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On-line deactivation of Au/TiO_2 for CO oxidation in H_2-rich gas streams

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Abstract

Au-based catalysts, known for ambient temperature CO oxidation, have to provide stable performance of up to 5000 h in order to be commercially applicable in automotive fuel cells. In this report, the on-line deactivation characteristics of Au/TiO_2 in unconventional PROX conditions are discussed. As opposed to CO removal from air, results in this report suggests that carbonates have a minor effect on deactivation of Au/TiO_2 in dry H_2-rich conditions. Also, no conclusive correlation between surface hydration and deactivation was observed. Rather, deactivation appeared to have occurred as a result of an intrinsic transformation in the oxidation state of the active species in the reducing operating conditions; a process which was reversible in an oxidizing atmosphere.

Keywords: Au/TiO_2; Deactivation; CO oxidation; Hydrogen; PROX

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1. Introduction

The production of hydrogen from hydrocarbon compounds such as methanol or natural gas is arguably the most feasible method of producing large quantities of hydrogen in the foreseeable future. One disadvantage of hydrocarbon reforming is the fact that CO is a typical by-product and has to be removed to sub-ppm levels in order for the Pt-catalyzed anodes in the fuel cell to perform optimally [1–5]. Conventional PROX systems treat the exit stream from the low temperature water–gas-shift reactor in fuel processors for CO removal and thereafter the diluted hydrogen stream is fed to a PEM fuel cell as fuel. Typical streams for PROX are at 80–120 °C and contain large amounts of water and CO_2. Recent results have shown that Au/Fe_2O_3 is a good catalyst for CO removal under these conventional conditions [6]. In an alternative system, hydrogen permeable membranes (e.g. Pd) or PSA units purify the post water–gas-shift stream and the concentrated hydrogen fuel, with some CO/CO_2 contamination, is passed to the fuel cell. CO tolerant anode catalysts such as PtRu/C tolerate the last traces of CO.

In this work, an unconventional PROX system is envisaged that could treat the partially purified hydrogen stream, from e.g. PSA, which has been dried and compressed for storage [7]. Partial purification could significantly lower the cost of hydrogen production. The catalyst for such an unconventional PROX system would have to operate, or at least light-off, at the ambient temperature of the stored hydrogen and have high selectivity for CO oxidation in this very hydrogen-rich atmosphere. Gold-based catalysts have well known ambient temperature activity and show selectivity for CO oxidation and as such appear as a good choice for an unconventional PROX system. In this report, temperature, water content, and CO and CO_2 concentrations have been chosen that better reflect unconventional PROX than the conventional case.

1.1. Gold-based catalysts for CO oxidation

Gold-based catalysts have been extensively studied over the past two decades and have involved a range of metal oxide

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supports such as TiO_2, Fe_2O_3, CeO_2, Al_2O_3, ZnO, SiO_2, Co_3O_4, MnO_2, Mn_3O_4, MgO, and SnO_2. Although the necessity of having both gold nanoparticles and a metal oxide support for catalytic activity has generally been confirmed, one ongoing debate concerns the nature of the active species. Some authors suggest that ionic gold provides the active sites for CO oxidation [8,9] whereas others claim metallic gold to be the active species [10,11]. It has also been suggested that both ionic and metallic gold is essential for catalytic activity [12].

Although metal oxide supported gold catalysts have an intrinsic advantage over other CO oxidation catalysts, it has been shown that they tend to deactivate with storage and/or time on-line [13–17]. Deactivation of Au metal-oxide catalysts for the CO oxidation has previously been ascribed to the accumulation of carbonate species, which can block access of CO and O_2 to the active sites [13,14]. The formation of carbonate-species can occur by the adsorption of CO_2 in air (i.e. in storage) or from CO_2 present in the reactant or product gas mixture (i.e. on-line). It has been reported that the addition of H_2O can prevent the deactivation of Au/α-Fe_2O_3 [13] and Au/Al_2O_3 [15] and may enhance the rate of decomposition of carbonate species by reactive conversion to bicarbonate species, which are thermally less stable. Manzoli et al. [17] reported that hydrogen reduced the deactivation of Au/ZnO catalysts by inhibiting the formation of transient intermediates and stable carbonates on the support. FTIR studies suggested the reduction of the amount of stable species at the interface resulted from the lowered basicity of the reactive oxygen at the metal support interface. Hydrogen inhibition of formate and carbonate formation was also observed by Shumacher et al. [18] using Au/TiO_2 catalysts.

