Low-Temperature CO Oxidation over Co₃O₄/Al₂O₃

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The oxidation of CO over $\text{Co}_3\text{O}_4/\gamma$ -Al₂O₃ at room temperature (21°C) has been studied in a continuous-flow reactor system with oxidising and reducing pretreatment, at varying stoichiometric ratios, and by using isotope-labeled ¹⁸O₂. The fresh catalyst was characterised by temperature-programmed reduction and temperature-programmed oxidation. CO deactivates the oxidised catalyst but the rate of deactivation can be suppressed by having a high O₂/CO ratio. The isotope study showed that the oxygen participating in the oxidation of CO comes from oxygen bound to the cobalt oxide surface. Finally, a mechanism for the CO oxidation over Co₃O₄/ γ -Al₂O₃ is proposed. © 2000 Academic Press

Key Words: CO oxidation; low temperature; cobalt oxide; isotopelabeled oxygen; reaction mechanism; catalyst pretreatment; deactivation.

INTRODUCTION

The low-temperature CO oxidation over Co₃O₄ and other metal oxide-based catalysts has been studied by several groups (1–9). Studies of the oxidation of hydrocarbons over cobalt oxide-based catalysts also exist in the literature (10-13). Our group has previously observed that it is only preoxidised cobalt oxide catalysts that show high low-temperature activity (14). The activity over prereduced cobalt oxide is much lower. Thormählen et al. (14) reported a T_{50} (the reactor inlet temperature at which the conversion of the reactant is 50%) of -63° C for preoxidised CoO_x/Al₂O₃ compared to 157°C for the prereduced catalyst. We have also seen that the surface layer of the reduced catalyst is easily oxidised by O2(g) even at room temperature (14). The purpose of this work is to further understand the mechanisms behind the low-temperature activity of the Co₃O₄ catalyst and explain the difference in activity between the preoxidised and the prereduced catalyst.

METHODS

Catalyst Preparation

 γ -Al₂O₃ was prepared by calcining boehmite (AlOOH, Disperal from Condea, Germany) at 600°C for 8 h. The γ -

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Al₂O₃ was sieved to obtain a powder with particles between 125 and 210 μ m and a BET area of 165.4 m²/g. A 13.6 g portion of Co(NO₃)₂ · 6H₂O of pro analysi grade from Merck, Germany, was diluted in distilled water and 15.0 g of γ -Al₂O₃ powder was added to form a slurry. A 0.5 ml aliquot of 25% NH_{3(aq)} was added to raise the pH. The slurry was freeze dried for 24 h, calcined at 550°C for 90 min, and then ground to reobtain the original particle size. The BET surface of the 20 wt% Co₃O₄/ γ -Al₂O₃ catalyst thus produced was found to be 70.6 m²/g.

Reactor System

The catalyst was tested in a continuous-flow reactor system consisting of a vertical quartz tube reactor (6 mm inner diameter) placed in an oven, where the temperature could be controlled between 20 and 600°C. The temperature was measured with thermocouples upstream of the reactor bed as well as in the reactor bed. The argon was 99.9997% pure, O₂, H₂, and CO₂ 99.998% pure, and CO 99.997% pure, all supplied by Air Liquide. The ¹⁸O₂ was prepared by mixing ${}^{18}O_2$ (isotope content 96.26% ${}^{18}O$) from Larodan Fine Chemicals AB with 99.999% pure argon from AGA to obtain a 6 vol% ¹⁸O₂/argon gas mixture. The gases in the outlet of the reactor were detected by a Balzers QMS 200 quadrupole mass spectrometer. M/e=2(H₂), 28 (CO), 32 (¹⁶O₂), 36 (¹⁸O₂), 40 (Ar), 44 (C¹⁶O₂), 46 $(C^{16}O^{18}O)$, and 48 $(C^{18}O_2)$ were followed, and the signals were calibrated by flowing different concentrations of H₂, CO, O₂, and CO₂ through the empty reactor. The M/e = 28signal was corrected for contribution from CO₂ to obtain the CO concentration.

Catalyst Testing

Six different types of experiments (see Table 1) were performed:

(1) Temperature-programmed reduction (TPR) and temperature-programmed oxidation (TPO) repeated one after the other several times on the fresh catalyst.

(2) CO oxidation over the prereduced and the preoxidised catalyst, while heating it in a temperature ramp.



