JOURNAL OF CATALYSIS **156**, 219–228 (1995)

Application of the Transient Response Technique to the Study of $CO + NO + O_2$ Interaction on $Cu_xCo_{3-x}O_4$ Catalysts

D. Panayotov, M. Khristova, and D. Mehandjiev

Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, 1113 Sofia, Bulgaria

Received June 3, 1994; revised April 21, 1995; accepted May 12, 1995

NO + CO interaction has been studied in the temperature range 60 to 240°C on the $Cu_xCo_{3-x}O_4$ spinels, where $x = 0.3$, 0.54, and 0.94. At temperatures up to the "light-off" temperature, where degrees of surface reduction below 50% of monolayer oxygen are realized, the formation of N_2O is an important intermediate step of the NO + CO reaction. At higher temperatures, degrees of surface reduction up to several monolayers are attained and a route of direct NO reduction to N_2 becomes important. On oxidized surfaces large amounts of NO are adsorbed which, however, are inactive towards reduction. Under oxidizing conditions the $NO + O_2 + CO$ interaction proceeds with slow reoxidation of the catalyst surface. The activity towards NO reduction even in oxidizing conditions is found to increase with increasing copper content (x). This is attributed to the enhanced capability of catalysts with $x \geq 0.5$ to accumulate reduced sites in the surface layer.

1. INTRODUCTION

Copper-containing catalysts have attracted the attention of many investigators in the past two decades because of their activity in the catalytic reduction of NO in the presence of oxygen. Recently a review on this catalytic system has been published by Bosch and Jansen (1). In the early 1970s Bauerle *et al.* (2) found that copper chromite has an activity towards the NO + CO reaction which is comparable to that of some noble metal catalysts, even in the presence of oxygen. Copper cobaltite, ferrite, and manganite in solid solution with $NiAl_2O_4$ or $ZnAl_2O_4$ have been studied by Leech and Campbell (3) in simultaneously proceeding reactions of CO and hydrocarbon oxidation, NO reduction, and water–gas shift reaction. Selective catalytic reduction of NO by hydrocarbons in the presence of O_2, SO_2, and H_2O over copper ion-exchanged zeolites has been studied by Iwamoto *et al.* (4). Selective reduction of NO by water-soluble oxygen-containing organic compounds over Cu–ZSM-5 zeolite has been proposed by Monreuil and Shelef (5). The catalytic decomposition of NO has been studied on Cu–ZSM-5 zeolites by Iwamoto *et al.* (6) and Li and Hall (7), on superconductors such as copper-containing perovskites by Shimada *et al.* (8), and on perovskite-like cuprates by Halasz *et al.* (9).

In previous papers we have shown that the spinels $Cu_xCo_{3-x}O_4$ have a higher activity towards NO reduction with CO to N_2O and N_2 than do the oxides CuO and Co_3O_4 (10, 11). We have also found that under the conditions of a stoichiometric NO + CO mixture the surface of $Cu_xCo_{3-x}O_4$ spinels is in a reduced state (11, 12).

The following stoichiometric equations present the proceeding of the catalytic process of NO reduction and the secondary process of the catalyst surface reduction:

$$2\,NO + CO = N_2O + CO_2 \quad [1]$$

$$2\,NO + 2\,CO = N_2 + 2\,CO_2 \quad [2]$$

$$M_sO + CO = M_s + CO_2; \quad [3]$$

here M_sO and M_s are the oxidized and reduced surface sites, respectively.

The reduced surface may be partially reoxidized by treatment with a NO + Ar mixture, where N_2O and N_2 are evolved in the gas phase as the products of NO reduction (11):

$$M_s + 2\,NO = M_sO + N_2O \quad [4]$$

$$2\,M_s + 2\,NO = 2\,M_sO + N_2. \quad [5]$$

In the presence of oxygen in the inlet gas flow (a $NO + CO + O_2$ mixture), the catalytic reaction

$$O_2 + 2\,CO = 2\,CO_2 \quad [6]$$

also takes place, in competition with the NO reduction.

Unsupported $CuCo_2O_4$ (13) and supported $CuCo_2O_4/\gamma\text{-}Al_2O_3$ (14) preserve, up to a certain level, their activity towards NO reduction when a stoichiometric NO + CO mixture is switched to a $NO + CO + O_2$ mixture having a 40% excess of oxidants. Under the same conditions CuO sharply loses its activity (15) irrespective of the fact that its surface is also in a reduced state under the conditions

0021-9517/95 $12.00

of a stoichiometric NO + CO mixture. Angelov *et al.* (16) have shown that the resistance of $Cu_xCo_{3-x}O_4$ catalysts to SO_2 in the CO + O_2 reaction increases substantially at x values higher than 0.3.

In the present paper the transient response technique is applied to a study of the interactions of NO + CO + Ar and NO + CO + O_2 + Ar gas mixtures with the surfaces of $Cu_xCo_{3-x}O_4$ spinels, where $x = 0.3$, 0.54, and 0.94. The aim is to elucidate the relation between the rates of the reactions of NO reduction to N_2O and N_2 and the surface state of the catalysts, as well as to find a suitable model for the inhibiting role of oxygen towards the reduction of NO.

2. EXPERIMENTAL

2.1. Sample Preparation and Characterization

A sample of $Cu_xCo_{3-x}O_4$ spinel was prepared by evaporation of an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ taken in an appropriate ratio (Cu : Co). The dry residue was ground and heated in air. The final decomposition temperature was 350°C. The method of synthesis and the data on the chemical and structural characterization of the samples were previously reported (10). The X-ray phase analysis showed that the $Cu_xCo_{3-x}O_4$ samples had a spinel structure and no additional phases were present. The BET surface area of the samples was 14 m^2/g for $Cu_{0.3}Co_{2.7}O_4$, 12 m^2/g for $Cu_{0.54}Co_{2.46}O_4$, and 4 m^2/g for $Cu_{0.94}Co_{2.06}O_4$.

2.2. Catalytic Test

The powdered $Cu_xCo_{3-x}O_4$ catalysts were previously pelleted, and then a 0.3–0.6 mm fraction was withdrawn. About 1.5 g (0.8 cm^3) of the catalyst was placed into the reactor (diameter 8 mm, catalyst layer height 15 mm).

The catalytic experiments were carried out in a flow apparatus described previously (11). The transient response method (17) was applied and a concentration step change was the technique mainly used to follow the interaction of the gas phase with the catalyst surfaces. Two gas lines assuring an alternate use of two gas flows with different compositions and concentration steps such as Ar/NO + CO + Ar, NO + CO + Ar/NO + (NO + CO) + Ar, and NO + CO + Ar/O_2 + (NO + CO) + Ar were realized. Argon (purity 99.999% vol.) supplied by Chimco, Vratza, was used as a carrier gas at a total gas flow rate of 440 cm^3/min (space velocity 33,000 h^{-1}). Nitric oxide was obtained by dropping a $FeSO_4$ solution (10% H_2SO_4) into a $NaNO_2$ solution. Carbon monoxide was prepared by dropping HCOOH into a concentrated H_2SO_4 at 110°C. Both NO and CO were then passed sequentially through a concentrated solution of NaOH and a column filled with solid KOH. The contents of N_2O, N_2, and O_2 in the NO and CO_2 in the CO were found not to exceed the sensitivity levels of the applied methods for analysis (20 ppm). Oxygen (purity 99.999% vol., from Chimco, Vratza) was used without further purification.

