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Article

Pt-CeO₂/SiO₂ catalyst for CO oxidation in humid air at ambient temperature

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ABSTRACT

CO self-poisoning and slow surface kinetics pose major challenges to a CO oxidation catalyst that should work at ambient temperature. Furthermore, the presence of moisture would cause passivation of the catalyst. A highly active ceria promoted Pt catalyst (4%Pt-12%CeO₂/SiO₂; conversion $\geq 99\%$ at low (< 500 ppm) and high (> 2500 ppm) CO concentrations) was developed for CO oxidation at ambient temperature in humid air. Catalyst preparation variables such as Pt and CeO₂ loading, ceria deposition method, drying and calcination conditions for the ceria and Pt precursors were optimized experimentally. The activity was correlated with surface properties using CO/H₂ chemisorption, O₂-H₂ titration, X-ray diffraction and BET surface area analysis. The method of CeO₂ deposition had a significant impact on the catalytic activity. CeO₂ deposition by impregnation resulted in a catalyst that was three times more active than that prepared by deposition precipitation or CeO₂ grafting. O₂-H₂ titration results revealed that the close association of ceria and Pt in the case of CeO₂ deposition by impregnation resulted in higher activity. The catalyst support used was also crucial as a silica supported catalyst was five times more active than an alumina supported catalyst. The particle size and pore structure of the catalyst support were also crucial as the reaction was diffusion controlled. The drying and calcination conditions of the ceria and Pt precursors also played a crucial role in determining the catalytic activity. The Pt-CeO₂/SiO₂ catalysts with Pt > 2.5 wt% and CeO₂ > 15 wt% were highly active (TOF > 0.02 s⁻¹) and stable (conversion $\geq 99\%$ after 15 h) at ambient conditions.

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1. Introduction

CO is harmful to humans as well as the environment [1]. For example, exposure to 10 ppmv of CO for 8 h has adverse effects on the nervous system [2]. CO poisoning alone causes 3500 to 4000 deaths every year in the US [3]. Since the adsorption or absorption of CO is inadequate at ambient conditions ($T \leq 50$ °C, 10%–95% RH), the removal of CO by catalytic oxidation to CO₂ is the most viable option for neutralizing CO in indoor air. However, CO oxidation at low temperature ($T \leq 50$ °C) is diffi-

cult because of slow surface kinetics and strong CO self-poisoning of the catalyst. Also, catalysts that are active at high CO concentrations due to the high heat of reaction, e.g. Hopcalite (mixture of CuO_x and MnO_x), show poor activity at low CO concentrations.

The presence of moisture can deactivate a catalyst. For example, water vapor deactivates copper–manganese mixed oxide catalysts by forming an inactive hydroxide layer on the surface. Furthermore, water vapor can suppress catalytic activity for CO oxidation, e.g., water vapor blocks active sites on

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gold-based catalysts [4]. Therefore, a CO oxidation catalyst that is highly active at ambient conditions ($T \leq 50\text{ }^{\circ}\text{C}$, 10%–95% RH) over a wide range of CO concentrations is desired. CO oxidation over noble metals is also characterized by the self-inhibition of the active sites, also called CO poisoning. However, in the case of noble metals, water vapor can reduce the effect of catalyst CO poisoning by preventing CO island formation on the metal surface [5].

Ceria supported metal oxide catalysts [6–9] as well as ceria supported noble metal catalysts [10–12] have been investigated in detail for catalytic CO oxidation at ambient temperatures. Ceria can act as an oxygen reservoir and the presence of ceria can stabilize the noble metal dispersion [12]. Furthermore, a study of CO oxidation using ceria supported noble metal catalysts found that the oxidation mechanism involved a reaction between the lattice oxygen from ceria and CO adsorbed on the noble metal [13]. Furthermore, noble metal deposition on ceria can increase the oxygen storage capacity of the ceria [14]. Also, ceria showed superior reducibility on the nano-scale compared to bulk ceria [15]. In light of these observations, we studied the effect of ceria as a promoter for supported Pt catalysts for CO oxidation.

The catalyst preparation variables significantly impact the surface properties of the catalyst and, in turn, the catalytic activity. Therefore, the effect of the different catalyst preparation variables was investigated in detail. The impact of ceria deposition methods (deposition precipitation, grafting (anchoring), or incipient wetness impregnation) on ceria and Pt dispersion as well as catalytic activity was investigated by oxygen-hydrogen ($\text{O}_2\text{-H}_2$) titration and catalytic activity measurements. The role of the support (silica or alumina) as well as that of the support pore size was also investigated. Ceria and Pt loadings were optimized experimentally and their effect on the surface properties was studied as well.

The active metal distribution profile is crucial, particularly in the case of highly exothermic and diffusion controlled reactions [16]. The precursor drying conditions determined the ratio of “precursor salt crystallite nucleation rate” to “crystal growth rate”, and this ratio in turn determined the crystal size of the precursor salt [17]. These precursor salt crystallites were then thermally decomposed during calcination to get the active metal (oxide). Hence, the drying and calcination conditions significantly affect the metal (oxide) dispersion and distribution profile [18,19]. The calcination temperature has been shown to have a significant effect on Pt dispersion [20–24]. Therefore, the selection of the drying and calcination conditions is critical in the development of a highly active catalyst and was investigated for the ceria and Pt precursors.

Finally, the performance and stability of the catalyst for CO oxidation at ambient temperature ($25\text{ }^{\circ}\text{C}$) was tested in humid (10%–90% RH) as well as dry conditions over a wide range of CO concentration (250–2500 ppm of CO) in air.

2. Experimental

2.1. Catalyst preparation methods and materials

Except for the study involving the effect of ceria deposition method, all the catalysts were prepared by the successive incipient wetness impregnation (successive IN) method. The steps followed for this method were: (a) impregnation of a ceria precursor on the silica support followed by drying and calcination, and (b) impregnation of a Pt precursor on the ceria-silica support followed by drying and calcination. The ceria precursor used was cerium(III) nitrate hexahydrate (REacton® 99.99%, Alfa Aesar). The effects of various catalyst preparation variables were investigated by preparing different catalysts by changing the variable to be considered while keeping unchanged all the other preparation conditions. The preparation conditions followed in each of these studies are given in the relevant sections.

2.1.1. Ceria deposition method and catalyst support selection

The effect of various ceria deposition methods was studied by preparing 4%Pt-22%CeO₂/SiO₂ catalysts using three different ceria deposition methods, namely, incipient wetness impregnation (IN) method, deposition precipitation (DP) method and grafting (GR) method. During the preparation of ceria/silica by IN, the silica support (Davisil® 645, Sigma Aldrich) was impregnated with a cerium(III) nitrate hexahydrate (REacton® 99.99%, Alfa Aesar) solution, then dried overnight at $100\text{ }^{\circ}\text{C}$ and calcined at $300\text{ }^{\circ}\text{C}$ for 2 h in air. The preparation of ceria/silica by the DP method was carried out as reported by Reddy et al. [25]. Briefly, cerium(III) ammonium nitrate (99.9%, Sigma Aldrich), DI water, and silica (Davisil® 645) were mixed together and aqueous NH₄OH was added dropwise with stirring until the pH = 8. The resulting product was then filtered and washed with DI water followed by drying overnight at $100\text{ }^{\circ}\text{C}$ and calcination at $300\text{ }^{\circ}\text{C}$ in air for 2 h. The preparation of ceria/silica by grafting (GR) was carried out according to the procedure given by Bensalem et al. [26]. Briefly, a suspension of silica (Davisil® 645) in a benzene solution of cerium(III) acetylacetonate (Sigma Aldrich) was heated at $60\text{ }^{\circ}\text{C}$ with reflux for 2 h. The resulting products were filtered and dried overnight at $100\text{ }^{\circ}\text{C}$ and then calcined in air at $300\text{ }^{\circ}\text{C}$ for 2 h. The 22%CeO₂/SiO₂ prepared by these three different methods were then impregnated with the Pt precursor (diammine dinitro platinum (DADNP), 8.2 wt% in dil. NH₄OH, Strem Chemicals) and were then dried at $100\text{ }^{\circ}\text{C}$ overnight and calcined at $400\text{ }^{\circ}\text{C}$ for 3 h.

For the catalyst support selection study, 4%Pt-22%CeO₂ were deposited on SiO₂ (Davisil® 645) and $\gamma\text{-Al}_2\text{O}_3$ (Alumina catalyst support, Alfa Aesar) with similar surface properties (SA: $300\text{ m}^2/\text{g}$, PV: 1.15 mL/g , APS: $120\text{--}150\text{ \AA}$). The catalysts were prepared using the IN method and the preparation parameters employed have been given above.

To understand the impact of the surface area and pore size of the support on CO oxidation activity, 2.5%Pt-16%CeO₂/SiO₂ catalysts were prepared using five different silica supports (Merck 10180, Grade 7734, Merck 10184, Davisil LC 250, and Davisil (644+645)). The Pt and ceria loadings were chosen based on the lowest pore volume of the supports studied so that the impregnation was carried out in one step only. The effect of particle size on CO oxidation activity of 4%Pt-

16%CeO₂/SiO₂ catalyst was studied for 60–750 μ m particles. To minimize batch variation in catalyst preparation, larger catalyst particles were crushed and sieved to obtain the desired particle sizes.

