Catalysis by Coordinatively Unsaturated Surface Compounds of Chromium(II), Iron(II), Cobalt(II) and Nickel(II) on Silica Gel. II. Decomposition of N_2O, Reduction of N_2O by CO and Oxidation of CO by O_2

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The coordinatively unsaturated surface compounds of chromium(II), iron(II), cobalt(II) and nickel(II) on silica gel catalyse the reduction of N_2O by CO, the oxidation of CO by O_2 and, with the exception of chromium(II), the decomposition of N_2O. No simple increase or decrease of the catalytic activity was observed in the series from chromium to nickel. On the basis of the chemisorption of N_2O, CO and O_2 by the surface compounds reaction mechanisms are discussed including the reduction of NO by CO.

In the first paper of this series[1] we reported the catalytic activity of the four coordinatively unsaturated surface compounds of chromium(II),[2] iron(II),[3] cobalt(II)[4] and nickel(II)[5] on silica gel for the decomposition of NO and the reduction of NO by CO.

On the basis that firstly CO,[2-5] and N_2O[6] in the case of chromium(II), are known to be chemisorbed by the coordinatively unsaturated surface compounds and secondly that O_2 reacts with some of these compounds (chromium(II),[2] iron(II)[3]), catalytic reactions may be expected. In fact for cobalt(II), the catalytic oxidation of CO by O_2 has been observed previously.[4]

EXPERIMENTAL

The preparation of the catalyst samples has been described previously for chromium(II),[1] iron(II),[3] cobalt(II)[4] and nickel(II).[5] The metal content of the samples was 0.7 % for iron(II) and 0.6 % for the others.

The catalytic reactions were performed with the samples placed in a column with an inner diameter of 8 mm, a heated length of 200 mm and an effective sample mass of about 6 g. The gases were dried before entering the column by a molecular sieve and phosphorus pentoxide. The gas flow was adjusted to 10 ml/min for N_2O (N_2O decomposition), 5 ml/min for both N_2O and CO (N_2O reduction by CO), 2 ml/min for O_2 and CO with 16 ml/min for N_2 (CO oxidation by O_2) and 12, 5 and 3 ml/min for CO, N_2O and NO, respectively (N_2O/NO reduction by CO).

N_2O, NO, N_2, CO and O_2 were determined using a Perkin-Elmer F 17 gas chromatograph equipped with a separation column filled with molecular sieve 13 X, mesh 45/60.

RESULTS

N_2O decomposition. During the decomposition of N_2O only one reaction occurs:

$$N_2O \rightarrow N_2 + \tfrac{1}{2}O_2$$

In contrast to the NO decomposition[1] the catalytic activity is higher for cobalt(II) than for iron(II) and is also higher for all three surface ions than for the decomposition of NO (Fig. 1). As in the case of the NO decomposition, the oxygen produced destroys the surface compound of chromium(II) by oxidising it to chromium(VI) and therefore no catalytic activity was observed in this case.

N_2O reduction by CO. Only one reaction occurs also during the reduction of N_2O by CO:
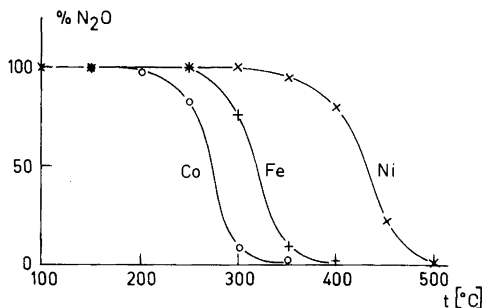
$$N_2O + CO \rightarrow N_2 + CO_2$$
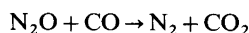
Fig. 1. Decrease of N_2O over iron(II), cobalt(II) and nickel(II) on silica gel as a function of temperature for the decomposition of N_2O.

The nickel(II) surface compound has a relatively high catalytic activity in this reaction, while the three other surface ions show the same order when compared to the reduction of NO by CO (Fig. 2). Again the catalytic activity is higher for the reduction of N_2O than for NO.

Oxidation of CO by O_2. Also here only one reaction has to be considered:

$$O_2 + 2CO \rightarrow 2CO_2$$

During this reaction the highest activity is shown by iron(II), followed by nearly equal activity for chromium(II) and nickel(II) (Fig. 3). Cobalt(II) has the lowest activity.

