

Parametric Study on the Deactivation of Supported Co_3O_4 Catalysts for Low Temperature CO Oxidation

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Abstract: This study focused on the influences of a variety of reaction parameters and guest molecules such as H_2O and C_3H_8 on the deactivation of supported Co_3O_4 catalysts for CO oxidation. Additionally, the physical features of and carbon deposition on some samples after the reaction under the chosen conditions were determined by BET and X-ray diffraction as well as by carbon analyses to deduce the precursors associated with catalyst deactivation. Activity maintenance profiles of the catalysts for CO oxidation at 100 °C significantly depended on the support for Co_3O_4 nanoparticle dispersion, the loading, the preparation technique and the calcination temperature. The best on-stream performance was achieved using a 5% $\text{Co}_3\text{O}_4/\text{TiO}_2$ catalyst prepared by the incipient wetness method followed by calcination at 350 °C. All the reaction parameters chosen here such as the reaction temperature, the feed gas composition of CO, O_2 , H_2O , and C_3H_8 , and the gas space velocity strongly influenced the extent of catalyst deactivation during CO oxidation and also the rate of catalyst deactivation. However, the deactivation behavior is very complicated. No appreciable changes in the surface area, the porosity, and the phase of the Co_3O_4 nanoparticles and their size occurred even for the samples that were severely deactivated. Significant deposition of carbon on the catalysts after the reaction was visible and it depended on the reaction parameters chosen here. Consequently, this extensive parametric study on the deactivation of catalysts during oxidation and with the chosen reaction parameters and guest gases can lead to an understanding of the deactivation precursors that are associated with carbonaceous species including carbonates and surface free carbon.

Key words: carbon monoxide; oxidation; supported cobalt oxides; deactivation; reaction parameters; feed compositions

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Advanced vehicles with homogeneous charge compression ignition (HCCI) engines have been reported to dramatically reduce NO_x ($\text{NO} + \text{NO}_2$) and particulate matter (PM) emissions [1,2]. However, unburned hydrocarbons (HCs) and CO greater than 1% exist in typical HCCI exhaust gases at temperatures up to 280 °C [3]. One of the problems associated with the successful introduction of full HCCI engine-driven vehicles to the advanced automotive market is the development of catalysts that are highly active at low temperature to control engine-out emissions. Many catalysts have been evaluated for low-temperature CO oxidation and some systems are promising for application and are an alternative to precious metals. Unsupported, supported, and promoted Co_3O_4 catalysts [3–9] are very active for CO oxidation even at temperatures far below room temperature such as at –77 °C but these catalysts possess weak durability during the oxidation reaction although the extent of deactivation and its rate depends on the kind of catalyst and the reaction conditions. This is one of the major challenges before their application to emissions control in HCCI automobiles.

Various precursors that affect the durability of Co_3O_4 catalysts during low-temperature CO oxidation have been proposed and representative precursors are carbonates [4–6,9–11] and guest molecules particularly H_2O even at sub-ppm concentrations [4,9,10,12], surface free carbon [6,11], reconstruction of the Co_3O_4 surface [11], and Co_3O_4 sintering [13]. All these precursors are closely or weakly related to the deactivation of the Co_3O_4 catalysts during oxidation and they vary with preparation techniques, the supports and promoters used, and the excursions to activate them by calcination and pretreatment. They also vary because of the chosen conditions such as the reaction temperature and the feed gas composition etc. Few, if any, studies have been reported for a systematic comparison of the dependence of these variables on the time-on-stream activity of Co_3O_4 -based catalysts for CO oxidation and several earlier reports are of particular interest for these low temperature applications although some documents [3,10,12,14,15] have dealt with calcination and reaction conditions, which affected the durability of these catalysts in low temperature CO oxidation and this is discussed be-

low.

The calcination temperature can result in a significant difference in the activity of Co₃O₄/TiO₂ catalysts for CO oxidation, as found in our earlier work [3]. Based on an extensive characterization of this catalyst by TPD (temperature-programmed desorption), XPS (X-ray photoelectron spectroscopy), and XRD (X-ray diffraction) measurements, two predominant types of CoO_x species have been found to exist with this sample: clean Co₃O₄ nanoparticles, which are present after calcination at 450 °C and highly active for CO oxidation at 100 °C, and completely Co_n-TiO_{n+2}-overlaid Co₃O₄ particles with $n = 1$ and 2 that are produced upon calcination at 570 °C and that have no activity during CO oxidation. Similarly, Shao et al. [14] reported CeO₂-promoted Co₃O₄ catalysts with CO oxidation activity dependent on the calcination temperature and the preparation technique. The calcination of unsupported Co₃O₄ at 300 °C gave the best duration of 8 h for total CO oxidation (100% CO conversion) at room temperature [15]. The extent of deactivation during CO oxidation over a sample of Co₃O₄ at -76 °C changed as a result of space velocities, as observed by Cunningham et al. [10] who reported that after 1 h on-stream 100% CO conversion was achieved in a flowing mixture of 1% CO in air that was dried to ppb levels and the time was shortened because of the high space velocity. Haruta and colleagues [16] proposed the strong influence of pretreatment conditions, particularly gas compositions, and temperatures on the longevity of unsupported Co₃O₄ catalysts for CO oxidation at 0 °C and it was obvious that the best activity maintenance at ca. 100 h was obtained after pretreatment at 150 °C for 40 min in a flow of 1% CO in air, and this was compared to that pretreated under either air or N₂.