2.1.2. Platinum and ceria loading

The effect of Pt loading on catalytic activity was studied by preparing (1.25–10 wt%)Pt-20 wt% ceria/silica catalysts by the successive incipient wetness impregnation method. The maximum amount of Pt that can be loaded in one impregnation cycle was determined to be 5 wt% Pt based on the Pt precursor (DADNP) solution used for the preparation and the pore volume of the ceria/silica support (1.0 mL/g). Therefore, in order to get different loadings of Pt, either a diluted Pt precursor solution was used (for Pt loading < 5 wt% Pt) or multiple Pt impregnation cycles were carried out for Pt loading > 5%. The effect of ceria loading was investigated by preparing 4 wt%Pt-(4–27 wt%)CeO₂/SiO₂ catalysts by the successive IN method. In order to get different loadings of ceria for the given pore volume of the support silica, ceria precursor solutions of different molarities were prepared. However, the process of depositing ceria on silica was carried out in one impregnation cycle only. The preparation conditions followed for the successive impregnation method were given in the previous section.

2.1.3. Pt precursor drying and calcination condition selection

The effect of the Pt precursor drying and calcination conditions on Pt dispersion and catalytic activity was studied by preparing 2%–4%Pt-16%CeO₂/SiO₂ catalysts using diammine dinitro platinum (DADNP) (8.2 wt% in dil. NH₄OH, Strem Chemicals) as a Pt precursor. The other preparation conditions were: (a) silica support used was Davisil® 645; (b) the ceria precursor was dried overnight at 75 °C and calcined at 300 °C for 2 h in air.

2.2. Catalyst testing

The reaction gas used for the experiments was 50–1000 ppm of CO in air (RH: 0–95%). The CO concentration was chosen to be less than 1000 ppm (adiabatic temperature rise $\leq$ 10 °C) to maintain close to isothermal operation of the reactor. Air and CO (5% CO in N₂, from Airgas) streams were controlled using mass flow controllers. These streams were mixed and a part of the stream was passed through a water saturator to get 0–95% RH in the resulting stream. Depending on the RH level required, the flow of the gases flowing through the water saturator was regulated with a manual control valve. The RH was measured using an RH detector. The CO concentration in the reaction gas was measured using an Agilent® gas chromatograph (GC). The GC was calibrated using standard gases. The outlet CO concentration was measured using an electrochemical sensor (detection limit 0.1 ppm CO). The sensor was calibrated using a standard gas obtained from RAE Systems. A tubular Pyrex reactor with a glass frit support for the catalyst powder was used for the experiments. In order to get a uniform flow in the catalyst bed, a thin layer of quartz wool was used before the catalyst bed. The tubular reactor was also wrapped

with a heating strip to maintain the reactor temperature.

2.3. Catalyst characterization

Powder X-ray diffraction (XRD) was performed using a Rigaku Miniflex with a Cu source at 30 kV and 15 mA. The XRD patterns were obtained at 0.5°/min. The catalyst samples were manually ground. The crystallite sizes were calculated by the Scherrer equation from the observed spectra using the Jade software.

Brunauer-Emmet-Teller (BET) surface areas (SAs), pore volumes (PVs) and average pore size (APS) were obtained using a Quantachrome AS1 surface area and pore size analyzer using N₂ adsorption at –196 °C. The BET surface area analysis employed a five point method and the PV and APS were estimated at a relative pressure (p/p_0) of 0.995.

Chemisorption was performed using the same Quantachrome AS1 instrument. The ceria surface areas were estimated by O₂ chemisorption and the Pt surface areas were estimated from CO and H₂ chemisorption studies. A stoichiometry of (1:1) was assumed for (CO:Pt) and (H:Pt) for chemisorption at 30 °C. For O₂ chemisorption on ceria at 30 °C, adsorption of 2 μ mol O₂/m² of ceria was assumed [27]. In order to get reproducible isotherms of CO/H₂ from Pt chemisorption, the pre-treatment sequence followed was: (a) cleaning (200 °C, 1 h, He), (b) evacuation (200 °C, 2 h, vacuum), (c) reduction (300 °C, 1 h, H₂) and (d) adsorbed H₂ removal (300 °C, 2 h, vacuum). Since the H₂ treatment at 300 °C reduced most of the surface ceria [27], the same pretreatment sequence was followed for O₂ chemisorption on ceria.

Static O₂-H₂ titration was carried out using the same Quantachrome AS1 instrument used to determine the total ceria surface area, Pt dispersion, and ceria surface area accessible to spilled-over H₂ and in contact with Pt. The detailed protocol and theoretical basis for the protocol as it relates to ceria promoted Pt catalysts have been reported by Salasc et al. [27]. Briefly, Salasc et al. [28] found that in a system of noble metal-ceria, H₂ reduction at 300 °C reduced only the “noble metal and ceria surface” and bulk CeO₂ reduction required a significantly higher temperature ($T > 477$ °C). Furthermore, Salasc et al. [27] found that in the presence of a noble metal, the ceria surface adjacent to the noble metal can be reduced even at room temperature due to the spillover of H₂ onto the ceria surface. Based on this surface chemistry, a novel protocol was developed that can be used to find the total CeO₂ surface area, total Pt surface area and the CeO₂ surface area in contact with Pt for Pt-CeO₂/SiO₂ catalysts.

Briefly, the sequence of steps followed during O₂-H₂ titration was: (a) catalyst pretreatment, (b) O₂ chemisorption at 30 °C, (c) H₂ titration at 30 °C, (d) O₂ titration at 30 °C, (e) catalyst pretreatment, and (f) H₂ chemisorption at 30 °C. The sequence of catalyst pretreatment steps followed during this study was the same as given in the previous paragraph (chemisorption pretreatment). From the O₂ and H₂ uptake values obtained in O₂-H₂ titration, by using the adsorption and reaction chemistry involved in the ceria promoted Pt catalysts [27], the following characteristics of the catalysts were determined: Pt dispersion,

ceria surface area, and ceria surface area in contact with Pt. The surface reactions during O₂-H₂ titration are outlined in Table 1.

Temperature-programmed reduction (TPR) of the catalyst samples (0.2 g) was carried out using 15 mL/min of 5% H₂ in Ar in the temperature range of 20–750 °C at a heating rate of 10 °C/min. In order to get reproducible results from TPR, the pre-treatment steps followed were: (a) oxidation (400 °C, 2 h, 5% O₂ in Ar) and (b) cleaning (500 °C, 1 h, Ar). H₂ consumption was estimated from the changes in thermal conductivity.

3. Results and discussion

Each catalyst preparation variable was studied independent of the others. Therefore, the catalyst preparation variables used for a particular study (for example, drying and calcination of the Pt precursor) may not utilize the optimum parameters obtained from other studies (e.g. Pt content or ceria content). However, the trends in the activity would remain the same, which is expected based on the surface characterization results and the understanding of the reaction kinetics. The aim was to understand the impact of different catalyst preparation variables and thus optimize the catalytic activity of the Pt-ceria/silica catalyst.

3.1. Ceria deposition method selection

3.1.1. Activity measurements, Pt dispersion and ceria XRD results

The effects of various ceria deposition methods were studied by comparing the activity of 4%Pt-22%CeO₂/SiO₂ catalysts prepared by the three different ceria deposition methods: incipient wetness impregnation (IN), deposition precipitation

Fig. 1. Powder XRD patterns for SiO₂ and 22%CeO₂/SiO₂ samples prepared by the different methods. (a) Incipient wetness impregnation (IN); (b) Grafting (GR); (c) Deposition precipitation (DP).

(DP, process by Reddy et al. [25]) and grafting (GR, process by Bensalem et al. [26]). CO oxidation activity, Pt dispersion and estimated ceria crystallite sizes (XRD and O₂ titration) data for the catalysts are given in Table 2. The observed XRD spectra are given in Fig. 1.

The ceria deposition method has a significant impact on catalytic activity. Ceria deposition by the IN method resulted in the most active catalyst (reaction rate 5.77 μmol g⁻¹ s⁻¹) compared to the catalysts prepared by ceria deposition by GR method (rate 1.96 μmol g⁻¹ s⁻¹) and by ceria deposition by DP method (rate 1.31 μmol g⁻¹ s⁻¹). The O₂ chemisorption results given in Table 2 showed that ceria deposition by grafting resulted in smaller ceria crystallites (CeO₂ crystallite size 3.00 nm) compared to deposition by the IN method (6.60 nm). Furthermore, the H₂ chemisorption analysis results given in Table 2 revealed that the Pt dispersion for the catalysts prepared by ceria graft-

Table 1

Reactions occurring during O₂-H₂ titration of ceria promoted noble metal catalysts.