TABLE 1

Experiment	Pretreatment	Inlet gas composition	Temperature
(1a) TPR	None ^a /(1b)	5% H ₂	21°C to 550°C at 10 K/min
(1b) TPO	(1a)	10% O ₂	21°C to 550°C at 10 K/min
(2a) Light-off	Reduction in 5% H ₂ at 550°C	$2\% \text{ CO} + 1.17\% \text{ O}_2$	21°C to 550°C at 10 K/min
(2b) Light-off	Oxidation in 10% O ₂ at 550°C	$2\% \text{ CO} + 1.17\% \text{ O}_2$	21°C to 550°C at 10 K/min
(3) CO oxidation with different oxygen concentrations	Oxidation in $10\% O_2$ at $550^{\circ}C$	$2\% \text{ CO} + x\% \text{ O}_2;$ $x = 0.83, 1.0, 1.17, 1.5, 2.0, {}^b 3.0$	$21^{\circ}C$ and $50^{\circ}C$
(4) CO oxidation over ¹⁸ O-labeled catalyst	Reduction in 5% H ₂ followed by oxidation in 6% ¹⁸ O ₂ at 550°C	$2\% \ C^{16}O + 1.17\% \ ^{16}O_2$	21°C
(5) CO_2 exchange ^c	Same as in (4)	$1.5\% C^{16}O_2$	21°C
(6a) Deactivation	Same as in (4)	$1.67\% C^{16}O + 0.98\% {}^{18}O_2$	21°C for 90 min
(6b-1) TPD	(6a)	100% Ar	21°C to 550°C at 10 K/min
(6b-2) TPO	(6a)	10% O ₂	$21^\circ C$ to $550^\circ C$ at 10 K/min

Experimental Conditions

Note. All experiments were performed with 68 ± 2.2 mg of Co_3O_4/Al_2O_3 . The total gas flow was 20 nml/min and argon was used as balance. ^{*a*} The first TPR was performed on the fresh catalyst.

 $^{b}x = 2.0$ only performed at 50°C.

^cThis experiment was also performed on γ /Al₂O₃ (BET = 165.4 m²/g).

(3) CO oxidation with several different oxygen concentrations, over the preoxidised catalyst. The experiments were performed at 21°C and at 50°C. (See Table 3.)

(4) CO oxidation at 21° C over a cobalt oxide catalyst preoxidised with isotope-labeled ¹⁸O.

(5) Exchange of oxygen in gas-phase CO_2 over a cobalt oxide catalyst preoxidised with isotope-labeled ¹⁸O.

(6) Temperature-programmed desorption (TPD) and temperature-programmed oxidation (TPO) of the deactivated catalyst.

RESULT AND DISCUSSION

1. TPR and TPO of the Fresh Catalyst

The results from the TPR and TPO experiments are presented in Fig. 1. The TPR of the fresh catalyst (curve 1 in Fig. 1a) shows one large peak at about 432° C and a small broad peak at about 140° C. When the catalyst was oxidised and the second TPR was recorded, the main peak shifted to 370° C (curve 3). The small broad peak at 140° C was still present. The two subsequent oxidations followed by TPR did not change the TPR profile substantially. The TPR curves were integrated to get the total H₂ consumption during the reduction. The result is presented in Table 2. The TPO profile of the catalyst that has been reduced once (curve 2 in Fig. 1b) shows one large peak at about 245°C. The two subsequent reductions followed by TPO did not change the TPO profile, apart from a slight decrease in peak maximum (curves 4 and 6). The TPO curves were integrated to get the total O₂ consumption during the oxidation. The result is presented in Table 2.

As seen from the area under the TPR graph, the cobalt is only reduced to 55-62% of total reduction (Table 2).



FIG. 1. (a) Temperature-programmed reduction (TPR) and (b) temperature-programmed oxidation (TPO) of the fresh Co_3O_4/Al_2O_3 catalyst. The H_2 and O_2 consumptions are defined as inlet minus detected outlet gas-phase mole fractions. The numbers indicate the order in which the experiments were conducted.

TABLE 2

Hydrogen Consumption in TPR and Oxygen Consumption in TPO Calculated as Percentage Reduction of Co_3O_4 to Co^0 for TPR and as Percentage Oxidation of Co^0 to Co_3O_4 for TPO

TPR	Reduction (%)	TPO	Oxidation (%)	Difference (Red-Ox)
1	61.6	2	53.2	8.4
3	55.4	4	45.9	9.5
5	58.0	6	47.9	10.1
7	55.4			

Note. The numbers 1–7 correspond to the run numbers in Fig. 1.

