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Microemulsion Prepared Pt in Ceria: Catalytically Active for Water Gas Shift Reaction but Totally Inert for Methanation

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Abstract A core–shell Pt in ceria type of catalyst prepared by a microemulsion technique shows high activity for both water gas shift and reverse water gas shift reactions but it does not catalyze methanation from carbon oxides and hydrogen feeds at all, whereas Pt-ceria catalysts prepared by traditional methods are effective for all these reactions under comparable reaction conditions. This clearly reveals the fact that the nature of active sites for shift reactions is different from those of methanation reactions, where a special metal-support interface in catalysts created by microemulsion offers the differentiation.

Keywords Microemulsion · Water gas shift · Noble metal · Ceria · Interface · Methane

1 Introduction

Noble metal (NM)/ceria based catalysts have been extensively investigated in recent years [1–8] for the WGS reaction ($CO + H_2O \rightleftharpoons CO_2 + H_2$, $\Delta G^\circ_{298} = -28.6\,\mathrm{kJ\,mol^{-1}}$ in order to produce more H_2 rich feeds from reformate mixtures. In terms of volume produced, hydrogen is by far the most important component. For the majority of energy (fuel cells) and chemical applications, hydrogen must be of high purity, and carbon oxides, in particular carbon monoxide (a strong catalyst poison), must be reduced to very low levels (ppm) [9]. Thus, developing a more active NM/ceria based catalyst over the less active Cu-based catalyst technology used in small WGS reactors is currently under intense investigation for both mobile and stationary applications. However, much of the research in this area reported in the literature has involved the use of an artificial gas mixture (CO/H_2O) for the WGS study rather than the use of reformate which contains high levels of hydrogen and carbon dioxide. The effects of these gas mixtures on the WGS reaction are not yet clear over the NM/ceria catalysts, though the direct use of reformate would be practically more relevant than using an artificial gas mixture. One immediate technical problem is that at high levels of hydrogen and carbon oxides, other side reactions could also be simultaneously taking place during the WGS catalysis. For example, the methanation reactions:

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)},\quad \Delta G^\circ_{298} = -140.6\,\mathrm{kJ\,mol^{-1}} \qquad \text{(Reaction 1)}$$

$$CO_{2(g)} + 4H_{2(g)} \rightleftharpoons CH_{4(g)} + 2H_2O_{(g)},\quad \Delta G^\circ_{298} = -113.1\,\mathrm{kJ\,mol^{-1}} \qquad \text{(Reaction 2)}$$

In addition, formation of higher hydrocarbons via the Fischer–Tropsch process from reformate mixture, at the given high levels of hydrogen and carbon oxides, is also thermodynamically favorable, particularly at elevated pressures.

$$(n+1)H_{2(g)} + 2nCO_{(g)} \rightleftharpoons C_nH_{2n+2(g)} + nCO_{2(g)}$$

$$(2n+1)H_{2(g)} + nCO_{(g)} \rightleftharpoons C_nH_{2n+2(g)} + nH_2O_{(g)}$$

Such like n-butane as follows:

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$$5H_{2(g)} + 8CO \rightleftharpoons C_4H_{10(g)} + 4CO_{2(g)}, \quad \Delta G^\circ_{298} = -493.2\,\mathrm{kJ\,mol^{-1}} \qquad \text{(Reaction 3)}$$

$$9H_{2(g)} + 4CO_{(g)} \rightleftharpoons C_4H_{10(g)} + 4H_2O_{(g)}, \quad \Delta G^\circ_{298} = -379.3\,\mathrm{kJ\,mol^{-1}} \qquad \text{(Reaction 4)}$$

These side reactions are known to be unimportant over the traditional Cu or Cr based WGS catalysts, since the C–O bond is likely to remain intact (associative adsorption of CO) before it is converted into CO_2 during the WGS. However, NMs are able to dissociatively adsorb CO leading to the breakage of C–O linkage on their surfaces, hence favoring the formation of methane and higher hydrocarbons under hydrogen rich conditions. In fact, a significant quantity of methane and high hydrocarbons has indeed been detected during the WGS study over the NM/ceria (prepared by traditional methods) by workers at Synetix, Johnson Matthey [10]. Thus, the high selectivity for the WGS reaction is required over the competing reactions of methanation and Fischer–Tropsch, as these can lower the H_2 content of the final feed.