Operation	Reaction	Explanation
O ₂ chemisorption (OC)	$\text{Pt}_s + (\text{Ce}_2\text{O}_3)_s + \text{O}_{2(g)} = \text{Pt}_s\text{-O}_{\text{ads}} + (2\text{CeO}_2)_s$	O ₂ chemisorption: Pt and reduced ceria surface
H ₂ titration (HT)	$\text{Pt}_s\text{-O}_{\text{ads}} + 1/2 \text{H}_{2(g)} = \text{Pt}_s\text{-H}_{\text{ads}} + \text{H}_2\text{O}$	Stoichiometric reaction of H ₂ with adsorbed O
	$((2\text{CeO}_2)_s.\text{Pt}_s) + \text{H}_{2(g)} = ((2\text{CeO}_2)_s.\text{Pt}_s)\text{HH}$	Hydrogen spillover to ceria adjacent to Pt
O ₂ titration (OT)	$\text{Pt}_s\text{-H} + 3/4 \text{O}_{2(g)} = \text{Pt}_s\text{-O}_{\text{ads}} + 1/2 \text{H}_2\text{O}$	Stoichiometric reaction of O ₂ with adsorbed H
	$((2\text{CeO}_2)_s.\text{Pt}_s)\text{HH} + 1/2 \text{O}_{2(g)} = ((2\text{CeO}_2)_s.\text{Pt}_s) + \text{H}_2\text{O}$	O ₂ reacts with spilled over H ₂ on ceria
H ₂ chemisorption (HC)	$\text{Pt}_s + 1/2 \text{H}_{2(g)} = \text{Pt}_s\text{-H}_{\text{ads}}$	H ₂ chemisorption on surface Pt

All the reactions are occurring on surface species (Pt: Pt_s, (CeO₂): (CeO₂)_s, and (Ce₂O₃): (Ce₂O₃)_s).

Table 2

Effect of ceria deposition method and support on activity and O₂-H₂ titration analysis.

Catalyst	Reaction rate (μmol g ⁻¹ s ⁻¹)	Uptake (μmol/g)				CeO ₂ SA (m ² /g)	CeO ₂ , Pt SA (m ² /g)	Pt, SA (m ² /g)	Pt %D	CeO ₂ crystallite size (nm)	
		OC	HT	OT	HC					Titration	XRD
4%Pt-22%CeO ₂ /SiO ₂ -DP	1.31	77.24	110.5	72.34	46.17	15.5	7.31	4.45	36	10.1	ND
4%Pt-22%CeO ₂ /SiO ₂ -GR	1.96	160.8	242.9	135.4	57.60	51.6	31.7	5.55	45	3.00	ND
4%Pt-22%CeO ₂ /SiO ₂ -IN	5.77	101.3	199.6	108.8	53.58	23.9	20.9	5.16	42	6.60	7.30
4%Pt-22%CeO ₂ /Al ₂ O ₃ -IN	1.05	107.2	254.7	120.2	86.64	10.3	5.95	8.35	68	15.2	5.00
22%CeO ₂ /SiO ₂ -IN	NA	44.55	NA	NA	NA	22.28	NA	NA	NA	5.60	7.20
5%Pt/Al ₂ O ₃	0.23	NA	NA	NA	80.2	NA	NA	7.71	63	NA	NA
5%Pt/SiO ₂	0.61	NA	NA	NA	20.12	NA	NA	1.94	16	NA	NA

All the values expressed in terms of per gram of the catalyst.

CeO₂, Pt: ceria accessible to spilled over H₂, adjacent to Pt; NA: Not applicable, ND: Not determined.

Activity test conditions: 500 ppm CO in air, catalyst bed depth 3.2 mm (0.25 g Cat. + 66% inert silica), face velocity 45 cm/s, particle size 150–250 μm, reactor ID 1.9 cm, Humidity 50% RH, temperature 25 °C.

ing (D : 45%) and the IN method (D : 42%) were comparable (instrumentation error, % D : $\pm 1\%$). Therefore, the catalytic activity results cannot be explained by the ceria or Pt dispersion alone.

Holmgren et al. [12] have shown that in the case of Pt/ceria catalysts, the Pt-ceria interfacial area provided the active sites for CO oxidation. The transfer of lattice oxygen from ceria to an adjacent Pt site was deemed to be responsible for the CO oxidation activity [12]. Furthermore, Aboukais et al. [29] showed that in the case of ceria supported Pt catalysts, superoxide radicals (O_2^-) in the ceria lattice reacted with CO adsorbed on adjacent Pt sites which resulted in higher CO oxidation activity. Therefore, the Pt-ceria interfacial area was crucial for the catalytic activity.

In the case of Pt/ceria catalysts, the Pt-ceria interfacial area is relatively easy to estimate when the Pt dispersion is known. However, in the case of ceria promoted Pt/silica or Pt/alumina catalysts, the estimate of the Pt-ceria interfacial area would be difficult. However, the extent of Pt deposition on the ceria crystallites in the case of ceria promoted Pt catalysts can be estimated. The ratio of “CeO₂ surface area (SA) in contact with Pt” to the “total CeO₂ surface area (SA)” would give the proportion of ceria deposited with Pt. A value of “zero” for this ratio would indicate no deposition of Pt on ceria crystallites and a value of “one” being that all ceria crystallites were deposited with Pt crystallites. These two quantities (“CeO₂ SA in contact with Pt” and “total CeO₂ SA”) can be estimated from O₂-H₂ titration.

3.1.2. Analysis by O₂-H₂ titration

The “total CeO₂ SA” and “CeO₂ SA in contact with Pt” were estimated for the different ceria deposition methods from O₂-H₂ titration, and the ratio of these two quantities was estimated as well. The O₂-H₂ titration was carried out using a unique protocol developed by Salasc et al. [27]. During this O₂-H₂ titration, initial H₂ reduction (HR) at 300 °C reduced the noble metal and created oxygen vacancies on the ceria surface. This was followed by O₂ chemisorption (OC) during which oxygen was taken up by the ceria surface to fill the oxygen vacancies and the noble metal also adsorbed oxygen. Therefore, a combined uptake of O₂ on CeO₂ and Pt can be determined. The OC was followed by H₂ titration (HT) and during HT, a stoichiometric reaction between hydrogen and adsorbed oxygen on Pt takes place. Also, H₂ adsorbed on Pt metal. Furthermore, hydrogen would also spillover onto the adjacent ceria surface. The HT was followed by O₂ titration (OT) during which the reaction between oxygen and the adsorbed hydrogen on Pt takes place and oxygen also undergoes a stoichiometric reaction with the hydrogen that migrated to the ceria surface. Also, O₂ adsorbed on Pt. Finally, to estimate the Pt surface area, hydrogen chemisorption (HC) was performed.

When the H₂ uptake from HC, by considering the stoichiometry, was subtracted from the O₂ uptake from OC, the resulting O₂ uptake was that by the ceria surface alone. This thus enabled the estimate of the total CeO₂ SA. Furthermore, when the H₂ uptake from HC, considering the stoichiometry, was subtracted from the O₂ uptake from OT, the result was the O₂ uptake due to the reaction between O₂ and the hydrogen that migrated to the

ceria surface adjacent to Pt. This thus enabled the estimate of the ceria SA in contact with Pt. Using the O₂-H₂ titration protocol OC, HT, OT, and HC uptake values were obtained and are summarized in Table 2. Then the total CeO₂ SA, total Pt SA, and CeO₂ SA in contact with Pt were estimated and are given in Table 2. The CeO₂ SA in contact with Pt thus estimated is the “ceria accessible to the spilled-over H₂” from the adjacent Pt. During the O₂-H₂ titration of Pt/Ceria, Salasc et al. [27] found that the uptake of O₂ was 2 $\mu\text{mol}/\text{m}^2$ of ceria SA and that the ratio of the total CeO₂ SA (123 m^2/g) and the CeO₂ SA in contact with Pt (112 m^2/g) was close to unity. In other words, if all the Pt was in contact with ceria, the ratio of CeO₂ SA in contact with Pt and total CeO₂ SA would be close to unity.

During this study, it was found that the ratio of the “CeO₂ SA in contact with Pt” (20.9 m^2/g) and the “total CeO₂ SA” (23.9 m^2/g) was close to unity for the catalyst prepared by ceria deposition by the IN method (ratio: 0.88). However, the ratio of the CeO₂ SA in contact with Pt (31.7 m^2/g) and the total CeO₂ SA (51.6 m^2/g) was less than 2/3 in the case of ceria deposition by GR (ratio: 0.61), and less than 1/2 in the case of ceria deposition by DP (ratio: 0.47). Based on these ratios, it was deduced that there were ceria grains which were not deposited with Pt in the catalysts prepared by either DP or GR method. The interfacial area between Pt and ceria would be higher for the catalysts prepared using the IN method since most of the ceria grains were deposited with Pt. Larger Pt-ceria interfacial areas would result in higher CO oxidation activity. The experimental results showed that the catalyst prepared using the IN method for ceria deposition resulted in highly active catalysts. Therefore, the Pt-ceria interfacial area was the key for the CO oxidation activity of the catalyst.

During the Pt precursor calcination, segregation of ceria and Pt can take place if the ceria crystallites are small, e.g., by the grafting method. The incipient wetness impregnation method resulted in larger ceria crystallites, providing anchoring sites for Pt and therefore, for equivalent Pt loading, resulted in a larger Pt-CeO₂ interfacial area.

