

NOTE

Metal-Support Interactions in Rh/CeO₂, Rh/TiO₂, and Rh/Nb₂O₅ Catalysts as Inferred from CO₂ Methanation Activity

In the last two decades the study of metal–support interactions and their relevance in catalysis have been widely investigated, following the discovery by Tauster *et al.* of the so-called strong metal–support interaction (SMSI) effect (1). Since it is generally recognized that the reducibility of the oxide is a major factor in determining SMSI effects, ceria, owing to its reducibility, may be a good candidate to exhibit this kind of interaction. Several authors have in fact suggested that CeO₂ undergoes strong interaction with the supported metal after treatment under H₂, in the way originally defined, thus meriting the acronym SMSI (2). On the contrary, recent studies carried out by Bernal *et al.* (3) have found compelling evidence which indicates that Rh/CeO₂ does not enter a SMSI state, at least after reduction at 773 K. Since it is generally recognized from the recent literature that conventional chemisorption studies cannot be profitably used to characterize Rh/CeO₂ interaction under H₂ (3–5), we decided to analyze metal–support interaction further by comparing the catalytic properties of Rh/CeO₂ with those of Rh supported on other reducible oxides like TiO₂ and Nb₂O₅, which are known to show a SMSI behaviour.

Nb₂O₅ was prepared by precipitation with excess NH₄OH from a methanolic solution of the corresponding chloride followed by drying for 15 h and calcination at 823 K for two h. The surface area, as measured by N₂ adsorption, was 97 m²/g. CeO₂ was prepared by adding NH₄OH dropwise to a solution of Ce(NO₃)₃ · 6H₂O. The resulting oxide was filtered, dried for 15 h, and calcined at 823 K for two h (surface area 18 m²/g). TiO₂ (Degussa P25) with a surface area of 51 m²/g was used. Rh-loaded catalysts (1 wt.%) were prepared by incipient wetness from a RhCl₃ · 3H₂O solution. The impregnated catalysts were first dried at 373 K for 15 h and then calcined at 823 K for two h. CO₂ methanation was chosen as a probe reaction to test the catalytic behaviour following the methodology and the experimental procedure previously described (6). We have used three different catalytic approaches: (1) catalytic activity in steady-state conditions, (2) catalytic activity in pulse conditions, and (3) catalytic measurements using a very dilute mixture of reactants.

The activity under steady-state conditions is reported in Table 1. As can be seen, a small positive effect following

high-temperature reduction (HTR) is observed for TiO₂-based catalyst, while Rh/Nb₂O₅ shows a remarkable decrease in the CH₄ formation rate. A decrease in the reaction rate is also observed with Rh/CeO₂, whose steady-state activity decreases by approximately 50% after reduction at 773 K. We have also followed the procedure of initially cycling the catalysts through a HTR and an oxidation at 673 K before measuring the catalytic activity. We have done this because previous work (5, 7) indicates some sintering following the initial HTR but a reproducible particle size for Rh thereafter. Following this procedure it is shown that the activity of the HTR Rh/CeO₂ under steady-state conditions is similar to the activity of the same catalyst after low-temperature reduction (LTR).

The analysis of data, collected under both pulse and unsteady-state continuous conditions, reveals a different picture. The results under pulse mode are reported in Fig. 1. A CO₂ pulse in hydrogen is converted into CH₄ after reduction at 473 K in all the catalysts tested. The effect of a high-temperature reduction at 773 K completely suppresses the catalytic activity in Rh/Nb₂O₅, while for Rh/TiO₂ a decrease of one order of magnitude is observed. However, while Rh/TiO₂ after subsequent pulses slightly recovers the activity, with Rh/Nb₂O₅ the conversion remains unchanged, even after several CO₂ pulses, and only a treatment with a pulse of O₂ at the reaction temperature restores the methanation activity to values similar to those observed after LTR (Fig. 1). In the case of Rh/CeO₂ a totally different, almost opposite behaviour is observed. High-temperature reduction causes the catalyst to convert as much as three times the quantity converted after a low-temperature reduction but the activity soon decreases due to a fast deactivation, which brings the catalyst back to a situation similar to that observed after a LTR.

The activity has also been tested under unsteady-state continuous conditions using a procedure, described previously in Ref. (6), which allowed the accurate determination of reaction rate vs time also under initial conditions. The profile of activity vs time at the beginning of reaction is reported in Fig. 2. The behaviour is consistent with that observed in pulse conditions with minor differences mainly related to the catalyst recovery rate. The initial activity after reduction at 773 K is *totally suppressed* with

TABLE 1
CO₂ Methanation under Steady-State Conditions and H₂ Chemisorption^a

Catalyst	CH ₄ formation rate ^b			H/Rh ^c	
	LTR	HTR	LTR ^d	LTR	HTR
Rh/CeO ₂	120	60	75	0.90	0.56
Rh/TiO ₂	1500	1900	1390	0.33	0.02
Rh/Nb ₂ O ₅	3300	70	3100	0.49	0.01

^a Reaction conditions: Temperature, 463 K; CO₂/H₂/He = 1/3/4; total flow, 48 ml/min; GHSV = 2500–3000 h⁻¹; LTR, reduction at 473 K for 2 h; HTR, Reduction at 773 K for 2 h.