In our previous communication, we reported that the new class of microemulsion prepared NM/ceria catalysts which show a comparable or even higher catalytic activity towards the WGS reaction than those catalysts prepared by traditional methods [11]. Our preliminary observation was that this new type of catalysts also inhibits methane formation at elevated temperatures.

In this paper, we have further investigated the methane inhibition effect with respect to the unusual architecture of the microemulsion prepared NM/ceria catalysts (unique morphology) as compared to those catalysts prepared by traditional methods.

2 Experimental

2.1 Microemulsion Prepared Pt/CeO_2 Catalysts

The typical procedure for preparing 5 wt.% Pt/ceria catalysts by the microemulsion (MEs) technique is as follows: a cationic surfactant, cetyltrimethylammonium bromide, CTAB was added into dry toluene with vigorous stirring. A water to surfactant ratio, W, of 30 was employed in this synthesis. A suspension of CTAB in toluene was formed immediately. Then, the Pt precursor salt solution with ceria was prepared by dissolving an appropriate amount of $(NH_4)_2PtCl_6$ into the DI water. The aqueous solution of Pt precursor salt was then added dropwise to the suspension of CTAB in toluene and was stirred overnight. A solution of 0.22 g of sodium hydroxide pre-dissolved in 1.630 mL of DI water was added into the reaction mixture and stirred for 2 h before adding a solution of 0.6060 g of cerium(III) nitrate hexahydrate. It is noted that the final water to surfactant molar ratio of the resulting mixture was maintained at 30 as in the MEs method. The reaction mixture was aged for 6 days with constant stirring. After the ageing step, the reaction mixture was centrifuged for 20 min at 1000 rpm in order to collect the product. The product was then washed with EtOH at least four times to remove surfactants. The solution was repeatedly centrifuged after each washing. The solid product obtained was dried overnight in air. The catalysts were then pre-treated with the reactant gas mixture (8% CO, 10% CO_2, 1% CH_4, 32.5% H_2 balancing with N_2) at 400 °C before catalytic testing.

2.2 Co-Precipitation Prepared Pt/CeO_2 Catalyst

A total of 2 wt.% Pt/ceria catalysts synthesised by the co-precipitation method were prepared as follows. A total of 0.1541 g of ammonium tetrachloroplatinate(II), $(NH_4)_2PtCl_4$, was dissolved in a 100 mL aqueous solution of 0.2 M cerium(III) nitrate hexahydrate, $Ce(NO_3)_3 \cdot 6H_2O$, and sprayed into a 250 mL ammonia solution under a constant stirring. The precipitate was allowed to age at room temperature with stirring for another 2 h. Then, it was collected by centrifugation at 1,000 rpm and washed twice with water and once with ethanol to remove any remaining ammonia and reaction by-product. The solid was dried at 60 °C in a vacuum oven for 2 h. Then, it was dried in a flowing stream of nitrogen at 100 mL min^{-1} at a temperature ramp of 2 °C min^{-1} from room temperature to 350 °C and then held for further 5 h. After the drying procedure, it was pre-reduced with 50 mL min^{-1} hydrogen at programming of 2 °C min^{-1} up to 250 °C and held for further 3 h.

2.3 Wet Impregnation Prepared Pt/CeO_2 Catalyst

A total of 5 wt.% Pt/ceria catalysts synthesized by wet impregnation were prepared as follows. Cerium(III) nitrate hexahydrate was calcined in static air with temperature programming (25 °C min^{-1}) from room temperature to 600 °C and was held at 600 °C for a further 10 h. Ammonium tetrachloroplatinate(II) or hexachloroplatinate(IV) was dissolved in D.I. water. The Pt-precursor solution was then wet impregnated onto the calcined ceria. The product was dried under air with temperature programming (5 °C min^{-1}) from room temperature to 100 °C and was held at 100 °C for a further 10 h. The catalyst was then calcined in a flowing stream of nitrogen at 30 mL min^{-1} with temperature programming (20 °C min^{-1}) from room temperature to 500 °C and was held for a further 2 h.