Another generally accepted mechanism for catalyst deactivation is growth in the size of the gold particles [19–21]. This effect is more prevalent when catalysts are exposed to high temperatures and/or if species such as chlorine (Cl^-) are present that lead to high gold atom mobility and sintering of the gold nanoparticles.

Although the above mentioned are possible explanations for the deactivation phenomena of metal oxide supported gold catalysts, an exact mechanism for deactivation has not yet been fully revealed; nor whether the same mechanism operates for CO oxidation in oxygen-rich (i.e. air) or hydrogen-rich (i.e. PROX) conditions or the effect of CO_2 and H_2O on catalyst stability. These issues were addressed in this paper with specific focus on the online deactivation characteristics of Au/TiO_2 in dry, cylinder stored CO contaminated H_2 for fuel cell applications.

2. Experimental

Preparation and pretreatment conditions have a significant effect on the activity and stability of Au-based catalysts [22–24]. In this work the Au/TiO_2 catalysts were prepared via deposition-precipitation of gold from diluted $HAuCl_4$ onto Degussa P25 TiO_2. Gold solution was heated to 70 °C and the pH adjusted to 7.5 with Na_2CO_3. TiO_2 was added to the stirred Au solution in a single step and the pH (HNO_3/Na_2CO_3) and temperature maintained for 1 h. The catalyst was filtered and washed with high purity water in a five-stage washing cycle and then dried at 120 °C for 14 h. A fraction of the catalyst (30 mg) was packed in a 4 mm diameter U-tube glass reactor that was immersed in a temperature controlled water bath. A thermocouple was inserted into the catalyst bed to monitor the bed temperature.

The initial deactivation of a 5 wt.% Au/TiO_2 catalyst was determined by introducing 80 ppm CO in H_2 with a 2% air bleed stream to the catalyst for 24 h at 25 °C and at a mass hourly space velocity (MHSV) of $2000\ \mathrm{l}\ \mathrm{g_{cat}}^{-1}\ \mathrm{h}^{-1}$. The gas samples were analysed by GC with a Pulse Discharge Helium Ionisation Detector (PDHID). Fourier transform infrared spectroscopy (FTIR) was used to analyse the surface of the catalyst before and after the 24 h on-line deactivation test.

The influence of CO_2 on deactivation was investigated by co-introducing 2000 ppm CO_2 with the reaction mixture above.

The effect of surface hydration on deactivation was investigated by heating the catalyst reactor to 60 °C thereby decreasing the relative humidity in the U-tube reactor and preventing the accumulation of liquid water.

3. Results and discussions

Fig. 1 shows the deactivation characteristics of a 5 wt.% Au/TiO_2 catalyst operating in 80 ppm CO in H_2 and a 2% air bleed stream. The CO conversion decreased from approximately 65% to less than 20% within 24 h. Also shown in Fig. 1 is the influence of CO_2 on the rate of deactivation. Although the presence of 2000 ppm CO_2 in the reaction gas mixture caused the initial CO conversion to decrease by approximately 8%, the overall rate of deactivation was similar to that of the non-CO_2 containing feed stream. In addition, the conversion levels from the CO_2 and non-CO_2 containing feed streams seemed to converge after approximately 13 h on stream and remained identical for the remainder of the test. The experiment shows that additional CO_2 does not significantly increase the rate of deactivation, which implies (assuming carbonate build-up deactivates) that gas phase CO_2 is not significantly absorbed as carbonate under the reaction conditions. Initially the large excess of CO_2 does lower activity, implying some absorption of CO_2 but in the end the catalyst achieves the same state under both conditions. Indirectly it also suggests that surface bound carbonates are mostly derived directly from the oxidation of surface bound CO and not from reverse absorption of released product CO_2. FTIR analysis supports the final state of the catalyst being similar under both conditions with respect to carbonate absorption, as shown in Fig. 2. Since no significant change in the adsorbed carbonate is seen, the role of carbonate accumulation in the deactivation is undefined. Equally the adsorbed carbonate may be a spectator species and the deactivation a result of other changes in the catalyst.

