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The effects of rare earth oxides on the reverse water–gas shift reaction on palladium / alumina

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The interaction between palladium and ceria, both supported on alumina, has been explored in the context of the reverse water–gas shift reaction. Specific rates of reaction were greater over catalysts containing ceria. The reaction kinetics were consistent with reaction between dissociatively adsorbed hydrogen and dissociatively adsorbed carbon dioxide, a reaction which is accelerated by migration of adsorbed oxygen across the metal surface to the ceria surface.

Keywords: reverse water–gas shift; palladium; ceria; lanthana; praesodymia

1. Introduction

The role of rare earth oxides in car exhaust catalysts is varied and complex [1]. The addition of lanthana mainly provides thermal stability to the washcoat [2,3]. Ceria was added originally as an oxygen storage component [1]. It has also been suggested to provide stability to the surface area [4], to promote noble metal dispersion [5,6] and to promote catalytic reactions [7,8] by interacting with precious metals [4].

In general, addition of ceria to metallic catalysts has been found to enhance their activity. The presence of ceria in steam reforming catalysts increases activity and selectivity and reduces carbon formation [8]. Addition to car exhaust catalysts promotes the water–gas shift reaction [4,7] although this promotion may be transitory, depending on the composition of the exhaust gas. Herz and Sell [9] concluded that, for platinum–ceria–alumina catalysts, increased carbon monoxide conversion resulted from oxygen released by ceria while, over platinum–rhodium–ceria–

alumina catalysts, increased conversion resulted from promotion of the shift reaction. Promotion of the water–gas shift reaction was also observed during methanation reactions over palladium–rare earth oxide–silica catalysts [10], the order of promotion being found to be $CeO_2 > PrO_2 > La_2O_3$.

As part of a systematic study of the preparation and use of ceria containing catalysts, the interaction between palladium and ceria, supported on alumina has been explored in the context of the reverse water–gas shift reaction. In that the reduction–oxidation capacity of ceria has been suggested to be an important factor, comparisons were made with palladium–praesodymia–alumina, where oxidation–reduction cycles can also be expected to occur [11]. Since ceria may also stabilise the noble metal, further comparisons were made with palladium–lanthana–alumina, where stabilisation is known to occur [2,3] but oxidation–reduction is unlikely [11].

The reverse water–gas shift reaction is an interesting test reaction despite the fact that it has not been widely used, since methanation may also occur in the system [12]. As a result, both activity and selectivity can be used to probe the efficiency of catalysts,

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{1}$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O\,. \tag{2}$$

2. Experimental

All of the catalysts were prepared by an incipient wetness impregnation of the γ-alumina, using solutions of rare earth nitrates or palladium chloride (acidified with hydrochloric acid) sourced from Fisher Scientific. Rare earth nitrates of purity 99.99% were obtained from Aldrich and γ-alumina from Norton (type SA-6173). After addition of the appropriate solution the catalyst precursors were left for 1 h and then dried by heating at 100°C for 1 h followed by a further 16 h at 130°C. Finally, the catalyst precursors were calcined in air for 24 h at 400°C. The palladium / rare earth oxide / alumina catalysts were prepared by sequential impregnation/calcination of first the rare earth nitrate and then the palladium chloride. For all of the catalysts, the palladium loading was 1 mole per 100 moles of alumina (1 mol%). A rare earth element loading of 10 atom percent (at%) relative to alumina was used to study the effects of lanthana and praesodymia, while both 5 and 10 at% loadings of ceria were investigated.

Total catalyst surface areas were measured by a nitrogen adsorption–desorption BET method. Metal surface areas were measured by carbon monoxide chemisorption at 0°C on a Coulter Omnisorb CX 100 instrument. Before admission of carbon monoxide, samples were reduced for 1 h in pure hydrogen at 400°C.

Catalyst testing was carried out in a conventional continuous flow system operated at one atmosphere total pressure. Reactant and product analysis was carried out using a Gow Mac series 550 TCD gas chromatograph with a silica gel column. For each experimental run ca. 400 mg of catalyst in a 5 mm i.d. tube reactor was used. Each sample was reduced by first heating to 400°C in 5% hydrogen/nitrogen and maintaining this temperature for 1 h and then switching the gas supply to pure hydrogen for a further hour. Finally the catalyst was brought to the initial reaction temperature (usually 260°C) under helium. Activity testing was usually carried out with a standard gas mixture (10% carbon dioxide, 10% hydrogen and 80% helium from CIG Hytec) with a flow rate of 25 cm^3/min. The product stream was diluted in order to ensure that any product water remained in the gas phase at ambient temperature. Kinetic studies were carried out as described below. Rates were calculated from the product analysis using the differential reactor approximation

$$\text{rate} = \frac{X_{CO} + X_{CH_4}}{W} F ,$$

where X_i is the mole fraction of component i in the exit stream, F is the total molar flow rate and W is the weight of the catalyst.