2.4 Catalysts Testing

The product gas mixtures were analysed by an online GC using a PERKIN ELMER Auto System XL equipped with a methanator and a flame ionization detector (FID). The size of a sample loop was 1.0 mL. A packed GC column of Carbosphere 80/100 (6 ft × 1/8 in. outer diameter) was used to separate CO, CO_2 and CH_4 from the gas mixtures at an oven temperature of 150 °C within 5 min. After the separation, CO and CO_2 were converted to CH_4 by the Ni catalyst installed in the methanator prior to their analysis by the FID. It is noted that two condensers kept in an ice/water bath were installed between the gas exit of the reactor and the inlet of a GC in order to trap any remaining water from the product mixture otherwise the separation efficiency of the GC column would have been impaired. Also, the product gas analysis was carried out by FID equipped with methanator hence only carbon containing gases were detected.

3 Results and Discussion

Table 1 summarizes the CO fractional conversions of WGS reactions (mainly to CO_2 and H_2) and methane formation (a minor reaction from hydrogenation of carbon oxides) over the various catalysts at 400 and 500 °C, respectively [11]. It is interesting to find that the co-precipitated Pt/ceria gives a significant quantity of methane formation (1.01% from *methanation* of carbon oxides on metal surface) from the gas mixture at 500 °C. Equally, the Pt/ceria catalyst prepared by the wet impregnation shows a lower activity towards the WGS due to the low surface area ceria, but it yields a measurable quantity of methane. It is noted that despite the fact that both the microemulsion and co-precipitation prepared 5% Pt/ceria catalysts show very similar CO conversions, the microemulsion prepared Pt/ceria sample displays no activity for methane formation under identical conditions. Addition of gold to platinum in the microemulsion prepared catalyst can also improve the WGS activity with no methane formation. These results suggest clearly an interesting fact that the nature of active sites for methanation (known to take place on extended metal ensemble surface [12]) may not be the same for WGS giving the possibility of optimising metal containing catalysts for WGS without methane formation.

Further to these methane assessments under WGS conditions, the noble metal-ceria samples prepared by the traditional co-precipitation method and microemulsion method were carefully examined and compared for their methanation activity under different feed compositions, namely:

(a) same reformate but further enriched with H_2;
(b) same reformate but without adding water;
(c) CO and H_2 diluted in N_2.

Figure 1 shows that the traditional co-precipitation catalyst gives an increasing quantity of methane formation compared with the blended methane level at 500 °C depending on the H_2 content (a flow of pure H_2 blended into the WGS mixture), which is in a clear contrast to the MEs-5 wt.% Pt/ceria catalyst that again gives absolutely no methane formation at all H_2 levels.

Another assessment on methanation activity over the two different catalysts (conventional co-precipitation 2% Pt/eria as compared to the best 5% Pt, 5% Au/ceria microemulsion catalyst) was conducted using the same reformate mixture but this time, without adding water to the system. The feed gas composition was 1% CH_4, 8% CO, 10% CO_2, 32.5% H_2 balanced with N_2 under the same

Table 1 Comparison of WGS and methanation activities of various catalysts

Catalyst	WGS activity[c]	CH_4 formation[d]	Dispersion[e] (d^f)
$Cu/ZnO/Al_2O_3$[a]	55.4	0.03	n.d.
Co-precipitated 2% Pt/ceria[a]	58.6	13.6	14.2 (6.4)
Wet impregnated 5%Pt/ceria[a]	53.2	1.51	20.3 (4.4)
MEs-5% Pt/ceria[b]	62.5	0.0	0.8 (58.4)
MEs-5%Pt, 5%Au/ceria[b]	70.6	0.0	1.8 (50.4)

[a] Catalysts prepared by traditional methods

[b] Using microemulsion method, each metal particle is embedded in a thin overlayer of ceria

[c] WGS activity expressed as a percent of CO conversion using 0.77% CH_4, 6.15% CO, 7.68% CO_2, 24.99% H_2, 23.08% H_2O balanced with N_2 at GHSV of 108, 000 h^{-1} at 400 °C

[d] Methane formation is defined as percent of methane gained with respect to the input 0.77% CH_4 at 500 °C

[e] Percent metal dispersion measured by CO chemisorption

[f] Theoretical metal diameter, *d*, based on CO chemisorptions (notice that XRD shows no metal peaks, whereas small metal clusters <2 nm are observed only by a high-resolution TEM)

