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NO decomposition and reduction by C_3H_6 over transition metal oxides supported on MgF_2

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Abstract

The monooxides copper, manganese, molybdenum and chromium catalysts supported on MgF_2 were tested in NO decomposition and reduction by propene. The effect of the oxides content, time on stream and O_2 concentration in reaction mixture during NO reduction on their catalytic activity was investigated. All the catalysts showed the optimum active phase concentration corresponding to 2–4 wt.% of the metal. For the best copper catalyst an effect of introduction of another oxide (manganese or chromium oxide) on the catalytic performance was studied. The double copper-manganese oxide sample containing 2 wt.% Cu and 4 wt.% Mn was proved to ensure the best catalytic performance.

Keywords: NO decomposition; NO reduction; Reducing agent; Transition metal oxide

1. Introduction

Nitrogen oxides emitted to the atmosphere with exhaust gases are harmful to the environment and much effort has been made to eliminate them, especially NO (90–95% of the total NO_x). The most effective of the hitherto proposed methods of NO removal are the catalytic processes of NO conversion to N_2. They can be conducted by direct decomposition of NO or by reduction with an appropriate reducing agents [1]. The best performance in both these reactions is achieved with noble metals as catalysts, however, transition metal oxides have been proposed as less expensive alternative.

The idea of this work was to study the performance of transition metal oxides supported on an unconventional support—MgF_2. Such systems have been studied earlier and have shown high activity and selectivity in NO reduction [2,3]. Magnesium fluoride has not been very popular as a support although its structure, physico-chemical and catalytic properties have been well established [4]. It has been tested as a support of different oxide and metallic phases shown to be active and effective catalysts in such reactions as NO reduction [2,3]. MgF_2 is characterised by an almost chemically inert surface and good thermal stability up to 500 °C. It has mesoporous structure, its surface area reaches 45 m^2/g after calcination at 400 °C. This support was used to prepare a series of monooxide catalysts of different contents of copper, manganese, molybdenum and chromium and double oxide catalysts consisting of copper oxide together with Mn or Cr oxides. The catalysts were tested in NO decomposition and reduction by C_3H_6 under different concentration of oxygen in the reacting mixture. Hitherto there have been no literature data on the behaviour of such systems in NO decomposition reaction.

2. Experimental procedures

Magnesium fluoride was obtained by adding small amounts of $MgCO_3\cdot Mg(OH)_2$ to aqueous solution of hydrofluoric acid. The precipitate was aged, dried at 105 °C and calcined at 400 °C for 4 h. The details of preparation were given in [2]. The M_x/F (M = Cu, Cr, Mn, Mo; F = MgF_2) catalysts were obtained by impregnation of MgF_2 powder of 0.25–0.50 mm grain size with aqueous solutions of $Cu(NO_3)_2\cdot 3H_2O$, $Cr(NO_3)_3\cdot 9H_2O$, $Mn(CH_3COO)_2\cdot 4H_2O$ and $[(NH_4)_6Mo_7O_{24}]\cdot 4H_2O$, respectively. The precursors of the catalysts were dried for 24 h at 105 °C and calcined for 4 h at 400 °C. The co-impregnated samples $CuO–MnO/MgF_2$ (Cu_2Mn_x/F) and $CuO–CrO/MgF_2$ (Cu_2Cr_x/F) were obtained in the same way by impregnation of magnesium fluoride with aqueous solutions of the mixtures of $Cu(NO_3)_2\cdot 3H_2O + Mn(CH_3COO)_2\cdot 4H_2O$ and

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$Cu(NO_3)_2{\cdot}3H_2O + Cr(NO_3)_3{\cdot}9H_2O$, respectively. The amounts of copper(II) nitrates and chromium(III) nitrates or manganese(II) acetate introduced into the solutions were chosen to ensure the desired Cu/Cr or Cu/Mn weight ratio from 0.5 to 4.0.