In Fig. 3 the catalytic activity of a sample of iron(II) pretreated in a vacuum at 300 °C (low compared with the pretreatment temperature of 1000 or 800 °C (Cr) for the other samples used in this work) is shown to be very low. In fact, the catalytic activity increases only when the tempera-
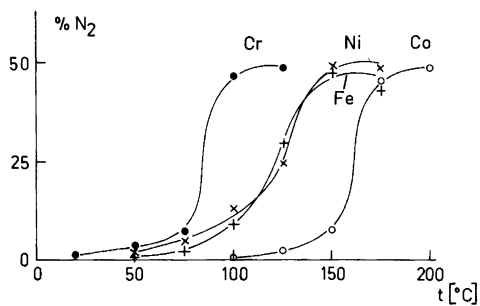

Fig. 2. N_2 production by N_2O reduction with CO over chromium(II), iron(II), cobalt(II) and nickel(II) on silica gel as a function of temperature.
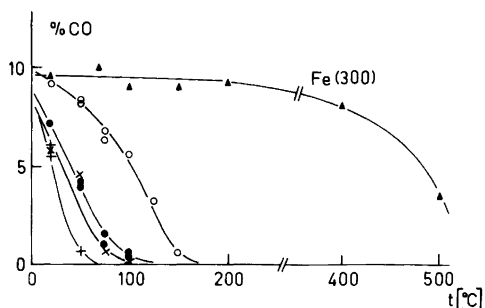

Fig. 3. CO decrease during oxidation of CO by O_2 over chromium(II), iron(II), cobalt(II) and nickel(II) on silica gel (pretreatment at 1000 °C/10^{-2} Torr) and iron(II) (pretreatment at 300 °C) *versus* temperature.

ture is raised to a value at which the coordinatively unsaturated iron(II) surface compound is produced.[3] This is an indication that the coordinatively unsaturated surface ions really are the catalytic centers in this reaction. This does not hold for chromium(II) because of its oxidation to chromium(VI). On the basis of the above observation and with the results of both the NO decomposition and the NO reduction by CO[1] in mind, the conclusion that the coordinatively unsaturated surface compounds are the catalytic centers is thought to be valid also for the other two catalytic reactions above.

Combined reduction of NO and N_2O by CO. For the NO reduction by CO the problem of whether N_2O is only a reaction product formed in a distinct temperature region[1,7] or an intermediate reaction product[8,9] is still not resolved in a satisfactory way. For this reason the combined reduction of NO and N_2O by CO was examined. Three reactions may occur:

1. $2 NO + 2CO \rightarrow N_2 + 2 CO_2$
2. $2 NO + CO \rightarrow N_2O + CO_2$
3. $N_2O + CO \rightarrow N_2 + CO_2$

This catalytic reaction was only examined with iron(II). As Fig. 4 shows the N_2O only reacted after all NO had been transformed to N_2O (or N_2), although the reaction of N_2O alone with CO takes place at a lower temperature than that of NO with CO. This indicates that as long as NO is not transformed entirely it is bound to the catalytic active sites and blocks them.
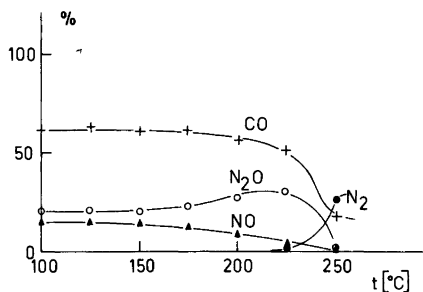
Fig. 4. Combined reduction of NO and N_2O by CO over iron(II) on silica gel versus temperature.

Scheme 1.

DISCUSSION

During the reduction of NO by CO, the first product after raising the temperature is N_2O (later replaced by N_2) while during decomposition of NO only N_2 is produced. In contrast to this difference the catalytic activity decreases nearly in the same order from chromium(II) to nickel(II) (reduction of NO by CO) or from iron(II) to nickel(II) (decomposition of NO). This may point to a reaction model in which the rate-determining step involves the same intermediate species or partly so.[1]

The catalytic activity of the three surface metal ions during the decomposition of N_2O can be correlated with the adsorption enthalpy of the N_2O chemisorption (at least qualitatively), which has the values 34, 12, 20 and 9 (arbitrary scale, 760 Torr/20 °C) for chromium(II), iron(II), cobalt(II) and nickel(II), respectively.[10] In contrast to the decomposition of NO, which reaches in the best case [iron(II)] only 75 % conversion[1] and is possibly controlled by product O_2, the decomposition of N_2O reaches 100 % (Fig. 1). While it may be concluded that during the decomposition of NO the reaction product O_2 can be readsorbed and react with the two adsorbed nitrogen atoms to yield the starting compound again, i.e. the surface compound with the two adsorbed NO molecules (Scheme 1), this cannot occur for the decomposition of N_2O.

The order of the catalytic activity between nickel(II) and cobalt(II) for the decomposition of N_2O is the reverse of that for the reduction of N_2O by CO. This may be an indication that N_2O and CO compete for adsorption at the catalytic sites. In fact the adsorption enthalpies of CO lie in the same range as those of N_2O with values of 26, 14, 20 and 28.5 (arbitrary scale, 760 Torr/20 °C) for
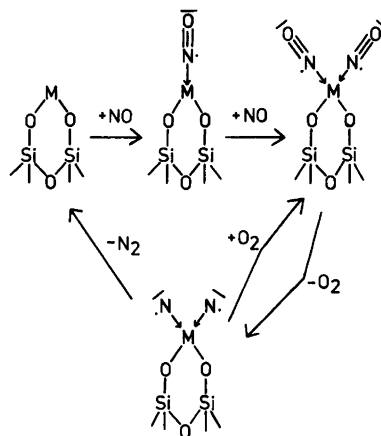
chromium(II), iron(II), cobalt(II) and nickel(II), respectively. However, a simple quantitative correlation does not exist.