Earlier studies including the previous studies discussed above have covered very limited variables among a variety of reaction parameters such as metal loading, calcination and reaction temperature, reactant concentration, and types of guest gases and their amounts. However, incomparable experimental conditions have been used in these studies. These points explain the difficulty in extracting useful information about the deactivation of Co₃O₄ catalysts during CO oxidation at low temperatures. Therefore, we report on an extensive and systematic study into the influence of all these parameters on the deactivation of supported Co₃O₄ catalysts for CO oxidation to assist in a fundamental understanding of the loss in on-stream activity maintenance as well as to improve their durability during the oxidation reaction. However, this study is not intended to be a comprehensive approach to the deactivation mechanisms related to the precursors mentioned above and our proposal regarding this issue will be reported in future.

1 Experimental

1.1 Preparation of the catalysts

Anatase-type TiO₂ (Millennium Chemicals, DT51D) and SiO₂ (Davisil) with respective specific surface areas (S_{BET}) of 83 and 365 m²/g were used to prepare supported Co₃O₄ catalysts. Before dispersing Co₃O₄ onto the fine powder supports they were calcined at 570 °C for 4 h in a flowing mixture of 21% O₂-79% He (Praxair, 99.999%) at 1 L/min. TiO₂- and SiO₂-supported samples containing 1% and 5% Co₃O₄ were prepared by the incipient wetness (IW) method in which an aqueous solution of Co(NO₃)₂·6H₂O (Aldrich, 99.999%) was impregnated dropwise as described elsewhere [3,17]. These catalysts were designated “IW” in parenthesis to distinguish them from the sample obtained using the ion exchange (IE) method described below. A 1% Co₃O₄/TiO₂ catalyst was prepared using the IE technique in which the H⁺ sites of the surface OH groups were replaced with Co²⁺ ions in an aqueous solution of Co(NO₃)₂·6H₂O at a pH of 9.8, as given elsewhere [17,18]. After this preparation, all the catalysts were dried in air overnight at 110 °C and stored in a desiccator for later use. The physicochemical properties of the prepared catalysts are listed in Table 1.

Table 1 Physicochemical properties of the supported Co₃O₄ catalysts

| Catalyst | S_{BET} (m ² /g) | Pore diameter (nm) | Pore volume (cm ³ /g) | Co ₃ O ₄ size ^a (nm) | Carbon amount (%) |
|---|---|--------------------------|--|---|-------------------------|
| TiO ₂ | 83 | 16.0 | 0.343 | — | 0.013 ^b |
| SiO ₂ | 365 | 8.2 ^c | — | — | — |
| 1% Co ₃ O ₄ /TiO ₂ (IW) | — | — | — | — | — |
| 1% Co ₃ O ₄ /TiO ₂ (IE) | — | — | — | — | — |
| 5% Co ₃ O ₄ /TiO ₂ (IW) ^d | 78 | 13.1 | 0.271 | 11.0 | 0.014 ^e |
| 5% Co ₃ O ₄ /SiO ₂ (IW) ^d | — | — | — | — | — |

^aBased on XRD peaks.

^bAfter calcination at 570 °C for 1 h in simulated flowing air.

^cWith pores of 3.4 and 11.3 nm.

^dNominal.

^eAfter calcination at 350 °C for 1 h in simulated flowing air.

1.2 Catalytic CO oxidation

Activity maintenance profiles for CO oxidation over the Co₃O₄/TiO₂ and Co₃O₄/SiO₂ catalysts under the chosen conditions were measured using a gas phase continuous flow U-shaped Pyrex reactor in a tubular electric furnace coupled with a Hanyoung Model NP200 PID temperature controller. An appropriate amount of the catalysts (0.2–0.35 g) was placed above a quartz wool plug in the Pyrex reactor and routinely calcined unless otherwise specified at 350 °C for 1 h in a flow of simulated air at 200 ml/min using a Brooks

5850E mass flow controller (MFC) before the CO oxidation reaction was allowed with the reaction parameters chosen here. He was purified by passing it through a moisture trap and an Oxytrap (Alltech Assoc.), and O₂ was also purified in a similar manner. Details of this reaction system have been given elsewhere [3].

A gas mixture consisting of 0.5%–5% CO (AGT, 99.998%) and 0.5%–10% O₂ in flowing He at a total flow rate of 200 ml/min, corresponding to gas hourly space velocities (GHSV) of 6000–24000 h⁻¹, was passed continuously through the catalyst bed for CO oxidation at the given reaction temperatures. These were designated T_r to distinguish them from the calcination temperatures (T_c) and the standard reaction temperature was 100 °C unless otherwise stated. To study the influence of H₂O and C₃H₈ on the deactivation of the 5% Co₃O₄/TiO₂(IW) catalyst the respective feed stream compositions were 3% O₂/5.8% H₂O and 7% O₂/1% C₃H₈ in flowing 1% CO in He. The CO cylinder that was made of aluminum was used here to avoid surface contamination of the catalyst samples by metallic carbonyls such as Fe(CO)₅ and Ni(CO)₄ because these volatile carbonyls can easily form by the reaction of highly pressurized gas phase CO with the walls of steel cylinders that contain Fe and Ni [19,20]. C₃H₈ (Research Grade, 99.9%) in an aluminum cylinder was purchased from Scott Specialty Gases (currently Air Liquide America Specialty Gases). All the gas flow rates during the on-stream activity measurements were controlled using Brooks 5850E and MKS Type 1179A MFCs. All the gases used were purified by flowing them through a moisture trap and an Oxytrap (Alltech Assoc.). The products were analyzed using an on-line, computer-controlled Shimadzu 2014 gas chromatograph equipped with a thermal conductivity detector and an Alltech CTR I column [3].

1.3 Characterization of the deactivated samples

To determine whether or not a change in the surface area and pore size distribution of the 5% Co₃O₄/TiO₂(IW) catalyst after CO oxidation under different on-stream excursions occurs, the physical features of the samples of interest were measured using a Micromeritics ASAP 2010 instrument. Before allowing N₂ adsorption on each sample at the liquid N₂ temperature (–196 °C) the system was evacuated for 1 h at room temperature and finally at 90 °C overnight in vacuum. The specific surface area was determined according to the BET multipoint technique and the size distribution of the pores present in the pretreated samples was analyzed by the Barrett-Joyner-Halenda (BJH) model using a desorption isotherm.