Reduction of nitrogen oxide was carried out by propene in the presence of oxygen in a flow reactor at temperature 370 °C. The flow rate of the reaction gases (NO ($\geq$99.999), C_3H_6 ($\geq$99%) and O_2 ($\geq$99.999) diluted in helium ($\geq$99.999)) was 35 ml/min (GHSV = 21 000 h^{-1}), and the content of individual components was selected to provide a desired proportions of NO and O_2. The reaction products were subjected to chromatographic analysis. 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 paper presents the activities of the catalysts after 2 h on stream determined at different values of the R coefficient corresponding to the reducing $R < 1$, stoichiometric $R = 1$, and oxidising $R > 1$ conditions. This coefficient was calculated from the formula given by Tanaka et al. [5]:

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

The catalysts activity in the decomposition of NO was tested by the continuous method. The conditions of the catalytic tests were as follows: pretreatment at 370 °C for 2 h in helium (20 ml/min) reaction temperature 370 °C, catalyst weight 0.1 g, gas mixture: 1% NO in He (flow rate 15 ml/min), GHSV = 9000 h^{-1}. The reaction products were subjected to chromatographic analysis. The content of N_2 and NO in the products was analysed.

3. Results and discussion

In this study, magnesium fluoride was used as a support of selected transition metal oxides: copper, chromium, molybdenum and manganese. The obtained catalysts were tested in the reaction of NO reduction by propene and decomposition of NO.

In our preliminary study it was established that the monooxide catalysts supported on MgF_2 showed the optimum activity in the stoichiometric conditions ($R = 1$) at the concentrations of ~2 wt.% Cu and 3–4 wt.% Cr, Mo, Mn [6]. Therefore, in Fig. 1 the monooxide catalysts' activities in NO reduction are shown for the optimum concentrations of the metals: 2 wt.% Cu and 4 wt.% of the other metals. The most active was the copper catalyst.

The mono- and double oxide catalysts were tested in the NO reduction with propene as a function of the oxygen content in the reaction mixture, Fig. 1. All the systems were characterised by a high, almost 100% selectivity of NO reduction to N_2. No formation of N_2O, often accompanying NO reduction processes over metallic catalysts, was detected [7,8]. Under the oxidising conditions the propene was oxidised, which decreased the conversion of NO.

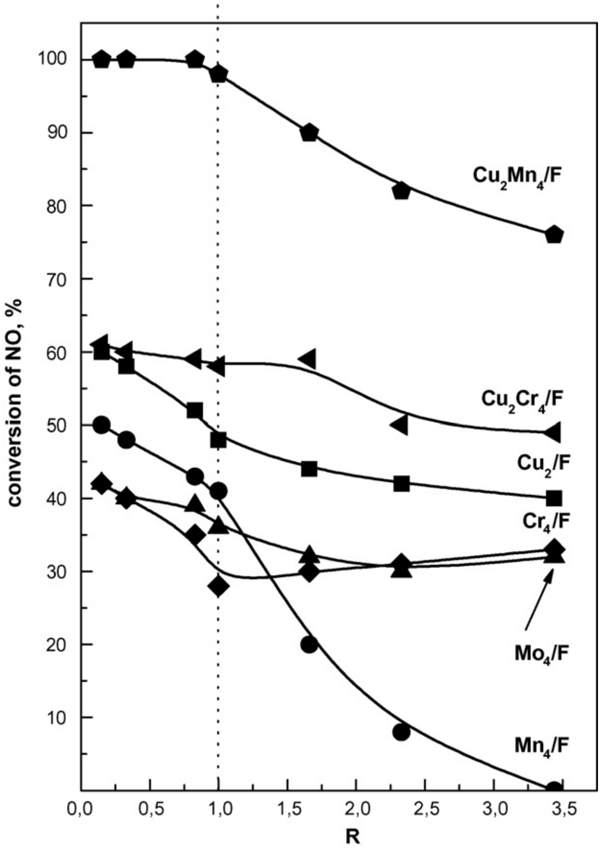

Fig. 1. The activity of mono- and double oxide catalysts in reduction of NO by propene in different redox conditions ($R < 1$ reducing, $R = 1$ stoichiometric and $R > 1$ oxidising conditions).