Similarly, the catalytic activity of the surface ions during the oxidation of CO by O_2 may be explained by the assumption that for cobalt(II) and nickel(II) CO is predominantly adsorbed while for chromium(II) and iron(II) O_2 is bonded more strongly. For the latter two surface ions, chromium(II) forms by oxidation to chromium(VI) the most strongly bonded oxygen and may be relatively difficult to reduce thereafter,[2] at least when compared with the product of the oxidation or chemisorption of iron(II) and oxygen.

Fig. 4 shows that in a mixture of NO, N_2O, CO, N_2 and CO_2 the most strongly bound molecule is NO. The same was observed by measuring the adsorption enthalpies and it should be noted that this was also shown for transition metal oxide catalysts.[11] However, this does not provide a solution to the problem of whether N_2O is a necessary intermediate or only a reaction product in a certain temperature region. The following discussion may provide some arguments for the case of a reaction product in a certain temperature region only.

In Ref. 1 it was observed that only for chromium(II) does N_2O reach the peak value of nearly 33 % during the reduction of NO by CO. For iron(II) nearly 18 % (for both the preparation temperatures of 1000 and 500 °C), for cobalt(II) 25 % and for nickel(II) 21 % were found. Similar observations have been reported by other authors.[12] The best explanation for this behaviour seems to

be the assumption that while N_2O is produced, the additional reaction step to N_2 has already begun in the case of iron(II), cobalt(II) and nickel(II). Such a reaction is thought to be proof of the reaction mechanism in Ref. 1, as it seems rather unlikely that N_2O can displace NO at the catalytic active centers while NO is still in the gas mixture. However, as will be shown below, N_2O may be reduced by CO at higher temperatures under these conditions.

In Ref. 12 (Fig. 1) NO surplus (CO/NO: 1.2/1.9) was used and an unusual reaction was observed. At appropriate conditions NO was reduced almost entirely to N_2O at certain temperatures. However at higher temperatures, when the product of the reduction is N_2, NO reappeared and reached nearly half of its initial value. If N_2O is an absolute intermediate of the NO reduction then this observation would mean that N_2O disproportionates at higher temperatures than NO and N_2. Such a reaction was not observed during the decomposition of N_2O mentioned above and is most unlikely as the $N=N$ bond should be conserved. However, in the reaction mechanism where N_2O is only produced at a certain temperature region, an apparent disproportionation is occurring as the formation of N_2 is taking place after the reduction of the second NO molecule (Ref. 1).

Fig. 3 in Ref. 12 has the initial conditions $N_2O:CO:NO$ of 0.7, 1.4 and 2.2 and with increasing temperature additional N_2O is produced, as would be expected, to give ratios of the above gases of 1.2, 0.7 and 1.0 (220 °C). At 300 °C all N_2O reacts to N_2, while the amount of NO in the gas phase rises again (0, 0, 1.5). The reduction of N_2O in the presence of NO can be explained by the assumption that after

the complex with two NO molecules at the transition metal ion surface compound is formed, CO and N_2O compete for the fifth coordination site. More specifically, it may be suggested that after a CO molecule has been chemisorbed, reacted to CO_2 and a chemisorbed nitrogen atom and left the surface ion, an N_2O molecule may be chemisorbed, react to N_2 by oxidising the adsorbed nitrogen atom to NO and desorb as an N_2 molecule (Scheme 2).

This reaction mechanism does not discredit the result of the above discussion that N_2O is only a product in a certain temperature region, because in that case nearly all NO had reacted and so the basis for the above reduction does not exist.

All five catalytic reactions discussed above are known to occur also on transition metal oxides. This seems to be a basis for applying reaction mechanisms and models of the catalytic center gained for the reactions with the coordinatively unsaturated surface compounds on silica gel, as shown above, also to transition metal oxide surfaces. It may be further suggested that the coordinatively unsaturated surface compounds on silica gel may be used as "model surface sites" of transition metal oxides.
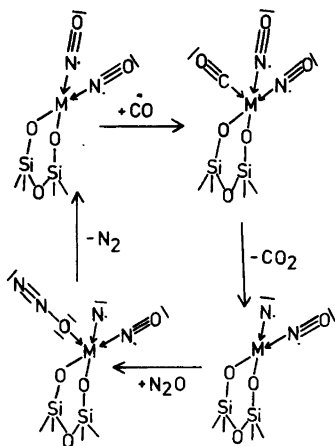
Scheme 2.

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