Metal–support interactions in the catalytic oxidation of carbon monoxide

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The catalytic oxidation of carbon monoxide has been studied over transition metal oxides in the absence and presence of platinum. A characteristic activity pattern was observed in both cases, with platinum reducing the temperature at which oxidation was initiated by between 20 and 200 K. The results show that platinum–metal oxide interactions are important in the system. These appear to involve the reaction of carbon monoxide adsorbed on the metal with oxygen associated with the metal oxide lattice.

Keywords: carbon monoxide oxidation, metal support effects, catalytic oxidation, metal oxide supports, precious metal catalytic oxidation

1. Introduction

The catalytic oxidation of carbon monoxide is an important reaction which has been studied in great depth. Vehicle exhaust catalysis [1], carbon dioxide lasers [2], catalytic combustion [3] and mine rescue devices [4] are only four of the many applications of the process.

Both platinum group metals and transition metal oxides have been found to catalyse the oxidation. Platinum group metals were some of the earliest catalysts identified [1,5] and are still used in vehicle exhaust catalysts [1]. The extent of surface coverage by oxygen and carbon monoxide has been found to vary with reaction conditions [5,6], an effect that can lead to oscillations, hysteresis [7] and to changes in relative activity patterns [8].

Surface carbonate species are thought to be important intermediates in the oxidation of carbon monoxide over transition metal oxides [5,9]. Formation of these species has been suggested to involve lattice oxygen [9] although, at least in the case of NiO, this is open to some doubt [10].

In recent years there has been considerable interest in the use of catalysts which contain both metals and metal oxides [2,11–13]. Pt/SnO_2 catalysts have been found to promote the oxidation of carbon monoxide at room temperature [2] as have $Pt/CoO_x/SiO_2$ catalysts [13]. Interactions across the metal–oxide interface have been suggested to be important, with carbon monoxide adsorbed on the metal reacting with oxygen species associated with the oxide [11,12].

In an attempt to explore the importance of such interactions, the oxidation of carbon monoxide on platinum supported on a range of metal oxides has been investigated.

2. Experimental

A flow system was used to study catalytic activity. 0.3 g catalyst was packed between thermocouples in a 4 mm i.d. quartz reactor. Gas flows were monitored using Brooks 5850 D mass flow controllers. Inlet and outlet gases were separated using a CTR1 column (2 m, 303 K) and analysed using a TCD (Gow Mac series 580). The reactor was placed in the constant temperature zone of a furnace which could be heated at 3 K min^{-1} or maintained isothermal (± 1 K).

Catalysts were pre-treated at 723 K in hydrogen overnight and then cooled. Mixtures of oxygen and carbon monoxide (typically 15% O_2 : 5% CO) were then admitted at a total flow rate of 50 ml min^{-1}. The catalyst was slowly heated until the system lit off. The temperature at which 50% conversion was observed (T_{50}) and the rate of reaction were used to assess activity once reproducible results could be obtained.

Transition metal oxide catalysts were prepared using the incipient wetness technique. γ-Al_2O_3 particles were reduced to 212–300 micron size by grinding and sieving and mixed with solutions of metal nitrates calculated to give an oxide loading of 10%. The slurries were heated to 330 K for 2 h and then dried (383 K, 16 h) and calcined in air (674 K, 4 h). Vanadia catalysts were prepared from oxalates [14].

Platinum catalysts were prepared by impregnating previously prepared oxide catalysts with chlorplatinic acid solutions, designed to give a loading of 3% Pt. Catalysts were subsequently treated as the oxide catalysts.