The catalytic reactor was placed in an oil bath with permanent mixing by a magnetic mixer. A coiled electric heater and a Pt/Pt–Rh thermocouple connected to a thermal control unit (Specac, England) were used to change or to keep constant the catalyst bed temperature regime. At a constant temperature regime the bed temperature fluctuations were found not to exceed ±1°C.

The concentrations of NO or NO_x (NO + NO_2), N_2O, CO, CO_2, and O_2 were continuously measured by gas analyzers and the data were collected by a CSY-10 personal data station. The analysis of NO and NO_2 (thermal converter for NO_x to NO) was carried out on an UNOR 5N.3 NDIR (Maihak, Germany) gas analyzer. The inlet concentration of CO was controlled by an UNOR 5 NDIR gas analyzer. The concentration of the outlet CO and CO_2 was measured by Infralyt 2106 (ex-GDR) NDIR gas analyzers. IR analysis by a Specord 75 IR spectrophotometer using a 1-m folded path gas cell (Specac, England) was performed for determining the N_2O outlet concentration. The O_2 content was measured by an electrochemical cell. A gas chromatograph (Pye Unicam, England) with a calibrated volume sampler and a column with a molecular sieve was applied to the analysis of N_2.

We have proposed (18) the so-called redox index RO as a measure of the deviation of a gas flow composition from the stoichiometric one corresponding to the interactions of the reductant CO with the oxidants NO and O_2. RO can be calculated by the following ratio of the inlet gas concentrations:

$$RO = [CO]/\{[NO] + 2\,[O_2]\}. \qquad [7]$$

A redox index equal to 1.0 corresponds to stoichiometric mixtures NO + CO or O_2 + NO + CO for the reactions [1] or [1] and [6], respectively. In this study the redox index RO was varied within the range 0.5–1.35.

To find a good step function for a particular gas (NO or CO), blank experiments were performed with a quartz insert instead of an active sample in the reactor. The transient response to the step changes Ar/NO + Ar and NO + Ar/Ar (as well as Ar/CO + Ar and CO + Ar/Ar) was found to be less than 15 sec. The quantity of the gas (NO or CO) filling or leaving the reactor volume during the transient period was estimated to be about 5 μmol at a gas concentration of 1200 ppm and a total gas flow rate of 440 cm^3/min.

Data on the quantity of a gas consumed, formed, or desorbed during the experiments were obtained by the integration of the area below the response curve.

The quantity of CO_2 formed during the reaction (3), i.e., during the interaction of CO with oxygen from the catalyst surface, was calculated on the basis of the mass balance equation

$$CO_{2(\text{catalyst reduction})} = CO_{2(\text{total})} - CO_{2(\text{NO reduction})}. \quad [8]$$

The effective degree of catalyst surface reduction may be calculated relative to unit specific surface area, because unsupported samples of the catalysts were used. Additionally, the effective degree of surface reduction may be presented as monolayers of removed oxygen by using the value approximated for the amount of oxygen contained in one monolayer of the oxide spinel surface (1.48×10^{19} atom/m^2 (19)).

Prior to the introduction of the reaction gas mixture NO + CO + Ar into the reactor, a sample of $Cu_xCo_{3-x}O_4$ was preheated in an Ar flow for 1 h at 240°C. We will call below in the text such a sample, thermally treated in an inert atmosphere, a "fresh sample." Afterwards, the temperature was decreased to the desired level, while the Ar flow was continuously fed through the reactor.

3. RESULTS AND DISCUSSION

3.1. Surface State of the $Cu_xCo_{3-x}O_4$ Catalysts and NO + CO Interaction

The interaction of a NO + CO + Ar gas mixture with the surfaces of all the $Cu_xCo_{3-x}O_4$ ($x = 0.3$, 0.54, and 0.94) spinels was studied in a set of experiments carried out successively at 60, 80, 100, 130, 170, and 240°C. The activity of a catalyst towards NO reduction to N_2O and N_2 was calculated as average rate of NO reduction, i.e., the amount of NO (in mmol) converted into N_2O or N_2 on 1 m^2 catalyst surface area per 1 h. Data on the activity of the three catalysts towards the NO reduction to N_2O and N_2 are presented in Fig. 1a. Figure 1b shows the corresponding data on the cumulative degree of catalyst surface reduction (in monolayers removed oxygen) achieved after the catalyst has worked successively at each temperature of the set 60, 80, . . . , and 240°C.

As can be seen from Fig. 1, the activity of $Cu_xCo_{3-x}O_4$ catalysts in the conversion of NO to N_2O and N_2 and also the degree of catalyst surface reduction are enhanced with an increase in the Cu content of the samples.

The character of the activity vs temperature curves for the NO reduction to N_2O (having a maximum) and to N_2 (monotonic increase) is analogous to that observed as for oxide (2, 20, 21) and for noble metal catalysts (2, 22, 23). For the three catalysts the "light-off" temperature, i.e., the temperature at which 50% conversion of NO is attained, is around 100°C. This temperature is slightly lower than the temperature (130°C) at which a maximum in the average rate of NO reduction to N_2O is observed. The correspondence between these two temperatures is suggested (22, 23) as evidence for the importance of the N_2O formation according to reaction [1] for the overall mechanism of NO reduction.

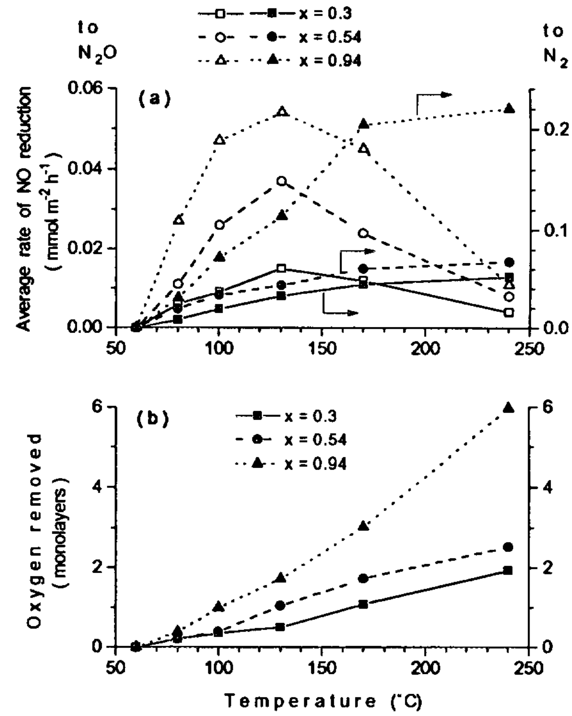

FIG. 1. Summarized results on the activity and the degree of reduction of $Cu_xCo_{3-x}O_4$ spinels attained when the steady state for both the NO + CO reaction and the catalyst reduction are achieved in a NO + CO + Ar gas mixture. (a) Temperature dependence of the average rates of NO conversion to N_2O and N_2. (b) Degree of surface reduction of the $Cu_xCo_{3-x}O_4$ spinel catalysts.