Fig. 2 shows the FTIR spectra of Au/TiO_2 before and after the 24 h CO oxidation tests. An intense broad band at 3600–3000 cm^{-1} in the OH-stretching region typifies this spectrum. In the 1800–1100 cm^{-1} region, an intense band at 1612 cm^{-1} can be observed which is due to δ(HOH) [25,26]. The medium- to

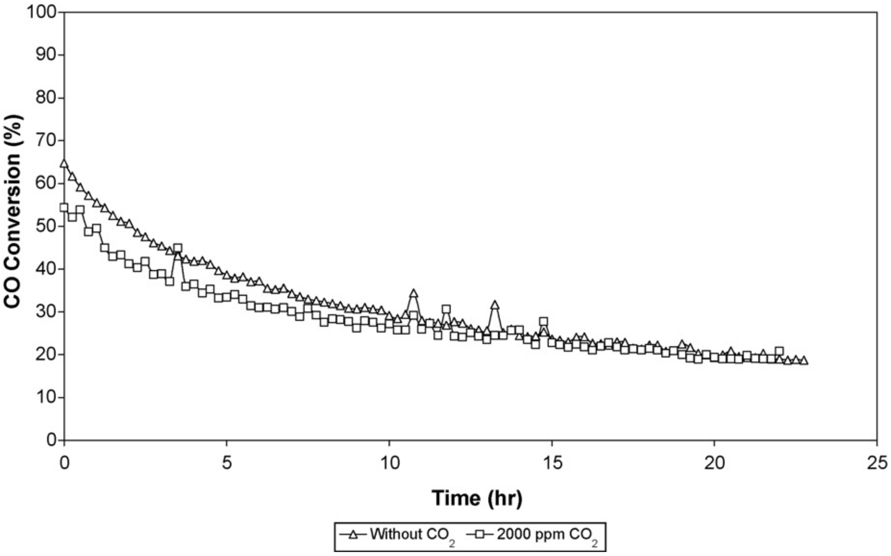

Fig. 1. Influence of 2000 ppm CO_2 on deactivation of a 5 wt.% Au/TiO_2 granulate catalyst (80 ppm CO, balance H_2, 2% air bleed, MHSV = 2000 l g_{cat}^{-1} h^{-1}, 25 °C).

low-intensity bands at 1410 and 1196 cm^{-1} may be assigned to either monodentate or uncoordinated carbonate species [27], or to bicarbonate species [28] adsorbed on the support, although carboxylate species also have absorption bands in the same region [25].

From Fig. 2, it is evident that both the Au/TiO_2 catalysts tested in 80 ppm CO, with and without CO_2, yielded similar spectra, but they were distinct compared to the spectrum of the fresh/untested catalyst. The results clearly show a marked accumulation of H_2O and a marginal increase in the amount of adsorbed CO_3^{2-} species during online CO oxidation. (Note that the baseline in the 1500–800 cm^{-1} region was lower for the fresh catalyst than for those tested.) These results indicated that hydration of the catalyst's surface might play as great or even a greater role in deactivation than the accumulation of carbonate species. In an attempt to promote the hydration effect, the catalyst bed was heated to 60 °C in a temperature controlled water bath, while the inlet gas temperature remained constant at 25 °C. It is well known that the selectivity for CO oxidation in hydrogen over Au/TiO_2 falls rapidly with increasing temperature below 100 °C [18,29], thus the rate of water production increases at 60 °C relative to 25 °C. The lower selectivity is supported by the small increase in CO conversion at 60 °C as shown in Fig. 3 (oxygen consumption was not monitored to confirm the lower selectivity). It is evident that the increase in temperature had a limited effect on the deactivation characteristics, which is interpreted as water production, under these relatively dry unconventional PROX conditions, has a limited