Total surface area of the catalysts was measured by adsorption of nitrogen. Metal surface areas were measured using carbon monoxide adsorption. A stoichiome-

Table 1
Total and platinum surface area ($m^2\ g^{-1}$)

Catalyst on γ-Al_2O_3	Total surface area ($m^2\ g^{-1}$)	Catalyst on γ-Al_2O_3	Total surface area ($m^2\ g^{-1}$)	Metal surface area ($m^2(Pt)\ g^{-1}$)
γ-Al_2O_3	200	Pt/Al_2O_3	190	5
NiO	180	Pt/NiO	170	5
Co_3O_4	170	Pt/Co_3O_4	173	4
Fe_2O_3	183	Pt/Fe_2O_3	174	2.4
MnO_2	170	Pt/MnO_2	181	3
Cr_2O_3	181	Pt/Cr_2O_3	182	3.5
V_2O_5	184	Pt/V_2O_5	178	3
CuO	198	Pt/CuO	189	4

Table 2
Temperatures at which 50% CO conversion occurs [a]

Catalyst on γ-Al_2O_3	T_{50} (K)	Catalyst on γ-Al_2O_3	T_{50} (K)
Co_3O_4	429	Pt/Co_3O_4	362
CuO	462	Pt/CuO	398
MnO_2	502	Pt/MnO_2	379
NiO	573	Pt/NiO	389
Cr_2O_3	562	Pt/Cr_2O_3	377
Fe_2O_3	513	Pt/Fe_2O_3	375
V_2O_5	632	Pt/V_2O_5	406
		Pt	386

[a] Gas flow = 15% O_2 : 5% CO : 80% He. Residence time 6×10^{-3} g min mol^{-1}.

try of 1 was assumed [15]. Values are summarised in table 1.

3. Results and discussion

Preliminary studies showed that homogeneous oxidation was important only at temperatures significantly in excess of those pertinent to catalytic oxidation.

Initial tests were carried out to compare the temperatures at which 50% conversion was reached over different catalysts (light off temperatures, T_{50}). As the temperature of the reactor was increased, the temperature of the catalyst bed and the conversion of carbon monoxide followed a characteristic path (figure 1). Catalysts containing platinum always lit off at lower temperatures, and the rate of rise of conversion with applied temperature was very steep. Values of T_{50} are summarised in table 2, and it is clear that differences between catalysts were larger than the potential error from calculating values from the light off curves.

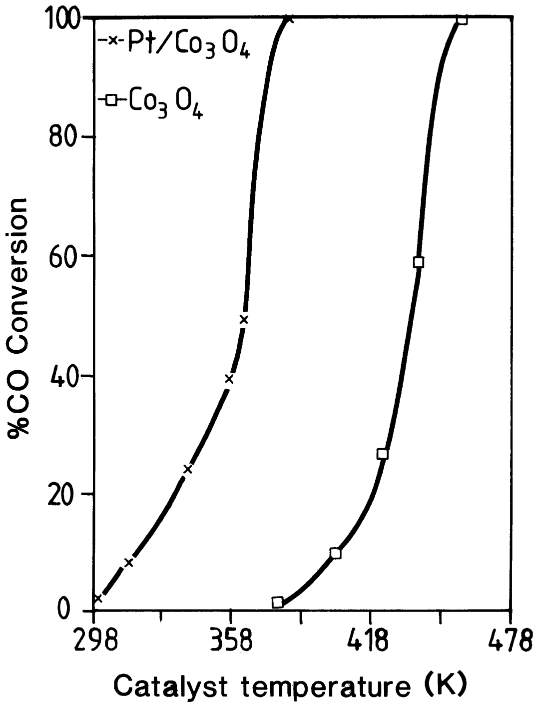

Figure 1. Activity profiles for Co_3O_4 and Pt/Co_3O_4 catalysts. Gas flow 15% O_2 : 5% CO : 80% He at 50 ml min^{-1}. Temperature increased at 3 K min^{-1}. Catalyst 0.3 g.

Light off values are almost certainly affected by mass transfer. As a result, initial rates of oxidation were determined at carbon monoxide conversions of less than 10%. The furnace temperature was maintained at 343 K and initial rates determined (table 3). Specific reaction rates were calculated using the metal surface areas reported in table 1. All tests were repeated until reproducible results were obtained: a fresh catalyst was usually on line for ca. 10 h before this point.

It was clear from table 3 that specific rates were highest with Pt/Co_3O_4 and Pt/MnO_2 as found by Mergler et al. [13]. Rates were lowest with Pt/V_2O_5 and Pt/NiO but, even in these systems, the presence of a metal oxide increased the reaction rate (table 3).

