Co-precipitated copper zinc oxide catalysts for ambient temperature carbon monoxide oxidation: effect of precipitate aging atmosphere on catalyst activity

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A study of the effect of the aging atmosphere on the activity of co-precipitated copper zinc oxide catalysts for the ambient temperature oxidation of carbon monoxide is described and discussed. Four aging atmospheres are reported: air, N_2, H_2 and CO_2, and both the precipitation and the aging of the precipitate were carried out by flowing these gases through the precipitation cell at constant pH and temperature. For all atmospheres, the surface area of the final CuO–ZnO catalyst increases with aging time and, consequently, the specific activity (mol CO converted/g catalyst/h) also increases. However, the intrinsic activity (mol CO converted/m^2/h) initially decreases with aging time before attaining a steady level. The highest activity catalysts were obtained using air as the aging atmosphere and TPR studies indicate that this catalyst is less readily reduced. Catalysts prepared using CO_2 as the aging atmosphere have lower activity, although the surface areas of these catalysts are not markedly lower. The study demonstrates that selection of the appropriate aging atmosphere, as well as the aging time, is an important parameter for the preparation of co-precipitated catalysts.

KEY WORDS: co-precipitated catalysts; N_2; H_2; CO_2; copper zinc oxide.

1. Introduction

Copper zinc oxide catalysts are important commercially in the conversion or preparation of synthesis gas [1,2]. Although the industrially used catalysts normally contain additional compounds, e.g. Al_2O_3 or MgO, that act as structural promoters, it is generally agreed that the active components comprise copper and zinc oxide [3–9]. These catalysts are prepared using a co-precipitation procedure in which the reaction parameters have to be closely controlled; these include reagent concentration, pH, temperature, aging time and calcination temperatures. When copper zinc oxide catalysts are used in synthesis gas reactions, the final calcined precipitate is usually carefully reduced in dilute hydrogen to give a material containing a high dispersion of small copper crystallites supported on zinc oxide [2].

Recently, there has been renewed interest in the design of catalysts for the oxidation of carbon monoxide at ambient temperature. Current commercial catalysts are based on hopcalite, a mixed copper manganese oxide ($CuMN_2O_4$) [10–13]. These catalysts are important in respiratory protection in military, mining and space applications. Supported gold nanocrystals have also been found to be effective catalysts for this reaction, although they have yet to be used commercially [14,15]. Both the supported gold nanocrystals and the copper manganese mixed oxide catalysts are prepared using a co-precipitation procedure. We have shown that the time for which the precipitate is left in contact with the preparation media, a process known as precipitate aging, is of critical importance with respect to controlling the catalyst structure and activity [12,16]. In an earlier communication [17] we have shown that co-precipitated and unreduced copper zinc oxides are also effective catalysts for the oxidation of carbon monoxide at ambient temperature. In a detailed structural study of catalysts aged in an air atmosphere, we have shown that the aging process leads to the formation of solid solutions of copper oxide and zinc oxide together with copper nanoparticles [18]. Although it is now recognized that the process of precipitate aging is crucial in the overall preparation procedure, there are still very few studies in which it is investigated. In particular, the effect of different aging atmospheres has not been studied. In this paper, we now address this aspect of catalyst preparation and we present the results showing the effect of the aging atmosphere on the preparation and activity of copper zinc oxide catalysts.

2. Experimental

2.1. Catalyst preparation

The copper zinc oxide catalysts were prepared using the following standard co-precipitation procedure in

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which all conditions were maintained constant except that the atmosphere was varied. Catalysts were prepared using a co-precipitation technique. Aqueous solutions of $Cu(NO_3)_2{\cdot}3H_2O$ ($0.25\,mol\,l^{-1}$, Aldrich, 99.999%) and $Zn(NO_3)_2{\cdot}6H_2O$ ($0.25\,mol\,l^{-1}$, Aldrich, 99.999%) were pre-mixed in a 2 : 1 ratio. The solution was stirred, heated to 80 °C in a round-bottomed flask fitted with a condenser and equilibrated with air at $20\,ml\,min^{-1}$, flowing through the flask for 5 min. An aqueous solution of Na_2CO_3 ($0.25\,mol\,l^{-1}$, Aldrich, 99.999%) was added to the continuously stirred flask until a pH of 7.0 was attained. At this stage a gas selected from air, N_2, H_2 or CO_2 ($20\,ml\,min^{-1}$) was passed through the solution and the precipitate allowed to age between 30 and 300 min while the pH was maintained constant at 7.0. After aging, the precipitate was recovered by filtration, washed several times with hot distilled water, dried in air (120 °C for 16 h) and subsequently calcined in static air (550 °C for 6 h) to produce the catalyst.

