



Pretreatments of Co_3O_4 at moderate temperature for CO oxidation at -80°C

Yunbo Yu^{a,1}, Takashi Takei^a, Hironori Ohashi^{a,b}, Hong He^c, Xiuli Zhang^c, Masatake Haruta^{a,*}

^a Department of Applied Chemistry, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan

^b Japan Science and Technology Agency (JST), CREST, 4-1-8 Hon-cho, Kawaguchi, Saitama 332-0012, Japan

^c Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Haidian District, Beijing 100085, China

ARTICLE INFO

Article history:

Received 22 April 2009

Revised 31 July 2009

Accepted 3 August 2009

Available online 8 September 2009

Keywords:

CO oxidation

Moisture

Pretreatment

Surface oxygen vacancy

Tricobalt tetraoxide

ABSTRACT

Heterogeneous catalysts that can work at ambient temperature are useful for in-door air quality control, pure gas production for fuel cells and semiconductors, gas sensing, and so forth. Deposition of gold nanoparticles on base metal oxide is known to provide highly active catalysts for CO oxidation at temperatures below room temperature. Here we report that some select base metal oxides such as Co_3O_4 , MnO_2 , and NiO are intrinsically active catalysts for CO oxidation below 50°C when pretreated at moderate temperature between 150 and 250°C in a stream of non-reducing dry gases, for example, dry air, CO in air, or N_2 . These metal oxides are p-type semiconductors and form surface excess oxygen adsorbed at oxygen vacancies which are created by the above pretreatments.

© 2009 Elsevier Inc. All rights reserved.

1. Introduction

Heterogeneous catalysts that can work at ambient temperature are useful for in-door air quality control [1], purification of H_2 for fuel cells [2], pure N_2 and O_2 gas production from air in the semiconductor industry [3], gas sensing [4] and so forth. Until now, only methanol and its decomposed derivatives such as HCHO , HCOOH , H_2 , and CO can be oxidized at room temperature over noble metal catalysts and base metal oxide catalysts [5]. Especially, CO oxidation has been most extensively and intensively studied because it is a structure sensitive reaction and the simplest reaction for mechanistic study.

Some base metal oxides such as Co_3O_4 , NiO , and a mixture of MnO_2 and CuO (called Hopcalite) are known to be active at room temperature for CO oxidation [6], but not in the presence of moisture. We have already reported that Co_3O_4 and NiO show catalytic activity for CO oxidation below -40°C when moisture content is below 1.0 ppm [7]. Recently, Co_3O_4 nanorods calcined at 450°C have been found to exhibit surprisingly high activity for CO oxidation at -77°C even in a moist atmosphere [8]. This presents the second condition that a select base metal oxide is intrinsically active as a catalyst below room temperature when specifically active crystalline planes are preferentially exposed at the surface.

Pretreatment in oxidative or reductive atmosphere at high temperatures ($>500^\circ\text{C}$) has often been used to change the structure of the catalyst particles [9,10] in order to improve the catalytic activity. Pretreatment in air at moderate temperatures such as 200°C [11,12] has also been performed to yield clean surfaces; catalyst reconstruction during this process does not take place substantially. Sadykov and co-workers [13,14] have shown that pretreatment in He at 350°C resulted in the surface reconstruction of Co_3O_4 to enhance the formation of weakly bound oxygen species and therefore the catalytic activity. These findings have motivated us to consider that pretreatment in neutral (neither oxidizing nor reducing) atmospheres may be more effective for enhancing catalytic activity than those in oxidizing and reducing atmospheres; however, to date no work has been yet focused on this issue.

In this study, CO oxidation has been chosen to study the influence of moderate temperature pretreatments ($\leq 300^\circ\text{C}$) on the catalytic activity of pure base metal oxides. Particular attention was paid to the effect of the kinds of gases, temperature, and moisture level for the pretreatments on the catalytic activity of Co_3O_4 . Surprisingly, pretreatments in dry air and even in inert or reducing-oxidizing dry atmospheres (N_2 or CO/air) in the temperature range of 150 – 250°C dramatically enhance the catalytic activity of Co_3O_4 , MnO_2 , and NiO , when they were calcined at relatively low temperatures below 400°C . CO oxidation can take place even at a temperature as low as -80°C in the case of Co_3O_4 . This enhancement can be ascribed to the formation of surface oxygen vacancies, which may provide a novel guideline for the creation of base metal oxide catalysts with high activity at low temperatures.

* Corresponding author. Fax: +81 42 677 2821.

E-mail address: haruta-masatake@center.tmu.ac.jp (M. Haruta).

¹ Present address: Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Haidian District, Beijing 100085, China.

2. Experimental

2.1. Catalyst preparation

Tricobalt tetraoxide (Co_3O_4) was prepared by calcination at 300 °C of the precipitates obtained by adding an aqueous solution of $\text{Co}(\text{NO}_3)_2$ to an aqueous solution of Na_2CO_3 (1.2 times of the stoichiometric amount) [11]. Typically, cobalt nitrate hexahydrate [$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 98.0%, Wako Pure Chemical Industries Ltd.], 17.361 g was dissolved in 500 ml of distilled water. The aqueous solution of $\text{Co}(\text{NO}_3)_2$ was heated to 70 °C and poured into 500 ml of aqueous Na_2CO_3 solution heated at 70 °C, followed by further aging at 70 °C for 1 h. During preparation, the solution was vigorously stirred. The precipitate was thoroughly washed with distilled water and filtered. The solid obtained was dried at 100 °C overnight in air and calcined in air at 300 °C for 4 h to transform into Co_3O_4 . Other metal oxides such as Mn_2O_3 , Fe_2O_3 , and NiO were prepared in a similar manner to those for Co_3O_4 and by calcination in air at 800, 400, and 400 °C for 4 h, respectively. Active MnO_2 was prepared by the oxidation of $\text{Mn}(\text{NO}_3)_2$ in aqueous solution with KMnO_4 followed by calcination in air at 300 °C [15].

Titanium dioxide (P25, 50 m^2/g in BET surface area), Fe_3O_4 (4.8 m^2/g), CuO nanopowder (33 nm in diameter, 29 m^2/g), and CeO_2 (166.4 m^2/g) were purchased from Nippon Aerosil, Wako Pure Chemical Industries, Sigma-aldrich, and Daiichi Kigenso Kagaku Kogyo Co. Ltd., respectively.

2.2. Characterization of metal oxides

BET (Brunauer, Emmett, and Teller) surface areas were determined by nitrogen adsorption at -196 °C by using a surface area and porosity analyzer (Micromeritics Tristar, Shimadzu Corporation, JP). The low concentration of moisture in the dry gas was measured by a cryogenic optical dew point meter (Hycosmo II S1200, Osaka Sanso Kogyo Ltd, JP) after flowing the gas for 2 h at a rate of 100 ml/min, while the high concentration of moisture in wet air was measured by a dew point analyzer (DPO-3D, Osaka Sanso Kogyo Ltd, JP) under the same conditions.