The symbatic increase in the average rate of N_2 production (Fig. 1a) and in the amount of removed surface oxygen (Fig. 1b) when the temperature is increased above the light-off temperature (100–130°C) reflects the importance of the reduced surface sites for the formation of N_2 via reaction [2] in the high-temperature region (170–240°C).

The validity of these suggestions for the NO + CO reaction proceeding on the $Cu_xCo_{3-x}O_4$ catalysts is confirmed by the transient data observed during the above experiments. In Figs. 2a and 2b the data observed at 80°C with the catalysts $Cu_{0.3}Co_{2.7}O_4$ and $Cu_{0.94}Co_{2.06}O_4$ are presented. It can be seen that with both catalysts at 80°C an interaction of CO with the catalyst surface starts first, yielding CO_2 (curve 5). Simultaneously, the rate of the catalytic conversion of NO to N_2O is accelerated and an S-shaped response is detected for the N_2O formation. The difference between curves 5 and 6 shows the part of CO_2 formed via the reaction (3), i.e., the reduction of catalyst. The start of N_2O increase (C_{N_2O}) corresponds to a degree

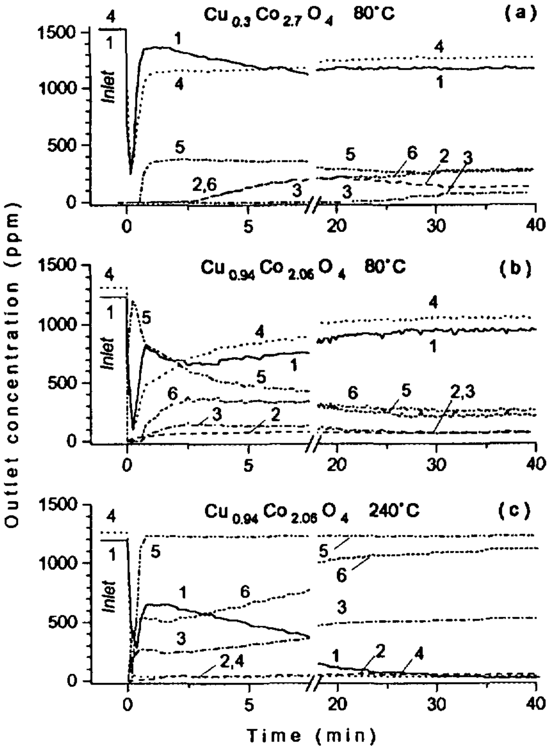

FIG. 2. Transient responses obtained after the concentration step Ar/NO + CO + Ar. (a) Catalyst $Cu_{0.3}Co_{2.7}O_4$; 80°C; NO + CO + Ar flow (1530 ppm NO + 1530 ppm CO). (b and c) Catalyst $Cu_{0.94}Co_{2.06}O_4$; 80°C and 240°C, respectively; NO + CO + Ar flow (1230 ppm NO + 1320 ppm CO). *Transient curves:* 1, NO; 2, N_2O; 3, N_2; 4, CO; 5, CO_2 (observed) total; and 6, CO_2 (calculated, Eqs. [1] and [2]) formed in the NO + CO interaction.

of 3–4% of monolayer surface reduction. In the case of $Cu_{0.3}Co_{2.7}O_4$ catalyst N_2 appears (Fig. 2a) much later than N_2O, only after extraction of about 21% of a monolayer oxygen. It is noteworthy that the increase in N_2 concentration corresponds to a decrease in N_2O concentration. In the case of $Cu_{0.94}Co_{2.06}O_4$ catalyst the start of N_2 formation is only slightly delayed. The delayed response of N_2 as compared to that of N_2O is an indication of the importance of N_2O formation as an intermediate step of N_2 formation via reaction [2]. The transient data observed with the $Cu_{0.54}Co_{2.46}O_4$ catalyst at 80°C were close to those for $Cu_{0.3}Co_{2.7}O_4$.

The transient data obtained with all three catalysts at higher temperatures (corresponding to the data shown in Fig. 1) revealed that the type of N_2O and N_2 response is changed from an S-shaped curve at 80–100°C, to a monotonic one at 130°C, and to an instantaneous one at 170–240°C. Although the N_2 response curves appeared instantaneously at 170–240°C they also contain a transient part of monotonic increase. In Fig. 2c the transient data observed with the $Cu_{0.94}Co_{2.06}O_4$ catalyst at 240°C are presented. The monotonic part of the response curves reflects the process of formation of new active surface for the catalytic reduction of NO before the attainment of a new steady state for the NO + CO reaction. Therefore, the instantaneous part of the transient responses describes the initial state of catalyst surface while the monotonic part reflects the changes in this state caused by the secondary process of catalyst surface reduction. In Table 1 the amounts of surface oxygen removed (in monolayers) at a definite temperature while the steady state for the N_2 formation is achieved are presented. From the data in Table 1 it may be deduced that at temperatures around and above 130°C the formation of the catalyst surface reduced layer governs the rate of NO to N_2 conversion during the transient period, i.e., where the degrees of reduction are around and above 0.5 of a monolayer.

We suggest that there are at least three reasons which may account for this observation. The first is that at temperatures above 130°C the mechanism of NO + CO interaction is changed so that the utilization cycles of both reactants (NO and CO) are separated on the surface, as observed in the case of CO + O_2 reaction on oxide (Co_3O_4, CuO, etc.) catalysts (24). Then the rate of catalyst reoxidation by the dissociated NO (as a stage of N_2 formation) will increase with the increase in the degree of catalyst reduction, i.e., with the increase in the number of surface reduced sites. The second reason is the change in the energy of oxygen bonding to the oxide surface (q_s). In Ref. (25) it is illustrated that the activity (reaction rate **r**) and selectivity of a wide number of oxide catalysts correlate well with q_s (lg **r** linearly decreases with q_s), when heterogeneous reactions with participation of molecular oxygen are

TABLE 1

Amounts of Surface Oxygen (in Monolayers) Reacted by CO Via Reaction [3] While the Steady State for the NO to N_2 Conversion Is Achieved at a Definite Temperature

Catalyst	Amounts of reacted surface oxygen via reaction [3] (monolayers)				
	80°C	100°C	130°C	170°C	240°C
$Cu_{0.3}Co_{2.7}O_4$	0.21 (0.21)[a]	0.15 (0.35)	0.11 (0.50)	0.25 (1.08)	0.69 (1.93)
$Cu_{0.54}Co_{2.46}O_4$	0.22 (0.22)	0.15 (0.38)	0.35 (1.05)	0.5 (1.73)	0.7 (2.57)
$Cu_{0.94}Co_{2.06}O_4$	0.20 (0.38)	0.3 (0.99)	0.4 (1.72)	1.05 (3.1)	2.1 (5.96)

Note. A stoichiometric NO + CO gas mixture and stepwise elevation of temperature are applied.