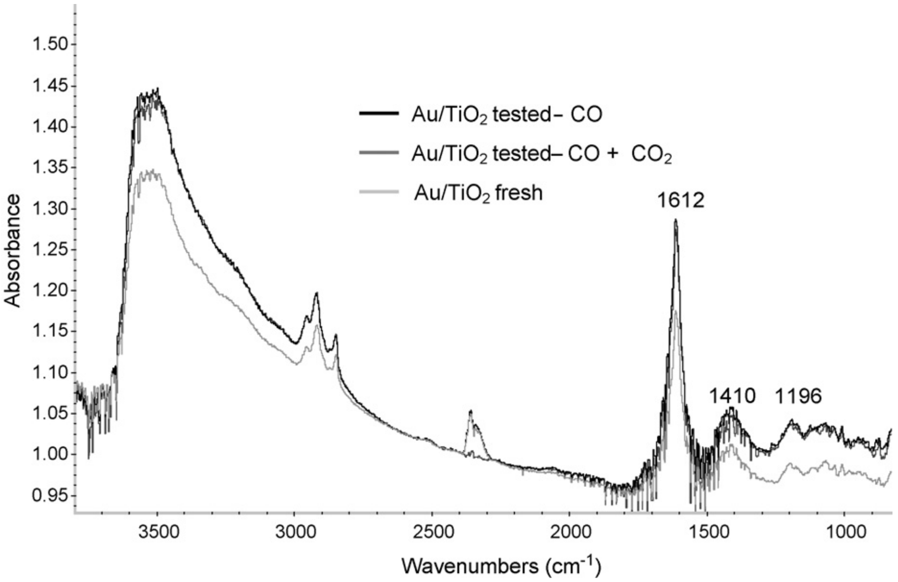

Fig. 2. FTIR spectra recorded before and after CO oxidation over Au/TiO_2 (5 wt.% Au/TiO_2, CO oxidation tests: 80 ppm CO in H_2, 2% air, with or without 0.2% CO_2, MHSV = 2000 l g_{cat}^{-1} h^{-1}, 25 °C, 23 h online operation).

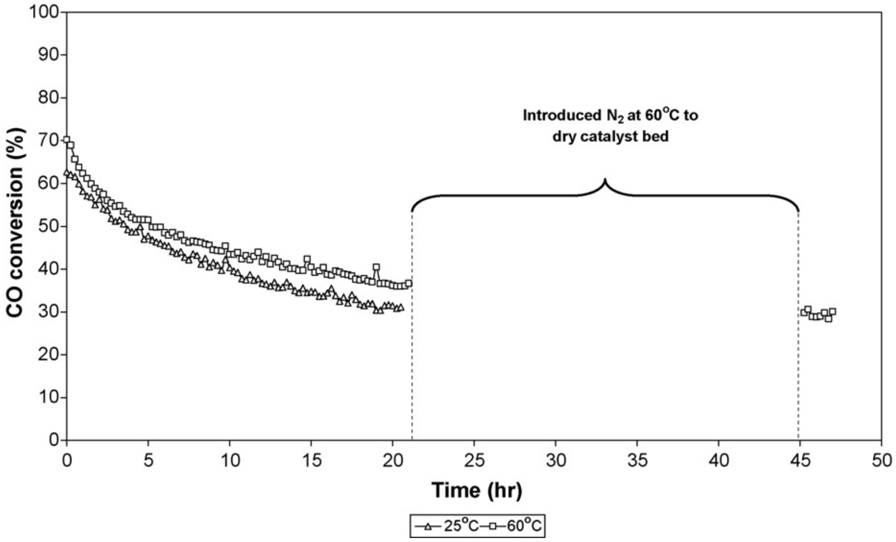

Fig. 3. Influence of catalyst bed temperature and drying on the deactivation of a 5 wt.% Au/TiO_2 granulate catalyst (50 ppm CO in H_2, 2% air, 2000 ppm CO_2, MHSV = 2000 l g_{cat}^{-1} h^{-1}).

effect on the deactivation. In an attempt to dry the catalyst in situ, or at least lower the adsorbed water content on the catalyst, dry N_2 was introduced to the heated catalyst bed (60 °C) at 960 ml min^{-1} for 24 h. However, from Fig. 3 it is evident that this had no distinct effect on the deactivated catalyst. It is therefore clear that the accumulation of water on the catalyst's surface is not the dominating deactivation mechanism.

The question that remained at this stage of the investigation was whether deactivation of the Au/TiO_2 catalysts is due to an intrinsic transformation in the catalytic properties of Au/TiO_2. Examples of such transformations are the change in the oxidation state of the perimeter gold species, i.e. Au^{x+} or Au^0, and/or the reduction of the surface of the support surrounding the gold particles [30]. Various researchers have different opinions concerning what is the active form of gold [8–11]. Bond and Thompson [12] proposed an interesting mechanism, suggesting that it is not exclusively ionic or metallic gold that causes gold-based catalysts to be active, but that the presence of both may be necessary. Visco et al. [31] have also observed a decrease in activity during on-line operation and have ascribed this effect to the reduction of Au^{x+} ions by carbon monoxide to Au^0, although an initial increase in activity has been observed before reaching a stable high level [32]. Elsewhere it has been demonstrated [33], using in situ X-ray absorption spectroscopy and TPR, that CO and/or CO–H_2 mixtures cause reduction (and activation) of gold in carefully prepared Au–TiO_2 originally containing Au(III). Further, there is evidence [34] that a partial reduction of gold is associated with high CO oxidation activities for several supported Au catalyst systems. The deactivation mechanism due to over reduction of ionic gold to metallic gold by carbon monoxide [31] in air is of concern since, for the application in this study, the gas mixture will