2.2. Catalyst testing

The catalysts were tested for CO oxidation using a fixed-bed laboratory microreactor. Typically CO (5% CO in He, $5\,ml\,min^{-1}$) and O_2 ($50\,ml\,min^{-1}$) were fed to the reactor at controlled rates using mass flow controllers and passed over the catalyst (100 mg) maintained at 20 °C. The products were analyzed using on-line gas chromatography with a 3 m packed Carbosieve column. These conditions are equivalent to a total gas hourly space velocity of $33\,000\,h^{-1}$ and CO concentration of 0.45 vol%. Under these conditions the adiabatic temperature rise is <7 °C and, consequently, the reactor temperature could readily be maintained isothermally at 20 °C.

Temperature-programmed reduction (TPR) studies were carried out using a Micromeritics TPD/TPR 2900 system. Typically, a calcined catalyst sample (25 mg) was heated from ambient to 300 °C under flowing hydrogen ($50\,ml\,min^{-1}$) with a temperature ramp of $10\,°C\,min^{-1}$.

3. Results and discussion

A set of catalyst precursors and calcined catalysts were prepared using air, N_2, H_2 and CO_2 as the aging atmospheres with aging times of 0–300 min. The surface area of the calcined materials generally increased with aging time for all four aging atmospheres (table 1). The precursors were largely found to be amorphous by powder X-ray diffraction (figure 1) and generally comprised gerhardite ($Cu_2(OH)_3NO_3$), rosasite ($(Cu/Zn)_2CO_3(OH)_2$), aurichalcite ($(Cu/Zn)_5(CO_3)_2(OH)_6$), malachite ($Cu_2CO_3(OH)_2$) and tenorite (CuO). It is clear that the aging atmosphere affected the structure of the initial precursor. However, examination of the calcined catalyst using powder X-ray diffraction showed the materials all to be similar and comprise poorly crystalline CuO and ZnO. Using the Scherrer equation it is possible to determine the crystallite sizes of these two oxides and these data are given in table 1. In general, for all the aging atmospheres, as the aging time is increased from 0 to 300 min, the crystallite size of both the CuO and ZnO decreases markedly. This is in line with an increase in the surface area determined by N_2 adsorption. The material prepared using air has the highest crystallite sizes for CuO and ZnO, but this material also has the highest surface area, which indicates that the small nanocrystals must have some porosity.

The calcined catalysts were investigated for the oxidation of carbon monoxide at ambient temperature and the results are shown in figure 2 and table 2. All catalysts

Table 1
Characterization of calcined catalysts

Aging time (min)	Aging atmosphere											
	Air			N_2			H_2			CO_2		
	Surface area ($m^2\,g^{-1}$)	Crystallite size (nm)[a]		Surface area ($m^2\,g^{-1}$)	Crystallite size (nm)[a]		Surface area ($m^2\,g^{-1}$)	Crystallite size (nm)[a]		Surface area ($m^2\,g^{-1}$)	Crystallite size (nm)[a]	
		CuO	ZnO		CuO	ZnO		CuO	ZnO		CuO	ZnO
0	14	189	76	10	35	26	9	89	76	6	115	113
30	26	143	69	18	34	24	16	32	20	11	70	53
60	29	79	69	27	29	24	25	22	14	26	69	53
120	36	51	57	32	28	19	34	17	11	28	20	33
150	38	38	56	65	26	17	35	19	13	32	19	25
165	49	37	35	41	26	16	42	21	13	33	16	18
180	46	32	33	40	25	13	41	15	8	38	14	9
300	42	27	28	43	22	9	45	10	6	40	14	7

[a] Determined from line broadening using the Scherrer equation.