XRD measurements were conducted with samples of the 5% Co₃O₄/TiO₂(IW) catalyst after calcination at 350 °C

following CO oxidation under the chosen reaction conditions to determine if the size of the Co₃O₄ nanoparticles could be altered and compared to that of a fresh sample. Co₃O₄ (Aldrich, 99.995%) was used as-received as a reference. XRD spectra of all the samples were collected ex situ using a Rigaku D/MAX2500 PC diffractometer equipped with a Cu K_α ($\lambda = 0.15406$ nm) radiation source and a graphite monochromator. During data collection the respective X-ray tube voltage and current were 40 kV and 20 mA. Each sample was loaded into a thin quartz holder with a diameter of 12 mm and placed in a diffractometer and scanned between 2θ values of 10° to 80° at a normal scanning rate of 1.0°/min. Following this, a high resolution scan where the peaks of the Co₃O₄ phase are visible was obtained at a rate of 0.1°/min to acquire more accurate Co₃O₄ peaks for the catalyst samples. The average crystallite sizes for Co₃O₄ were determined based on the line width at half height of the XRD peak at $2\theta = 31.26^\circ$ at the crystallographic (220) plane using the Scherrer equation with Warren's correction for instrumental line broadening.

The amount of carbonaceous materials deposited on the 5% Co₃O₄/TiO₂(IW) samples that had undergone CO oxidation under different reaction parameters were determined using a LECO CS-600 Carbon/Sulfur analyzer combined with a high-frequency induction furnace and a solid-state infrared (IR) detector. A sample of each catalyst (0.15 g) was loaded into a crucible and then 0.3 g of pure tungsten powder, as a combustion accelerator, was added onto the top of the sample before placing the crucible in the furnace in which the sample-accelerator was rapidly combusted in a flow of O₂ to form CO₂ that was detected by the IR detector to quantify the amount of the carbonaceous species present in chosen samples. The O₂ was purified by passing it through Alltech moisture, hydrocarbon, and CO₂ traps.

2 Results and discussion

2.1 Effect of the reaction parameters chosen

Co₃O₄ catalysts with different supports, prepared using different techniques and with a different Co₃O₄ content were used to determine their effect on the duration of activity during CO oxidation at 100 °C, and the results are shown in Fig. 1. The initial activity (85%) was obtained for the 1% Co₃O₄/TiO₂(IW) sample after calcination at 350 °C, and it decreased rapidly with time and became zero after 7 h. In contrast, the 1% Co₃O₄/TiO₂(IE) catalyst gave no activity. The noticeable difference between the IW and IE samples may be associated with the difficulty in abstracting surface oxygen that is bound chemically to the Co³⁺ sites in an octahedral coordination on which CO is adsorbed [6,9,21] because the latter is expected to predominantly consist of

isolated Co oxides on TiO_2 , thereby indicating a very strong Co_3O_4 - TiO_2 interaction. Consequently, the IW method is preferable for the preparation of supported Co_3O_4 catalysts for CO oxidation.

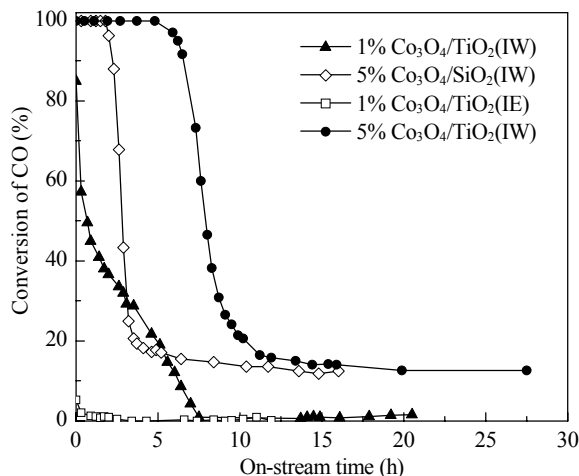


Fig. 1. Activity maintenance profiles for CO oxidation at 100 °C over the $\text{Co}_3\text{O}_4/\text{TiO}_2$ and $\text{Co}_3\text{O}_4/\text{SiO}_2$ catalysts with different Co_3O_4 loadings and prepared using different techniques.

The 5% $\text{Co}_3\text{O}_4/\text{TiO}_2$ (IW) catalyst gave 100% conversion up to 5 h on-stream and then its activity decreased to 15% within 6 h (Fig. 1). When CO oxidation was allowed for the 5% $\text{Co}_3\text{O}_4/\text{SiO}_2$ (IW) sample, this catalyst gave much shorter residence over the total CO oxidation period although the steady-state conversion was similar to that observed for the TiO_2 -supported sample. Finally, when bare TiO_2 and SiO_2 were used for CO oxidation at 100 °C they were all completely inactive as they gave CO conversions of less than 1% over 9 h (not included here), and this agrees well with earlier results [3,22,23]. All CO conversions were consistent with CO_2 production amounts during the course of the reaction. Based on these observations, we believe that the duration of the CO oxidation reaction at 100 °C significantly depends on the amount of Co_3O_4 and its chemical nature, which is influenced by the preparation techniques and the supports used.