This corresponds to a mean oxidation state of 1.0-1.2 for the cobalt after reduction at 550° C. To obtain reduction to metallic cobalt, the temperature must be raised above 550° C. Comparing the areas under the TPR and the TPO profiles, one notices a systematic difference (Table 2) between the degree of reduction and the degree of oxidation. The degree of reduction seems to be higher than the corresponding oxidation. The explanation for this difference is that, in the TPO experiment, oxygen is consumed already at room temperature during the preconditioning before the temperature ramp was started, as has been reported by Thormählen *et al.* (14).

Arnoldy and Moulijn (15) assigned reduction in the region 440-500°C to surface Co³⁺ ions or mixed Co³⁺- Al^{3+} oxidic crystallites and reduction in the region 280-380°C to Co₃O₄ crystallites. This corresponds well with the main peak in the first TPR profile (curve 1 in Fig. 1a), respectively the main peak for the repeated TPR profile after the first reduction and oxidation (curves 3, 5, and 7 in Fig. 1a). One explanation for the shift in temperature for the main peak in the TPR profile is that the first reduction followed by oxidation transforms Co³⁺ ions or mixed $Co^{3+}-Al^{3+}$ oxidic crystallites into Co_3O_4 crystallites. The Co₃O₄ crystallites are then stable in the sense that, upon subsequent reduction, the cobalt will return to crystallites again once the catalyst is oxidised. It is also possible that the difference between the first TPR (curve 1 in Fig. 1a) and the subsequent TPR (curves 3, 5, and 7 in Fig. 1a) might be due to the fact that the fresh catalyst contains impurities that are removed during the first TPR and/or TPO. These impurities might be nitrates not completely removed during the calcination, or water or hydrocarbons from the air.

2. Light-Off

The prereduced catalyst lights off with a temperature of 50% conversion, T_{50} , of 150°C. Full conversion is reached at about 265°C. The preoxidised catalyst lights off with $T_{50} = 80^{\circ}$ C. The light-off curve shows a shoulder and reaches full conversion at about 215°C. Preoxidation of the catalyst thus lowers the T_{50} by 70 K compared to prereduction. This re-

sult is in contradiction to some previous results (8, 13) where the opposite was shown, but in agreement with newer results (14). The explanation for these contradicting results may lie in the cobalt oxide catalyst's high sensitivity to water. Cunningham et al. (5) have shown that only 3 ppm of water in the gas feed increases the T_{50} by about 100 K. In the present experiments the gases were very pure and contained less than this amount. Another explanation might be the difference in volume flow rate between the present experiments and the previous ones. Here the volume flow rate (at standard conditions) per milligram of cobalt oxide was about 70 times lower than that reported in (13). An increase in flow rate will shift the T_{50} in the light-off experiments to higher temperatures, and the shift will be different for reduced and oxidised catalysts if the activation energies are different.

3. CO Oxidation with Varying O₂ Concentration

The result of the reaction between CO and O2 with varying O₂ concentration is presented in Table 3. The value S indicates the stoichiometric ratio for the reaction, i.e., $S = 2[O_2]/[CO]$. S = 1 thus corresponds to a stoichiometric mixture. It is clear that the higher the oxygen concentration (higher *S*) the higher is the CO conversion. The catalyst deactivates with time, and the deactivation is faster when the stoichiometric ratio is low. It should be noted. however, that due to the integral reactor behaviour, less deactivation would be seen at higher conversion levels. At 21°C, even with a high excess of oxygen, a certain amount of deactivation occurred, but at 50°C almost no deactivation occurred with S > 2.0. This behaviour is consistent with a reaction mechanism where CO and O2 are competing for the same sites on the catalyst surface, and where CO irreversibly blocks the sites if it cannot react with oxygen. The strength of CO blocking under reaction conditions is not

TABLE 3

Conversion in CO Oxidation Initially and after 60 Min of Reaction

	React	ion at 21°C	Reaction at 50°C	
S	Initial CO conversion (%)	CO conversion after 60 min (%)	Initial CO conversion (%)	CO conversion after 60 min (%)
0.83	74	68	77	73
1.0	87	75	91	85
1.17	90	79	97	91
1.5	92	84	98	95
2.0	а	а	98	97
3.0	92	88	98	97

Note. The reaction was performed at 21° C and at 50° C over the Co₃O₄/Al₂O₃ catalyst first oxidised in 10% O₂ at 550°C. The reaction mixture consisted of 2% CO and different concentrations of O₂, as indicated by the stoichiometric number *S. S*=2[O₂]/[CO].