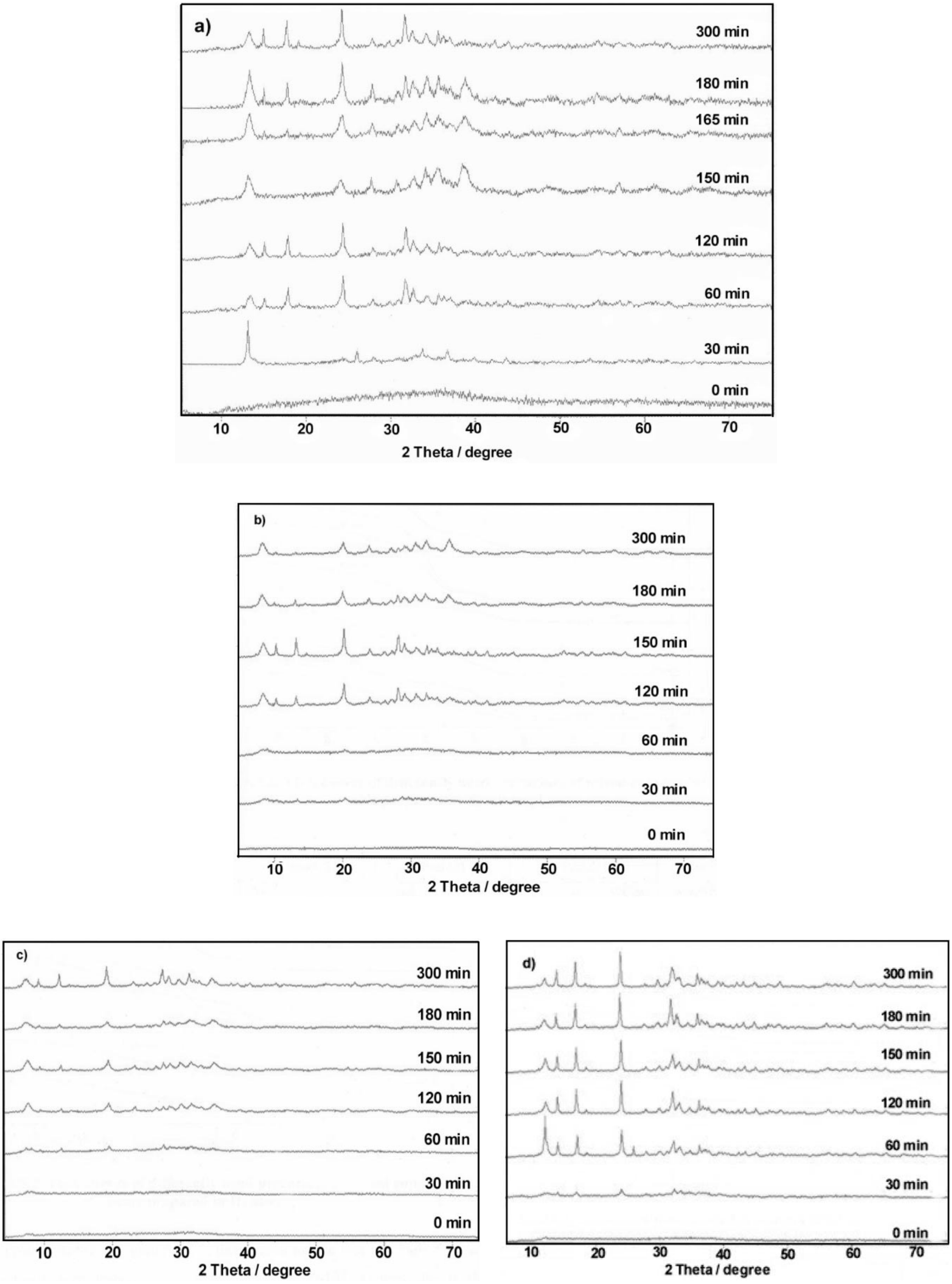

Figure 1. X-ray powder diffraction patterns of the catalyst precursors prepared in different aging atmospheres: (a) air; (b) N_2; (c) H_2; (d) CO_2.

Table 2
CO conversion over aged calcined catalysts[a]

Aging time (min)	Aging atmosphere							
	Air		N_2		H_2		CO_2	
	Intrinsic activity[b]	Specific activity[c]	Intrinsic activity[b]	Specific activity[c]	Intrinsic activity[b]	Specific activity[c]	Intrinsic activity[b]	Specific activity[c]
0	8.9	1.2	10.0	1.0	11.1	1.0	12.5	0.75
30	8.2	2.1	8.3	1.5	9.4	1.5	8.5	0.94
60	8.4	2.4	6.9	1.9	7.5	1.9	4.8	1.3
120	6.9	2.5	6.4	2.0	6.4	2.2	4.9	1.4
150	6.7	2.5	6.4	2.2	6.1	2.1	4.1	1.3
165	6.6	3.2	5.9	2.4	5.8	2.4	4.0	1.3
180	6.5	3.0	6.1	2.4	6.1	2.5	4.3	1.6
300	6.7	2.8	5.9	2.5	5.8	2.6	4.5	1.8