The activities of the catalysts depended on the oxygen concentration. The next in activity in the reducing conditions ($R < 1$) that is the manganese catalyst, was rapidly loosing its activity in the oxidising conditions ($R > 1$). The activities of the manganese and chromium catalysts were close and only a bit lower in the oxidising conditions. Double oxide systems proved the most active in the oxidising conditions, in particular the copper-manganese catalyst. The optimum of oxide phases loading corresponded to 2 wt.% Cu and ~4 wt.% Mn, Fig. 2.

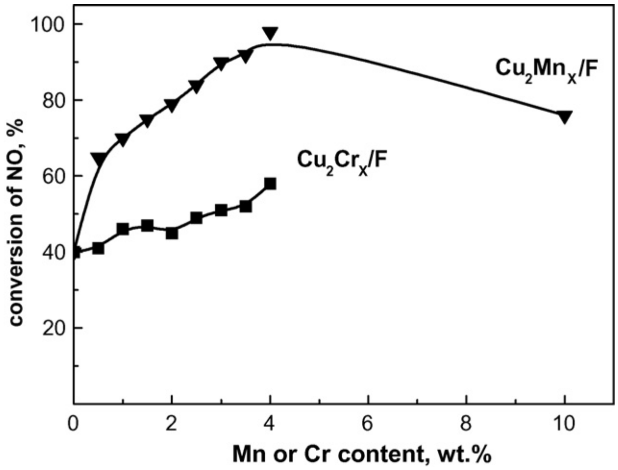

Fig. 2. The activity of double oxide catalysts in the NO reduction by propene for $R = 1$ as a function of Mn and Cr content.

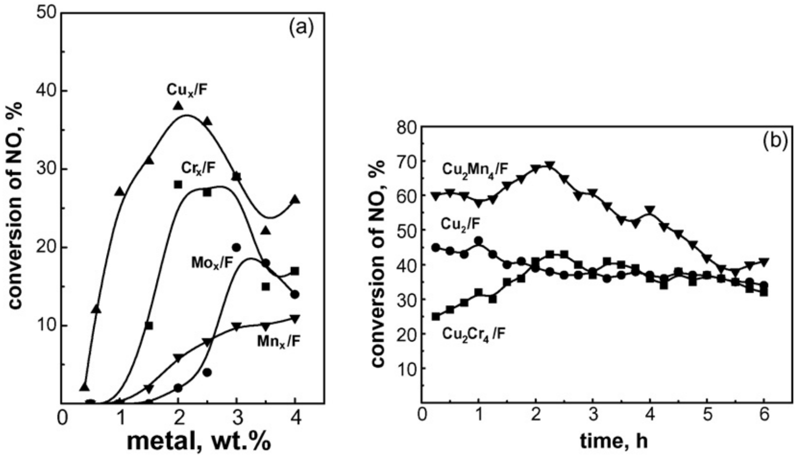

Fig. 3. The activity of the catalysts in the decomposition of NO for the monooxide catalysts as a function of metal content (a) and for the copper monooxide and double oxide catalysts as a function of time on stream (b).

The introduction of the chromium phase into the catalyst gave a rather low increase in the activity.

The catalysts obtained were also tested in the NO decomposition reaction. Fig. 3a presents the activity of the catalysts in the NO decomposition versus the loading with the active phase. The most active proved the copper catalysts and the sequence of activities of the monooxide catalysts was: Cu > Cr ~ Mo > Mn. All the monooxide catalysts studied, except the least active one with manganese oxide, revealed the optimum activity in the range corresponding to 2–3 wt.% of the metal. As complex systems often show higher activity than monooxides, an attempt was made to combine the most active CuO phase with chromium oxide (the next in active in the series) and with the least active manganese oxide. The proportion of copper to the other metal of 1:2 was assumed on the basis of the highest activities of these samples in NO reduction with propene. The addition of manganese oxide (Fig. 3b) caused an increase in the copper catalyst activity, decreasing with time to a value comparable with that of the monooxide copper catalyst. The addition of chromium caused an initial decrease in the copper catalyst activity, but with time the activity of the double oxide sample increased to reach a value comparable with that of the monooxide copper catalyst.