Transmission electron microscopy (TEM) observation was carried out by using a JEOL/JEM-2000FX. X-ray photoelectron spectra (XPS) were measured on a Shimadzu/Kratos ESCA 3400 using $\text{Mg K}\alpha$ X-ray source (100 W) after pretreatment in different atmospheres such as in air, N_2 , and CO/air for 40 min within the temperature range of 100–250 °C, which is similar to the conditions of catalytic activity tests for CO oxidation. Binding energies are referenced to the $\text{C}(1s)$ binding energy of adventitious carbon contamination taken to be 284.6 eV. X-ray diffraction (XRD) analyses were performed with a RINT-TTR III diffractometer (Rigaku Corporation, JP) using $\text{Cu K}\alpha$ radiation at 50 kV and 300 mA after different pretreatments which are similar to XPS measurements.

2.3. CO oxidation after different pretreatments

The catalytic tests for CO oxidation were carried out in a fixed-bed quartz reactor (i.d. = 5 mm), containing 0.15 g of catalyst samples. A standard reaction gas containing 1.0 vol% CO, 99 vol% air, and 1.8 ppm H_2O was fed directly from the cylinder without purification. In all the cases pretreatments were performed at desired temperatures for 40 min in a stream of dry air (3.4 ppm H_2O), wet air (13,840–15,780 ppm H_2O), 1.0 vol% CO in air, N_2 (1.6 ppm H_2O), 1.0 vol% CO in N_2 (2.6 ppm H_2O), or 5.0 vol% H_2 in N_2 (2.8 ppm H_2O) at a flow rate of 50 ml/min. After pretreatments under different conditions, the catalyst sample was cooled down to room temperature and then the feed gas was switched to reaction gas.

The conversion of CO was measured at the steady state; usually 30 min after the catalyst bed temperature was settled down. The temperature was usually lowered from room temperature by using methanol/liquid nitrogen mixture contained in a vacuum bottle. To maintain constant temperature (change within 1 °C), small amount of liquid nitrogen was carefully added into the bottle for 10 min each time, and two vacuum bottles containing the mixture were used alternately. When CO conversion at room temperature was below 100%, the catalyst was heated by a resistive heater until 100% CO conversion is reached. The concentrations of CO and CO_2 in the inlet and outlet streams were measured by using an automatic sampling gas chromatograph (GC8A, Shimadzu Corporation).

2.4. Kinetic measurements

Kinetic measurements were carried out in different temperature ranges depending on the pretreatment conditions: in the range of -23 to 23 °C after pretreatments at room temperature, in the range of -41 to -21 °C after pretreatment at 150 °C in wet air, and in the range of -81 to -49 °C (after operated at -90 to -49 °C for 5 h for obtaining steady state) after pretreatment at 150 °C in dry air, CO in air, or N_2 . The stream containing 0.2–1.0 vol% CO in air (excess oxygen) and the stream containing 1.0–20 vol% O_2 and 1.0 vol% CO in N_2 (excess oxygen) were fed for the measurements of rate dependency on the partial pressure of CO and of O_2 , respectively. The gas hourly space velocity was changed in the range of 1.2×10^4 – 6.1×10^4 h^{-1} ml/g cat in order to keep CO conversion below 15% for realizing a differential reactor assumption.

2.5. Oxygen temperature-programmed desorption (O_2 -TPD) and CO temperature-programmed reduction (CO-TPR)

O_2 -TPD and CO-TPR experiments were performed at Automated Catalyst Characterization System (Autochem 2920, Micromeritics, USA) equipped with a mass spectrometer (QIC 20, Hiden, UK) by using 0.20 g catalyst powder. After pretreatments at different conditions, the sample was cooled down to -70 °C, and then exposed to O_2 at the same temperature. After 60 min, the feed gas was switched to He (or 5.0 vol% CO in He for CO-TPR experiments) for purging the system for 60 min and then the temperature was raised at a ramp of 10 °C/min from -70 to 600 °C in a stream of He at 30 ml/min (or 5.0 vol% CO in He for CO-TPR experiments) and the mass signal of O_2 ($m/z = 32$) (or mass signal of CO ($m/z = 28$), O_2 ($m/z = 32$), and CO_2 ($m/z = 44$) for CO-TPR) was recorded simultaneously. The purity of O_2 , N_2 , and He in cylinders was above 99.99%. To estimate the amount of different oxygen species, the O_2 -TPD profiles of the samples after different pretreatments were deconvoluted and then the integrated peak area was obtained.

3. Results

3.1. The catalytic activities of metal oxides for CO oxidation after different pretreatments

The morphology and crystalline nature were investigated by using TEM and XRD. The mean diameter of Co_3O_4 calculated from the peak width by using the Scherrer's equation was 11 nm. A specific surface area of 129 m^2/g was obtained by BET analysis. After pretreatments in different atmospheres at 150 °C for 40 min, CO oxidation over Co_3O_4 was performed in a reaction stream of air containing 1.0 vol% CO and 1.8 ppm moisture. The reaction curves are shown in Fig. 1. Dry air pretreatment gives surprisingly high

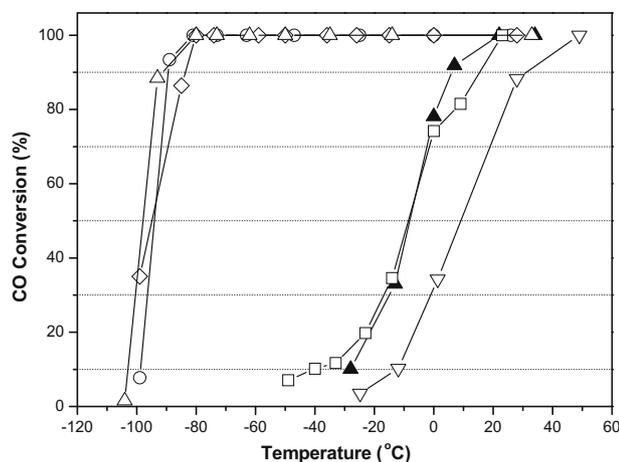


Fig. 1. The influence of pretreatment atmosphere on CO oxidation over Co_3O_4 . Reaction conditions: 0.15 g catalyst sample, 1.0 vol% CO in air, 50 ml/min. In all the cases pretreatment was performed at 150 °C for 40 min in dry air (Δ), wet air (\blacktriangle), 1.0 vol% CO/air (\diamond), N_2 (\circ), 1.0 vol% CO/N_2 (\square), or 5.0 vol% H_2/N_2 (∇).

catalytic activity for CO oxidation. Even at a temperature as low as -80 °C, 100% CO conversion was obtained. Pretreatments in the reactant gas, 1.0 vol% CO/air and in N_2 also lead to 100% CO conversion at -80 °C. In contrast, after the pretreatment in 1.0 vol% CO/ N_2 , complete oxidation of CO occurred only above room temperature. A similar result was obtained by the pretreatment in 5.0 vol% H_2/N_2 , indicating that the reductive pretreatments depress the catalytic activity of Co_3O_4 .