Activity maintenance profiles for the 5% $\text{Co}_3\text{O}_4/\text{TiO}_2$ (IW) catalysts that were calcined at 250, 450, and 570 °C for CO oxidation at 100 °C are shown in Fig. 2. The preceding activity maintenance data of the catalyst prepared by calcination at 350 °C is included for comparison and will be used for the same purpose below. The supported Co_3O_4 catalyst that was calcined at 250 °C gave 50% conversion at the beginning of the oxidation but its activity decreased with time. For the 5% $\text{Co}_3\text{O}_4/\text{TiO}_2$ (IW) sample that was calcined at 450 °C the catalyst already gave a conversion of 90% just after oxidation had begun. However, it gradually became deactivated. For the catalyst calcined at 570 °C, 70% CO

conversion was obtained at the onset of oxidation and the deactivation behavior was comparable to that observed after calcination at 250 °C. This implies that the 350 °C calcination product that gives a total conversion at approximately 5 h is good as a catalyst.

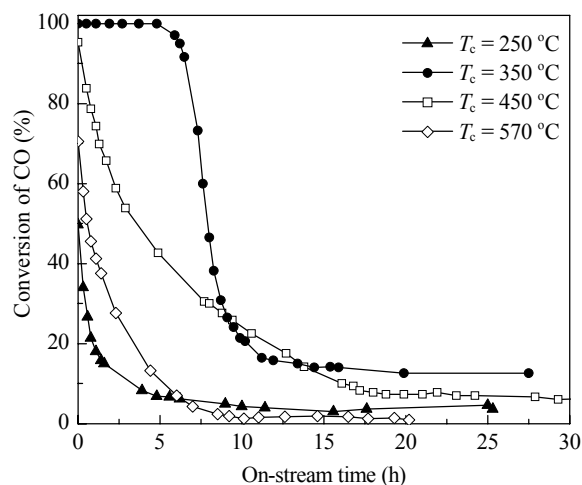


Fig. 2. Durability of sample activity for the 5% $\text{Co}_3\text{O}_4/\text{TiO}_2$ (IW) catalyst after calcination at different temperatures and upon CO oxidation at 100 °C.

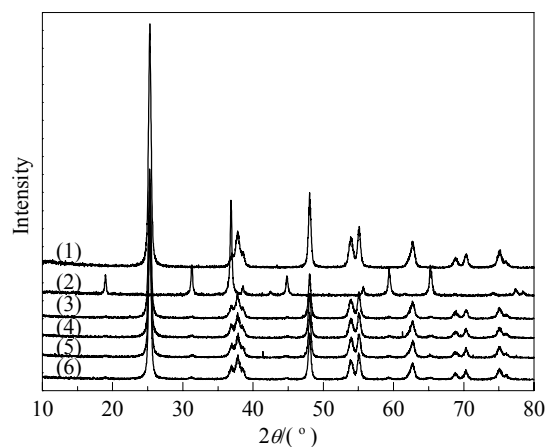


Fig. 3. XRD spectra for 5% $\text{Co}_3\text{O}_4/\text{TiO}_2$ (IW) after calcination at different temperatures. (1) TiO_2 , (2) Co_3O_4 , 5% $\text{Co}_3\text{O}_4/\text{TiO}_2$ (IW) calcined at: (3) 250, (4) 350, (5) 450, and (6) 570 °C.

The cobalt species in the 5% $\text{Co}_3\text{O}_4/\text{TiO}_2$ (IW) catalysts are Co_3O_4 nanoparticles regardless of the calcination temperatures between 250 to 570 °C, as shown in Fig. 3 in which the original intensity of the XRD patterns for all the samples was reduced by 30%–70% to allow for an easier comparison. There were no discernable XRD peaks for the $\text{Co}_n\text{Ti}_{n+2}$ compounds even in the catalyst samples calcined at 450 and 570 °C (Fig. 3(5) and (6)), as expected. Calcination at these high temperatures might produce completely and/or partially $\text{Co}_n\text{Ti}_{n+2}$ -overlaid Co_3O_4 particles, as proposed previously [3]. Based on the results regarding the

influence of calcination excursions on the maintenance of activity profiles and the XRD spectra of 5% $\text{Co}_3\text{O}_4/\text{TiO}_2(\text{IW})$ after calcination at different temperatures, the calcination temperature of the catalyst plays a particular role in catalyst deactivation, and this observation is very consistent with the results reported for Co_3O_4 -based systems [3,12,14,15]. Our earlier $\text{Co}_3\text{O}_4/\text{TiO}_2$ catalysts [3] that had been prepared using shaped TiO_2 with small amounts of (in)organic binders revealed that the best maintenance of activity was obtained at a calcination temperature of 450 °C and this discrepancy may be because of the presence of binders.

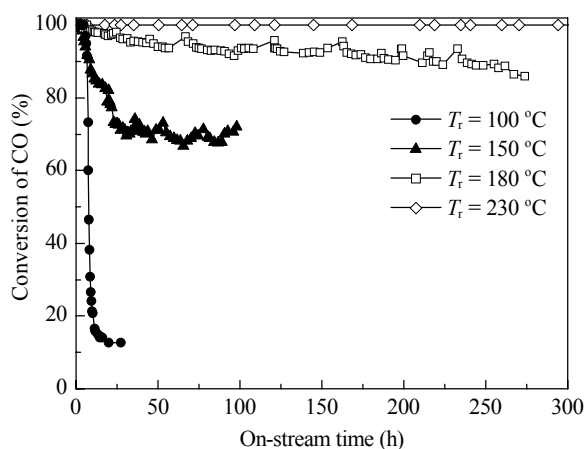


Fig. 4. Effect of reaction temperature on the on-stream performance during CO oxidation over 5% $\text{Co}_3\text{O}_4/\text{TiO}_2(\text{IW})$ that was prepared by calcination at 350 °C.