The most active of the double oxide catalysts Cu_2Mn_4/F, was subjected to more catalytic tests in NO reduction by propene to establish the stability of its performance, Fig. 4. In the reducing and neutral conditions ($R \leq 1$) its activity remained unchanged. Only in the excess of oxygen the catalyst was initially unstable but after ~8 h its activity stabilised at ~70%.

A comparison of activities of the catalysts studied in NO reduction with propene and NO decomposition has shown that the catalysts most active in the former reaction are also the most active in the latter. It is in agreement with one of the proposed schemes of NO reduction [9] in which the NO molecule undergoes decomposition on the catalyst surface and the oxygen liberated is used for oxidation of the hydrocarbon.

The same sequence of the catalysts studied according to their activity in NO reduction with propene and NO decomposition suggests that similarly active complexes participate in both these processes. In the monooxide catalysts such active complexes are well dispersed metal oxides. In the most active double oxide copper-manganese catalyst the most probable active complex is the spinel $CuMn_2O_4$. As follows from Fig. 2, the maximum activity of the copper-manganese catalyst is achieved at the weight ratio Cu/Mn = 1/2, almost the same as the proportions of copper and manganese in the spinel $CuMn_2O_4$. In a mixture of unsupported CuO-MnO oxides, they react forming spinel at 500 °C [10]. The reaction starts at 400 °C, but above 500 °C the spinel structure becomes more crystalline. Such spinel was reported on Cu-Mn catalysts supported on γ-Al_2O_3 [11]. The MgF_2 support was found to favour the reaction between the copper and manganese oxides towards the spinel formation as it was reported. According to our XRD study, calcination of CuO-MnO supported on MgF_2 at 400 °C leads to the appearance of the crystalline $CuMn_2O_4$ phase [12]. It seems reasonable to suppose that the amorphous spinel phase appears already in lower temperatures. To sum up, the well-dispersed amorphous-crystalline copper-manganese spinel is the most active phase catalysing NO reduction with propene and NO decomposition.

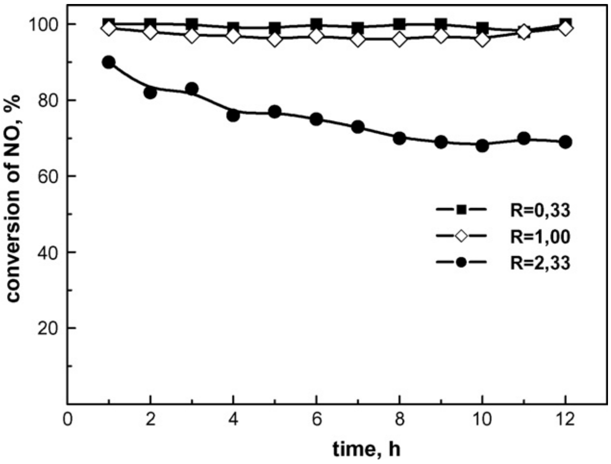

Fig. 4. The changes in the activity of Cu_2Mn_4/F-4 catalyst in the NO reduction by propene in different reduction conditions with the time on stream.

4. Conclusions

1. MgF_2 is a very good and promising support for transition metal oxides active in the NO reduction by propene and NO decomposition.
2. In these two reactions the most active catalysts are those containing copper oxide.
3. Manganese oxide has been found the best additive for the copper catalysts from among the oxides studied.
4. The active phase in the copper-manganese catalyst is the $CuMn_2O_4$ spinel.

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