[a] Reaction conditions: CO (5% CO in He, 5 ml min^{-1}), O_2 (50 ml min^{-1}), catalyst (0.100 g), 20 °C, GHSV = 33 000 h^{-1}, 0.45% CO.
[b] 10^{-5} mol CO converted/m^2/h, experimental accuracy $\pm 0.2 \times 10^{-5}$ mol CO converted/m^2/h.
[c] 10^{-4} mol CO converted/g/h, experimental accuracy $\pm 0.02 \times 10^{-4}$ mol CO converted/g/h.

show an initial deactivation at the start of the catalyst evaluation but, subsequently, a steady-state activity is attained and this is maintained for over 500 min (table 1). The effect of aging atmosphere and times on the steady-state CO conversion is shown in figure 3. It is apparent that, as the aging time is increased for all the gas atmospheres, the CO conversion increases and the highest conversions are observed for the air-aged samples (figure 3). Catalysts are usually compared in terms of their specific activity (mol CO converted/g catalyst/h) and these data are given in table 2. However, as the aging process significantly increases the surface area of the calcined materials, it is important to consider the intrinsic activity (mol CO converted/m^2/g) which normalizes the catalyst activity with respect to surface area. From this, it is concluded that the intrinsic activity generally decreases to a steady value as the aging time is increased from 0 to 300 min. At the steady-state value, the highest intrinsic activities are observed for the air-aged samples. The intrinsic activity for the N_2-aged

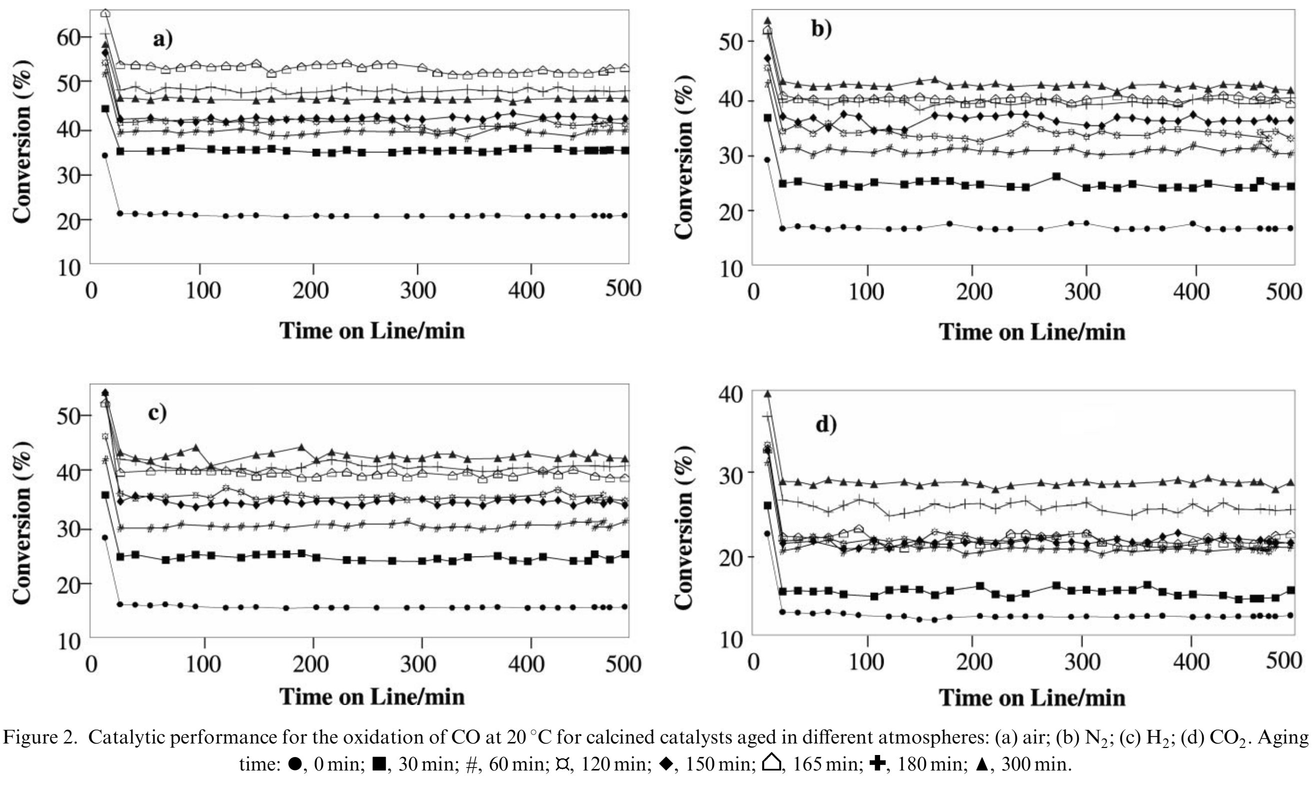

Figure 2. Catalytic performance for the oxidation of CO at 20 °C for calcined catalysts aged in different atmospheres: (a) air; (b) N_2; (c) H_2; (d) CO_2. Aging time: ●, 0 min; ■, 30 min; #, 60 min; ¤, 120 min; ◆, 150 min; ⌂, 165 min; ✚, 180 min; ▲, 300 min.