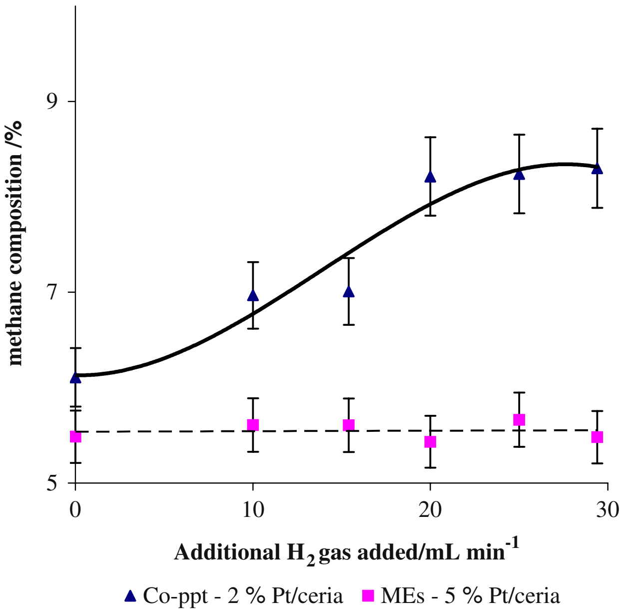

Fig. 1 Methane formation over the two catalysts, MEs-5% Pt/ceria and Co-ppt-2% Pt/ceria, using a reformate of 0.77% CH_4, 6.15% CO, 7.68% CO_2, 24.99% H_2, 23.08% H_2O balanced with N_2 (thus 5.6% methane content with respect to all carbon-containing gases as a baseline) at GHSV of 108, 000 h^{-1} at 500 °C blending with a pure H_2 feed

GHSV (with respect to the reformate). The results of this study are summarized in Figs. 2 and 3. As shown in Fig. 2, the traditionally prepared 2% Pt/ceria catalyst (co-precipitation catalyst) produces a large quantity of methane from the mixture while the microemulsion 5% Pt, 5% Au/ceria and 5% Pt/ceria (not shown) catalysts again gives only a small amount of methane at above 500 °C.

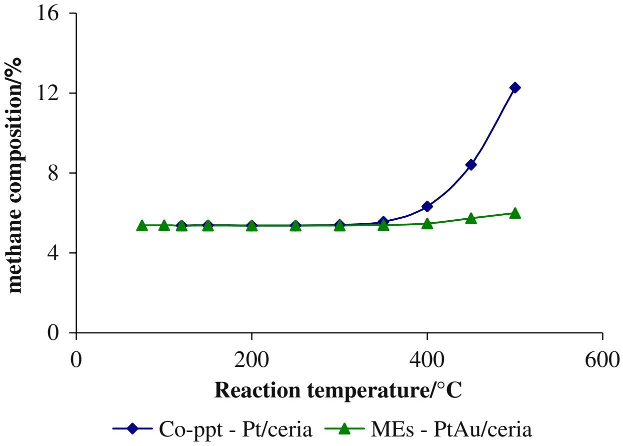

Fig. 2 A plot of % CH_4 composition with respect to all carbon content in the product gas mixture versus reaction temperature over different tested catalysts in the presence of a reformate of 8% CO, 10% CO_2, 1% CH_4, 32.5% H_2 balanced with N_2 (initial methane content is 5.26% with respect to all carbon-containing gases as a baseline)

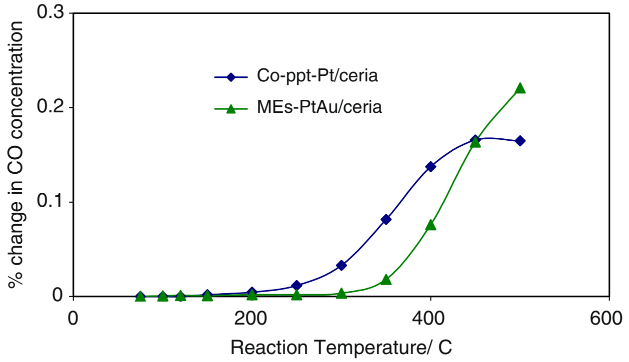

Fig. 3 A plot of % change in CO (with reference to the original CO concentration) versus reaction temperature over catalyst prepared by a traditional method (co-precipitation 2% Pt/ceria) as compared to 5% Pt, 5% Au/ceria microemulsion catalyst in the presence of a reformate of 8% CO, 10% CO_2, 1% CH_4, 32.5% H_2 balanced with N_2