Pretreatment in wet air supplied by an air compressor, containing 13,840–15,780 ppm H_2O , leads to 100% CO conversion at 22 °C, which is 102 °C higher than in the case of dry air pretreatment. It has been reported that the concentration of moisture in the feed gas has a great influence on the catalytic activity of Co_3O_4 for CO oxidation [11,16]. Our present results show that the concentration of moisture in the pretreatment gases also greatly affects the rate of CO oxidation. The catalytic activity after pretreatment in air, CO/air, or N_2 is much higher than that previously obtained under similar conditions, where 100% CO conversion was achieved only when the catalyst temperature was raised to about 60 °C [11]. It was reported that calcination temperature has strong influence on the catalytic activity of Co_3O_4 for low temperature CO oxidation [17]. We have also studied the influence of calcination temperature and found, as shown in Table 1, that the calcination at 300 °C gave much higher catalytic activity for CO oxidation than the calcination at 400 °C.

Table 1

The catalytic performance of Co_3O_4 and $\text{Au}/\text{Co}_3\text{O}_4$ previously reported for low temperature CO oxidation.

Catalyst	Calcination temperature (°C)	Pretreatment conditions	SV (h^{-1} ml/g cat)	Moisture in the feed (ppm)	T_{50} (°C)	T_{100} (°C)	Ref.
Co_3O_4	400	Air, 200 °C	20,000	0.85	-54	^a	[11]
				3	50	60	
				6000	90	120	
$\text{Au}/\text{Co}_3\text{O}_4$	400	Air, 200 °C	20,000	0.85	^a	-76, 45 min	[18]
Co_3O_4 honeycomb	827	2% O_2 , 227 °C	^a	-63 ^b	-43 ^b		
Co_3O_4	300	Air, 200 °C	5000	Dried ^c	^a	-78, 4 h	[12]
Co_3O_4 nanorod	450	20% O_2/He , 450 °C	15,000	3	^a	-77, 6 h	[8]
Co_3O_4	300	Air, 200 °C	20,000	1.8	-95	-80	This work
				1.8	-13	28	
				1.8	-58	0	

^a No information.

^b Measured for transient reaction with a temperature ramp of 20 °C/min from -123 to 227 °C.

^c Pretreatment and reaction gases were dried by using molecular sieve and silica gel.

Table 2

Conversion of CO in CO oxidation at -80 °C over Co_3O_4 after pretreatments at different temperatures.

Pretreatment atmosphere	Pretreatment temperature (°C)					
	25	50	100	150	200	250
N_2 (%)	0.4	0.4	77.0	100	89.9	80.1
CO/air (%)	0.5	0.6	78.8	100	98.6	98.0
Dry air (%)	0.3	0.2	0.6	100	100	81.3
Wet air (%)	0.3	0.9	1.0	1.3	1.2	2.3

Note: Before CO oxidation measurements, the catalysts were pretreated in different atmospheres at different temperatures for 40 min. Reaction conditions: 0.15 g catalyst sample, 1.0 vol% CO in air, 50 ml/min.

The influence of pretreatment temperature was also studied on CO oxidation over Co_3O_4 at -80 °C (Table 2). Pretreatments in dry air, CO/air, or N_2 at 150, 200, or 250 °C give surprisingly high catalytic activity (CO conversion above 80%) at -80 °C, whereas pretreatments at room temperature and at 50 °C under all atmospheres result in low conversion of CO, below 1.0%. At 100 °C, pretreatments are effective only in CO/air and N_2 , namely, under reducing–oxidizing or inert gas atmospheres. These results as a whole imply that the formation of oxygen vacancies can be correlated to the genesis of low temperature catalytic activity. In contrast, after pretreatments by wet air at room temperature to 250 °C, CO conversions at -80 °C are always below 3%, demonstrating that the concentration of moisture in the pretreatment gas has a great influence on the catalytic activity of Co_3O_4 .

After pretreatment in CO/air at 150 °C, CO oxidation was performed at -73 °C (Fig. 2). The CO conversion remains to be 100% during the initial 3 h time-on-stream (TOS) and then decreased gradually to 50% after 8 h. After dry air pretreatment at 150 °C, 100% CO conversion at 0 °C was maintained for 37 h. Interestingly, pretreatment in N_2 and in CO/air at 150 °C provides much longer durability than air pretreatment, maintaining 100% CO conversion at 0 °C until 70 and 98 h. Pretreatment in CO/air shows the longest durability among the three kinds of pretreatment atmospheres, therefore providing a simple and in situ regeneration method for the practical use of Co_3O_4 catalysts for CO oxidation.

Pretreatment temperature also changes the durability of Co_3O_4 for CO oxidation. After pretreatment in N_2 at 200 °C, 100% CO conversion was maintained at 0 °C for 91 h, which is longer than after the pretreatment in the same atmosphere at 150 °C. Wang et al. [12] reported that Co_3O_4 calcined at 300 °C was able to maintain 100% conversion in CO oxidation longer than 8 h at 25 °C and about 4 h at -78 °C, but under dry conditions. So far, the best performance for low temperature CO oxidation in the presence of moisture (3 ppm) has been achieved by Co_3O_4 nanorod catalysts, prepared by morphology-controlled synthesis using ethylene gly-

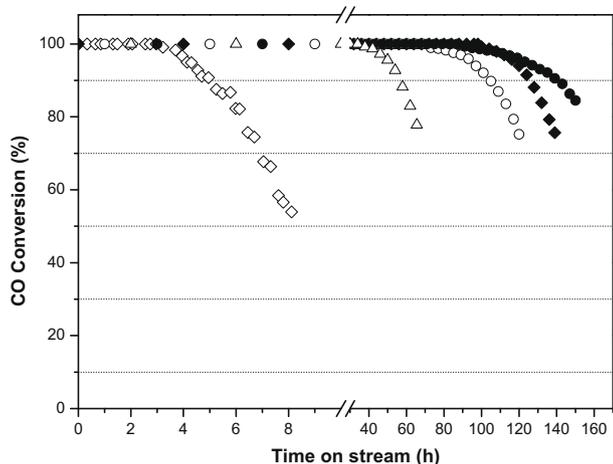


Fig. 2. Durability of Co_3O_4 for CO oxidation under different conditions: at -73°C after pretreatment in 1.0 vol% CO/air at 150°C (\diamond), at 0°C after pretreatment in dry air at 150°C (\triangle), at 0°C after pretreatment in N_2 at 150°C (\circ), at 0°C after pretreatment in 1.0 vol% CO/air at 150°C (\blacklozenge), and at 0°C after pretreatment in N_2 at 200°C (\bullet).

col as an organic solvent and by calcination at 450°C . Complete conversion of CO was maintained for 6 h at -77°C and for more than 55 h at 25°C in the presence of 3 ppm moisture [8].