The estimated ceria crystallite sizes from XRD and O₂-H₂ titration were not in agreement for the catalysts prepared by the DP method. The DP method resulted in significant amounts of amorphous ceria, which would explain the absence of ceria peaks in the XRD spectra. Similar results were obtained by other researchers as well, e.g., Craciun et al. [30] observed less than 30% crystalline ceria in ceria/silica samples prepared by the DP method (calcined at 500 °C) and the amount of amorphous ceria increased with decreasing calcination temperature. In our study, the calcination temperature for ceria/silica was 300 °C.

There was a possibility that H₂ spillover on CeO₂ can take place during H₂ chemisorption. However, it has been shown by Salasc et al. [27] that this was not the case for Pt-CeO₂/Al₂O₃ systems. During this study, O₂ chemisorption of only 22% CeO₂/SiO₂ prior to Pt deposition was also performed. The total CeO₂ SA from this O₂ chemisorption study (22.3 m^2/g) was comparable to the total CeO₂ SA estimated for 4%Pt-22%CeO₂/SiO₂ from O₂-H₂ titration (23.9 m^2/g). As per the O₂-H₂ titration protocol, if there were any hydrogen spillover on

CeO₂ during H₂ chemisorption, the value of the total CeO₂ SA estimated from O₂-H₂ titration would have been lower. Furthermore, the ceria crystallite sizes estimated from O₂-H₂ titration for ceria deposition by the IN method (6.6 nm), given in Table 2, were in close agreement with those estimated from XRD spectra (7.3 nm, Table 2).

3.2. Catalyst support selection

3.2.1. Type of support

The effect of the catalyst support on CO oxidation activity was studied by preparing the ceria promoted Pt catalyst on SiO₂ and γ -Al₂O₃ supports (SA: 300 m²/g; PV: 1.0–1.15 mL/g; APS: 120–150 Å) using the IN method. CO oxidation activity results and estimated ceria crystallite sizes (XRD and O₂ titration) for these catalysts are given in Table 2. The total CeO₂ SA, Pt dispersion and CeO₂ SA in contact with Pt were estimated from O₂-H₂ titration and are given in Table 2. Ceria dispersion as well as Pt dispersion was better on the alumina supported catalysts compared to the silica supported catalysts. However, the silica supported catalyst showed significantly better CO oxidation activity (rate: 5.77 $\mu\text{mol g}^{-1} \text{s}^{-1}$) compared to the alumina supported catalyst (rate: 1.05 $\mu\text{mol g}^{-1} \text{s}^{-1}$).

The ratio of “CeO₂ SA in contact with Pt” to the “total CeO₂ SA” in the case of the alumina supported catalyst was 0.58, and that in the case of the silica supported catalyst was 0.88. Therefore, the amount of Pt deposition on the ceria promoter and in turn the Pt-ceria interfacial area would be larger in the case of the silica support compared to the alumina support. A larger Pt-ceria interfacial area would result in better CO oxidation activity for the silica supported catalyst.

Pt deposition on a support is determined by the support surface properties (iso-electric point (IEP)) as well as the Pt precursor properties (pH and nature of Pt species in the solution) [31]. Depending on the type of precursor salt used for impregnation, the Pt species would be present in the form of cationic, anionic or non-ionic species in the precursor solution. When the pH of the Pt precursor solution is higher than the IEP of the support, then the support is negatively charged and is surrounded by cations to maintain electro-neutrality [31]. Deposition of the Pt species on the support would then take place by cation exchange or ligand exchange. However, when the Pt species in the precursor solution was anionic or neutral in charge, then the deposition would be difficult [32]. The deposition in such cases would be followed by crystallization of the precursor salt during drying of the precursor, resulting in poor dispersion. When the pH of the solution is the same as the IEP of the support, then the support remains neutral in charge and the deposition of the Pt species takes place by adsorption.

The Pt precursor used during this study was diammine dinitro platinum(II) (DADNP) in water (with dilute NH₄OH, pH of 8–8.5). The Pt species in the precursor solution were non-ionic (neutral in charge, as shown by Iida et al. [32]). Silica has an IEP of 2 [31], ceria has an IEP of 8–8.2 [33] and γ -Al₂O₃ has an IEP of 7–8. Therefore, during impregnation by the DADNP precursor, SiO₂ would be negatively charged and surrounded by NH₄⁺ ions and alumina and CeO₂ would be neutral in charge due to

their IEP being close to the pH of the precursor solution.

In the case of the ceria/silica system, the neutral Pt precursor would be weakly adsorbed on a neutral ceria support until saturation and the remaining precursor would deposit on the silica support after solvent evaporation during drying. During solvent evaporation, the salt crystallizes and deposits on the support resulting in poor dispersion. Therefore, the Pt dispersion on silica using a Pt precursor with neutral Pt species in solution would be poor. However, the interaction with ceria although a weak adsorption would lead to better Pt dispersion. The H₂ chemisorption results support this hypothesis as the Pt dispersion (Table 2) improved with the addition of the CeO₂ promoter on SiO₂ supported Pt catalysts from 16% (no ceria) to 42% (22 wt% ceria). So, in the case of the ceria/silica system, most of the ceria grains would be deposited with Pt.

In the case of ceria/alumina, the IEP of the support and promoter are very close: alumina (7–8), CeO₂ (6.8–8.6). Therefore, any type of Pt precursor (cationic, anionic or non-ion) in any type of solution (basic or acidic pH) would result in non-preferential weak adsorption of Pt precursor on both alumina and silica. As can be seen from the estimated Pt dispersion values (H₂ chemisorption), the addition of ceria did not change the Pt dispersion significantly for the alumina supported catalysts (63% to 68%). So, in the case of ceria/alumina system, the ceria grains may or may not get deposited with Pt due to the non-preferential deposition of Pt on ceria and alumina.

The addition of ceria resulted in better Pt dispersion on the silica supported catalysts. One reason for the better Pt dispersion on ceria/silica due to the addition of ceria was the ability of ceria to inhibit Pt metal sintering during high temperature calcination, which would also support the preferential deposition of Pt on ceria. The basicity of the support (IEP) thus determined the distribution of Pt on the support and the promoter. This in turn determined the Pt-ceria interfacial area and CO oxidation activity of the catalysts.

The estimated ceria crystallite sizes from XRD (5.0 nm) and O₂-H₂ titration (15.2 nm) were not in agreement for the catalysts prepared by the incipient wetness impregnation method on the γ -Al₂O₃ support. This can be explained by the ability of the γ -Al₂O₃ support to stabilize the Ce³⁺ ions against re-oxidation at room temperature, as shown by Moral et al. [34]. The stabilization of the Ce³⁺ ions by the γ -Al₂O₃ would lead to a lower O₂ uptake during OC and over-estimation of the size of the CeO₂ crystallites. However, the estimated ratio of “CeO₂ SA in contact with Pt” to the “total CeO₂ SA” would not change due to the stabilization of Ce³⁺ ions, as shown by Salasc et al. [27].

3.2.2. Effect of support particle size and support surface properties

In order to investigate if CO oxidation on Pt-ceria/silica catalyst was diffusion controlled or reaction controlled, the effect of particle size on activity was studied. The results are given in Fig. 2. It can be said that the reaction was significantly diffusion limited. When the particle size was reduced from 750 to 75 μm , the change in the reaction rate was almost double at 25 °C. The effect of diffusion limitation was severe at higher temperatures.

Fig. 2. Effect of particle size on the catalytic activity of 4%Pt-16%CeO₂/SiO₂ catalyst with 1% H₂O in air.

The Weisz-Prater parameter (C_{WP} : ratio of actual reaction rate to that of diffusion [35]; $C_{WP} > 1$: diffusion limited reaction) was calculated for all the particles and are given in Table 3. When the value of the C_{WP} is much greater than 1, internal diffusion limitation is more severe for the reaction. The reaction was significantly internal diffusion controlled as seen from the C_{WP} values even at room temperature. For example, C_{WP} values for the 450 and 250 μm particles were 42.8 and 12.9, respectively. However, the C_{WP} values were close to 1 for the 45–75 μm particles, indicating internal diffusion limitation was not significant for the smaller particles at room temperature. At the higher temperature (50 °C), the increase in effective diffusivity was negligible compared to the increase in the reaction rate. Therefore C_{WP} values were higher at 50 °C compared to 25 °C. For example, the C_{WP} values were 1.14 and 2.07 for the 45–75 μm particles at 25 and 50 °C, respectively. In addition, in order to find out if the reaction was external diffusion limited, Mears' criterion [35] was used. The estimated values for the different particle sizes are given in Table 3. From Mears' criterion, it was clear that the reaction was not external diffusion controlled.

The effect of the silica support surface properties on the catalytic activity of 2.5%Pt-16%CeO₂/SiO₂ was studied by using five different silica supports. The CO activity results of these catalysts and the silica support and catalyst surface properties are given in Table 4. As expected, the support surface area had a major impact on the Pt and CeO₂ dispersions. Supports with a larger surface area showed increased Pt and CeO₂ dispersion, as seen from the XRD and chemisorption results. Since ceria is

Table 3

Estimated Weisz-Prater parameters and Mears' criteria for 4%Pt-16%CeO₂/SiO₂.