[a] In parentheses are given the values of the cumulative degrees of catalyst reduction attained at a steady state for both the NO + CO reaction and the catalyst reduction, corresponding to Fig. 1b.

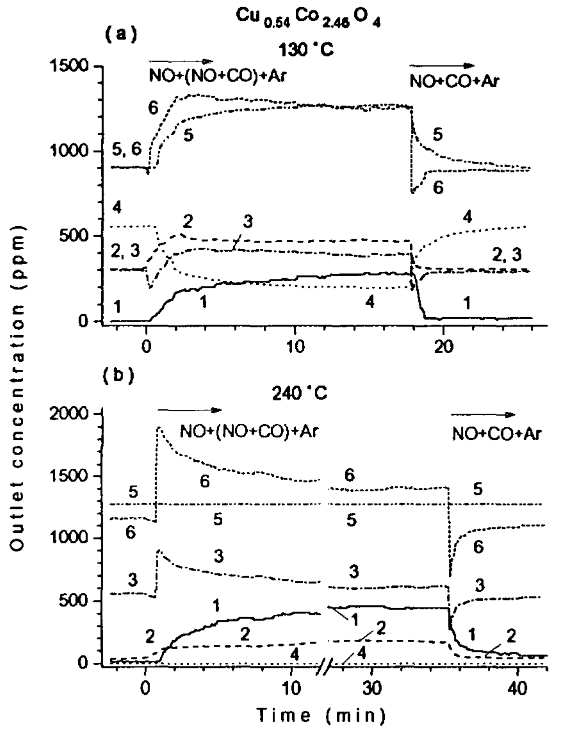

FIG. 3. Transient responses obtained after the concentration step NO + CO + Ar/NO + (NO + CO) + Ar. Catalyst $Cu_{0.54}Co_{2.46}O_4$. (a) 130°C; NO + CO + Ar flow (1210 ppm NO + 1460 ppm CO); NO + (NO + CO) + Ar flow (1990 ppm NO + 1460 ppm CO). (b) 240°C; NO + CO + Ar flow (1210 ppm NO + 1270 ppm CO); NO + (NO + CO) + Ar flow (2030 ppm NO + 1270 ppm CO). *Transient curves:* 1, NO; 2, N_2O; 3, N_2; 4, CO; 5, CO_2 (observed) total; and 6, CO_2 (calculated, Eqs. [1] and [2]) formed in the NO + CO interaction.

considered. This also concerns the reactions of NO and N_2O decomposition (25). In general, the value of q_s increases when the degree of oxide reduction is increased (in the cases of Co_3O_4, CuO, etc.). The third reason is that at these temperatures and high degree of reduction a diffusion of oxygen from the catalyst bulk to the catalyst surface may proceed with remarkable rate (which is also related to the q_s). Hence oxygen left by dissociated NO on the active (reduced) surface sites and oxygen migrated to these sites will compete for the interaction with CO which will cause a retardation of N_2 formation.

The above hypothesis that the dissociation of NO molecules may be a stage of the reaction mechanism of NO reduction was examined in separate experiments. In these experiments the concentration of NO in a NO + CO + Ar gas mixture was increased above the stoichiometric value by additional feed of NO. A redox index of RO = 0.75 was realized; i.e., a 25% excess of NO was supplied according to the stoichiometry of reaction (2) (NO to N_2 conversion). The experiments were carried out at 130 and 240°C with fresh samples of the catalyst $Cu_{0.54}Co_{2.46}O_4$ and the results are presented in Figs. 3a and 3b, respectively. Before the experiments the steady state for both the NO + CO reaction and the catalyst reduction was attained.

At both temperatures (130 and 240°C), the increase in the inlet concentration of NO causes an increase in the outlet concentration of both products of NO reduction (N_2O and N_2). The fact that curves 6 are overlying curves 5 indicates that NO is converted not only via reaction with CO (as measured by CO_2 formation, curve 5) but also by reoxidation of catalyst surface (as measured by the difference between curves 6 and 5).

At 130°C (Fig. 3a) a false start transient response (initial decrease before growing) is observed for the N_2 formation. According to Kobayashi (17) this is an indication that the reactant (nitric oxide) inhibits the product (nitrogen) formation. This means that the NO is adsorbed on free reduced sites which are needed for NO dissociation. On the other hand, the fact that the N_2O response precedes that of the N_2 response suggests that the formation N_2O may be a stage of N_2 formation.

At 240°C (Fig. 3b) an overshot type of response is observed for N_2, while the N_2O response shows some induction period, after which it monotonically increases. According to Kobayashi (17) an overshot type of response for a product (N_2) may be observed when the concentration of surface active sites is decreased during the reaction. In our case the number of surface reduced sites decreased because of their reoxidation by dissociated NO, as no CO was available to keep the surface in a reduced state (CO is fully consumed, curve 4). At the end of the NO + (NO + CO) + Ar stage (Fig. 3b) the amount of oxygen transferred from NO to the catalyst surface is significant, about 40% of a monolayer. However, the NO to N_2 reduction at the expense of catalyst reoxidation continues to proceed, as shown by curves 3 and 6.

When the opposite step NO + (NO + CO) + Ar/NO + CO + Ar is realized (Figs. 3a and 3b), the steady-state concentrations of N_2O and N_2 (characteristic for the NO + CO + Ar flow) are restored, but that of N_2 happens more slowly. The fact that curve 5 is overlying curve 6 indicates that restoration of the catalyst surface reduced state proceeds.