Long term experiments were carried out to establish if any of the rare earth oxides enhanced resistance to thermal deactivation [13]. The experimental procedure for these tests involved determining the activity of a fresh catalyst, heating it at 800°C in flowing helium 16 h, cooling to reaction temperature and re-determining the activity.

3. Results and discussion

Under the standard test conditions, all catalysts were active above ca. 240°C. The equilibrium conversion for reaction 1 is about 10% at 240°C and about 16% at 300°C for an equimolar $CO_2 : H_2$ feed [12]. All experiments were carried out under conditions such that less than ca. 30% of equilibrium conversion was achieved. This allowed calculation of reaction rates in the absence of significant back reaction.

Initial attention was focused on the stabilisation of the support [13]. Although ageing conditions were not extreme, decreases in total surface area were always observed (table 1).

The determination of active surface area of these type of catalysts is not simple. Conventionally, carbon monoxide adsorption is used to measure metal surface area [14]. There are, however, problems with the technique in that the adsorption stoichiometry may change during ageing [14] and that Pd–CeO_2 interactions may occur which give species that do not adsorb CO but are catalytically active [4].

One approach to this dilemma is to use a reaction such as methanation to titrate adsorbed carbon monoxide on active sites on the solid [15,16]. The necessary

Table 1
Thermal stability of catalysts

Catalyst	Total surface area (m^2/g)		Apparent metal surface area[a] (m^2/g)	
	fresh	aged[b]	fresh	aged[b]
Pd/Al_2O_3	230	170	62	24
$Pd/La_2O_3/Al_2O_3$	200	184	nm	nm
$Pd/PrO_2/Al_2O_3$	240	180	nm	nm
$Pd/CeO_2/Al_2O_3$	200	165	7	9

[a] Assuming 0.7 molecules CO/surface Pd atom and 1.27×10^{19} exposed Pd atoms/m^2. nm = not measured.

[b] Ageing involved heating in helium for 16 h at 800°C.

assumption is, however, that those sites active for methanation are also active for the reverse water–gas shift reaction. This is not necessarily valid.

In a preliminary attempt to measure active surface area, measurements of CO adsorption were carried out. These showed that the apparent surface area based on the amount adsorbed increased during ageing (table 1). Should Pd–CeO_2 interactions occur, the apparent area should decrease unless the new species can also adsorb CO. Such a decrease was not observed. As a result, the CO adsorption technique was adopted to give a relative measure of active surface area in the systems.

The catalysts were then used to promote the reverse water–gas shift reaction. Carbon monoxide was the dominant product (table 2). The selectivity to methane varied as the catalyst aged (table 2). The selectivity to methane over ceria containing catalysts was low (table 2) and, in contrast to Pd/Al_2O_3, decreased on ageing the catalyst. The effect of flow rate on selectivity is shown in fig. 1. The fall in selectivity with flow rate suggested that methane was a secondary product, formed by hydrogenation of carbon monoxide, and the occurrence of this reaction was con-

Table 2
Characteristics of catalysts for the hydrogenation of carbon dioxide

Catalyst	Methane selectivity[a] (%)	Rate[b] (μmol CO_2/g min)	Rate/unit active area (μmol CO_2/min m^2)
Pd/Al_2O_3			
fresh	22	2.1	0.034
aged	39	1.1	0.046
$Pd/La_2O_3/Al_2O_3$	30	1.6	–
$Pd/PrO_2/Al_2O_3$	24	2.0	–
$Pd/CeO_2(5)/Al_2O_3$	13	2.7	–
$Pd/CeO_2(10)/Al_2O_3$			
fresh	19	4.4	0.63
aged	0	4.3	0.48

[a] Methane selectivity = (moles of methane × 100)/(moles of methane + moles of carbon monoxide).

[b] With standard mixture at 260°C.