Particle size (μm)	C_{WP} at 25 °C	C_{WP} at 50 °C	Mears' criterion at 25 °C	Mears' criterion at 50 °C
600–850	96.96	88.17	0.149	0.135
300–600	42.79	49.27	0.084	0.096
180–300	12.85	21.74	0.034	0.058
125–180	5.59	10.63	0.019	0.036
75–125	2.76	5.54	0.011	0.023
45–75	1.14	2.07	0.006	0.011

Test conditions: Humidity 1% H₂O, reactor ID 1.9 cm, catalyst 0.05 g (inert silica: 0.5 g)

known to stabilize noble metals [12], it would be prudent to say that the larger surface area along with the higher ceria dispersion resulted in better Pt dispersion. As expected, the final catalysts had lower BET SAs and PVs compared to the pristine supports due to Pt and promoter deposition and thermal treatment. The catalysts prepared from supports with larger SAs showed a larger drop in the BET SA and PVs. The supports with narrower pore openings showed an increase in the APS with deposition of Pt and ceria, which was clear indication of the blocking of the narrower pores in the catalyst. The supports with wider pore openings showed a decrease in the APS which could be due to pore narrowing or a combined effect of pore narrowing and pore blocking.

The catalytic activity was not directly proportional to the SA or Pt/ceria dispersions. The catalysts prepared on a support with a larger SA (Merck® 10180, TOF: 0.028 s⁻¹) performed poorly in comparison with those prepared on a support with a lower surface area (Davisil® (644+645), TOF: 0.052 s⁻¹). Therefore, the effect of mass transport properties can explain these results.

The effective diffusivity of CO inside these porous catalysts was estimated and given in Table 4. The mean free path for CO estimated at room temperature was 6.5×10^{-8} (in m) [36]. When the ratio of "mean free path (l)" to the APS of the support is greater than 10 ($l/\text{APS} > 10$), the diffusion is mainly Knudsen diffusion [36]. Therefore, for supports with $\text{APS} \leq 60$ Å, the diffusion was assumed to be Knudsen diffusion. For the other supports, the diffusion was assumed to be combined bulk and Knudsen diffusion. The bulk diffusivity was estimated using Chapman-Enskog kinetic theory [37]. Although the tortuosity and particle porosity would be different for the different supports, due to the lack of experimental data, a tortuosity value of

Table 4

Effect of type of silica on catalyst properties and catalytic activity of 2.5%Pt-16%CeO₂/SiO₂.

Type of silica	Support			Catalyst			Reaction rate ($\mu\text{mol g}^{-1} \text{s}^{-1}$)	TOF (s ⁻¹)	Pt (%D)	D_p of CeO ₂ (nm) XRD	D_{eff} (mm ² /s)
	BET SA (m ² /g)	PV (mL/g)	APS (Å)	BET SA (m ² /g)	PV (mL/g)	APS (Å)					
Merck 10180	750	0.68	40	417	0.52	50	2.26	0.028	63.3	4.7	12.3
Grade 7734	550	0.80	60	370	0.57	61	2.45	0.036	53.3	6.8	18.1
Merck 10184	330	1.00	100	296	0.82	111	2.59	0.038	52.5	7.7	29.4
Davisil LC 250	330	1.65	250	236	1.05	179	2.82	0.045	48.6	8.3	66.2
Davisil (644+645)	300	1.15	150	259	0.91	141	2.89	0.052	43.0	7.7	42.5

Activity test conditions: Humidity 50% RH, temperature 25 °C, reactor ID 1.9 cm, particle size 63–200 μm , catalyst 0.25 g (+ 50% inert SiO₂), face velocity 30 cm/s, CO 250 ppm in air.

three ($\tau = 3$) and a particle porosity of 0.6 ($\varepsilon_p = 0.6$) was assumed for these catalysts for estimating the effective diffusivity. The effective diffusivity of CO for the Davisil® (644+645) supported catalyst (APS: 141 Å, D_{eff} : 42.5 mm²/s), was almost 3.5 times that of the effective diffusivity of CO for the Merck® 10180 supported catalyst (APS: 50 Å, D_{eff} : 12.3 mm²/s). The catalysts with wider pore openings have a larger effective diffusivity and resulted in better catalytic activity.

These observations clearly indicated that the reaction was diffusion controlled. The effect of mass transport limitation can be minimized by using a support with a smaller particle size and wider pores. However, the selection of support particle size would involve the trade-off between performance and pressure drop. Depending on the application requirements, therefore, the selection of particle size should be done judiciously. During this study, considering the application requirements, an average particle size of 200 µm was chosen.

3.3. Effect of precursor drying and calcination conditions

During this study, the effect of drying and calcination conditions on both the ceria and Pt precursors were studied in detail.

3.3.1. Effect of ceria precursor drying conditions

The impact of the ceria precursor drying conditions on catalytic activity was studied. The CO oxidation rates as well as XRD and O₂ chemisorption results are given in Table 5. Surface characterization revealed that the drying rate affected the ceria dispersion and in turn the catalytic activity. The CeO₂ crystallite size increased with increasing drying temperature or drying rate (drying at 40 °C: 6.4 nm; drying at 125 °C: 7.9 nm). The catalyst with a better ceria dispersion (greater CeO₂ SA) resulted in a higher activity. Since CeO₂ provided sites for Pt deposition and the Pt-ceria interfacial area was responsible for catalytic activity, a higher ceria SA improved catalytic activity. The rate of drying can dictate the distribution profile of the active metal (oxide) on the support and the different metal distribution profiles such as homogeneous, egg-shell, egg-white and egg-yolk are given in Fig. 3.

In the case of a strong precursor-support interaction, the rate of drying would not affect active species dispersion unless the precursor concentration is significantly higher [18]. For higher precursor concentrations, the support would get over-saturated and the rate of drying can affect the distribution

Fig. 3. Active metal distribution profile in the catalyst.

profile and in turn the dispersion [18]. Faster drying rates would result in increasingly egg-shell like distribution profiles while slower drying rates could yield an almost homogeneous profile in the case of higher precursor concentrations. Furthermore, a higher concentration of the solute would result in a poor dispersion for distribution profiles other than the homogeneous distribution profile [38]. During this study, the pH of the ceria precursor (cerium(II) nitrate) solution (pH $\approx$ 6–7) was higher than the IEP of the silica support (IEP $\approx$ 2). Furthermore, the ceria precursor solution would yield cerium cations (Ce³⁺) in the impregnating solution resulting in strong precursor-support interaction. However, during this study, the precursor concentration in the solution was significantly higher, considering the desired ceria loading (16 wt%). So, a faster drying rate (drying at 125 °C) may have resulted in an egg-shell like profile and a slower drying rate (drying at 40 °C) may have resulted in a more uniform ceria distribution profile. Since ceria loading was higher, a uniform ceria distribution would result in a better ceria dispersion compared to the other distribution profiles. Thus, a slower drying rate of the ceria precursor (drying at 40 °C) resulted in higher catalytic activity.

3.3.2. Effect of ceria precursor calcination conditions

The effect of the ceria precursor calcination temperature on the catalytic activity was studied. The CO activity results and O₂ chemisorption and XRD analysis results are given in Table 5. The catalytic activity increased with increasing calcination temperature up to 300 °C and then dropped when the calcination temperature was raised to 350 °C. As expected, the CeO₂ dispersion decreased with increased calcination temperature as shown by XRD analysis as well as O₂ chemisorption. So, the catalytic activity was not a function of the CeO₂ dispersion alone.

The volcano type activity profile can be explained by two factors: (a) the total CeO₂ SA available for the Pt deposition, and (b) the property of CeO₂ to decorate the Pt crystallites during Pt precursor calcination [39]. The total CeO₂ SA available for the

Table 5

Effect of ceria precursor drying conditions and calcination temperature on catalytic activity and ceria dispersion.

Catalyst	Drying condition	Calcination temperature (°C)	Rate of reaction (µmol g ⁻¹ s ⁻¹)	D_p of CeO ₂ (nm) XRD	O ₂ chemisorption on CeO ₂	
					SA (m ² /g)	D_p (nm)
2.5%Pt-16%CeO ₂ /SiO ₂	Vacuum dry at 40 °C	300	1.96 (a)	6.4	14.43	6.5
2.5%Pt-16%CeO ₂ /SiO ₂	Overnight at 75 °C	300	1.62 (a)	6.5	13.71	6.9
2.5%Pt-16%CeO ₂ /SiO ₂	4 hours at 125 °C	300	1.08 (a)	7.9	13.02	7.2
2.0%Pt-20%CeO ₂ /SiO ₂	Vacuum dry at 40 °C	200	0.24 (b)	6.4	20.23	6.2
2.0%Pt-20%CeO ₂ /SiO ₂	Vacuum dry at 40 °C	250	2.04 (b)	6.8	19.13	6.6
2.0%Pt-20%CeO ₂ /SiO ₂	Vacuum dry at 40 °C	300	2.54 (b)	7.0	18.42	6.8
2.0%Pt-20%CeO ₂ /SiO ₂	Vacuum dry at 40 °C	350	1.74 (b)	7.1	17.11	7.3

Test conditions: (a) CO: 250 ppm; face velocity: 30 cm/s; catalyst: 0.25 g (+ 50% inert SiO₂); (b) CO: 300 ppm; face velocity: 45 cm/s; catalyst: 0.2 g (+ 50% inert SiO₂).