It was previously reported (11) that the reduced surface of $Cu_xCo_{3-x}O_4$ catalysts via NO + CO reaction may be only partially reoxidized by a treatment with a NO + Ar mixture. In this study we examine how an intermediate stage at fully oxidizing conditions (treatment with an O_2 + Ar gas flow) would influence the NO + CO reaction. This is also of practical interest concerning the NO_x neutralization. The study was performed with a fresh sample of the $Cu_{0.54}Co_{2.46}O_4$ catalyst at 240°C and the results are presented in Fig. 4. Previously, the sample was treated with a NO + CO + Ar mixture (with a stoichiometric composition) until the steady state for both NO + CO reaction and catalyst reduction was attained (4 monolayers

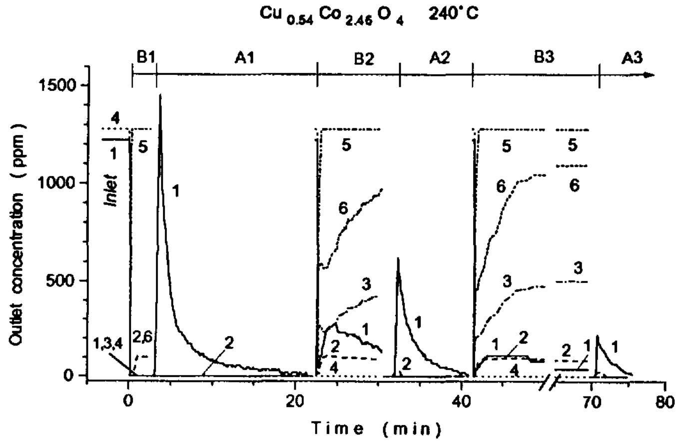

FIG. 4. Transient responses obtained at 240°C with the $Cu_{0.54}Co_{2.46}O_4$ catalyst during consequent concentration steps Ar/NO + CO + Ar. The catalyst has been previously reacted with a NO + CO flow until a steady state is achieved and then reoxidized for 1 h with an O_2 + Ar (550 ppm O_2) gas flow. A1–A3 stages with an argon flow; B1–B3 stages with a NO + CO + Ar flow (1230 ppm NO + 1280 ppm CO). *Transient curves:* 1, NO; 2, N_2O; 3, N_2; 4, CO; 5, CO_2 (observed) total; and 6, CO_2 (calculated, Eqs. [1] and [2]) formed in the NO + CO interaction.

of removed oxygen). The sample was then partially reoxidized by an O_2 + Ar flow (550 ppm O_2) for 1 h, so that only about 2 monolayers of surface oxygen were restored. After that, consequent reaction stages with a NO + CO + Ar flow (Fig. 4, B1–B3) and desorption stages with an Ar flow (Fig. 4, A1–A3) were carried out. In the first stage with the NO + CO + Ar gas flow (Fig. 4, stage B1) carbon monoxide is instantaneously converted into CO_2 on the partially reoxidized surface of the $Cu_{0.54}Co_{2.46}O_4$ catalyst. Although NO was fully consumed, only a low concentration of N_2O was registered and no N_2 was formed. During the first desorption stage (A1) a large amount of NO was desorbed (56 μmol NO) which was by a factor of 20 larger than that observed at a steady state for the NO + CO reaction. In the next reaction stages (B2 and B3) up front of the addition of NO + CO an instantaneous response with a following monotonic part was observed for N_2. The instantaneous response of N_2 in the stage B2 indicates that reduction of NO to N_2 may proceed only after desorption of NO previously adsorbed on the oxidized surface (in the first stage B1). The monotonic part of the N_2 response observed during reaction stages B2 and B3 reflects the restoration of catalyst surface reduced state, as was discussed above. Although at the end of the third stage (B3) the amount of extracted oxygen was 0.7 of a monolayer the amount of desorbed NO was still larger (by a factor of 3) than that at a steady state.

Therefore, when NO + CO + Ar mixture is fed to oxidized surfaces of $Cu_xCo_{3-x}O_4$ catalysts large amounts of NO are initially adsorbed even at high temperatures (240°C). Such high-temperature adsorption forms of NO are not surprising. In TPD experiments with $CuCo_2O_4$ (12) we have observed a desorption peak of NO with a T_{max} = 130°C and a wide shoulder of NO up to 270°C. Hierl *et al.* (26) have found that on an oxidized surface of copper–alumina spinel NO is adsorbed as nitrito and nitrato complexes, decomposing with evolution of NO_{gas} at high temperatures (desorption peaks at 217 and 412°C, respectively). Therefore, from the above results it may be deduced that the adsorption forms of NO on oxidized Cu_x-$Co_{3-x}O_4$ surfaces are inactive for the reduction of NO to N_2.

3.2. Surface State of the $Cu_xCo_{3-x}O_4$ Catalysts and NO + CO + O_2 Interactions

This study was performed with all three $Cu_xCo_{3-x}O_4$ catalysts. A set of consequent experiments was carried out at 130, 170, and 240°C. In the first experiment (at 130°C) fresh samples of the catalysts were used. Successive stages of Ar/NO + CO + Ar/O_2 + (NO + CO) + Ar/NO + CO + Ar were applied at each temperature. The concentration of O_2 in the O_2 + (NO + CO) + Ar mixtures was 650 ppm O_2, so that the feed composition contained about 50% excess of oxidants (redox index RO = 0.51). First, at each temperature a catalyst was treated with a NO + CO + Ar mixture. After achievement of steady states for both the NO + CO reaction and the catalyst reduction the concentration step change NO + CO + Ar/O_2 + (NO + CO) + Ar was performed. So the initial reduced state of a catalyst at a given temperature corresponds to that shown in Fig. 1b. The duration of the O_2 + (NO + CO) + Ar stage in all cases was 1 h.

At the three temperatures studied (130, 170, and 240°C) when oxygen was added to the NO + CO + Ar flow it was instantaneously and fully consumed with all the catalysts. Carbon monoxide was fully converted to CO_2. The material balance for O_2, NO, and CO consumption and N_2O, N_2 and CO_2 production showed that part of the oxygen (originating from O_2 and/or NO) is accumulated on the catalyst surface. As a consequence of this the surface oxidation state increases and the NO + CO reaction is perturbed. In Figs. 5a and 5b the transient data observed with the $Cu_{0.54}Co_{2.46}O_4$ catalyst at 130 and 240°C, respectively, are shown. In Fig. 6 data on the conversion degrees of NO to N_2 obtained during the O_2 + (NO + CO) + Ar stages are summarized and they are presented as a function of the amount of oxygen transferred to the catalyst surfaces.

At 130 and 170°C the rates of both reactions of NO reduction (to N_2O and N_2) gradually and simultaneously decrease. In the cases of $Cu_{0.3}Co_{2.7}O_4$ and $Cu_{0.54}Co_{2.46}O_4$ catalysts this decrease falls to zero. This is shown in Fig. 5a for the $Cu_{0.54}Co_{2.46}O_4$ catalyst at 130°C. In the case of

