Ethanol Promotion by the Addition of Cerium to Rhodium–Silica Catalysts

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The selectivity of rhodium-based catalysts is very dependent on the choice of support or the promotors. Cerium oxide is very effective for ethanol promotion when added to Rh/SiO₂ catalysts or used as support (70-80%ethanol selectivity). The role of the cerium oxide has been studied by various techniques, namely chemical trapping, Fourier-transform infrared spectroscopy and the use of probe molecules. The results show that when cerium oxide is added to rhodium catalysts, a new absorption band appears at 1725 cm⁻¹ in the infrared spectra which may be attributed to a CO molecule bonded through both the carbon and oxygen atoms. Such an interaction could be responsible for the formation and stabilization of the formyl species which, from chemical trapping experiments, is proposed as a key intermediate. These results and those obtained with probe molecules would be in accordance with a reactional pathway where the formyl species is a building block of the C₂-oxygenates and the acetaldehyde a primary product of the synthesis. In addition to its role in the activation of carbon monoxide towards hydrogenation, it is also shown that cerium oxide is responsible for the reduction of acetaldehyde to ethanol.

During the past decade considerable research effort has been devoted to carbon monoxide hydrogenation. Although our knowledge of the elementary steps of the reactions has greatly increased, some aspects are not fully understood.

The most important drawback of the classical syngas synthesis is its low selectivity. One of the goals of today's research is to find ways to diverge from the broad product spectra of an Anderson–Schulz–Flory type of distribution. This goal can be achieved either by the use of geometry-controlled catalysts (*e.g.* zeolites) or by the addition of adequate promoters. Among the different catalytic systems, rhodium-based catalysts are the most suitable for the study of the promotor and support effects. Indeed, drastic changes in selectivities can be reached with different supports or promotors,^{1, 2} and high ethanol selectivities can be reached with rare-earth-containing rhodium catalysts. Promotors can intervene at different steps of the ethanol synthesis, namely: (i) activation of carbon monoxide during its chemisorption, (ii) formation of the first C₁-intermediate (dissociation or hydrogenation), (iii) formation of the carbon–carbon bond and (iv) subsequent transformation of the primary reaction products.

The reactivity and selectivity tests showed that high ethanol selectivities are obtained on rhodium-silica catalysts containing cerium oxide (compared to rhodium-silica catalysts, where mainly hydrocarbons are obtained). This led us to study the role of cerium oxide in ethanol promotion by means of different methods (chemical trapping, the use of probe molecules and Fourier-transform infrared spectroscopy).

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				conversion $(^{\circ}_{0})^{a}$				
catalyst	CH4	total hydrocarbons	MeOH	AcH	EtOH	total oxygenates	to oxygenates	
5% Rh-0% Ce/SiO ₂	2.50	3.60		0.20	0.02	0.23	6	
5% Rh-0.5% Ce/SiO ₂	0.19	0.27	0.03	0.04	0.18	0.25	48	
5% Rh-2% Ce/SiO ₂	0.33	0.56	0.05	0.02	0.24	0.34	38	
5% Rh -5% Ce/SiO ₂	0.26	0.36	0.11	0.02	0.73	0.88	71	
5% Rh–CeO ₂	0.10	0.17	0.17	0.03	0.58	0.72	83	

Table 1. Reactivity of cerium-containing rhodium-silica catalysts at atmospheric pressure

Reaction conditions: catalyst 5% Rh-5% Ce/SiO₂; T = 180 °C; atmospheric pressure; weight of catalyst, 0.5 g; reduction temperature, 300 °C in hydrogen flow. ^a Conversion is expressed as (number of moles of CO converted in a given product)/(total number of moles of converted CO) and given after 8 h on stream.