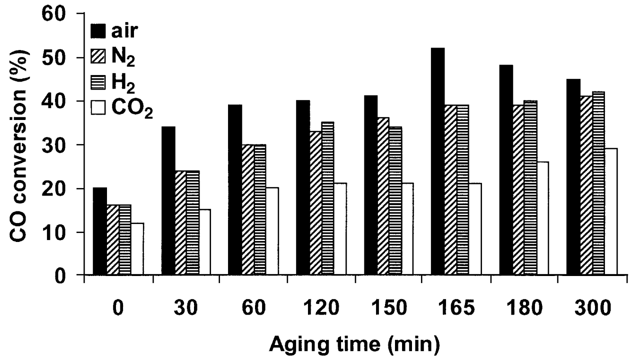

Figure 3. Effect of aging atmosphere and aging time on the steady-state CO conversion.

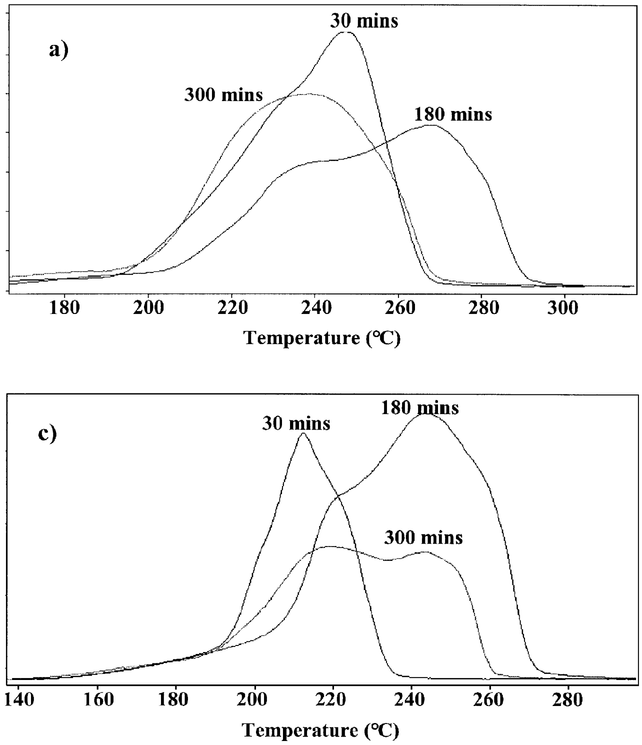

Figure 4. TPR data for calcined catalysts aged in different atmospheres: (a) air; (b) N_2; (c) H_2; (d) CO_2.

and the H_2-aged samples are very similar, whereas the intrinsic activity and specific activity of the CO_2-aged catalyst are significantly lower than those of the other catalysts. For an aging time ≥ 60 min, the order of catalyst activity is:

$$\text{air} > N_2 \sim H_2 \gg CO_2.$$

However, this activity order is reversed for the unaged samples. It is interesting to note that the catalysts aged in air and N_2 atmospheres give different intrinsic and specific activities. As the catalysts prepared using air as the aging atmosphere give improved performance, this indicates that the presence of oxygen may be an important preparation parameter.

To study the possible origin of the activity differences, the calcined catalysts prepared at 30, 180 and 300 min were characterized by TPR. These samples were considered to be representative of the aged catalysts. The data are shown in figure 4 for the four different aging atmospheres. From these data it is apparent that the air-aged materials are reduced by H_2 at higher temperatures when compared with the other samples.

It is clear from this initial study that air-aged catalysts give the highest catalyst activity, which may possibly be related to the reducibility of the copper zinc oxide material (figure 4). The previous detailed structural study of the air-aged catalyst [18] showed that the catalyst comprised solid solutions of Cu in ZnO and Zn in CuO as well as a much lower concentration of discrete Cu nanocrystals, and this would require a further detailed study. However, it can be concluded from this initial study that the aging atmosphere is an important parameter in the co-precipitation catalyst preparation procedure. It is a parameter that has been largely neglected in previous studies, but it is a parameter worthy of further study.

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