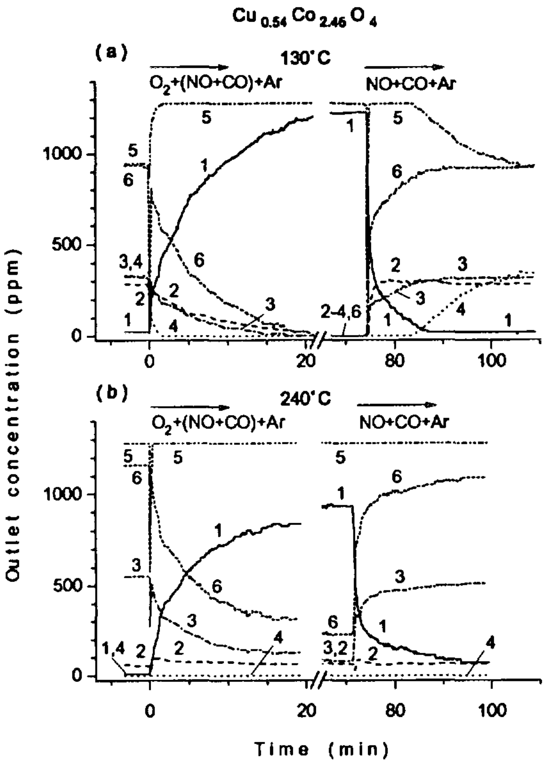

FIG. 5. Transient responses obtained with the $Cu_{0.54}Co_{2.46}O_4$ catalyst during the concentration steps NO + CO + Ar/O_2 + (NO + CO) + Ar/NO + CO + Ar; NO + CO + Ar flow (1230 ppm NO + 1280 ppm CO); O_2 + (NO + CO) + Ar flow (1230 ppm NO + 1280 ppm CO + 650 ppm O_2), RO = 0.51; (a) 130°C; (b) 240°C. *Transient curves:* 1, NO; 2, N_2O; 3, N_2; 4, CO; 5, CO_2 (observed) total; and 6, CO_2 (calculated, Eqs. [1] and [2]) formed in the NO + CO interaction.

$Cu_{0.94}Co_{2.06}O_4$ catalyst the concentrations of N_2O and N_2 decreased only to some intermediate level.

At 240°C with all the three catalysts (as shown in Fig. 5b for $Cu_{0.54}Co_{2.46}O_4$) the rate of NO reduction to N_2O was initially even slightly increased under oxygen addition to a NO + CO + Ar flow, but after that almost constant low concentrations were measured. The rate of NO to N_2 reduction gradually decreases to some level for the time of experiments (1 h). As shown in Fig. 6 the quasi-steady-state conversion of NO to N_2 is higher for the $Cu_{0.94}Co_{2.06}O_4$ catalyst (25%) and almost equal (17%) for the $Cu_{0.3}Co_{2.7}O_4$ and $Cu_{0.54}Co_{2.46}O_4$ catalysts.

The data in Fig. 6 also show that the conversion of NO to N_2 decreases exponentially with the increase in the amount of oxygen transferred to the catalyst surface. The dotted curves in Fig. 6 present an exponential fit of data by the equation $\eta = \eta_{\mathrm{st.st.}} + A \exp(-O_{\mathrm{tr.}}/t)$, where $\eta_{\mathrm{st.st.}}$ is the quasi-steady-state conversion of NO to N_2, $O_{\mathrm{tr.}}$ the amount of oxygen transferred in monolayers, and A, t are fitting parameters. Most probably the exponential decrease of η with increasing $O_{\mathrm{tr.}}$ reflects a linear relation between the energy of oxygen bonding (q_s) and $O_{\mathrm{tr.}}$, because η is proportional to $\exp(q_s)$ (25), but we have no data to confirm this suggestion. With the $Cu_{0.3}Co_{2.7}O_4$ and $Cu_{0.54}Co_{2.46}O_4$ catalysts the conversion of NO to N_2 falls to zero at achievement of about 0.35–0.4 of a monolayer at 130°C and around 0.75–0.8 of a monolayer at 170°C. These values are less than the corresponding steady-state degrees of catalyst reduction attained with NO + CO mixture (see Fig. 1b); i.e., the initial oxidation state of catalysts is only partially restored. At 240°C quasi-steady-state conversions of NO to N_2 are attained around 0.9 of monolayer oxygen transferred. With the $Cu_{0.94}Co_{2.06}O_4$ catalyst, quasi-steady-state conversions of NO to N_2 are attained at about 0.2 of monolayer at 130°C, 1.5 monolayers at 170°C and 0.8 of monolayer at 240°C.

After the back switch of gas flows O_2 + (NO + CO) + Ar/NO + CO + Ar both reactions of NO reduction (to N_2O and N_2) respond instantaneously, as shown in Fig. 5. However, the steady-state concentrations of N_2 are achieved only after restoration of the surface reduction state characteristic for the NO + CO reaction. The difference between curves 5 and 6 corresponds to the part of

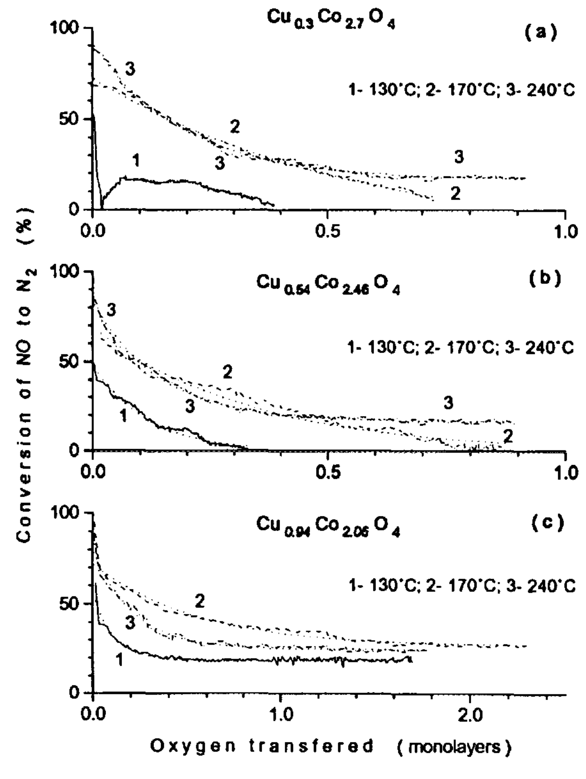

FIG. 6. Changes in the conversion of NO to N_2 with the increase in the amount of transferred oxygen after the concentration step NO + CO + Ar/O_2 + NO + CO + Ar. Consecutive experiments carried out at 130, 170, and 240°C. The duration of the O_2 + NO + CO + Ar stage is 1 h and the conditions are identical to those in Fig. 5. 1, 130°C; 2, 170°C; 3, 240°C.

CO_2 which is formed via reaction [3], i.e., via depletion of surface oxygen (by CO) left on the catalyst surface during the NO + O_2 + CO interaction. The calculations showed coincidence between the amounts of oxygen transferred to the surface during the NO + O_2 + CO reaction and that afterwards extracted during the NO + CO reaction.

From the above results it may be suggested that when the NO + O_2 + CO interaction proceeds on $Cu_xCo_{3-x}O_4$ catalysts under oxidizing conditions (RO < 1) at temperatures of 130°C and above, the effect of oxygen on the NO + CO reaction cannot be explained by a blockage of the active sites for NO adsorption and reduction. If this were the case, then a sharp (instantaneous) decrease of the rates of NO reduction to N_2O and N_2 should be observed. Such a blocking effect of oxygen has been previously established by us in the case of CuO (15). A blocking effect of oxygen is also reported for some oxide catalysts, such as Cr_2O_3 (27, 28), CuO, and Co_3O_4 (29).