^aNot measured.

known, but from reduced Co/Al₂O₃, CO desorbs at about 100°C, as known from CO-TPD (13, 16). At 21°C it will thus probably form a strongly adsorbed unreactive species, but at 50°C the rate of CO desorption is high enough to prevent CO from irreversibly blocking the cobalt sites. If the oxygen concentration is high enough, O₂ will be able to compete with CO for the free sites, whereby the rate of CO blocking is limited.

4. CO Oxidation over an Isotope-Labeled Cobalt Oxide Catalyst

The result from this experiment with an ¹⁸O-preoxidised catalyst is presented in Fig. 2. When the reaction mixture $(CO + {}^{16}O_2, S = 1.17)$ is switched on, a certain amount of isotope-labeled C¹⁶O¹⁸O is formed in addition to the formation of $C^{16}O_2$. The amount of $C^{18}O_2$ formed is negligible. After about 10 min the C¹⁶O¹⁸O decreases to zero. As no ¹⁸O is introduced in the gas phase, this means that one of the oxygens in the CO₂ formed must come from the preoxidised catalyst surface, which will be partially reduced when reacting with CO. When the surface oxygen on the catalyst is consumed, no more C¹⁶O¹⁸O can be formed, which explains why the curve decreases to zero after about 10 min. The area below the curve for these first 10 min corresponded to 6.4 μ mol of C¹⁶O¹⁸O and was related to the total number of cobalt atoms in the catalyst, giving $C^{16}O^{18}O/Co = 0.038$. As in the previous experiment, where the deactivation of the catalyst was studied, the amount of CO₂ formed decreased with time. The presence of the about 8 times larger amount of C¹⁶O₂ compared to C¹⁶O¹⁸O in Fig. 2 may indicate that only a part of the surface atoms are involved in the reaction, since the gas-phase isotope fraction should be proportional to the active site abundance.



FIG. 2. Gas phase mole fractions of $C^{16}O_2$, $C^{16}O^{18}O$, and $C^{18}O_2$ in the outlet from the reactor as a function of time for the reaction between $C^{16}O$ and ${}^{16}O_2$ at $21^{\circ}C$. The Co_3O_4/Al_2O_3 catalyst was first preoxidised with ${}^{18}O$. The shaded area corresponds to $C^{16}O^{18}O/Co = 0.038$.

5. Exchange of Oxygen between CO₂ and the ¹⁸O-Preoxidised Catalyst

When the $C^{16}O_2$ is turned on, there is a formation of C¹⁶O¹⁸O that decreases after about 10 min. The C¹⁶O₂ curve levels off at the inlet concentration, and the amount of $C^{18}O_2$ formation was negligible. The area below the C¹⁶O¹⁸O curve for these first 10 min corresponded to 4.5 μ mol of C¹⁶O¹⁸O and was, as in the previous experiment, related to the total number of cobalt atoms in the catalyst, giving $C^{16}O^{18}O/Co = 0.027$. This ratio gives a measure of the fraction of cobalt atoms involved in the exchange reaction. CO_2 is proposed to adsorb on the cobalt oxide surface and exchange oxygen with the surface via the formation of a carbonate species. Formation of carbonate species on cobalt oxide has been observed by Finocchio et al. (11) with FTIR after exposing Co_3O_4 to CO_2 . When the same experiment was performed over pure γ -Al₂O₃, formation of C¹⁶O¹⁸O was also observed during the first 10 min, corresponding to 3.1 μ mol of C¹⁶O¹⁸O. It is known that carbonates may form on alumina upon CO₂ introduction (17), and exchange between CO₂ in the gas phase and oxygen on alumina has been reported at 27° C (18). This may explain the $C^{16}O^{18}O$ on pure Al_2O_3 .

6. TPD and TPO of the Deactivated Catalyst

The reaction between $C^{16}O$ and ${}^{18}O_2$ over the ${}^{18}O_2$ oxidised catalyst resulted in the formation of the CO_2 isotopes in the proportions 29% $C^{16}O_2$, 50% $C^{16}O^{18}O$, and 21% $C^{18}O_2$. These ratios stayed constant during the 90 min that the reaction took place. As in the previous experiments, a deactivation of the catalyst as a function of time could be seen. From the results in experiment 4, where CO reacted with one oxygen in the surface cobalt oxide, one would have expected only $C^{16}O^{18}O$ formation during the reaction. Instead, large amounts of both $C^{18}O_2$ and $C^{16}O_2$ were formed besides the $C^{16}O^{18}O$. This might be due to exchange of oxygen in gas-phase CO_2 and surface oxygen (either on cobalt oxide or on the alumina), as seen in the CO_2 exchange experiment.