The durability of the 5% $\text{Co}_3\text{O}_4/\text{TiO}_2(\text{IW})$ catalyst during CO oxidation at different reaction temperatures (T_r) was measured, as shown in Fig. 4. At $T_r = 150$ °C, the catalyst that was calcined at 350 °C gave 100% CO conversion until 4.5 h on stream after which its on-stream performance decreased gradually and it reached steady-state conversions near 70%. The duration of the total conversion was comparable to that obtained at 100 °C. The decreased rate in the on-stream activity of the catalyst for the oxidation at 180 °C was much slower than that observed at lower T_r values such as at 100 and 150 °C. The oxidation of CO at 230 °C retained an apparent total conversion even at approximately 300 h. It is clear that the extent of activity impairment in the oxidation reaction depends strongly on the reaction temperature, and this is in good agreement with earlier reports [9,15]. As the reaction temperature increases the deactivation rate becomes much slower and the steady-state activity becomes significantly higher suggesting a strong relationship between the deactivating precursors and the reaction temperature [9,11]. As already stated, this study did not aim to identify the deactivating precursors that results in catalyst deactivation. However, the observed behavior in on-stream

activity maintenance with respect to reaction temperature may offer us very useful information for the characterization of the used samples to enable us to determine the deactivation mechanism in future.

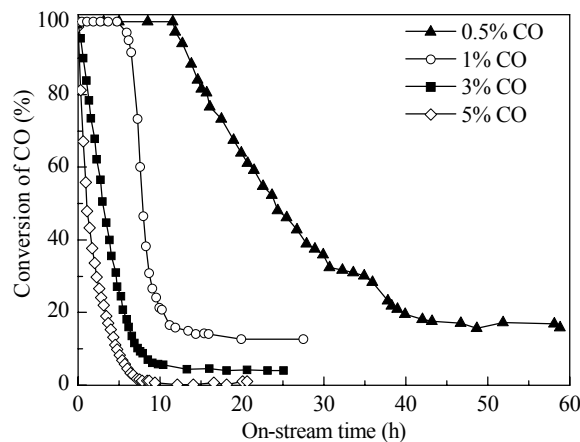


Fig. 5. Effect of CO concentration on activity impairment during CO oxidation at 100 °C over 5% $\text{Co}_3\text{O}_4/\text{TiO}_2(\text{IW})$ that was prepared by calcination at 350 °C.

Figure 5 shows the influence of CO concentration in the feed stream with 3% O_2 on deactivation during CO oxidation at 100 °C over 5% $\text{Co}_3\text{O}_4/\text{TiO}_2(\text{IW})$ after calcination at 350 °C. In the presence of 0.5% CO, the catalyst maintained 100% conversion over a longer time and it also gave much slower deactivation compared to the activity maintenance profile that was measured in a flowing mixture of 1% CO/3% O_2 . When the catalyst was subjected to high concentrations such as 3% and 5% CO the extent of activity maintenance hour at total conversion became shorter as a function of the concentration. The level of steady-state efficiency decreases as the CO concentration fed to the catalyst bed increases. These results indicate that a high CO concentration facilitates catalyst deactivation and suggests that the deactivation precursors and mechanism are closely related to the amount of CO that is exposed to the catalyst surface. As reported for low temperature CO oxidation with a 20% $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ catalyst [6,11] it is possible that the surface free carbon is formed by the CO disproportionation reaction: $2\text{CO} \rightarrow \text{C} + \text{CO}_2$. Surface free carbon can also be produced from CO adsorbed on the catalyst surface according to the following dissociation reaction [6]: $\text{CO} \rightarrow \text{C} + \text{O}$. Based on our results and earlier proposals of deactivation agents during low temperature CO oxidation with unsupported and supported Co_3O_4 -based catalysts [4–6,9–13,24] the deactivation because of carbonaceous materials such as carbonates and surface free carbon seems to be more probable.

To understand the deactivation precursors that results in a decrease in on-stream activity for the 5% $\text{Co}_3\text{O}_4/\text{TiO}_2(\text{IW})$

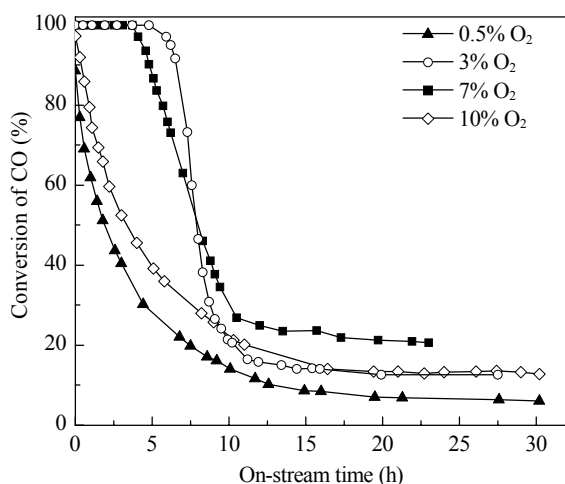


Fig. 6. Effect of O_2 concentration on the activity maintenance for CO oxidation at $100\text{ }^\circ\text{C}$ over 5% $\text{Co}_3\text{O}_4/\text{TiO}_2(\text{IW})$ that was prepared by calcination at $350\text{ }^\circ\text{C}$.

