CO and CO_2 Hydrogenation under Transient Conditions over Rh–CeO_2: Novel Positive Effects of Metal–support Interaction on Catalytic Activity and Selectivity

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The high temperature reduction at 773 K of Rh–CeO_2 catalysts induced a transient Rh–CeO_2 interaction which enhances the rate of CO and CO_2 hydrogenation; however, the activity dropped rapidly as a result of formation of water, which reoxidised CeO_{2-x}, restoring the normal behaviour.

The study of strong metal-support interaction (SMSI) and its relevance in catalysis have been widely investigated following the first report by Tauster and coworkers.[1] It has been reported that SMSI does not play an essential role in the promotion of CO hydrogenation;[2] on the contrary the activity after high temperature reduction (HTR) is somewhat lower than after low temperature reduction (LTR). This trend has been observed for several metal/reducible-oxide systems by numerous authors.[3] Moreover, water formed during the reaction destroys at least partially the SMSI state leading to steady state behaviour which is similar to that obtained after LTR.[4,5]

In the present study we have investigated the catalytic properties under transient and steady-state conditions of CO and CO_2 hydrogenation over Rh–CeO_2 obtained at different reduction temperatures. The reactivity under transient conditions over different rhodium supported oxides has also been compared. The catalyst (1% wt. Rh) was prepared by incipient wetness impregnation of CeO_2 with an aqueous solution of $RhCl_3 \cdot 3H_2O$. After drying, the catalyst was calcined at 673 K and then reduced *in situ* at 500 K (LTR) and 773 K (HTR). High surface area CeO_2 was prepared by hydrolysis of cerium nitrate with ammonia [Brunauer–Emmett–Teller (BET) surface area 62 $m^2\ g^{-1}$, total pore volume 0.17 $cm^3\ g^{-1}$]; X-ray diffraction showed the presence of crystalline CeO_2 with the fluorite structure. The hydrogenation reactions were carried out at 500 K in a transient-pulse microreactor by injecting CO or CO_2 pulses of known volume into an H_2 stream. Temperature programmed reduction showed the presence of two different kinds of Rh particles and it was evident that an important component of hydrogen adsorption was due to support reduction. The amount of CO uptake after low temperature reduction, measured by a pulse chemisorption technique at 300 K, was calculated to be 0.73 CO molecules per rhodium atom. The high temperature reduction almost completely suppressed CO chemisorption capabilities. However, H_2 uptake was only slightly affected by the reduction temperature (H/Rh = 0.84 after LTR and 0.58 after HTR).

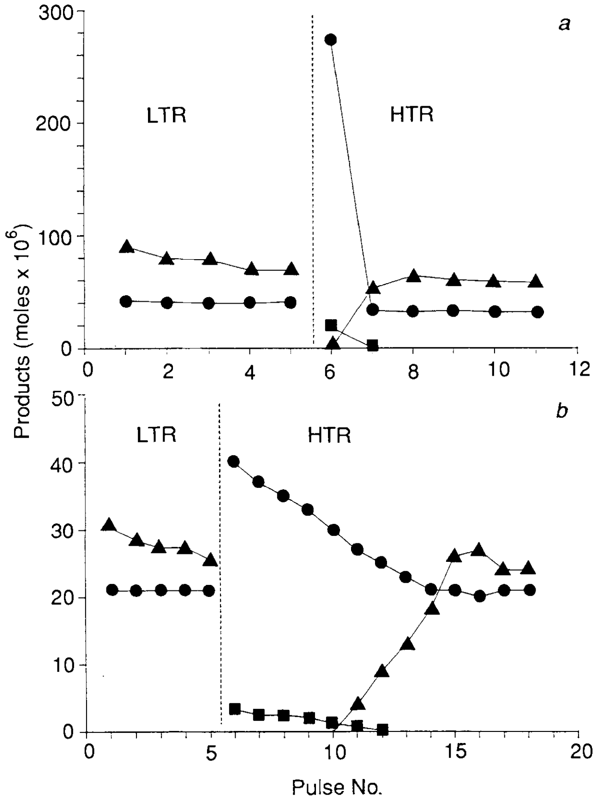

Fig. 1 Amounts of CH_4 (●), H_2O (▲) and C_2-C_3 hydrocarbons (■) formed from consecutive pulses of (*a*) CO_2 and (*b*) CO over Rh–CeO_2 catalyst in a H_2 flow following reduction at 500 K (LTR) and 773 K (HTR)