The results from the TPD and the TPO are presented in Fig. 3. Both TPD and TPO profiles have one peak at about 100°C. This peak contains 31% C¹⁶O₂, 49% C¹⁶O¹⁸O, and 20% C¹⁸O₂ in the TPD, and 27% C¹⁶O₂, 52% C¹⁶O¹⁸O, and 21% C¹⁸O₂ in the TPO. The different CO₂ isotope peaks are shifted somewhat in relation to each other in the order $T_{\text{peak}}(C^{16}O_2) < T_{\text{peak}}(C^{16}O^{18}O) < T_{\text{peak}}(C^{18}O_2)$. The TPO profile also has a peak at about 450°C, which contains only C¹⁶O₂. This peak is not present in the TPD profile. No CO formation was observed in either TPD or TPO.

The first peak in TPD and TPO profiles (at about 100° C) of the catalyst deactivated by the reaction between ${}^{18}O_2$ and C¹⁶O is similar in the two experiments (Fig. 3), i.e.,



FIG. 3. (a) Temperature-programmed desorption (TPD) and (b) temperature-programmed oxidation (TPO) of a mildly deactivated Co_3O_4/Al_2O_3 catalyst. The catalyst was first preoxidised with ¹⁸O and then deactivated by reacting 1.67% C¹⁶O and 0.98% ¹⁸O₂ for 90 min over it before TPD or TPO was performed.

the presence of this peak is independent of the presence of gas-phase oxygen. This indicates that it is a pure desorption peak. It is suggested that this peak is due to decomposition of surface carbonates formed during the reaction between $C^{16}O$ and $^{18}O_2$ prior to the TPD/TPO. Carbonates probably also form on the alumina support. The different CO_2 isotope peaks are shifted somewhat in relation to each other. This is probably due to a kinetic isotope effect in the decomposition of the carbonate to CO_2 (19, 20).

The second peak at about 450° C contained only C¹⁶O₂ and was present in the TPO profile but not in the TPD. This is consistent with oxidation of surface carbon, C_{surf}, with gas-phase O₂. C_{surf} might be formed in the CO disproportionation reaction (2CO \rightarrow C + CO₂), which was reported to occur over partially reduced CeO₂ at room temperature (21) and over Pt/CeO₂/Al₂O₃ at 300°C (22). It is also possible that another form of C, for example carbonate, during the TPO is transformed into graphitic C during heating of the catalyst sample.

Proposed Mechanism

From the experimental results, the following mechanism for the low-temperature CO oxidation over Co_3O_4/γ -Al₂O₃ is proposed:

(1) $CO_{(g)}$ is adsorbed on an oxidised cobalt site (probably Co^{3+}).

(2) The adsorbed CO reacts with an oxygen linked to the active Co^{3+} . CO_2 is formed and desorbs quickly. The result is a partially reduced site. The partially reduced site may consist of two Co^{2+} ions or may be regarded as an oxygen vacancy.

(3) The partially reduced site can undergo two different reactions.

(a) It can either be reoxidised by gas-phase oxygen to an active Co^{3+} site, or

(b) a CO can adsorb to the site and thus deactivate it. It is possible that the adsorbed CO thereafter undergoes dissociation or reacts with another CO to form CO_2 and C (CO disproportionation).

(4) Gas-phase CO_2 can react with the oxidised surface to form a carbonate species. The carbonate may exchange oxygen with the surface and desorb as CO_2 again.

Mechanisms similar to this have previously been proposed by, e.g., Mergler *et al.* (8) and Haruta *et al.* (3). The main difference is that the catalysts investigated also contained Pt (8) or Au (3). The authors propose that the CO is adsorbed to the Pt or Au site, while oxygen is supplied by the CoO_x . In this investigation it was shown that the reaction may take place without the presence of a noble metal, leading to the above-proposed mechanism. This redox mechanism is in accordance with what has previously been found for CO oxidation over metal oxide catalysts (1, 23).

CONCLUSIONS

The preoxidised catalyst shows higher activity for CO oxidation than the prereduced catalyst. Deactivation takes place at 21°C for the preoxidised catalyst, but the deactivation can be slowed by increasing the O₂/CO ratio. By raising the temperature to 50°C, no deactivation was seen over the preoxidised catalyst for $S \ge 2.0$. This behaviour is well explained by the above-proposed reaction mechanism. When the CO oxidation reaction proceeds, at least two forms of carbonaceous species are deposited on the catalyst. These are probably carbonates (both on the cobalt oxide and on the alumina support) and graphite-like C.

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