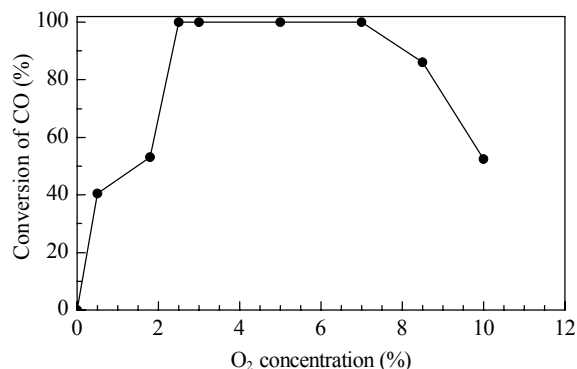


Fig. 7. Optimal O_2 concentrations for CO oxidation at $100\text{ }^\circ\text{C}$ over 5% $\text{Co}_3\text{O}_4/\text{TiO}_2(\text{IW})$ that was prepared by calcination at $350\text{ }^\circ\text{C}$. The conversion values for each corresponding O_2 concentration were chosen near 3 h on-stream.

catalyst during CO oxidation at $100\text{ }^\circ\text{C}$ the effect of oxygen on this catalytic system was examined and the results are given in Figs. 6 and 7. In the absence of O_2 in a feed bearing 1% CO no oxidation reaction occurred (not included here). The oxidation was activated by the introduction of 0.5% O_2 to the feed stream under which the catalyst showed 90% conversion for a very short time and then this activity decreased slowly. This means that oxygen, even in small amounts, is necessary to initiate this reaction over the catalyst [4]. The activity maintenance profile obtained during CO oxidation in flowing 10% O_2 was very similar to that observed under 0.5% O_2 although the onset and steady-state performances were better. For 3% and 7% O_2 in this reaction the deactivation behavior for the number of hours on-stream at which the catalyst gave 100% CO conversion, the deactivation rate and the level-down conversion were comparable with each other. Based on the influence of oxygen on the CO oxidation this indicates that an optimal O_2

content exists for this catalyst and it is between 2.5%–7%, as shown in Fig. 7 in which the conversion values that correspond to each O_2 concentration were chosen at 3 h on stream.

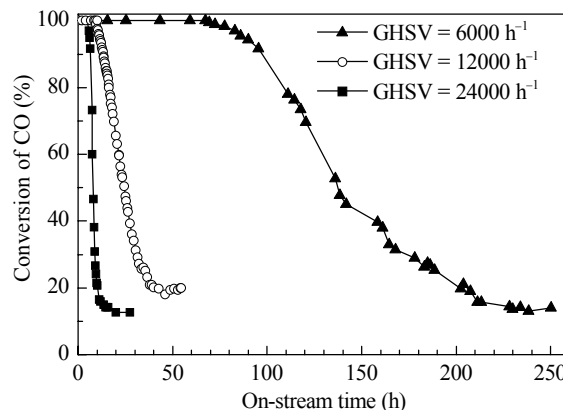


Fig. 8. Effect of gas hourly space velocity (GHSV) on the durability of 5% $\text{Co}_3\text{O}_4/\text{TiO}_2(\text{IW})$ that was prepared by calcination at $350\text{ }^\circ\text{C}$ for CO oxidation at $100\text{ }^\circ\text{C}$.

The gas space velocities noticeably influenced both the activity maintenance hours for 100% conversion and the rate of deactivation for CO oxidation at $100\text{ }^\circ\text{C}$ for the 5% $\text{Co}_3\text{O}_4/\text{TiO}_2(\text{IW})$ sample prepared by calcination at $350\text{ }^\circ\text{C}$, as shown in Fig. 8. At a GHSV value of 6000 h^{-1} , this catalyst gave a total oxidation activity over ca. 70 h on stream although it showed a gradual loss in activity after that time. When the reaction was carried out at higher GHSVs such as at 12000 and 24000 h^{-1} , faster deactivation was observed and this was consistent with the deactivation behavior reported for CO oxidation at $-76\text{ }^\circ\text{C}$ over an unsupported Co_3O_4 catalyst [10]. These results suggest that a carbonaceous species such as carbonates and surface free carbon [4–6,9–11] may be associated with catalyst deactivation because the catalyst had a shorter total oxidation time and a faster deactivation as its exposure to the feed stream increased.

2.2 Effect of H_2O vapor

Not only do HCCI combustion exhausts contain H_2O vapor with concentrations near 5% [25] depending on fuels, loads, and engine operations but Co_3O_4 -based systems are also very sensitive to this guest molecule [4,9,10,12]. Therefore, the tolerance of 5% $\text{Co}_3\text{O}_4/\text{TiO}_2(\text{IW})$ to water vapor was evaluated for CO oxidation at $230\text{ }^\circ\text{C}$ at which temperature this catalyst gave total conversion even at 300 h without any deactivation as shown in Fig. 4. The results are shown in Fig. 9 in which the first injection of 5.8% H_2O to a feed composition of 1% CO and 3% O_2 in flowing He was allowed after a 5 h on-stream operation under dry condi-

tions. The added water led to a severe decrease of 80% for CO oxidation activity and this was similarly indicated upon repeated cyclic operations between dry and wet feeds as marked by the arrows in Fig. 9.

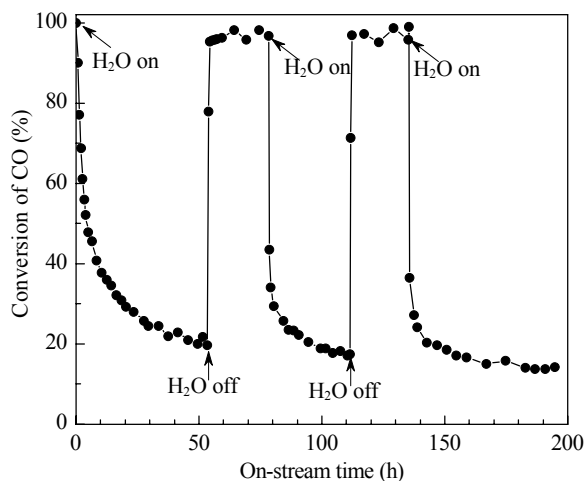


Fig. 9. Cyclic measurements of on-stream performance during CO oxidation at 230 °C in the presence and absence of 5.8% H₂O over 5% Co₃O₄/TiO₂(IW) that was prepared by calcination at 350 °C.