Pt deposition decreased with increased calcination temperature of the CeO₂ precursor, as indicated by the O₂ chemisorption data. During the calcination of the Pt precursor at 400 °C, due to the increased surface diffusion and sintering of the CeO₂, the Pt crystallites would be decorated by the CeO₂. So the extent of the Pt decoration would depend on the stability of the CeO₂ and in turn the CeO₂ precursor calcination temperature [39]. The extent of decoration would decrease with increased ceria precursor calcination temperature. Although a moderate amount of decoration of Pt by ceria would increase the catalytic activity by increasing the Pt-ceria contact area, significant decoration could result in a lower active surface area and lower activity.

At lower ceria precursor calcination temperature, the ceria SA for deposition would be larger, but significant ceria decoration of Pt would result in a lower active SA. At higher calcination temperatures of the ceria precursor, the ceria SA for Pt deposition would be lower and the ceria decoration would also be lower resulting in lower activity. The catalytic activity increased with increased calcination temperature of ceria precursor from 200 °C to 300 °C due to decreased ceria decoration. The catalytic activity decreased when the calcination temperature was increased from 300 °C to 350 °C because the ceria SA available for Pt dispersion was lower and the extent of Pt decoration by ceria was also lower.

3.3.3. Platinum precursor drying conditions

The type of support-precursor interaction, concentration of the precursor and precursor drying rate dictate the active metal (oxide) distribution profile on the support. The drying conditions play a crucial role in determining metal dispersion and metal distribution profile on the catalyst support. There are four general types of metal distribution profiles on a support, namely, homogeneous, egg-shell, egg-white, and egg-yolk [16,40] as shown in Fig. 3. The preparation conditions, CO activity results and estimated Pt dispersion and TOF values (from CO chemisorption) for the catalysts studied are given in Table 6. The catalytic activity (reaction rate) trend based on the drying conditions was 4 h at 125 °C (1.84 $\mu\text{mol g}^{-1} \text{s}^{-1}$) > overnight at 75 °C (0.91 $\mu\text{mol g}^{-1} \text{s}^{-1}$) > 6 h under vacuum at 40 °C (0.37

$\mu\text{mol g}^{-1} \text{s}^{-1}$). However, the observed trend for the Pt dispersion was opposite to that of the trend observed for the reaction rate. The difference in the estimated Pt dispersion for the catalysts with the best and the worst Pt dispersion was less than 4% whereas the accuracy of the instrument was within $\pm 2\%$. Therefore, the drying condition had a minor impact on the Pt dispersion of the catalyst. However, the precursor drying condition had a major impact on the catalytic activity. As can be seen from the comparison of the TOF of the catalysts prepared by different drying conditions: 4 h at 125 °C (0.037 s^{-1}) > overnight at 75 °C (0.018 s^{-1}) > 6 h under vacuum at 40 °C (0.007 s^{-1}). Since the drying condition had a minimal impact on the metal dispersion, the drying condition played a major role in determining the distribution profile of the Pt in the final catalyst resulting in significant difference in rate of reaction and TOF.

There are two important factors that affect the metal distribution profile on the support [18]: (1) type of adsorption of precursor on support, strong or weak; and (2) rate of drying, fast or slow. In the case of strong adsorption, the rate of drying does not affect the active metal distribution [18]. For weakly adsorbed precursors, the drying conditions have a significant impact on the metal distribution profile. When the drying rates are higher, egg-shell distribution profiles were obtained [18]. If the drying rate is low for weakly adsorbed precursor, then homogeneous metal distribution profiles were obtained [18]. As noted before, in the case of the Pt precursor (DADNP), a weak interaction existed between the support and the Pt precursor. During this study, drying at 125 °C for 4 h can be said to be a form of fast drying. Therefore, this resulted in a Pt metal distribution profile close to an egg-shell distribution profile.

The catalytic activity is a function of the type of reaction regime (kinetic or diffusion controlled reaction (DCR)) and the type of active metal distribution profile in the catalyst. For diffusion controlled reaction, an egg-shell profile would be favored, whereas for a kinetically controlled reaction the type of metal profile would not be a major contributing factor. Since CO oxidation on the Pt-ceria/silica catalyst was found to be a diffusion controlled reaction, an egg-shell or egg-white profile of the active metal on the support would be preferred. Therefore,

Table 6

Effect of Pt precursor drying and calcination conditions on reaction rate, Pt dispersion, and TOF.

Catalyst	Drying condition	Calcination time (h)	Calcination temperature (°C)	Reaction rate ($\mu\text{mol g}^{-1} \text{s}^{-1}$)	CO chemisorption on Pt		TOF (s^{-1}) (%D: CO chemi.)
					%D	D_p (nm)	
2.5%Pt-16%CeO ₂ /SiO ₂	Vacuum dry at 40 °C	4	400	0.37 (a)	52.4	2.2	0.007
2.5%Pt-16%CeO ₂ /SiO ₂	Overnight at 75 °C	4	400	0.91 (a)	49.4	2.3	0.018
2.5%Pt-16%CeO ₂ /SiO ₂	4 h at 125 °C	4	400	1.84 (a)	48.9	2.3	0.037
4.0%Pt-16%CeO ₂ /SiO ₂	4 h at 125 °C	4	300	0.84 (b)	54.1	2.1	0.0076
4.0%Pt-16%CeO ₂ /SiO ₂	4 h at 125 °C	4	400	1.54 (b)	49.4	2.3	0.0155
4.0%Pt-16%CeO ₂ /SiO ₂	4 h at 125 °C	4	500	9.04 (b)	40.3	2.8	0.109
4.0%Pt-16%CeO ₂ /SiO ₂	4 h at 125 °C	4	600	8.65 (b)	21.9	5.2	0.193
2.0%Pt-16%CeO ₂ /SiO ₂	4 h at 125 °C	1	500	0.70 (c)	43.1	2.6	0.016
2.0%Pt-16%CeO ₂ /SiO ₂	4 h at 125 °C	2	500	1.72 (c)	37.7	3.0	0.045
2.0%Pt-16%CeO ₂ /SiO ₂	4 h at 125 °C	3	500	0.65 (c)	33.9	3.3	0.019
2.0%Pt-16%CeO ₂ /SiO ₂	4 h at 125 °C	4	500	0.32 (c)	33.6	3.4	0.010

Activity test conditions: Humidity 50% RH, temperature 25 °C, reactor ID 1.9 cm, particle size 200 μm ; (a) Catalyst 0.5 g, face velocity 45 cm/s, CO 500 ppm; (b) Catalyst 0.2 g, face velocity 60 cm/s, CO 750 ppm; (c) Catalyst 0.5 g, face velocity 45 cm/s, CO 300 ppm.

the drying of the DADNP precursor at 125 °C for 4 h yielded a catalyst with higher activity.

3.3.4. Platinum precursor calcination temperature and time selection

The effect of Pt precursor calcination temperature on Pt dispersion and the catalytic activity are given in Table 6. A volcano type of correlation was found between catalytic activity and calcination temperature: 300 °C ($0.84 \mu\text{mol g}^{-1} \text{s}^{-1}$) < 400 °C ($1.54 \mu\text{mol g}^{-1} \text{s}^{-1}$) < 500 °C ($9.04 \mu\text{mol g}^{-1} \text{s}^{-1}$) > 600 °C ($8.65 \mu\text{mol g}^{-1} \text{s}^{-1}$). The Pt dispersion decreased with increased calcination temperature as follows: 300 °C (54.1%) > 400 °C (49.4%) > 500 °C (40.3%) > 600 °C (21.9%). A reduction in the Pt dispersion would have an adverse effect on catalytic activity; however, the catalytic activity increased with calcination temperature up to 500 °C. There can be two possible reasons for this relationship: (a) metal sintering or (b) decoration of Pt crystallites by CeO_2 .

Based on the earlier O_2 - H_2 titration analysis, it has already been established that the Pt- CeO_2 interfacial area was crucial to the catalytic activity. Also, in the case of Pt/ceria catalysts, ultra-thin films of ceria on Pt crystals have been found to be highly active CO catalysts [41]. As observed here, despite a reduction in the Pt dispersion, when the calcination temperature was increased to 500 °C, the activity was still increased. Therefore, the decoration of the Pt crystallites by ceria was the most probable cause of the decrease in Pt dispersion up to 500 °C. A similar behavior has been reported in the case of the Pt/ TiO_2 catalysts as well, where an increase in Pt doping in TiO_2 with increasing calcination temperature caused a decrease in Pt dispersion [21].

The effect of Pt metal sintering due to surface diffusion was probably significant only at calcination temperatures at or above 600 °C (based on Pt dispersion and activity values). In other words, a trade-off existed between the Pt dispersion and catalytic activity due to the decoration of the Pt crystallites by ceria, which most probably peaked at around 500 °C. This would also explain the significant jump in TOF from 0.109 s^{-1} for the calcination temperature of 500 °C to the TOF of 0.193 s^{-1} for the calcination temperature of 600 °C. While the activity per active site increased due to a higher Pt-ceria surface area, the total number of active sites decreased due to the higher calcination temperature.