In this study, significantly large enhancement in the catalytic activity and durability for low temperature CO oxidation (such as at around room temperature) was achieved over usual Co_3O_4 powder in the presence of moisture simply by optimizing pretreatment conditions. The influence of pretreatment conditions on CO oxidation was further studied over different kinds of base metal oxides and is shown in Fig. 3. In the case of Co_3O_4 , MnO_2 , and NiO , pretreatment in N_2 or CO/air always leads to higher catalytic activity for CO oxidation than pretreatment in wet air or reductive atmospheres. In the case of Fe_3O_4 , Fe_2O_3 , CuO , and CeO_2 , pretreatment in N_2 or in CO/air provided only marginal improvement in the cat-

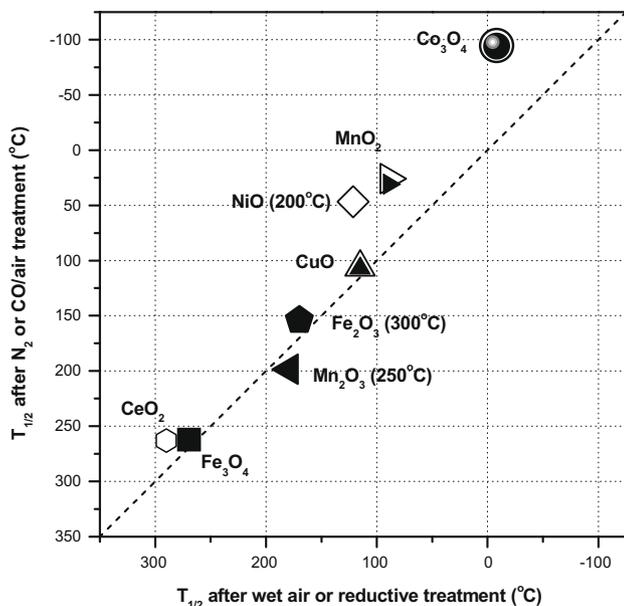


Fig. 3. Temperature for 50% CO conversion ($T_{1/2}$) after pretreatment in N_2 (solid mark) or 1.0 vol% CO/air (open mark) versus after pretreatment in wet air (or reductive atmosphere). The pretreatments were performed at 150°C unless otherwise noted in parentheses.

alytic activity. Over TiO_2 (P25) CO conversion was below 2% even at 300°C . As a result, the data for TiO_2 are not shown in Fig. 3.

3.2. Kinetic study of CO oxidation over Co_3O_4 after different pretreatments

To understand the relationship between pretreatment and the origin of high catalytic activity of Co_3O_4 for low temperature CO oxidation, XRD, XPS, O_2 -TPD, CO-TPR, and kinetic study were performed after different pretreatments. XRD patterns show that pretreatment in air, CO/air, N_2 , CO/ N_2 , or H_2/N_2 within a temperature range of 150 – 250°C hardly changed the bulk structure of Co_3O_4 . XPS results showed that the binding energy of cobalt and oxygen was hardly changed by pretreatment in air, N_2 , or CO/air within a temperature range of 100 – 250°C . Fig. 4 shows Arrhenius plots for the rate of CO oxidation over Co_3O_4 with different pretreatments. Pretreatments at 150°C in dry air, CO/air, and N_2 show almost the same reaction rates and apparent activation energy, 23–24 kJ/mol, suggesting a similar reaction pathway for CO oxidation. Xie et al. reported that Co_3O_4 nanorods showed almost the same activation energy of 22 kJ/mol for CO oxidation [8]. Pretreatments at room temperature and at 150°C in wet air gave much higher activation energy, 50–54 kJ/mol, suggesting that reaction pathway and/or rate-determining step might be changed. Pretreatments at room temperature in dry air, CO/air, and N_2 gave intermediate activation energies between 34 and 37 kJ/mol.

The dependence of CO oxidation rate on the concentrations of CO and O_2 after different pretreatments is shown in Table 3. As for dry air pretreatment, the reaction orders of CO and O_2 were 0.30 and 0.31, respectively. This result suggests a possibility that large amounts of CO and O_2 were adsorbed on the surfaces of Co_3O_4 , leading to weak dependencies of reaction rate on CO and O_2 concentrations and that the reaction rate is substantially controlled by the surface reaction. Pretreatment in CO/air and N_2 shows a little lower reaction order for O_2 (both 0.16) while a little higher order for CO (0.47 and 0.48, respectively) than dry air pretreatment. In contrast to the pretreatment in dry air, pretreatment in wet air obviously increases the reaction order of CO to 1.0 while hardly changes the reaction order of O_2 , 0.30, indicating that the pre-adsorption of moisture strongly suppresses the adsorption of CO and that CO and O_2 adsorb on different sites. Takita et al. [19]

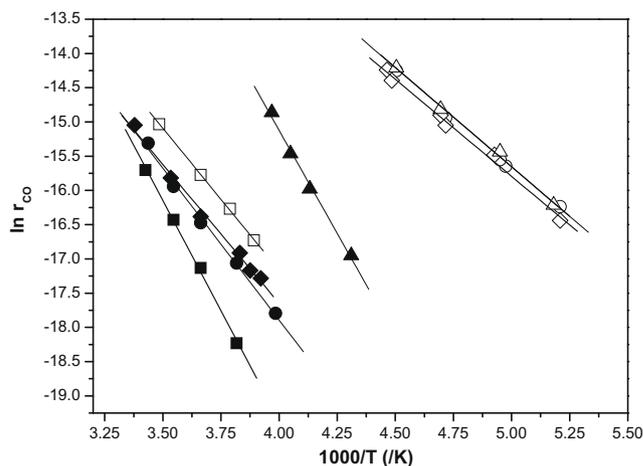


Fig. 4. Arrhenius plots for the rate of CO oxidation over Co_3O_4 after pretreatment in dry air at 150°C (\triangle), wet air at 150°C (\blacktriangle), dry air at room temperature (\square), wet air at room temperature (\blacksquare), 1.0 vol% CO/air at 150°C (\diamond), 1.0 vol% CO/air at room temperature (\blacklozenge), N_2 at 150°C (\circ), or N_2 at room temperature (\bullet). The feed gas consisted of 1.0 vol% CO and air as a balance and the gas hourly space velocity was changed in the range of 1.2×10^4 – $6.1 \times 10^4 \text{ h}^{-1} \text{ ml/g cat}$ in order to obtain CO conversion below 15% for a differential reactor assumption.