Two noticeable features are present in the cyclic measurements. One is a very quick reduction by 70% within 2 min during the dry activity upon feeding with water vapor as shown for the second and third cycles. After this, the CO conversions decreased very slowly with time. Another feature we observed is an immediate recovery to 100% CO conversion after turning off the water vapor feed and this completely reversible deactivation is reproducible. The first feature readily indicates the competitive adsorption of H₂O on Co³⁺ sites and their hydroxylation and this is in good accord with the results reported for unsupported Co₃O₄ [10,11]. The second feature implies that water vapor does not alter any of the chemical features of the Co₃O₄ nanoparticles present on TiO₂ but remarkably disturbs CO molecule access to them where CO is meant to be adsorbed. Consequently, under such a wet stream, catalyst deactivation may result from competitive H₂O adsorption on the active sites and also by surface hydroxylation, which may be minor although the deposition of carbonates could be accelerated on hydroxylated Co₃O₄ [4].

2.3 Effect of C₃H₈

It is of particular interest to see if C₃H₈ as a model HC gas that exists with CO in HCCI exhausts plays an appreciable role in deactivating the 5% Co₃O₄/TiO₂(IW) catalyst that was prepared by calcination at 350 °C for CO oxidation under the chosen conditions. The results are shown in Fig. 10. The substantial presence of 1% C₃H₈ in a flowing mix-

ture of 1% CO/7% O₂ in He facilitated the deactivation at 100 and 180 °C but did not at 230 °C. The instant the oxidation at 100 °C was initiated the catalyst only gave a 55% CO conversion and it was very quickly deactivated. The influence of C₃H₈ on deactivation at this temperature is dramatic because the catalyst gives total conversion for ca. 5 h in the absence of C₃H₈ in the feed stream. Comparing the extent of the maintenance in 100% CO conversion indicated that during CO oxidation at 180 °C, in the absence of C₃H₈, this guest could significantly induce additional deactivation of the catalyst. Simultaneous measurements of C₃H₈ conversion under this reaction condition were found to be less than 5%, irrespective of the reaction temperature (not shown here), which indicates that the catalyst is inactive during C₃H₈ oxidation even at 230 °C where CO was completely removed despite the co-existence of C₃H₈. This result is very consistent with the earlier publication of Xie et al. [9] who reported that when both CO and C₃H₈ are present in a feed gas stream CO is completely oxidized by a nano-rod-type Co₃O₄ catalyst at 200 °C and C₃H₈ oxidation is negligible. Consequently, the presence of C₃H₈ in the feed stream containing CO greatly affects the CO oxidation activity of the catalyst at low temperatures such as 100 °C and it seems that this catalyst deactivation is involved in the competing process of the adsorption of C₃H₈ on TiO₂-supported Co₃O₄ nanoparticles, which are the active sites for CO oxidation.

2.4 Physical properties of the deactivated samples

Some samples of the 5% Co₃O₄/TiO₂(IW) catalyst after CO oxidation with different reaction parameters that affect deactivation were characterized by BET and XRD measurements and carbon depositions were also analyzed. However, we do not expect that these characterizations will reveal the whole nature of the precursors with regards to catalyst deactivation. Regardless, this is consistent with the

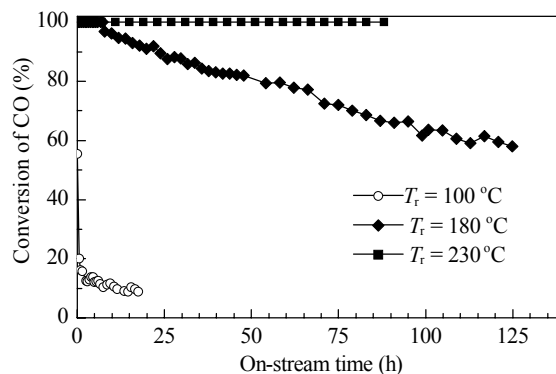


Fig. 10. Activity maintenance profiles for CO oxidation at 100–230 °C in the presence of 1% C₃H₈ over 5% Co₃O₄/TiO₂(IW) that was prepared by calcination at 350 °C.

Table 2 Physicochemical properties of the 5% Co₃O₄/TiO₂(IW) catalyst prepared by calcination at 350 °C followed by CO oxidation under the chosen conditions

| T_r (°C) | Reaction conditions | | | S_{BET} (m ² /g) | Pore diameter (nm) | Pore volume (cm ³ /g) | Co ₃ O ₄ size ^a (nm) | Carbon amount (%) |
|---------------|----------------------------|-------------|--------------------------|----------------------------------|-----------------------|-------------------------------------|--|----------------------|
| | GHSV (h ⁻¹) | [CO] (%) | [O ₂] (%) | | | | | |
| 100 | 6000 | 1 | 3 | 79 | 13.6 | 0.279 | 11.1 | 0.38 |
| 100 | 12000 | 1 | 3 | — | — | — | — | 0.093 |
| 100 | 24000 | 1 | 3 | 78 | 13.9 | 0.284 | 10.9 | 0.11 |
| 150 | 24000 | 1 | 3 | 81 | 13.7 | 0.281 | — | 0.053 |
| 180 | 24000 | 1 | 3 | — | — | — | 11.2 | 0.036 |
| 230 | 24000 | 1 | 3 | 77 | 13.2 | 0.273 | 10.8 | 0.012 |
| 100 | 24000 | 0.5 | 3 | 80 | 13.5 | 0.281 | 10.9 | 0.12 |
| 100 | 24000 | 3 | 3 | — | — | — | — | 0.19 |
| 100 | 24000 | 5 | 3 | 79 | 13.8 | 0.282 | 10.9 | 0.26 |
| 100 | 24000 | 1 | 0.5 | — | — | — | 11.0 | 0.12 |
| 100 | 24000 | 1 | 7 | — | — | — | — | 0.061 |
| 100 | 24000 | 1 | 10 | 78 | 13.3 | 0.275 | 10.8 | 0.041 |

^aBased on the XRD peaks.

limits of our present study, as stressed already.