Inspection of the activity patterns for the catalysts showed clear similarities with activity patterns predicted and measured by Dowden et al. [16,17]. Dowden had suggested that activity patterns for metal oxide catalysts could be explained in terms of the contribution of crystal field stabilisation energy in the oxide [16]. Experimental measurements for a range of reactions over various oxi-

Table 3
Specific rates of carbon monoxide oxidation over Pt/transition metal oxide catalysts at 343 K. Pressure = 101 kPa. Mass of catalyst 0.3 g

Catalysts on γ-Al_2O_3	Rate 343 K ($\mu mol\ g^{-1}\ min^{-1}$)	Specific rate ($\mu mol\ m^{-2}\ min^{-1}$)	E_A [a] ($kcal\ mol^{-1}$)
Pt/MnO_2	64.6	21.5	15 ± 2
Pt/CuO	36.7	9.2	17 ± 1
Pt/Co_3O_3	89.8	22.5	16 ± 1
Pt/Fe_2O_3	23.8	9.9	12 ± 2
Pt/NiO	9.2	1.8	39 ± 2
Pt/Cr_2O_3	20.4	5.8	21 ± 2
Pt/V_2O_3	9.9	3.3	29 ± 2
Pt/Al_2O_3	6.1	1.2	15 ± 2

[a] Apparent activation energy only based on initial rates.

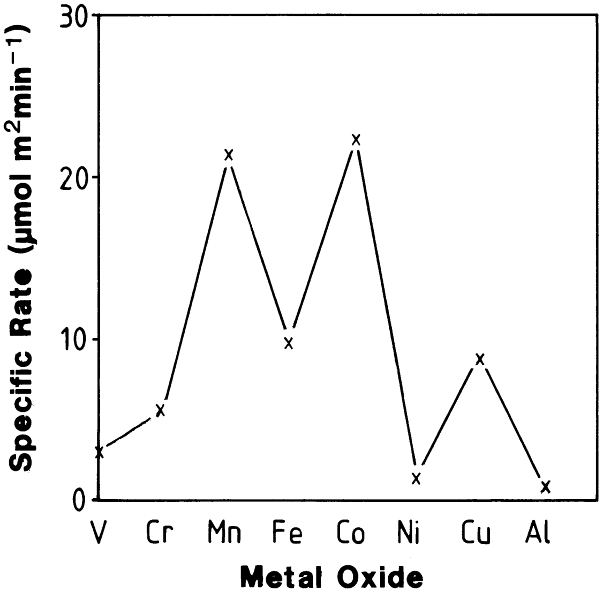

Figure 2. Specific activities of various catalysts. Conditions as figure 1 except for temperature (343 K).

des had shown that the predicted patterns did exist, with maxima at cobalt and manganese oxides [16,17]. In order to determine whether similar effects were important in the present system, specific reaction rates were plotted across the transition metal oxides. The plot showed a clear correlation with Dowden's predictions (figure 2), giving clear indication that catalytic activity was affected by the nature of the oxide, despite the presence of the more active Pt.

Carbon monoxide oxidation on Pt is inhibited by adsorption of carbon monoxide on the metal [5,6]. Any process which accelerates removal of the monoxide should accelerate the overall reaction. The most probable explanation of the results would be that adsorbed CO in the metal is reacting with oxygen associated with the metal oxide to produce gaseous carbon dioxide. Such a suggestion explains the observed results and is consistent with the suggestion of Mergler et al. [13] that dissociated oxygen formed at O vacancies on the metal oxide is involved in the oxidation.

A measure of support of this suggestion comes from values of the apparent activation energies reported in table 3. Where the support is not expected to provide oxygen (Pt/Al_2O_3) the apparent activation energy was 12 kcal mol^{-1}. In other cases, the variation in activation energies (table 3) reflected the ease of diffusion/reaction of dissociated oxygen on the oxidic support.

Metal–support interaction across the interface would thus seem to be a more wide spread phenomenon in oxidation catalysis than previously suggested. Catalyst preparation techniques that maximise catalyst–support interface while maintaining thermal stability are required in such systems. Studies of catalyst preparation procedures are in progress.

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