It is also interesting to find from Fig. 3 that for this gas mixture, no CO is consumed but in fact *produced* over the tested catalysts. The CO production can be explained due to the equilibrium of the reverse water gas shift (RWGS) reaction without the presence of water. Thus, both the tested catalysts are clearly active for the RWGS reaction giving a significant quantity of CO.

$$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)} \qquad \text{(Reaction 5)}$$

It is noteworthy that the co-precipitation catalyst activates the gas mixture to form CO at lower temperatures of 200 °C (more active) than our MEs catalyst, however, a very similar activity of the two Pt/ceria catalysts was previously observed for the forward WGS (Table 1). Thus, it is concluded that for the activation of the gas mixture for the RWGS it may not be necessary to use the same active site as in the case of the WGS especially more than one type of site is present (hydrogen activation is facilitated by metal surface in the RWGS). Nevertheless, it is interesting to find that both the RWGS and the WGS activities over the co-precipitation catalyst were leveled at above 400 °C, where a significant quantity of methane was produced in both cases. Thus, it is apparent that the methanation activity competes with the shift equilibrium over this temperature regime reducing the overall extents of the shift activity in the case of the traditional catalyst while such a competition is not significant in the MEs catalyst.

Methanation assessments over the two catalysts were also conducted under 8% CO, 32.5% H_2 balanced with N_2 at the same GHSV. Methane and carbon dioxide productions were observed, so their conversions were defined as: CH_4 production (%) = 100 × mole of CH_4/total mole of input carbons (CO, CH_4 and CO_2); CO_2 production (%) = 100 × mole of CO_2/total mole of input carbons (CO, CH_4 and CO_2).

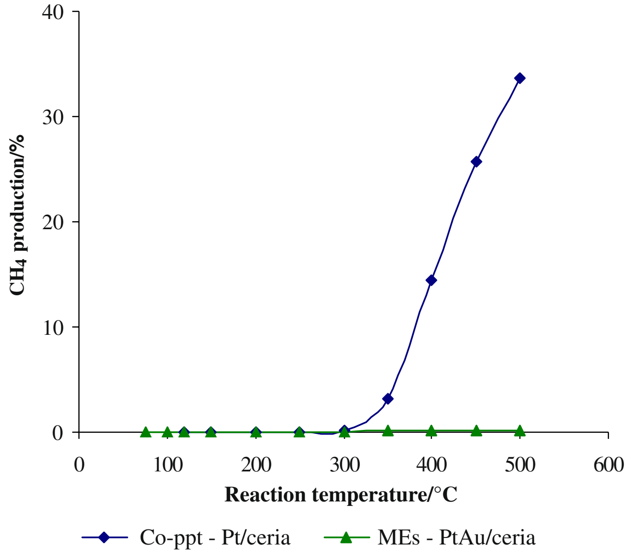

Fig. 4 A plot of methane production versus reaction temperature over co-precipitation and MEs catalysts towards methanation in the presence of 8% CO, 32.5% H_2 balanced with N_2 with the GHSV = 84,000 h^{-1}

As shown in Fig. 4, the co-precipitation catalyst clearly shows a high activity for methane production at above 300 °C, while the microemulsion catalyst again displays no activity for methane production for the whole temperature range studied. As seen from Fig. 5, the co-precipitation catalyst also produces a large quantity of CO_2 during the methanation reaction with a very similar temperature profile for both the CH_4 and CO_2 production curves, presumably the water formed from methanation could help to shift some of the CO gas to CO_2. On the other hand, a small quantity of CO_2 was detected over the MEs catalyst from 300 °C.

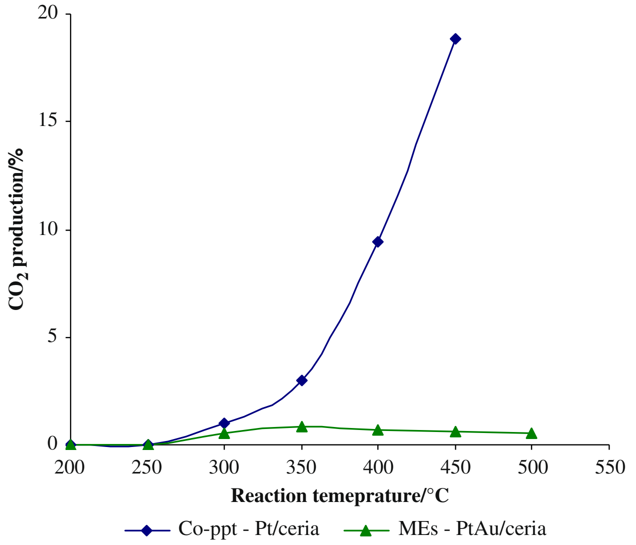

Fig. 5 A plot of CO_2 production versus reaction temperature over co-precipitation and MEs catalysts towards methanation in the presence of 8% CO, 32.5% H_2 balanced with N_2 with the GHSV = 84,000 h^{-1}