The catalytic results obtained under transient conditions (see Fig. 1) showed that in both CO and CO_2 hydrogenation the activity of the high temperature reduced Rh–CeO_2 catalyst is much greater than that of the corresponding catalyst after reduction at 500 K. C_2–C_3 hydrocarbons were detected during the first pulses, and in the case of CO_2 hydrogenation selectivities close to 10% were obtained. However, subsequent pulses lowered the catalytic activity reaching values which are only slightly lower than those of the low-temperature reduced catalyst. The interaction and the related catalytic activity enhancement could be fully restored by re-reducing the catalyst at 773 K, which provided evidence for process reversibility (see Table 1, note *d*).

The catalytic behaviour under transient conditions after reduction at 500 K and 773 K was compared to that obtained in a microflow reactor operating in continuous mode. Under such conditions, the activity of the Rh–CeO_2 catalyst does not show any positive effect due to high temperature reduction. The steady state activity for CO_2 methanation as measured at 500 K ($H_2 : CO_2 = 4 : 1$) was 0.0022 (moles CH_4)/(g_{cat} h) after LTR and 0.0015 after HTR and it did not vary with time on stream.

Methanation activities for CO_2 hydrogenation in transient conditions over different rhodium-supported catalysts are reported for comparison in the Table 1. The activity of

Table 1 Carbon dioxide hydrogenation over supported rhodium[a]

	Moles formed[b]		H/Rh[c]	
Support	LTR	HTR	LTR	HTR
CeO_2	42.5	271 327[d] 319[d]	0.84	0.58
SiO_2	6.6	7.9	0.55	0.71
TiO_2	36.2	3.7	0.33	0.02
Ta_2O_5	18.9	0.4	0.69	0.15
Nb_2O_5	25.0	trace	0.49	0.01

[a] Reduction temperature: LTR (500 K), HTR (773 K); reaction temperature: 500 K. [b] [(Moles of CH_4 formed)/catalyst (g)] 10^6. Values obtained after the first CO_2 pulse. [c] H_2 adsorption measured at 298 K by extrapolating at zero pressure the linear part of the isotherm. [d] Values obtained after successive re-reductions at 773 K.

$Rh-CeO_2$ catalyst after HTR is much higher than the activity of the other rhodium catalysts. Besides, among reducible supports, $Rh-CeO_2$ is the only catalyst positively affected by HTR; the other catalysts are transformed into a strongly inhibitory SMSI state which is shown by the suppression of H_2 chemisorption.

The fact that CeO_2 differs from other reducible supports which do not show this effect (TiO_2, Nb_2O_5, Ta_2O_5), may be due to its well known redox properties and to the related ability to create nests and vacancies on the surface and near-surface region.[6] The metal–oxide interaction may cause changes in catalytic activity through electronic effects as well as geometric effects mainly located at the $Rh-CeO_{2-x}$ interface. A mechanistic picture similar to that with Pd and Pt supported on CeO_2 and other reducible oxides[7] is suggested. In these cases it was proposed that cations or oxygen vacancies in the support interact with the oxygen of adsorbed CO (or CO_2) promoting the breaking of C–O bonds.

The oxidation properties of CO_2 and H_2O towards CeO_{2-x}[8] are probably responsible for the lability of the interaction state created after HTR. It is likely that by reaction with the water formed (which is completely adsorbed after the first pulses) and/or oxygen from CO or CO_2, the CeO_2 lattice is restored to its full complement of $O_2{}^-$ by filling the vacancies created after high temperature H_2 treatment. This is probably why this activity enhancement has never been observed over $Rh-CeO_2$ catalysts under stationary conditions.

These results represent to the best of our knowledge a unique insight into metal–support interaction, detectable only with the pulse technique, which appears to be a sensitive probe for studying the catalytic behaviour of these systems.

We are grateful to the 'Consorzio Universitario di Udine' for providing a grant for C. D. L. and to M.U.R.S.T. 40% for financial support of this work.

Received, 3rd December 1990; Com 0/05446A

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