Table 3
Kinetic parameters for CO oxidation over Co₃O₄ after different pretreatments.

Pretreatment atmosphere at 150 °C	Temperature range (°C)	Activation energy (kJ/mol)	Reaction order ^a			
			CO	Temperature (°C)	O ₂	Temperature (°C)
N ₂ ^b	–51 to –81	23	0.48	–60	0.16	–49
CO/air ^b	–49 to –81	24	0.47	–61	0.16	–61
Dry air ^b	–51 to –80	24	0.30	–71	0.31	–66
Wet air ^c	–21 to –41	50	1.0	–26	0.30	28

^a The stream containing 0.2–1.0 vol% CO in air (excess oxygen) and the stream containing 1.0–20 vol% O₂ and CO (1.0 vol%) in N₂ were fed for the measurements of rate dependency on the partial pressure of CO and of O₂, respectively. The gas hourly space velocity was changed in the range of 1.2×10^4 – 6.1×10^4 h^{–1} ml/g cat in order to keep CO conversion below 15% for realizing a differential reactor assumption.

^b Before rate measurements, CO oxidation was performed within the temperature range of –90 to –49 °C for 5 h to obtain steady state.

^c Before rate measurements, CO oxidation was performed within the temperature range of –41 to 28 °C for 30 min to obtain steady state.

also showed by TPD experiments that the pre-adsorption of water did not change the total amount of oxygen desorbed from the surface of Co₃O₄ even though it resulted in the rearrangement of different oxygen species.

3.3. Low temperature O₂-TPD and CO-TPR studies over Co₃O₄ after different pretreatments

To further investigate the relationship between adsorbed oxygen and pretreatment conditions, O₂-TPD experiments were carried out starting at –70 °C. In Fig. 5, four kinds of oxygen species are observed at the temperature ranges of –60 to 40 °C, 100–200 °C, 250–400 °C, and at above 400 °C, which could be assigned to molecular oxygen species adsorbed on oxygen vacancy (vO₂), surface oxygen ion bound with Co²⁺ and Co³⁺ (O_{ws}), surface oxygen ion bound with three Co³⁺ cations (O_{ss}), and bulk oxygen (O_B), respectively. The ratios of different oxygen species after different pretreatments were further estimated by the area of corresponding peak and are summarized in Table 4. After pretreatment in dry air

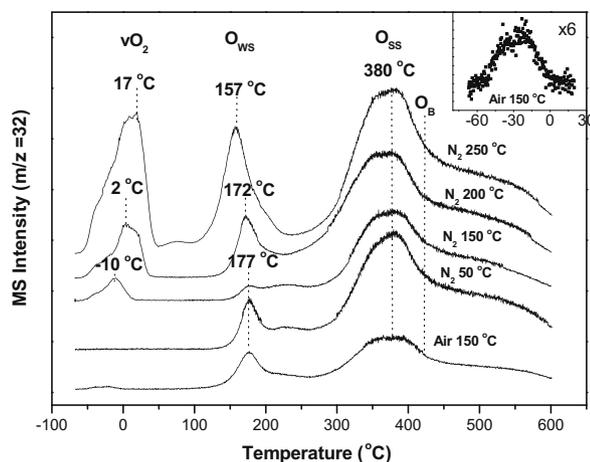


Fig. 5. O₂-TPD profiles of Co₃O₄ after different pretreatments. The procedures were as follows: (1) pretreatment of 0.2 g Co₃O₄ under different conditions for 40 min; (2) cooling down to –70 °C and O₂ adsorption for 1 h; (3) purging with He for 1 h; and (4) heating at a ramp of 10 °C/min from –70 to 600 °C in He and recording mass signal of O₂ ($m/z = 32$) simultaneously.

Table 4
The ratios of different oxygen species estimated by the area of corresponding peak.

	Air at 150 °C (%)	N ₂ at 50 °C (%)	N ₂ at 150 °C (%)	N ₂ at 200 °C (%)	N ₂ at 250 °C (%)
vO ₂	1.1	0	6.5	11.8	23.4
O _{ws}	18.0	6.1	4.3	7.1	14.9
O _{ss}	42.3	41.2	34.4	44.8	31.3
O _B	38.6	52.7	54.8	36.3	30.4

at 150 °C, in addition to peaks around 177 and 380 °C, a small amount of vO₂ (1.1%) was observed which desorbed at around –30 °C. After N₂ pretreatment at 50 °C, vO₂ was hardly observed, whereas increasing the pretreatment temperature to 150 °C in N₂ results in the formation of large amount of vO₂ (6.5%, desorbed from –60 °C and reached maximum at –10 °C). Further increase in the pretreatment temperature to 250 °C gradually raised the desorption temperature of vO₂ as well as the amount of vO₂. Taking into account that pretreatment at 150 °C in N₂ led to the highest catalytic activity for CO oxidation at –80 °C when pretreatments were carried out in a temperature range of room temperature to 250 °C, it is likely that weakly bound molecular oxygen species (vO₂) play a crucial role in CO oxidation at low temperatures and their amount and bonding strength can be tuned by the pretreatments. Namely, the lower the desorption temperature of vO₂ is, the more active Co₃O₄ is for low temperature CO oxidation. Meanwhile, pretreatment in N₂ at 150 °C forms more vO₂ than dry air pretreatment at the same temperature, which can explain why pretreatment in N₂ gives a little lower reaction order of O₂ than pretreatment in dry air.

So far many papers have discussed the relationship between the formation of oxygen species and the catalytic activity of Co₃O₄ for CO oxidation [13,17,20–24]. It has generally been accepted that adsorbed surface oxygen species play a key role in CO oxidation [13,17,20,21,24,25], while few have proposed that lattice oxygen has higher catalytic activity for CO oxidation than adsorbed species [22,23]. In view of the fact that 100% oxidation of CO over Co₃O₄ can occur at temperatures far below room temperature, the active oxygen species may desorb at lower temperatures. However, the desorption of oxygen on Co₃O₄ was investigated with a conventional TPD only above room temperature [13,19,24]. In this study, our TPD instrumentation has enabled us to observe that the desorption of oxygen species weakly bound with Co₃O₄ can occur at –60 °C after O₂ preadsorption at –70 °C. Further CO-TPR experiments show that this weakly bound oxygen could react with CO to form CO₂ at –40 °C (Fig. 6). It should be noted that, after O₂ preadsorption at –70 °C, the sample was purged with 5% CO/He at the same temperature for 60 min. Even in this purging process (the inserted graph in Fig. 6), CO₂ was formed at the initial stage, reaching a maximum amount soon after, and then the amount decreased gradually, which indicates sufficiently high reactivity of weakly bound oxygen with CO at –70 °C.

