the NO reduction by propane. This supposition seems highly probable in the light of results reported by many authors. For example, Lu et al. [7] who studied the activity of CuO in the reaction of NO reduction by isobutene in the presence of steam, reported a 30% decrease in the activity of $Cu/Al_2O_3$. This result was interpreted in terms of adsorption of OH group formed by water dissoci-

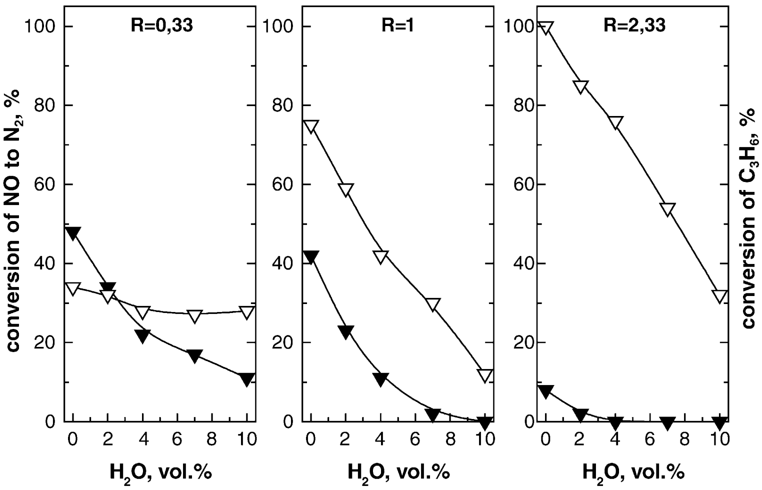

Fig. 3. The effect of steam on the activity of the $MFCu_2Mn_4$ catalyst for different redox ratios at 370 °C, after 2 h of the reaction. Conversion of NO to $N_2$ (filled symbols), conversion of propene (empty symbols).

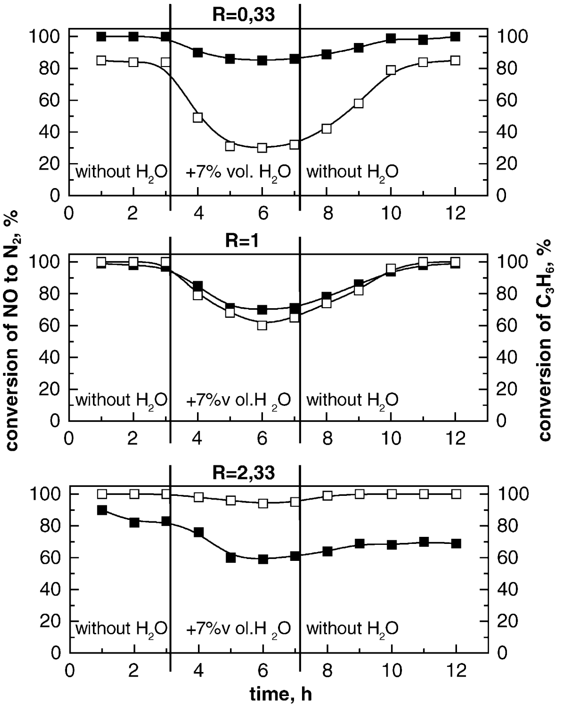

Fig. 4. The activity of the catalyst $MFCu_2Mn_4$ vs. the time of the reaction, after introduction of 7 vol.% of steam into the system at different redox ratios. The reaction was run at 370 °C. Conversion of NO to $N_2$ (filled symbols), conversion of propene (empty symbols).

ation at the copper centres. In the dissociation of water two sites metal–oxygen are involved. As a result of this process also other active centres can be eliminated, that is oxygen ions of Cu–O–Cu species being the sites of NO and propene adsorption in the reaction $NO + C_3H_6 + O_2$ [8,9]. According to Chen et al. [10] who studied $Cu/Al_2O_3$ catalysts in the reaction $NO + C_3H_6 + O_2$, the inhibiting effect of steam is a result of the active sites being blocked by $H_2O$, which prevents adsorption of the reagents: NO or propene. These suppositions were confirmed in [4,11].

The excess of oxygen in the presence of steam has an additional negative effect on the NO reduction with propene. The excessive oxygen can oxidise $Cu^+$ ions, disturbing the $Cu^+/Cu^{2+}$ equilibrium on the catalyst surface. It can also oxidise $C_3H_6$.

## 4. Conclusions

1. The binary system of copper and manganese oxides supported on $MgF_2$ is an active and selective catalyst in the process of nitrogen oxide reduction with propene.
2. The catalyst $MFCu_2Mn_4$ shows a high activity and selectivity in the presence of steam both at oxidising and reducing conditions.
3. The catalyst $MFCu_2Mn_4$ undergoes regeneration when the inflow of steam is stopped. However, at oxidising conditions its activity is partly permanently decreased.

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