To determine whether or not any change in the physical features of the 5% Co₃O₄/TiO₂(IW) catalyst prepared by calcination at 350 °C occurred following CO oxidation under the chosen reaction conditions, BET and XRD measurements were conducted for each sample of interest. These results are listed in Table 2 and compared to those of a fresh catalyst as given in Table 1. A fresh sample of the catalyst that was prepared by calcination at 350 °C had a surface area of 78 m²/g (Table 1) and even after CO oxidation with a variety of reaction parameters this value was unchanged as listed in Table 2. Characterization of the sample porosity after deactivation under the given reactions revealed no significant alteration in both the mean pore diameter and the pore volume, as compared in Tables 1 and 2. The fresh catalyst consisted of Co₃O₄ nanoparticles with an average crystallite size of 11.0 nm (Table 1). This catalyst contained Co₃O₄ with nanoparticle sizes of 11 ± 0.2 nm regardless of oxidation under different conditions as listed in Table 2 indicating no appreciable change in the phase of Co₃O₄ and its particle size, which agrees fairly well with a previous study [11]. Consequently, these measurements indicate that none of the CO oxidations conducted under different conditions led to a significant change in the physical properties of the catalysts including the surface area, the pore diameter and volume, and the phase of the Co₃O₄ nanoparticles and their size. However, severe deactivation occurred and the precursors that cause this catalyst deactivation do not visibly alter their physical properties.

The amounts of carbon deposited on the Co₃O₄-based catalysts after CO oxidation under the chosen reaction conditions are expected to help us to reasonably understand the deactivating agents. Therefore, carbon deposition on the 5% Co₃O₄/TiO₂(IW) catalyst samples after CO oxidation using

the different reaction parameters chosen here was determined and these results are also included in Table 2.

Only a trace amount of carbon (approximately 0.014%) was present in the fresh catalyst sample (Table 1), and this was an impurity in the TiO₂ support. As given in Table 2, using the fresh catalyst for CO oxidation under the given reaction conditions led to the deposition of a carbonaceous material and this depended significantly on the conditions employed. In all cases, the amount of carbon did not directly reflect the deactivation and its rate is shown in Figs. 4–6 and 8. These differences were obtained because these samples were subjected to different reaction conditions as well as incomparable time on-stream. Regardless, the extent of carbon accumulation in some cases can provide very useful information about catalyst deactivation during CO oxidation. The catalyst analyzed after CO oxidation at 230 °C for 300 h contained no carbon on the surface while 0.11% carbon was measured after oxidation for 30 h at 100 °C and 24000 h⁻¹, as listed in Table 2. Secondly, the amount of carbon found on the catalyst upon CO oxidation at 100 °C under identical conditions, except for the CO concentration, was proportional to the percentage levels of the CO feed (Table 2) but there was a significant difference between the on-stream hours allowed, as in the case of the 0.5% and 5% CO (Fig. 5). Thirdly, increasing the O₂ concentration for the oxidation gave less carbon deposition on the catalyst surface, as listed in Table 2. Finally, a sample of the catalyst that underwent 250 h on-stream CO oxidation at 100 °C and 6000 h⁻¹ gave much more carbon deposition (0.38%) than that measured after the reaction for on-stream times of less than 50 h under the same conditions but at higher GHSVs such as 12000 and 24000 h⁻¹, and this is given in Table 2 and Fig. 8. Based on these carbon content results the carbonaceous species that was deposited on the catalyst surface is

closely associated with the deactivation of the catalyst under the dry streams and they may primarily be carbonates and surface free carbon among the earlier proposed deactivation precursors, and competitive adsorption of O₂ and CO on the same Co³⁺ sites could occur because of the probable chemisorption of O₂ on Co₃O₄ [4,26], thereby resulting in the deactivation of the catalyst upon oxidation in high O₂ concentrations such as 10%.

3 Conclusions

The incipient wetness (IW) technique was found to be advantageous for the preparation of supported Co₃O₄ nanoparticles for CO oxidation at low temperatures, and a 5% Co₃O₄/TiO₂(IW) catalyst was found to have the best activity maintenance for low temperature oxidation upon calcination at 350 °C. The influences of the chosen reaction parameters and guest molecules (H₂O and C₃H₈) on the deactivation of the catalyst during oxidation are very complicated. The extent of catalyst deactivation and its rate are in reasonable agreement with the reaction temperatures, the CO concentrations fed to an inlet stream and the gas hourly space velocities. At a high temperature and low CO concentration as well as at a low gas hourly space velocities the catalyst shows less deactivation during oxidation although detailed profiles of activity maintenance varies with on-stream hours. The activity maintenance profiles of the catalyst for CO oxidation at 100 °C under different O₂ concentrations indicates that an optimal content of O₂ for the feed exists and that the competing process of Co₃O₄ nanoparticle adsorption is a part of the deactivation scheme. No appreciable changes in the surface area, the mean diameter of pores present in TiO₂ and their volume, and the size of the Co₃O₄ nanoparticles occur even for the catalyst samples that were severely deactivated upon oxidation under the chosen conditions. Some catalyst samples, after the reaction, have significant carbon deposition probably as carbonates and surface free carbon, and this depends strongly on the reaction variables chosen. These carbonaceous substances may play a significant role in catalyst deactivation. The substantial presence of H₂O in the chosen feed stream results in severe deactivation of the catalyst for CO oxidation, even at 230 °C, but this effect is completely reversible. In the presence of C₃H₈ as a guest molecule the extent of oxidation at low temperatures such as at 100 °C diminishes noticeably but does not do so at 230 °C.

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