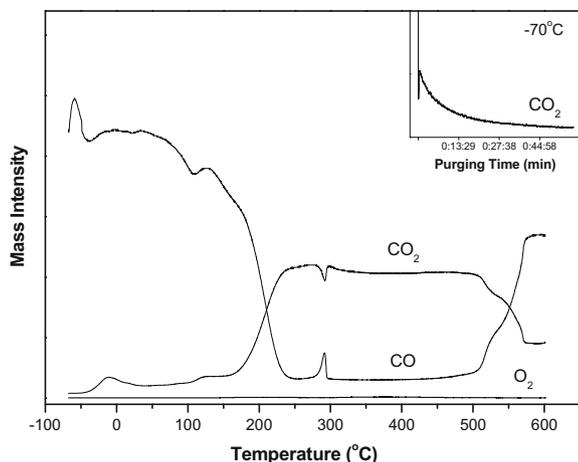


Fig. 6. CO-TPR profiles of Co_3O_4 after pretreatment in N_2 at 150°C . The procedures were as follows: (1) pretreatment of 0.2 g Co_3O_4 in N_2 at 150°C for 40 min; (2) cooling down to -70°C and O_2 adsorption for 1 h; (3) purging with 5.0 vol% CO in He for 1 h; and (4) heating at a ramp of $10^\circ\text{C}/\text{min}$ from -70 to 600°C in 5.0 vol% CO in He and recording mass signal of CO ($m/z = 28$), O_2 ($m/z = 32$), and CO_2 ($m/z = 44$), simultaneously.

4. Discussion

It is well known that supported gold catalysts exhibit high catalytic activity for CO oxidation at temperatures far below room temperature. The adsorption and activation of molecular oxygen are thought to be crucial to gold catalysts for low temperature CO oxidation [26–30]. The formation of adsorbed reactive oxygen species such as superoxide ion (O_2^-) can be correlated to the presence of surface oxygen vacancies on metal oxide support [29] or on the metal–support interfaces [26–29]. By using temporal analysis of product (TAP) techniques, Widmann et al. [31] found that the catalytic activity of Au/CeO₂ for CO oxidation was significantly improved by the removal of about 7% of the surface oxygen through pre-reduction with a few CO pulses, whereas over-reduction caused lower catalytic activity at the initial stage. Meanwhile, different kinds of superoxide species were also observed on the surfaces of CoO–MgO dilute solid solutions between -196 and 25°C by IR and EPR [32], and it was hypothesized that the superoxide species played an important role in CO oxidation over metal oxides at low temperatures [33,34]. These previous studies indicate that pretreatments in inert and reducing–oxidizing atmosphere such as N_2 and CO/air may lead to the creation of surface oxygen vacancies, where molecular oxygen is activated at low temperatures, resulting in the improved catalytic activity and/or durability.

Sadykov and co-workers [13,14] also studied the influence of pretreatment atmosphere on the formation of adsorbed oxygen species over Co_3O_4 calcined at 400°C . In comparison with O_2 pretreatment at 350°C , pretreatment in He at the same temperature enhanced the formation of weakly bound oxygen species over Co_3O_4 . In TPD starting at 25°C , the desorption of O_2 occurred at 27 – 97°C , which was much higher than the temperature for the desorption of molecular oxygen species adsorbed on Co_3O_4 calcined at 300°C in our TPD experiments. It is well known that the metal oxides prepared in air inevitably bear surface hydroxyl groups, which has been clearly identified by IR measurement [35]. As reported by Ciuparu et al. [36], a part of hydroxyls is known to be easily removed by pretreatment in the flow of H_2 at temperature below 700°C , thus creating surface oxygen vacancies. The relationship between the removal of surface hydroxyls and the formation of oxygen vacancies over Co_3O_4 during different pretreatment will be further investigated by IR spectroscopy in the near future.

XRD patterns show that Co_3O_4 is the only phase after calcination of the precipitate $\text{Co}(\text{OH})(\text{CO}_3)$ at 300°C in air. Tricobalt tetraoxide is a spinel type oxide which consists of cobalt (II) in tetrahedral sites (Co^{2+}) and cobalt (III) in octahedral sites (Co^{3+}) [20,37–39]. By successively substituting the Co^{2+} and Co^{3+} ions in Co_3O_4 with less active Zn^{2+} and Al^{3+} ions, respectively, it has been proved that the surface Co^{3+} of cobalt spinel oxide is essential for the genesis of high activity for CO oxidation while Co^{2+} is not useful for this reaction [37]. Intensive studies on the low temperature CO oxidation over Co_3O_4 have been performed by Jansson et al. [21,25,38], and it has been proposed that CO adsorption and reaction at low temperature take place on the surface octahedral sites (Co^{3+}). Preferred adsorption of CO is also found to occur at surface-exposed Co^{3+} sites while other sites such as sublayer Co^{3+} ions are sterically hindered and inaccessible for CO adsorption based on a DFT study [39].

As shown in Fig. 7 in the left-hand side structure presented by Broqvist et al. [39], there are two kinds of oxygen ions on Co_3O_4 (110) surface: one is bonded to one Co^{2+} and one Co^{3+} ion, while another is bound to three Co^{3+} ions as the nearest neighbors. Thus, the two surface oxygen ions on the Co_3O_4 (110) plane experience different crystal fields, which cause their electropositivities to differ, and thereby also their reactivities. In Fig. 7, these surface oxygen ions are hereafter denoted as O_{WS} and O_{SS} , representing the weaker and stronger local crystal field sites, respectively. As a result, two different surface oxygen vacancies can be formed by the oxygen abstraction from either O_{WS} or O_{SS} site, but the O_{WS} vacancies formation may be more feasible and lead to significantly longer lifetime than the O_{SS} vacancies [39]. The desorption peaks at 157 – 177°C in TPD study (Fig. 5) may correspond to the surface oxygen abstraction from O_{WS} site, which also gives an evidence that pretreatment at above 150°C is highly effective for CO oxidation by enhancing the formation of surface oxygen vacancies. The oxygen desorption starting at 250 – 300°C can be assigned to the surface oxygen abstraction from O_{SS} . The shoulder observed at around 420°C can be ascribed to the bulk oxygen (O_{B}) since this sample was calcined at 300°C .