The mechanism for CO methanation in the presence of H_2 has been intensively investigated in the past. It is accepted that this reaction will favorably take place on the *metal surface sites* through dissociative adsorption of CO molecules as shown in Reaction 6 with initial deposition of carbon and oxygen species on the extended metal ensemble surface [12]. Methane formation can take place from the reaction of carbon species with hydrogen on the *metal surface sites* (activated hydrogen, see Reaction 8). In the presence of excess CO, the surface oxygen species could react with it to form CO_2 (Reaction 7). Even without surface oxygen CO can still convert to CO_2 with carbon deposition on catalyst surface by Boudouard reaction (Reaction 9). Hence, such a mechanism could explain the simultaneous production of methane and carbon dioxide over our traditional co-precipitation catalyst. In contrast, it is surprising to find that our MEs catalyst containing the same noble metal component with a high activity for WGS shows no activity for methanation. The small quantity of carbon dioxide production at above 300 °C is likely to be derived from the stoichiometric reaction of CO with the lattice oxygen from ceria (Reaction 7), their depletion restricts the significant production of carbon dioxide (see Fig. 5).

$$CO_{(g)} \rightarrow C_a + O_a \qquad \text{(Reaction 6)}$$

$$CO_{(g)} + O_a \rightarrow CO_{2(g)} \qquad \text{(Reaction 7)}$$

$$C_a + 2H_{2(g)} \rightarrow CH_{4(g)} \qquad \text{(Reaction 8)}$$

$$2CO_{(g)} \rightarrow CO_{2(g)} + C_a \qquad \text{(Reaction 9)}$$

C_a and O_a represent carbon and oxygen adsorbed on the catalyst surface respectively.

A summary of the methanation activities at 500 °C over the traditional and MEs catalyst under different feeds is listed in Table 2. It is apparent that the two MEs catalysts are consistently showing a higher kinetic barrier for methane production than the traditionally prepared catalysts with the same chemical composition over different gas feeds.

As a result, this paper clearly reveals the unusual methanation inhibition effect of the microemulsion prepared supported metal catalysts as compared to those catalysts prepared by traditional methods. The clear conclusion is that the microemulsion prepared metal catalysts do not allow exposure of *surface metal sites* for catalyzing Reactions 6–9. Material characterization in our previous communications indeed confirmed that the core–shell morphology of the supported metal catalysts prepared by microemulsion. CO chemisorption suggested most metal sites are inaccessible to reactive gases and no characteristic

Table 2 Methane production over different preparation methods made Pt/ceria under different feed gas compositions

CH_4 production (%) at 500 °C	$Cu/ZnO/Al_2O_3$	Co-ppt[f]	Wet impregnation	MEs-Pt/CeO_2	MEs-$Pt/Au/CeO_2$
WGS conditions[a,b]	0.03	13.6	1.5	0.0	0.0
WGS conditions without H_2O[b,c]	–	133.2	–	–	Trace
H_2 enriched WGS conditions[b]	–	48.9	–	0.0	0.0
CO, H_2/N_2[d,e]	–	33.7	–	–	0.0

[a] Feed gas composition: 0.77% CH_4, 6.15% CO, 7.68% CO_2, 24.99% H_2, 23.08% H_2O balancing with N_2

[b] Percent of methane gain compared to the initial methane content in the feed gas

[c] Feed gas composition: 8% CO, 10% CO_2, 1% CH_4, 32.5% H_2 balancing with N_2

[d] Feed gas composition: 8% CO, 32.5% H_2 balancing with N_2

[e] Percent of methane in total carbon count in the gas mixture after reaction

[f] Co-precipitation

metal-carbonyl and formate species were detected under RWGS conditions [11, 13].