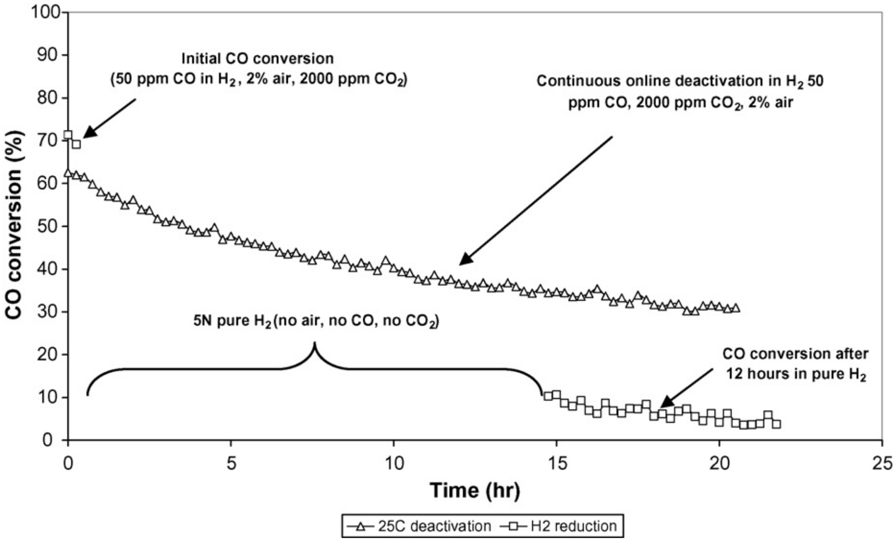

Fig. 4. Influence of 12 h 5N H_2 treatment on catalytic activity of a 5 wt.% Au/TiO_2 granulate catalyst (CO conversion from gas mixture containing 50 ppm CO in H_2, 2% air, 2000 ppm CO_2, MHSV = 2000 l g_{cat}^{-1} h^{-1}, 25 °C).

consists mainly of a reducing gas, namely hydrogen. If the mechanism proposed by Bond and Thompson is accurate, and if the deactivation effect proposed by Visco et al. is correct, then it might be possible that the apparent deactivation seen in the present investigation is due to an intrinsic, maybe irreversible, transformation in the catalytic/chemical properties of Au/TiO_2. To investigate this possibility, a 5 wt.% Au/TiO_2 catalyst was exposed to a gas mixture similar to that associated with the data shown in Fig. 3 (50 ppm CO, 2000 ppm CO_2, balance H_2 and a 2% air bleed) and the initial CO conversion was measured, there after the CO, CO_2, and air was removed and 5N pure H_2 was introduced for 12 h (thereby eliminating the possibility of deactivation due to the accumulation of carbonates or due to surface hydration). After 12 h in pure H_2 the initial gas mixture was re-introduced and the CO conversion measured. As is evident from Fig. 4, very significant deactivation occurred, much more severe than that presented in Fig. 3. This clearly indicates that, for this system, the accumulation of carbonates and water has minor effects on deactivation. The results in Fig. 4 might therefore indicate that the proposed "balance" between ionic and metallic gold [12] is distorted during online operation in a reducing (hydrogen) atmosphere. What supports this hypothesis even more is the fact that deactivation is more pronounced in the absence of oxygen, possibly due to faster reduction of the Au^{x+} to Au^0, as is evident from Fig. 4. It could be suggested that the severe deactivation might result from sintering of the Au nanoparticles under a hydrogen atmosphere, but several studies [35,36] have shown that hydrogen treatment of fresh Au/TiO_2 catalyst favors the formation of smaller Au particles. TEM images (not shown) of the catalysts prepared in this work show Au particles of similar or smaller sizes after hydrogen treatment of the freshly prepared catalysts, in agreement with literature [35,36]. Thus sintering of the Au appears not to be the dominant deactivation mechanism.