Based on the above results in combination with the hypotheses of CO oxidation over metal oxides at low temperatures [33,34], a possible scheme is proposed for the role of pretreatment and for the pathways of CO oxidation over Co_3O_4 . As shown in Fig. 7, pretreatment in inert and reducing–oxidizing atmosphere (N_2 and CO/air) at moderate temperatures enhances the formation of surface O_{WS} vacancies by oxygen removal from the O_{WS} sites and then leads to the formation of weakly bound oxygen species such as bridged $\text{Co}^{3+}-\text{O}_2-\text{Co}^{2+}$, which exhibits high reactivity toward adsorbed “end on” CO species on the surface-exposed Co^{3+} sites to form CO_2 even at -80°C . During this process, the dissociation of adsorbed O_2^- occurs and then atomic oxygen anion leaves the surface vacancies ($\text{Co}^{3+}-\text{O}^--\text{Co}^{2+}$). Considering that the reactivity of adsorbed O^- is a little higher than that of O_2^- [34], the CO oxidation can easily undergo to produce CO_2 , and then the surface O_{WS} vacancies are available again for O_2 adsorption. Also, it is indicated that the formation of adsorbed atomic oxygen anion may be the rate-determining step during the low temperature CO oxidation over Co_3O_4 after pretreatment in dry air, N_2 , and CO/air at above 150°C . It is reasonable that pretreatment in dry air is less efficient for the formation of surface O_{WS} vacancies than pretreatment in N_2 , or CO/air. Water molecules are more strongly adsorbed on Co^{3+} active sites than CO and thereafter retard the adsorption of CO [40], causing a sharp increase in the reaction order of CO.

As shown in Fig. 3, the catalytic activity of base metal oxides for CO oxidation decreased in the following sequence: $\text{Co}_3\text{O}_4 > \text{MnO}_2 > \text{NiO} > \text{CuO} > \text{Fe}_2\text{O}_3 > \text{Mn}_2\text{O}_3 > \text{Fe}_3\text{O}_4 > \text{CeO}_2 > \text{TiO}_2$, which approximately coincides with an increasing sequence of metal–oxygen bond energy of base metal oxides as reported by Boreksov

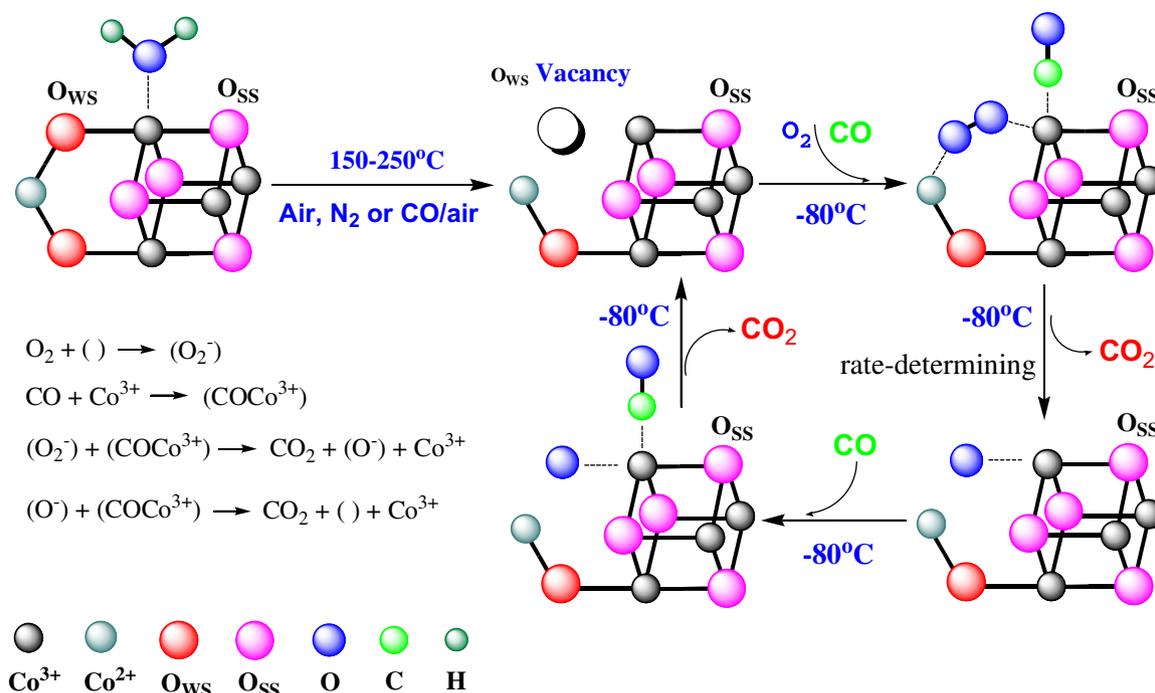


Fig. 7. A possible scheme for the role of pretreatment and CO oxidation pathways over Co_3O_4 . O_{SS} : surface oxygen ions of Co_3O_4 bonded to three Co^{3+} ions as the nearest neighbors, representing the stronger local crystal field sites; O_{WS} : surface oxygen ions of Co_3O_4 bonded to one Co^{2+} and one Co^{3+} ion, representing the weaker local crystal field sites. The oxygen removal from O_{WS} sites to form surface O_{WS} vacancies may occur preferentially to that from O_{SS} sites.

[41]: $Co_3O_4 < CuO < NiO \approx MnO_2 < Fe_2O_3 < TiO_2$. By taking into account the lower metal–oxygen bond energy of Co_3O_4 , MnO_2 and NiO , it is reasonably understood that pretreatment in N_2 or CO/air at moderate temperature is efficient for oxygen abstraction from the surface of these metal oxides to form surface oxygen vacancies, finally enhancing the adsorption of O_2 for CO oxidation. Cupric oxide, CuO , has metal–oxygen bond energy of 76–80 kJ/mol, which is similar to that of MnO_2 and NiO (80–84 kJ/mol) [41,42], however, pretreatment in N_2 or in CO/air offered only a marginal improvement in the catalytic activity. Sadykov et al. [14] proposed that pretreatment and activity measurement conditions can broadly vary the surface layer stoichiometry of Co_3O_4 , NiO , and MnO_2 , while CuO possesses a very narrow range of the surface non-stoichiometry, indicating that the surface non-stoichiometric variability may also contribute to the effect of pretreatment.

5. Conclusions

Atmospheres, temperature, and the moisture content in the pretreatments have a great influence on the catalytic activity of Co_3O_4 , MnO_2 , and NiO which are calcined at relatively low temperatures of 300 or 400 °C. They are p-type semiconductors having smaller metal–oxygen bond energy than other base metal oxides and are characterized by relatively large surface non-stoichiometric variability. These two properties can be correlated to the formation and stability of surface oxygen vacancies and lead to the high catalytic activity of Co_3O_4 , MnO_2 , and NiO for CO oxidation at a temperature as low as $-80^\circ C$. The other metal oxides are intrinsically much less active for CO oxidation at temperatures below 120 °C, and therefore pretreatment effect is small. This finding may provide a new guideline for the creation of low-temperature catalysts without using noble metals by optimizing pretreatment conditions.