The CO oxidation activity results and CO chemisorption results for the effect of calcination time are given in Table 6. The Pt dispersion decreased with increased calcination time. A volcano type correlation was found between the catalytic activity and calcination time, analogous to the calcination temperature effect 1 h ($0.70 \mu\text{mol g}^{-1} \text{s}^{-1}$) < 2 h ($1.72 \mu\text{mol g}^{-1} \text{s}^{-1}$) > 3 h ($0.65 \mu\text{mol g}^{-1} \text{s}^{-1}$) > 4 h ($0.32 \mu\text{mol g}^{-1} \text{s}^{-1}$). Since the aggregation of Pt crystallites by surface diffusion and Pt crystallites decoration by ceria are functions of calcination time, the change in Pt dispersion can be anticipated. The effect of calcination time on catalytic activity can be explained analogously to the calcination temperature and the catalytic activity in the case of the calcination temperature of 500 °C for the DADNP precursor peaked at about 2 h.

3.4. Effect of ceria content

Since the catalytic activity was found to be a function of the CeO_2 SA in contact with Pt, the effect of CeO_2 loading on the catalytic activity of 4%Pt- $\text{CeO}_2/\text{SiO}_2$ catalyst was analyzed by varying the CeO_2 content from 4 to 27 wt%. The XRD spectra were obtained for different CeO_2 contents and are given in Fig. 4. The catalytic activity, XRD analysis, and CO/ H_2 and O_2 chemisorption results are given in Table 7. The catalytic activity improved with increased CeO_2 content from 4% CeO_2 ($1.05 \mu\text{mol g}^{-1} \text{s}^{-1}$) to 22% CeO_2 ($5.77 \mu\text{mol g}^{-1} \text{s}^{-1}$); however, it decreased on going from 22% CeO_2 to 27% CeO_2 ($5.46 \mu\text{mol g}^{-1} \text{s}^{-1}$). Since the presence of CeO_2 in the Pt- $\text{CeO}_2/\text{SiO}_2$ catalyst has been attributed to the increased Pt dispersion, the increased CeO_2 content expectedly resulted in better catalytic activity. The Pt dispersion indeed improved with increased CeO_2 content. For example, Pt dispersions were 36% (CeO_2 : 4 wt%) and 52% (CeO_2 : 27 wt%) as determined by CO chemisorption. Furthermore, the TOF values increased with increased CeO_2 content (TOF: 0.01 s^{-1} and 0.05 s^{-1} for 4 and 22 wt% CeO_2 , respectively). Therefore, the increased CeO_2 SA, better Pt dispersion would have resulted in a larger Pt- CeO_2 interfacial area resulting in the improved activity with increased CeO_2 content.

However, the TOF values decreased from 22% to 27% of CeO_2 . This drop in the catalytic activity can be explained by the increased CeO_2 crystallite size and/or pore blockage and/or pore narrowing of the catalyst. The increased CeO_2 crystallite size would cause a reduced Pt-ceria contact surface area, thus reducing the catalytic activity. Furthermore, pore blocking would make the active sites inaccessible to the reactants, while pore narrowing would cause diffusion limitation. The results of the powder XRD and the O_2 chemisorption indicated that there was a significant increase in the CeO_2 crystallite size with increased CeO_2 content, particularly when the CeO_2 content was higher than 22 wt%, e.g., the CeO_2 crystallite size was 6.4 nm for 9 wt% ceria, whereas the CeO_2 crystallite size was 7.7 nm for 27 wt% ceria. This increased CeO_2 crystallite size may have diminished the catalytic activity.

In general, pore blocking would cause an increase in APS by blocking the smaller pores of the support; whereas pore narrowing would decrease the APS. The BET SA, PVs and APS were

Fig. 4. Powder XRD patterns for ceria on silica for various ceria content prepared by incipient wetness impregnation.

Table 7

Effect of ceria content on catalytic activity**, Pt and ceria dispersion and surface characterization.

Catalyst	Reaction rate ($\mu\text{mol g}^{-1} \text{s}^{-1}$)	Pt chemisorption (%D)		TOF (s^{-1}) (%D: CO chemi.)	CeO ₂ crystallite size (nm)		BET SA (m^2/g)	Pore vol- ume (mL/g)	Avg. pore size (Å)
		H ₂ chemi.	CO chemi.		O ₂ chemi.	XRD			
SiO ₂	NA	NA	NA	NA	NA	NA	319	1.14	143
4%Pt-4%CeO ₂ /SiO ₂ -IN	1.05	28	36	0.011	6.2	6.0	306	1.10	144
4%Pt-9%CeO ₂ /SiO ₂ -IN	1.57	30	37	0.016	6.4	6.4	293	1.03	141
4%Pt-15%CeO ₂ /SiO ₂ -IN	2.94	37	42	0.028	6.9	6.9	257	0.92	143
4%Pt-22%CeO ₂ /SiO ₂ -IN	5.77	42	46	0.049	7.0	7.3	248	0.87	140
4%Pt-27%CeO ₂ /SiO ₂ -IN	5.46	50	52	0.043	7.6	7.7	251	0.85	135

Activity test conditions: 500 ppm CO in air, catalyst bed depth 3.2 mm (0.25 g Cat. + 66% inert silica), face velocity 45 cm/s, particle size 150–250 μm , reactor ID 1.9 cm, humidity 50% RH, temperature 25 °C.

estimated for the catalysts with varying CeO₂ content by N₂ adsorption and are given in Table 7. The increase in CeO₂ content caused a decrease in BET SAs as well as PVs, e.g., the BET SA decreased from 306 to 251 m^2/g with the increase in the CeO₂ content from 4 to 27 wt%. The estimated APS did not show a significant change, e.g., the APS decreased from 143 to 135 Å on going from 4% to 27% CeO₂. Therefore, the increased CeO₂ content had a two-pronged effect on the catalyst, that of pore blocking as well as pore narrowing. By comparing the CO oxidation activity of the catalysts from 15% to 27% ceria loading, it can be said that the optimum value of ceria loading was in the range of 20%–25%.

3.5. Effect of Pt loading

An increase in the Pt content would affect the catalytic activity and Pt dispersion. In this work, the Pt content was varied from 1.25 to 10 wt%. The effect on the catalytic activity and catalytic surface properties was estimated and given in Table 8. As expected, an increased Pt content significantly increased the rate of reaction (Pt: 1.25%, reaction rate: 1.34 $\mu\text{mol g}^{-1} \text{s}^{-1}$; Pt: 5%, 3.13 $\mu\text{mol g}^{-1} \text{s}^{-1}$) and the Pt dispersion decreased substantially with increased Pt content (Pt: 1.25%, %D: 76%; Pt: 7.5%, %D: 31%). Therefore, the TOF values decreased with increased Pt content or increased Pt crystallite size.

Since the Pt–CeO₂ interfacial area was crucial to the activity of the catalyst, the formation of larger Pt crystallites would diminish the Pt–CeO₂ interfacial area, thus resulting in the decline of the rate of reaction on per surface Pt atom basis, i.e., TOF. Furthermore, an increase in the Pt loading after 7.5%

caused a significant drop in the TOF as well as the overall rate of reaction. This can possibly be a combined effect of increased Pt crystallite size, decreased Pt–CeO₂ interfacial area, and changes in the pore structure of the catalyst such as pore blocking and/or pore narrowing due to increased thermal treatments to get Pt content of greater than 5 wt% on the catalyst using successive impregnation steps. However, the BET SA analysis and pore volume, average pore size estimations did not show any major change in the catalyst surface properties when Pt content was increased from 5% to 7.5%. Based on these results an optimum Pt content would be in the range of 2.5–7.5 wt% Pt.

3.6. TPR results

Pt crystallites can be deposited either on the SiO₂ support or CeO₂ promoter. According to Holmgren et al., the Pt–CeO₂ interfacial area was responsible for the CO oxidation activity of Pt/ceria catalysts [12]. Therefore, the location of the Pt crystallites in the Pt–CeO₂/SiO₂ catalyst (Pt/CeO₂ or Pt/SiO₂) would determine the catalytic activity.

CO chemisorption cannot distinguish between Pt/CeO₂ and Pt/SiO₂. Therefore, TPR studies were performed on these catalysts. The H₂ uptake profiles are given in Fig. 5. In the case of CeO₂/SiO₂, two peaks were observed corresponding to CeO₂ surface reduction (490 °C) and bulk CeO₂ reduction (680 °C). The 16%CeO₂/SiO₂ sample as well as the 4%Pt-16%CeO₂/SiO₂ catalyst showed a bulk CeO₂ reduction peak at 670 °C.

Golunski et al. [42] have shown that CeO₂ surface reduction can occur at significantly lower temperature (< 250 °C) due to

Table 8

Effect of Pt loading on catalytic activity and surface characterization.