When the total concentration of oxidants (NO and O_2) exceeds the stoichiometric value required for interaction with CO according to reactions [1–3], oxygen gradually oxidizes the reduced catalyst surface and hence the centres responsible for the adsorption and activation of the NO molecule. In this way oxygen inhibits the reactions of NO reduction. The inhibiting effect of oxygen depends on the ability of a catalyst to accumulate reduced sites under stoichiometric (or reducing) conditions. The catalyst $Cu_{0.94}Co_{2.06}O_4$, having the highest capacity to accumulate reduced centres during the treatment with a NO + CO flow, has the highest activity for NO reduction in the presence of oxygen at temperatures 130–240°C.

On the basis of the results in this study it may be assumed that for the NO + CO reaction proceeding on $Cu_xCo_{3-x}O_4$ catalysts the overall scheme which is valid is that proposed by Gassan-zade *et al.* in the case of Cr_2O_3 (21) and also recently reported by Cho *et al.* (22) in the case of supported rhodium. According to this scheme, in addition to Eqs. [1] and [2], the following equation is assumed:

$$N_2O + CO \rightarrow N_2 + CO_2. \qquad (9)$$

The route of N_2 formation via reactions [1] and [9], i.e., via formation of N_2O as an intermediate step, is realized at low temperatures (below the light-off temperature) and also when low degrees of surface reduction are achieved. At high temperatures (130°C and above) and when the degrees of catalyst surface reduction are above 50% of monolayer oxygen removed the direct route of N_2 formation becomes important. At low temperatures and on oxidized surfaces creation of surface reduced sites is also needed for the adsorption of the NO molecule in an active form, and for the reduction of N_2O to N_2. In these cases N_2O and N_2 responses coincide well (with the second response being always retarded). At high temperatures and when highly reduced surfaces are achieved, direct dissociation of NO molecule on reduced centres is possible and reaction (2) is realized.

The correlation between the Cu content in the $Cu_xCo_{3-x}O_4$ samples and their activity towards NO reduction to N_2O and to N_2 and selectivity for N_2 formation, in NO + CO and in NO + O_2 + CO interactions, may be attributed to the capability of the catalysts to accumulate reduced centres.

An analogous relationship between the degree of catalyst reduction by CO and its resistance towards a poisoning effect of SO_2 on the CO + O_2 reaction has been found by Angelov *et al.* (16) for a series of $Cu_xCo_{3-x}O_4$ catalysts where $0 < x < 0.9$.

It should be pointed out that the catalytic activity of oxide spinels $M_I(M_{II})_2O_4$ (M_{II} = Fe, Mn, Cr, Co) is found to be mainly dependent on the nature of the octahedrally coordinated M_{II}^{3+} cations in the reactions of molecular oxygen isotopic exchange (30), oxidation of hydrogen and methane (31). For the decomposition of N_2O on $Ni_xMg_{1-x}Al_2O_4$ it is reported (32) that the catalytic activity of surface Ni^{2+} ions, which are exposed from octahedral sites of the spinel matrix, considerably exceeds the activity of surface Ni^{2+} ions exposed on tetrahedral sites. Recently, an analogous conclusion has been derived for the activity of $ZnMn_2O_4$, $ZnCo_2O_4$, and $CoAl_2O_4$ in gas-phase nitrobenzene reduction (33). It is also found that the activity of $Mn_xZn_{1-x}Al_2O_4$ spinels increases with x as does the content of Mn^{3+} in the octahedral position.

For the $Cu_xCo_{3-x}O_4$ spinels it was earlier established by magnetic susceptibility measurements (34), X-ray (35), and neutron diffraction (36) that they are partially inverted,

$$Cu_{x-y}^{2+}Co_{1-x}^{2+}Co_y^{2+}[Co_{2-y}^{3+}Cu_y^{2+}]O_4^{2-}, \qquad [10]$$

where $y > 0$ at $x > 0.3$. Hence, for the spinels with x above 0.3 the Co^{3+} and Cu^{2+} cations will reside together in the octahedral positions.

In Ref. (19) it was reported that for the $Cu_xCo_{3-x}O_4$ spinels the amount of the most reactive surface oxygen (that in the first monolayer) towards the reduction by CO increases sharply and the activation energy decreases with increasing copper content at $x \geq 0.5$. This is related to the increased ratio of Cu/Co in the surface layer (XPS study) as compared to the bulk for the samples with $x \geq 0.5$. In an XPS study (37) of the same series of $Cu_xCo_{3-x}O_4$ spinels a high-energy shoulder in the O 1*s* peak is observed whose area increases in direct proportion to the copper content. Therefore, the coexistence of Cu^{2+} and Co^{3+} in octahedral positions lessens the oxygen transfer to and from the catalyst surface even at low degrees of reduction (first monolayer oxygen). In this way an enhancement of the rates of catalytic reactions should occur when oxygen exchange with catalyst surface is an important stage of the reaction mechanism.

Hence, the increase in the activity of $Cu_xCo_{3-x}O_4$ spinels with increasing x for the reduction of NO may be rationalized if one assumes that the formation of surface reduced centres such as Cu^+ and Co^{2+} (both in octahedral positions) lessens the activation of the NO molecule and its interaction with CO to N_2O and N_2. Indeed in Ref. (12) a band at 2130 cm^{-1} is observed for CO adsorption on reduced surface of $CuCo_2O_4/Al_2O_3$ which was attributed to the Cu^+CO species. The intensity of this band drops instantaneously to zero when NO is admitted to a CO + He gas flow.

4. CONCLUSIONS

NO + CO and NO + O_2 + CO reactions on the $Cu_xCo_{3-x}O_4$ spinels (x = 0.3, 0.54, and 0.94) have been studied by the transient response technique. It is found that with increasing copper content the degree of surface reduction increases, which in turn favours NO conversion even in oxidizing conditions. A direct correlation is observed between the surface redox processes and the NO and CO conversions. During a stepwise elevation of temperature (60–240°C) at temperatures up to light-off temperature (100–130°C) the degrees of surface reduction are below 50% of a monolayer of oxygen and the formation of N_2O is an important intermediate step of the NO + CO reaction. In this temperature region the transient response data showed a coincidence of the responses of N_2O and N_2 owing to the consequence of the conversions of NO to N_2O and N_2O to N_2. At higher temperatures (above 130°C) degrees of surface reduction above one monolayer are attained and a route of direct NO reduction to N_2 becomes important. In this temperature region the transient responses of N_2 are much influenced (as compared to the responses of N_2O) due to the formation of a surface-reduced layer (in a NO + CO mixture) or to the reoxidation of surface (in NO + (NO + CO) + Ar and O_2 + (NO + CO) + Ar mixtures).

On oxidized surfaces large amounts of NO are adsorbed which, however, are inactive towards NO to N_2 reduction.