^b (Mol CH₄/g_{cat.} h) × 10⁵ measured after approx. 15 h on stream.

^c H₂ uptake as measured by extrapolation at zero pressure of the linear part of the isotherm at 298 K.

^d Activity measured after initially cycling the catalyst through an HTR and an oxidation at 623 K (see text).

catalysts based on Nb₂O₅ and TiO₂, while an enhancement is observed with Rh/CeO₂. The suppression of activity is not permanent; a slow increase of activity with time-on-stream is observed with Rh/Nb₂O₅, while Rh/TiO₂ shows a better recovery rate, which is in agreement with the behaviour observed under pulse mode. The initial suppression of activity is also in agreement with H₂ chemisorption data (Table 1), which indicate that accessible surface Rh is not available following HTR for typical "SMSI supports"; in contrast, only a moderate reduction of H₂ uptake is observed over Rh/CeO₂ after a high-temperature reduction.

It clearly appears from the results that steady-state activity measurements *are not indicative* of the properties

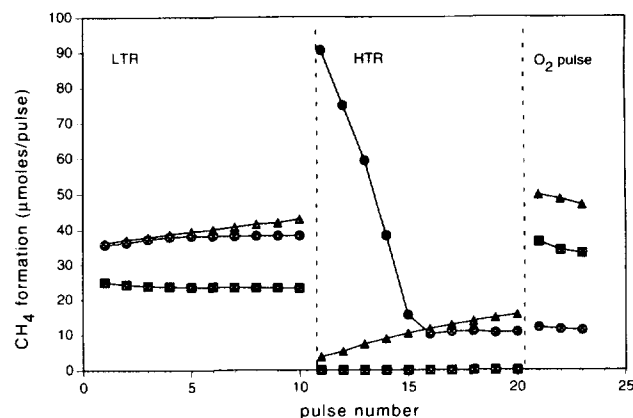


FIG. 1. CO₂ methanation under pulse conditions. Amounts of CH₄ formed from consecutive pulses of CO₂ (10–30 μl) over Rh/CeO₂ (●), Rh/TiO₂ (▲), and Rh/Nb₂O₅ (■) catalysts in H₂ flow at 473 K, following reduction at 500 K (LTR) and 773 K (HTR) and treatment with O₂.

of the samples that have been subjected to a high temperature reduction. Transient measurements under pulse and continuous conditions give a completely different but more reliable picture. The main features which deserve to be highlighted are the following: (i) for all reducible supports there is a dramatic effect of a high temperature reduction on the catalytic properties; (ii) the behaviour of Rh/CeO₂ is totally different from that observed with Rh on other reducible supports; (iii) the catalytic activity is consistent with suppression of H₂ chemisorption only for supports showing a classical SMSI effect; (iv) among such supports TiO₂ slightly differs from Nb₂O₅; (v) catalytic activity under steady-state conditions is not indicative of the presence or absence of a metal–support interac-

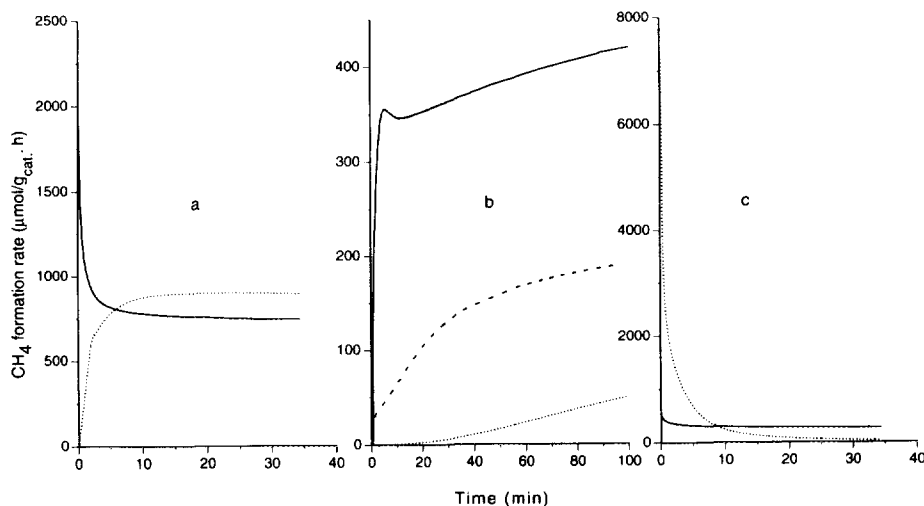


FIG. 2. CO₂ methanation under unsteady-state continuous conditions. Rate of CH₄ formation measured at 463 K after reduction at 473 K (—), 573 K (---), and 773 K (···) over Rh/TiO₂ (a), Rh/Nb₂O₅ (b), and Rh/CeO₂ (c).

tion, at least for CO₂ methanation; under these conditions Rh/CeO₂ is much less active than Rh on other supports, as already observed in CO hydrogenation (8).