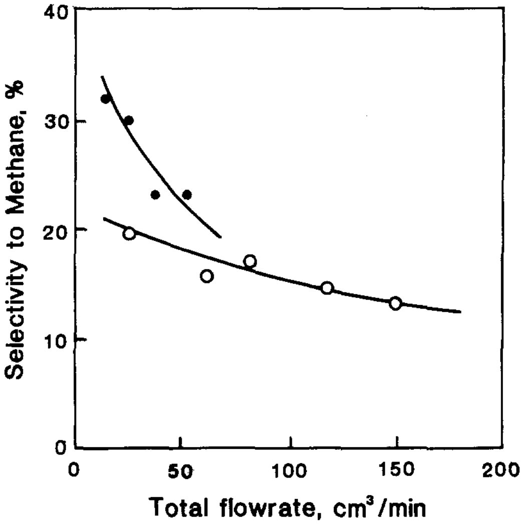

Fig. 1. Selectivity to methane as a function of total flow rate for reaction of a 10% CO_2/10% H_2 mixture at 260°C over Pd/Al_2O_3 (○) and $Pd/La_2O_3/Al_2O_3$ (●).

firmed by passing carbon monoxide and hydrogen over the catalyst. More methane was produced over fresh catalysts containing lanthana (table 2). Rieck and Bell [10] have also reported that the addition of lanthana to Pd/SiO_2 catalysts promotes methanation reactions.

Rates of conversion of carbon dioxide over different catalysts at 260°C are also reported in table 2. Rates were much faster over catalysts containing ceria, particularly when the apparent active surface areas were used to determine specific rates. This effect was not due to ceria/alumina, which was inactive as a catalyst over the temperature range studied.

The kinetics of the reaction were then studied using catalysts that did and did not contain ceria. The orders of reaction were determined by plotting log rate versus log concentration of one gas while the concentration of the other gas was held constant. The apparent activation energy was calculated for the range where initial rates could be measured (240–275°C). Results are summarised in table 3. Within experimental error, the kinetic relationships observed over both catalysts are the same, the differences in rate reflecting only the differences in rate constants and surface areas.

Table 3
Kinetic relationships for the reverse water–gas shift reaction

Catalyst	Apparent orders		Apparent activation energy (kJ/mol)
	CO_2	H_2	
Pd/Al_2O_3	0.44	0.45	73
$Pd/CeO_2(10)/Al_2O_3$	0.49	0.43	74

The differences in activity induced by ceria would seem to be best explained by a metal–support interaction in the presence of the test reaction. Interaction between noble metals and ceria is now well established [1,4,17] and both the metal and the surface of the ceria may be reduced by heating in hydrogen to ca. 180°C [4,18]. Ceria is known to have the ability to accommodate large amounts of hydrogen within the lattice [19]. With the reverse water–gas shift reaction as a test system, hydrogen is in excess, palladium and ceria will be reduced at ca. 260°C and hydrogen may be stored in both components. Carbon dioxide can then be expected to re-oxidise the ceria to form carbon monoxide [3,20]. Subsequent re-reduction of the ceria by hydrogen forms water and completes the reaction sequence.

If this is the case, one role of palladium would be to catalyse the reduction of ceria, with the ceria possibly being partly distributed across the surface of the metal [21]. Methanation would be expected to be catalysed by palladium, and the reduced apparent metal surface area observed with catalysts containing ceria (table 1) would be responsible for the reduced methane selectivity (table 2). Similar effects have been reported previously [16].

In an effort to confirm this explanation, tests were carried out with a catalyst containing praesodymia (table 2). Regrettably, after the tests were completed, a report was found that praesodymia produced from the corresponding nitrate is particularly stable [11]. As a result, a reduction/oxidation cycle cannot be expected.

It is necessary then to explain the similar kinetic relationships observed for catalysts that do an do not contain ceria (table 3). In that hydrogen would be expected to be present on both the metal and the ceria via adsorption on the metal, the half order in hydrogen – typical of the application of Langmuir–Hinshelwood arguments to dissociative adsorption – is not unexpected. The approximately half order in carbon dioxide is also typical of dissociative adsorption. The dissociative adsorption of carbon dioxide over model copper catalysts has also been reported by Campbell and Ernst [22]. The overall reaction can then be viewed as a reaction between dissociatively adsorbed hydrogen and dissociatively adsorbed carbon dioxide, a reaction which is accelerated by removal of oxygen from the active surface by migration to ceria. The acceleration obtained is reflected in the ca. tenfold increase in specific rates (table 2).

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