Under oxidizing conditions (redox index RO = 0.51), the NO + O_2 + CO interaction proceeds with a slow reoxidation of the catalyst surfaces, which in turn leads to a slow decrease in the conversion of nitric oxide. Therefore, oxygen has no blocking effect on the NO + CO reaction as established in the case of CuO (15, 28), Cr_2O_3 (26, 27), Co_3O_4 (28). The ability of catalysts to preserve activity towards NO reduction in NO + O_2 + CO is found to increase with increasing copper content (x). This is attributed to the enhanced capability of catalysts with $x \geq 0.5$ to accumulate reduced sites in the surface layer.

On the basis of the results of this study and the previous results obtained with analogous series of $Cu_xCo_{3-x}O_4$ spinels (10–16, 19, 34–37), it may be generalized that the presence of copper in the octahedral sublattice of cobalt spinels with copper content $x \geq 0.5$ leads to an increased activity towards CO + O_2 and CO + NO catalytic reactions. In other words, the blocking effect of SO_2 to CO + O_2 and of O_2 to NO + CO observed with CuO and Co_3O_4 may be eliminated when a spinel $Cu_xCo_{3-x}O_4$ is applied with copper content $x \geq 0.5$.

ACKNOWLEDGMENT

Financial support for this work from the Foundation for Scientific Investigations at the Ministry of Sciences and Education, Project X-411, is gratefully acknowledged.

REFERENCES

1. Bosch, H., and Jansen, F., *Catal. Today* **2,** 369 (1988).
2. Bauerle, G., Service, G., and Nobe, K., *Ind. Eng. Chem. Prod. Res. Develop.* **11,** 54 (1972).
3. Leech, C. A., and Campbell, L. E., *Adv. Chem. Ser.* **143,** p. 161, 1975 (Catal. Control Autom. Pollut., Symp., Washington, D.C., 1974).
4. Iwamoto, M., Mizuno, N., and Yahiro, H., *in* "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L. Guczi, F. Solymosi, and P. Tétényi, Eds.), p. 1285. Akadémiai Kiadó, Budapest, 1993.
5. Monreuil, C. N., and Shelef, M., *Appl. Catal. B Env.* **1,** L1 (1992).
6. Iwamoto, M., Yahiro, H., Tanda, K., and Mizuno, N., *J. Phys. Chem.* **95,** 3727 (1991).
7. Li, Y., and Hall, W. K., *J. Catal.* **129,** 202 (1991).
8. Shimada, H., Miyama, S., and Kuroda, H., *Chem. Lett.*, 1797 (1988).
9. Halasz, I., Brenner, A., Shelef, M., and Ng, K.Y.S., *in* "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L. Guczi, F. Solymosi, and P. Tétényi, Eds.), p. 2201. Akadémiai Kiadó, Budapest, 1993.
10. Mehandjiev, D., Panayotov, D., and Khristova, M., *React. Kinet. Catal. Lett.* **33,** 273 (1986).
11. Panayotov, D., Mehandjiev, D., and Khristova, M., *Appl. Catal.* **34,** 48 (1987).
12. Panayotov, D., Matyshak, V., Sklyarov, A., Vlasenko, A., and Mehandjiev, D., *Appl. Catal.* **24,** 37 (1986).
13. Panayotov, D., and Mehandjiev, D., *Appl. Catal.* **34,** 65 (1987).
14. Mehandjiev, D., Panayotov, D., and Bliznakov, G., Symp. "Stickoxyde" Wien, Rep. 139, Technische Universität, Wien, 1984.
15. Panayotov, D., and Mehandjiev, D., *in* "Proceedings, 10th International Congress on Catalysis," (L. Guczi, F. Solymosi, and P. Tétényi, Eds.), p. 1539, Akadémiai Kiadó, Budapest, 1993.
16. Angelov, S., Mehandjiev, D., Piperov, B., Zarkov, V., Terlecki-Baricevic, A., Jovanovic, D., and Jovanovic, Z., *Appl. Catal.* **16,** 431 (1985).
17. Kobayashi, M., *Chem. Eng. Sci.* **37,** 393 (1982).
18. Panayotov, D., and Mehandjiev, D., *in* "Proceedings, IVth International Symposium on Heterogeneous Catalysis," Part 2, p. 255. Varna, 1979. Publishing House of the Bulgarian Academy of Sciences, Sofia, 1979.
19. Angelov, S., Zhecheva, E., and Tyuliev, G., *React. Solids* **3,** 57 (1987).
20. Shelef, M., and Otto, K., *J. Catal.* **10,** 408 (1968).
21. Gassan-zade, G. Z., Sultanov, M. Y., and Alkhazov, T. G., *React. Kinet. Catal. Lett.* **7,** 397 (1977).
22. Cho, B. K., Shanks, B. H., and Bailey, J. E., *J. Catal.* **115,** 486 (1989).
23. Ng, K. Y. S., Belton, D. N., Schmieg, S. J., and Fisher, G. B., *J. Catal.* **146,** 394 (1994).

24. Boreskov, G. K., and Marshneva, V. I., *Dokl. AN USSR* **213,** 112, (1973).
25. Golodetz, G. I., "Heterogeneous Catalytic Reactions with Participation of Molecular Oxygen." Kiev, Naukova Dumka, 1977. [in Russian]
26. Hierl, R., Urbach, H. P., and Knözinger, H., *J. Chem. Soc. Faraday Trans.* **88,** 355 (1992).
27. Shelef, M., Otto, K., and Gandhi, H., *J. Catal.* **12,** 361 (1968).
28. Gassan-Zadeh, G. Z., Wood, M. E., and Alkhazov, T. G., *React. Kinet. Catal. Lett.* **34,** 225 (1987).
29. Alkhazov, T. G., Gassan-Zadeh, G. Z., Osmanov, M., and Sultanov, Yu., *Kinet. Katal.* **16,** 1230 (1975).
30. Muzykantov, V. S., Popovskii, V. V., Boreskov, G. K., Panov, G. I., and Shrabina, R. A., *Kinet. Katal.* **13,** 385 (1972).
31. Boreskov, G. K., Popovskii, V. V., and Sazonov, V. A., *in* "Proceedings, 4th International Congress on Catalysis, Moscow, 1968" (B. A. Kazanzky, Ed.), Vol. 1, p. 343. Adler, New York, 1968.
32. Cimino, A., and Schiavello, M., *J. Catal.* **20,** 202 (1971).
33. Maltha, A., Kist, H. F., Brunet, B., Ziokowski, J., Onishi, H., Iwasawa, Y., and Ponec, V., *J. Catal.* **149,** 356, (1994).
34. Angelov, S., Zhecheva, E., and Mehandjiev, D., *Compt. Rend. Acad. Bulg. Sci.* **36,** 1403 (1983).
35. Petrov, K., Karamaneva, T., Angelov, S., and Mehandjiev, D., *Mater. Res. Bull.* **16,** 637 (1983).
36. Krezhov, K., Petrov, K., and Karamaneva, T., *J. Solid State Chem.* **48,** 38 (1983).
37. Angelov, S., Tyuliev, G., and Marinova, Ts., *Appl. Surf. Sci.* **27,** 381 (1987).