Two important questions correspondingly arise: Why does Rh/CeO₂ differ from Rh on other reducible oxides, and, is there any simple model which can explain both types of behaviour? The occurrence of SMSI in Rh/TiO₂ and Rh/Nb₂O₅ is now well established; encapsulation of the metal by reduced oxide, as suggested by Resasco and Haller (7), is generally proposed to account for such interaction in the Rh/TiO₂ system. In our case the presence of traces of water and formation of atomic oxygen from CO₂ dissociation slowly reoxidize MO_x suboxides; this was already observed in the case of the CO/H₂ reaction, in which, owing to the presence of water generated from the reaction, a reversal of SMSI occurred (9). It should be noted that water is formed in CO₂ methanation in a concentration which is twice the concentration of water formed in CO/H₂ reaction, and hence the effects are expected to be more pronounced. This oxidation process is faster under continuous conditions where a continuous supply of both reactants favours the oxidation reaction. Under pulse mode, the switching between CO₂ pulse and a pure H₂ stream, might slow the oxidation process generated by CO₂ and water. This is probably the reason why under transient continuous conditions Rh/Nb₂O₅ slowly recovers the catalytic activity, while under pulse mode, only an additional treatment with O₂ restores the catalytic activity.

Several investigations on the M/CeO₂ system have focused on metal-support interaction since the discovery of SMSI, *but a definitive picture is still missing*. Already since the first studies it appeared that CeO₂ did not behave like other reducible oxides (10); in particular, several studies showed that H₂ chemisorption is not suppressed after a high-temperature reduction (3, 5, 10, 11), and no evidence for encapsulation of metal into CeO_x suboxides has been reported so far at these temperatures. However, the behaviour of CeO₂ has also been described as classical SMSI; recent careful studies by Cunningham *et al.* report on the formation of a strong metal-support interaction in Rh/CeO₂ even after reduction at moderate temperature (2a) and also Munuera *et al.* have described Rh-CeO₂ interaction after HTR as a classical strong metal-support interaction (12). Moreover, the metal precursor used for preparation of Rh/CeO₂ can also influence the redox behaviour of the support (13).

It is clear from the literature that the problem is still far from being solved, although right from the first studies, a great amount of information has been collected on Rh/CeO₂. We have recently reported that surface and especially bulk oxygen vacancies play an important role in determining the enhancement of reaction rate after a high-temperature reduction in Rh/CeO₂ and CeO₂-promoted

Rh/SiO₂ catalysts (6). We believe that the driving force leading to the activity enhancement we have observed originates from the formation of bulk vacancies which are generated after a reduction at high temperature; their subsequent annihilation by oxygen from CO₂ and water could bring about the subsequent fast deactivation (6). The important role of CeO₂ is also evidenced by the fact that this effect is observed over several noble metals supported on CeO₂, regardless of the metal employed (14); moreover, the use of different metal precursors (metal carbonyls or nitrates) or preparation of CeO₂ from different sources (like CeCl₃) does not affect this behaviour (15).

The observation of this strong enhancement in reaction rate, along with the lack of H₂ uptake suppression, strongly suggests that encapsulation of Rh into migrating CeO_x suboxides, with consequent physical blockage and suppression of catalytic activity, is not predominant in Rh/CeO₂, at least at these reduction temperatures. These indications are also corroborated by the results of Bernal *et al.* which did not find evidence for Rh encapsulation by the support by high-resolution electron microscopy (3).

Three other features should be accounted for to explain the difference in the catalytic behaviour between ceria and other reducible oxides: (1) the very well known capacity of CeO₂ to stabilize the dispersed noble metal after reduction (16, 17); (2) the possibility first envisaged by Fierro *et al.* (18) of incorporating hydrogen in the bulk of the oxide as a result of reduction at high temperature, with consequent removal of lattice oxygen; (3) the ability of CeO₂ to form several stable CeO_{2-x} suboxides through the progressive depletion of surface and bulk oxygen, which leads to the formation of oxygen-deficient phases with oxygen vacancies as predominant defects (19). On the contrary, TiO₂ and Nb₂O₅ are known to annihilate oxygen vacancies through collapse and shearing of the lattice with formation of crystallographic shear structures (19). These defects (and not oxygen vacancies) are the only ones responsible for deviation from stoichiometry in these oxides. In Rh/CeO₂, the presence of oxygen vacancies distributed throughout the bulk of the support is believed to be the driving force leading to CO₂ activation by extracting oxygen. During reaction, the replenishment of oxygen annihilates bulk vacancies, thus restoring the normal catalytic behaviour; under reaction conditions it is in fact not possible to regenerate bulk vacancies (6). In contrast, in TiO₂-type oxides, the reduction does not bring about the formation of oxygen vacancies, but the metal is buried by TiO_x suboxide, with the consequence of a complete suppression of catalytic activity. This negative effect is also destroyed by oxidation during reaction; however, in this case an increase in the activity is observed, connected with the release of Rh and restoring of the exposed catalytic sites.

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