Catalyst	Reaction rate ($\mu\text{mol g}^{-1} \text{s}^{-1}$)	CO chemisorption on Pt			TOF (s^{-1}) (%D: CO chemi.)	BET SA (m^2/g)	Pore volume (mL/g)	Avg. pore size (Å)
		%D	Crystallite size (nm)	Pt SA (m^2/g)				
1.25%Pt-20%CeO ₂ /SiO ₂ -IN	1.34	76	1.5	2.36	0.028	268	0.90	134
2.50%Pt-20%CeO ₂ /SiO ₂ -IN	2.46	51	2.2	3.13	0.038	260	0.88	135
3.75%Pt-20%CeO ₂ /SiO ₂ -IN	2.80	40	2.8	3.75	0.036	258	0.87	136
5.00%Pt-20%CeO ₂ /SiO ₂ -IN	3.13	39	2.9	4.83	0.031	249	0.84	136
7.50%Pt-20%CeO ₂ /SiO ₂ -IN	3.52	31	3.7	5.65	0.030	225	0.79	140
10.0%Pt-20%CeO ₂ /SiO ₂ -IN	2.74	27	4.1	6.78	0.019	230	0.78	136
5%Pt/SiO ₂	0.61	23	5.0	2.79	0.011	ND	ND	ND
SiO ₂	0.00	NA	NA	NA	NA	319	1.14	143

Activity test conditions: 500 ppm CO in air, catalyst bed depth 3.2 mm (inert silica: 50%–75%), face velocity 60 cm/s, particle size 150–250 μm , reactor ID 1.9 cm, humidity 50% RH, temperature 25 °C.

Fig. 5. TPR Profiles of 16%CeO₂/SiO₂ and 4%Pt-16%CeO₂/SiO₂.

H₂ spillover in the case of Pt/ceria. Further, Salasc et al. [27] observed a CeO₂ surface reduction peak at 480 °C in the case of Pt-CeO₂/Al₂O₃ catalysts due to the presence of ceria grains not deposited with Pt crystallites.

During this study, a CeO₂ surface reduction peak was not observed for 4%Pt-16%CeO₂/SiO₂ catalyst. Therefore, most of the ceria grains were deposited with Pt crystallites. However, the extent of Pt deposition on ceria for the catalyst could not be estimated from TPR.

The catalysts showed a reduction peak at 70 °C which might correspond to the reduction of Pt oxide species and subsequent H₂ spillover to CeO₂. The catalyst also showed a reduction peak at very low temperature (30 °C). According to Hardacre et al., [41] a thin film of ceria partially covering Pt metal was highly reducible (at $T \approx 50$ °C). The reduction peak at 30 °C was perhaps due to the presence of this highly reducible ceria. This reduction peak at 30 °C indicated a strong Pt-ceria interaction resulting in near room temperature ceria reducibility which would also explain the higher activity of the catalysts.

3.7. Activity maintenance of the catalyst

Based on the understanding of the catalyst preparation variables effects on catalytic activity, a catalyst with the optimum preparation conditions was prepared (Davisil 645 silica support; successive incipient wetness impregnation of ceria precursor; drying at 40 °C overnight; calcination at 30 °C for 2 h; DADNP precursor; drying at 125 °C for 4 h; calcination at 500 °C for 2 h and 4%Pt-22%CeO₂/SiO₂). This catalyst was then tested for activity stability at the selected “application conditions” such as the high CO concentration (2500 ppm, 90% RH) conditions for respiratory protection equipment and low CO concentration (250 ppm, 50% RH) for ultra-high efficiency applications. The results are given in Fig. 6.

The CO removal applications at high CO concentration demand the catalyst to be active (CO conversion >90%) for more than 4 h. The catalyst was highly active (CO conversion $\geq 99\%$) and stable (for more than 8 h) in the presence of high moisture and CO content (2500 ppm, 90% RH) as shown in Fig. 6(b).

The CO removal applications at low CO concentration demand the catalyst to be active (CO conversion >90%) for more than 12 h. The catalytic activity test at low CO concentration in

Fig. 6. Activity stability of 4%Pt-22%CeO₂/SiO₂ catalyst under different CO concentration and humidity regimes. Test conditions: temperature 250 °C, reactor ID 1.9 cm, particle size 150–250 μ m; (a) Face velocity 30 cm/s, catalyst bed depth 2.5 mm; (b) Face velocity 10 cm/s, catalyst bed depth 4.0 mm; (c) Face velocity 100 cm/s, catalyst bed depth 5.0 mm.

the presence of moisture (250 ppm CO, 50% RH at 25 °C) revealed that the catalyst was also highly active (CO conversion $\geq 99.5\%$) and stable for more than 15 h (Fig. 6(a)).

The catalyst was also tested under dry conditions (0% RH) at ambient temperature at low CO concentration (200 ppm). Under completely dry conditions (200 ppm, 0% RH, 25 °C), the catalyst was slowly deactivated. However, the catalyst regained activity completely after the introduction of moisture in the reaction gas, suggesting a reversible behavior. The experimental results under dry conditions indicated a progressive cumulative poisoning of the catalyst over time which was not observed in the presence of moisture. Therefore, the water vapor minimized the CO self-poisoning of the catalyst during CO oxidation at ambient temperature on the Pt-CeO₂/SiO₂ catalyst. A similar observation was made in the case of Pt/Al₂O₃ catalyst where the presence of water vapor helped break the CO islands formed on the active Pt sites [5]. Hence, in the case of the Pt-CeO₂/SiO₂ catalyst, the presence of water vapor was essential to maintain the catalytic activity at room temperature.

4. Conclusions

Ceria promoted Pt catalysts were active for CO oxidation in humid air. The ceria deposition method and type of support played an important role in the catalytic activity. The Pt-CeO₂ interfacial area was crucial to the activity of the catalyst, which was determined by O₂-H₂ titration. The deposition of ceria using the incipient wetness impregnation method resulted in the largest Pt-CeO₂ interfacial area and therefore the most active catalyst. Non-preferential deposition of Pt on ceria or alumina resulted in a smaller Pt-CeO₂ interfacial area and reduced activity of the catalyst in the case of an alumina supported Pt-CeO₂ catalyst. The (2.5%–7.5%)Pt-(20%–25%)CeO₂/SiO₂ catalyst was highly active at room temperature at low (CO < 500 ppm) and high CO (CO > 2500 ppm) concentrations in the presence of moisture. The drying and calcination conditions of the ceria and Pt precursors also played a crucial role in determining the active metal (oxide) dispersion and distribution on

the support and in turn the catalytic activity. Water vapor played a major role in maintaining the activity of the catalyst by minimizing CO self-poisoning of the catalyst. CO removal at ambient conditions using the Pt-CeO₂/SiO₂ catalyst for CO oxidation is an effective solution for neutralizing CO in indoor air and other CO filtration applications.

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Graphical Abstract

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Pt-CeO₂/SiO₂ catalyst for CO oxidation in humid air at ambient temperature

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Highly active Pt-Ceria/silica catalyst for low temperature CO oxidation in humid air has been developed. Effect of catalyst preparation variables was studied and the activity maintenance of the catalyst for different applications was investigated.

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Pt-CeO₂/SiO₂催化剂用于室温湿空气中CO氧化反应

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摘要: 开发室温CO氧化催化剂的主要挑战是CO自中毒和慢的表面动力学, 同时湿气的存在也可导致催化剂失活。本文开发了高活性CeO₂促进的Pt基催化剂4%Pt-12%CeO₂/SiO₂, 用于室温湿气(湿度10%–90%, 25 °C)中CO氧化反应, 在低CO浓度(< 500 ppm)和高CO浓度(> 2500 ppm)时, CO转化率高于99%。优化了催化剂制备变量, 如Pt和CeO₂负载量、CeO₂沉积方法、CeO₂和Pt前驱体的干燥和焙烧条件。采用CO/H₂化学吸附、O₂-H₂滴定、X射线衍射和BET比表面积测定表征了催化剂的表面特性, 并将其与催化剂活性相关联。

结果表明, CeO₂沉积方法对催化剂活性影响显著, 当用浸渍法沉积CeO₂时, 所得催化剂的反应速率(5.77 μmol/g/s)比用沉积沉淀法(1.96 μmol g⁻¹ s⁻¹)或CeO₂嫁接法(1.31 μmol g⁻¹ s⁻¹)制得催化剂的高3倍。O₂-H₂滴定结果表明, 当用浸渍法沉积CeO₂时, CeO₂和Pt的紧密结合导致了催化剂的高活性。催化剂载体的选择也非常重要, 硅胶负载的催化剂活性(5.77 μmol g⁻¹ s⁻¹)是氧化铝负载的(1.05 μmol g⁻¹ s⁻¹) 5倍。当反应受内扩散控制时, 催化剂载体的粒径和孔结构影响非常大。另外, CeO₂和Pt前驱体的干燥和焙烧条件对催化剂活性的影响至关重要。当Pt和CeO₂含量分别大于2.5和15 wt%时, 所得催化剂在室温条件下活性高(TOF > 0.02 s⁻¹), 稳定性好(反应15 h, CO转化率 ≥ 99%)。

关键词: 一氧化碳氧化; 催化剂; 铂; 二氧化铈; 二氧化硅; 前驱体; 氢氧滴定; 化学吸附; 程序升温还原

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