The key questions then include: why are the microemulsion catalysts still active for shift reactions without much exposed metal sites which are also thought to catalyze these reactions? and what is the nature of active sites in these catalysts in catalyzing the shift reactions? In another word, is there any prime difference in the nature of active sites of the ‘reverse morphology’ of ‘oxide enclosing on metal’ in microemulsion catalysts compared to the standard architecture of supported metal catalyst described as ‘metal particle on oxide support’ made by traditional methods?

There have been many mechanistic studies on WGS and RWGS reactions over traditionally synthesized noble metal-ceria catalysts in the literature. It is generally believed that these shift reactions are catalyzed by the cerium oxide surface promoted by the metal ingredients. There are broadly two schools of thought, namely regenerative (redox) mechanism and associative mechanism to explain the high activity of WGS using metal-promoted ceria catalysts [14–19]. The regenerative mechanism involves successive oxidation and reduction of the surface (Reactions 10 and 11). In this redox mechanism water dissociates completely to O_a and H_a and the O_a is then titrated by carbon monoxide. The elementary reactions are shown as follows:

$$\text{O-cat} + CO_{(a)} \rightarrow CO_2 + [\quad]\text{-cat} \qquad \text{(Reaction 10)}$$

$$H_2O + [\quad]\text{-cat} \rightarrow H_2 + \text{O-cat(rate-determining step)} \qquad \text{(Reaction 11)}$$

On the other hand, the associative mechanism involves reactions through adsorbed surface intermediates, such as a formate. Decomposition of formate then results in hydrogen and carbon dioxide products. In the formate mechanism, water dissociates to form OH_a, which then reacts with carbon monoxide to produce $HCOO_a$. This mechanism was summarized in the paper of Shido and Iwasawa who studied mechanism of the WGS reaction over CeO_2 and Rh/CeO_2 [20]. This postulation has then been backed by the studies from Jacobs and co-workers [3, 21, 22]. In addition, carbonate rather than formate surface species has been proposed as the main intermediate specie over reverse-WGS reaction which is thought to share the same mechanistic pathways as WGS under microscopic equilibrium [2, 23]. Very recently, Burch [24] has pointed out that the WGS mechanism is strongly dependent on the choice of experimental conditions while the similar point was previously made by various workers in this area. According to his analysis, the redox mechanism has been proposed to be important at higher temperatures with the implication that the associative mechanism is important at low temperatures with further possibility that surface carbonates or carboxylates could be important intermediates involved in the rate determining step.

Nevertheless, there is still no agreement on the nature of the active sites over conventional Pt on ceria catalysts in the literature, the conclusions of which could depend on particular catalysts and reaction conditions used. For example, Davis [25] proposed exposed NM sites on the surface of ceria to be crucial to shift activity, Flytzani-Stephanopoulos [1] attributed to the ionic Pt in ceria [11, 13].

Surely, the exposed metal sites in conventional prepared catalysts with well-known capability of dissociatively activations of small molecules such as CO and CO_2 and H_2 can catalyse both the methanation and shift reactions. But, in this special case, by eliminating the exposed metal sites on ceria, the unusual metal–metal oxide geometry of MEs catalysts has clearly shown to display superior beneficial methanation inhibition effect over the current catalyst systems for WGS. Thus, a simple and straightforward conclusion is that the extended metal surface must have been covered by the ceria leading to the absence of methanation activity.

Thus, the high WGS activity of the core–shell catalysts without much exposed metal sites must derive from the active ceria interface promoted by underneath metal core through the thin ceria encapsulation which provides the *active sites* for the WGS and RWGS shift activities under these conditions. However, it should be emphasized that the relative significance of this kind of observed catalysis over our core–shell samples compared to those of traditional exposed metal-ceria interface under different reaction conditions is not yet known.

4 Conclusion

From this work we show that a new class of microemulsion NM/ceria catalysts displays an unusual catalytic property. They are highly active for both WGS and RWGS reactions but they do not catalyze methanation from carbon oxides and hydrogen feeds at all. On the other hand, NM/ceria catalysts prepared by traditional methods are effective to catalyze all these reactions under comparable reaction conditions. This clearly reveals the fact that the nature of active sites for shift reactions is different from those for methanation reactions, where the special metal-support interface in catalysts prepared by microemulsion offers the differentiation. It is believed that this finding of a higher kinetic barrier for methanation of the microemulsion NM/ceria catalysts could be practically important with regard to potential applications of this new type of catalyst in both mobile and stationary WGS reactors.

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