Acknowledgments

The authors would like to acknowledge Mr. Y. Man of Beijing Research Institute of Chemical Industry for O_2 -TPD and CO-TPR

measurements. They also thank Prof. Y. Shimakawa and Dr. Y. Teng of Kyoto University for their advices concerning metal oxides preparation. Y. Yu also thanks Japan Society for the Promotion of Science (JSPS) for the financial support to his stay at TMU for 2 years as a postdoctoral fellow. This work was partly supported by Grant-in-Aid for Specially Promoted Research (19001005) of the Ministry of Education, Culture, Science and Sports, Japan. It was also partly supported by the National Natural Science Foundation for Creative Research Groups of China (50621804).

References

- [1] A.V. Nero Jr., *Scientific Am.* 258 (1998) 24.
- [2] M. Jacoby, *Chem. Eng. News* 2003, January 20, p. 32.
- [3] R. Jain, US Patent 5 110 569, 1992.
- [4] N. Funasaki, A. Henmi, S. Ito, Y. Asano, S. Yamashita, T. Kobayashi, M. Haruta, *Sens. Actuat. B* 14 (1993) 536.
- [5] M. Haruta, A. Ueda, S. Tsubota, R.M. Torres Sanchez, *Catal. Today* 29 (1996) 443.
- [6] F.S. Stone, *Adv. Catal.* 13 (1962) 1.
- [7] M. Haruta, M. Yoshizaki, D.A.H. Cunningham, T. Iwasaki, *Ultra Clean Technol.* 8 (1996) 117 (in Japanese).
- [8] X. Xie, Y. Li, Z.-Q. Liu, M. Haruta, W. Shen, *Nature* 458 (2009) 746.
- [9] Z. Qu, M. Cheng, W. Huang, X. Bao, *J. Catal.* 299 (2005) 446.
- [10] S.H. Kim, S.W. Nam, T.H. Lim, H.I. Lee, *Appl. Catal. B* 81 (2008) 97.
- [11] D.A.H. Cunningham, T. Kobayashi, N. Kamijo, M. Haruta, *Catal. Lett.* 25 (1994) 257.
- [12] Y.-Z. Wang, Y.-X. Zhao, C.-G. Gao, D.-S. Liu, *Catal. Lett.* 116 (2007) 136.
- [13] V.A. Razdobarov, V.A. Sadykov, S.A. Veniaminov, N.N. Bulgakov, O.N. Kovalenko, Yu.D. Pankratiev, V.V. Popovskii, G.N. Kryukova, S.F. Tikhov, *React. Kinet. Catal. Lett.* 37 (1988) 109.
- [14] V.A. Sadykov, S.F. Tikhov, S.V. Tsybulya, G.N. Kryukova, S.A. Veniaminov, V.N. Kolomiichuk, N.N. Bulgakov, E.A. Paukshtis, V.P. Ivanov, S.V. Koshcheev, V.I. Zaikovskii, L.A. Isupova, L.B. Burgina, *J. Mol. Catal. A* 158 (2000) 361.
- [15] S.B. Kanungo, *J. Catal.* 58 (1970) 419.
- [16] F. Grillo, M.M. Natile, A. Glisenti, *Appl. Catal. B* 48 (2004) 267.
- [17] M.J. Pollard, B.A. Weinstock, T.E. Bitterwolf, P.R. Griffiths, A.P. Newbery, J.B. Paine III, *J. Catal.* 254 (2008) 218.
- [18] P. Thormählen, M. Skoglundh, E. Fridell, B. Andersson, *J. Catal.* 188 (1999) 300.
- [19] Y. Takita, T. Tashiro, Y. Saito, F. Hori, *J. Catal.* 97 (1986) 25.
- [20] D. Perti, R.L. Kabel, G.J. Mccarthy, *AIChE J.* 31 (1985) 1435.
- [21] J. Jansson, M. Skoglundh, E. Fridell, P. Thormählen, *Top. Catal.* 16/17 (2001) 385.
- [22] H.-K. Lin, C.-B. Wang, H.-C. Chiu, S.-H. Chien, *Catal. Lett.* 86 (2003) 63.

- [23] C.-B. Wang, C.-W. Tang, H.-C. Tsai, M.-C. Kuo, S.-H. Chien, *Catal. Lett.* 107 (2006) 31.
- [24] Y.-Z. Wang, Y.-X. Zhao, C.-G. Gao, D.-S. Liu, *Catal. Lett.* 125 (2008) 134.
- [25] J. Jansson, *J. Catal.* 194 (2000) 55.
- [26] M. Haruta, *CATTECH* 6 (2002) 102.
- [27] G.C. Bond, D.T. Thompson, *Gold Bull.* 33 (2000) 41.
- [28] J. Guzman, S. Carrettin, J.C. Fierro-Gonzalez, Y. Hao, B.C. Gates, A. Corma, *Angew. Chem., Int. Ed.* 44 (2005) 4778.
- [29] J. Guzman, S. Carrettin, A. Corma, *J. Am. Chem. Soc.* 127 (2005) 3286.
- [30] J.A. van Bokhoven, C. Louis, J.T. Miller, M. Tromp, O.V. Safonova, P. Glatzel, *Angew. Chem., Int. Ed.* 45 (2006) 4651.
- [31] D. Widmann, R. Leppelt, R.J. Behm, *J. Catal.* 251 (2007) 437.
- [32] E. Giamello, Z. Sojka, M. Che, A. Zecchina, *J. Phys. Chem.* 90 (1986) 6084.
- [33] G.I. Golodets, J.R.H. Ross, *Language* (Eds.), *Heterogeneous Catalytic Reaction Involving Molecular Oxygen*, *Studies in Surface Science and Catalysis*, vol. 15, Elsevier, Amsterdam–Oxford–New York, 1983, p. 280.
- [34] J.V.D. Berg, A.J.V. Dillen, J.V.D. Meijden, J.W. Geus, in: J.P. Bonnelle, B. Delmon, E. Derouane (Eds.), *Surface Properties and Catalysis by Non-Metals*, D. Reidel Publishing Company, 1983, p. 493.
- [35] M.I. Zaki, H. Knözinger, *Mater. Chem. Phys.* 17 (1987) 201.
- [36] D. Ciuparu, Y. Chen, S. Lim, Y. Yang, G.L. Haller, L. Pfefferle, *J. Phys. Chem. B* 108 (2004) 15565.
- [37] K. Omata, T. Takada, S. Kasahara, M. Yamada, *Appl. Catal. A* 146 (1996) 255.
- [38] J. Jansson, A.E.C. Palmqvist, E. Fridell, M. Skoglundh, L. Österlund, P. Thormählen, V. Langer, *J. Catal.* 211 (2002) 387.
- [39] P. Broqvist, I. Panas, H. Persson, *J. Catal.* 210 (2002) 198.
- [40] A.J. Goodsel, *J. Catal.* 30 (1973) 175.
- [41] G.K. Borekov, *Kinet. Catal.* 8 (1967) 878.
- [42] A. Bielanski, *J. Haber, Catal. Rev. Sci. Eng.* 19 (1979) 1.