If the hypothesis discussed above is valid, then reactivation of the catalyst might be possible in an oxidizing atmosphere by withdrawing electrons from perimeter site gold atoms, thereby re-establishing the proposed "balance" between Au^0 and Au^{x+}. This was investigated by systematically introducing air, oxygen, and ozone (Ozone Industries Ltd. AirMaid 3280, 100 mg O_3/h) to the catalyst after deactivation ("over-reduction") in pure H_2. The results are shown in Fig. 5, from where it is evident that the H_2 deactivation effect observed in Fig. 4 has been confirmed. A 3 h treatment in 45 ml min^{-1} air (period 21–23 h in Fig. 5) had a very small effect on reactivation. However, on-line deactivation continued when the test gas mixture was reintroduced (period 23–25 h in Fig. 5). Significant reactivation was observed following an 18 h treatment in 45 ml min^{-1} pure oxygen. The CO conversion increased from 18% to over 43%. In addition, the on-line stability appeared to have increased following the 18 h O_2 treatment (period 42–45 h in Fig. 5). The activity was further increased to 50% after a 2 h treatment in 45 ml min^{-1} O_3. These results support the hypothesis that both Au^0 and Au^{x+} are essential for CO oxidation. These experiments have shown a reductive deactivation of the catalyst that in line with other literature studies has been interpreted to mean reduction of the active Au species. However, the possibility of deactivation/reactivation due to the reduction/oxidation of the support surrounding the gold particles cannot be excluded, as recently reported by Moreau and Bond [30]. Studies into the oxidative changes of the support in the catalysts prepared in this study are ongoing.

4. Conclusions

The deactivation of Au/TiO_2 catalysts in a dry hydrogen-rich atmosphere has stimulated research into understanding the mechanism of deactivation. Results in this article suggest that the accumulation of carbonate species and surface hydration have a minor, if any, effect on the on-line deactivation of Au/TiO_2 under the unconventional PROX conditions used in this work. Rather, it was found that deactivation is more likely to be due to an intrinsic transformation in the catalytic properties of the catalyst; by distorting the proposed balance between Au^0

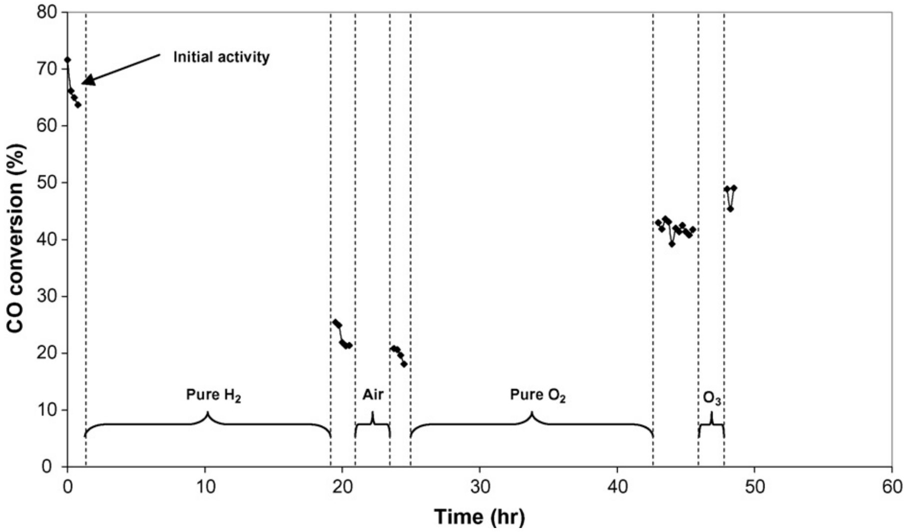

Fig. 5. Influence of reducing/oxidizing atmosphere on the catalytic activity of a 5 wt.% Au/TiO_2 granulate catalyst (50 ppm CO, 2000 ppm CO_2, balance H_2, 2% air bleed, MHSV = 2000 l g_{cat}^{-1} h^{-1}, 25 °C).

and Au^{x+} through reducing Au^{x+} to Au^0. This process was reversible by exposing the catalyst to oxidizing atmospheres.

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