Results and Discussion

Reactivity and Selectivity of Cerium-containing Catalysts

The effect of addition of cerium oxide to a rhodium-silica catalyst containing 5% Rh, denoted 5% Rh-SiO₂, in the conversion of carbon monoxide and the oxygenate's selectivity has been studied for various amounts of cerium oxide and different reaction conditions. The results at atmospheric pressure are presented in table 1. The mean particle sizes determined by X-ray spectroscopy on two different catalysts (5% Rh/SiO₂ and 5% Rh-5% Ce/SiO₂) after overnight reduction at 325 °C by pure hydrogen are the same (48 Å).

The addition of even a very low concentration of cerium oxide considerably depresses hydrocarbons formation, without a noticeable change in the total amount of oxygenates, but shifts the selectivity from acetaldehyde to ethanol. Upon further addition of cerium oxide the conversion to hydrocarbons remains almost constant, whereas the formation of oxygenates (mainly ethanol) increases. On a rhodium–silica catalyst (without CeO_2) the main oxygenated product is acetaldehyde, while in the presence of cerium oxide the selectivity shifts to ethanol. This shift to ethanol seems to be at variance with the hydrogenating power of the catalyst, since hydrocarbon formation is the highest on the rhodium–silica catalyst. This can be explained either by the formation of acetaldehyde and ethanol on different sites or by a promoting effect of Ce on the hydrogenation of the acetaldehyde.

The results at a higher pressure (20 atm) and a higher temperature (280 °C) are summarized in table 2. They are similar to those at atmospheric pressure as far as the hydrocarbon formation and the oxygenate selectivity are concerned. Furthermore, they show that the low methanol activity is not related to thermodynamic limitations, since at 280 °C and 20 atm the equilibrium CO conversion into methanol is 8.5%.

Influence of the Gas Flow Rate

The variation of selectivity with the gas flow rate shows that for a longer contact time we have a higher oxygenate selectivity (table 3). First this means that the hydrocarbons are not produced by secondary reactions of the oxygenates (decarbonylation or dehydration). Secondly, the fact that the acetaldehyde is much less affected than ethanol suggests either that acetaldehyde is further converted into ethanol or that ethanol is formed by another mechanism. The reduction temperature of the catalyst is also

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		CO	conversio	n (%)ª	ţ		1 4 1
catalyst	CH4	total hydrocarbons	MeOH	AcH	EtOH	total ^b oxygenates	to oxygenates
5% Rh-0% Ce/SiO	。 25	32		2.5	0.3	2.8	8
5% Rh-0.5% Ce/Si	Ö, 4	4.4		0.3	1.7	2.3	34
5% Rh-2% Ce/SiO	, 4.4	4.6	0.3	0.2	2.2	2.8	36
5% Rh-5% Ce/SiO	3.0	3.1	0.3	0.1	1.7	2.5	45
5% Rh/CeO ₂	2.2	2.4	0.3	-	1.2	1.5	38

Table 2. Reactivity of cerium-containing rhodium-silica catalysts at 20 atm

Reaction conditions: T = 280 °C; P = 20 atm; gas flow 2 dm³ h⁻¹; reduction temperature 375 °C; weight of catalyst 0.5 g. ^{*a*} See table 1. ^{*b*} Other oxygenates are present mainly as methyl- and ethyl-acetates.

		pro	oduct co	onversion (%)			coloctivity
flow rate /dm ³ h ⁻¹	total hydrocarbons	total oxygenates	CH4	МеОН	AcH	EtOH	AcO-	to oxygenates
1	9.1	12.1	8.4	1.6	0.2	7.1	3.2	57
2	3.5	1.8	3.5	0.6	0.11	1.1		34
4.2	1.1	0.4	1.1	0.35	_	0.06	-	27

Table 3. Influence of the gas flow rate

Reaction conditions: T = 280 °C; P = 50 atm; catalyst weight 0.5 g; reduction temperature 375 °C; catalyst 5% Rh-5% Ce/SiO₂.

important for C_2 -oxygenates activity of these cerium oxide-containing catalysts. An optimum was observed at 375 °C.

These results show clearly the promotion of ethanol by cerium oxide. To understand better the role of the cerium oxide, its possible effects on different elementary steps were studied.

Adsorption of Carbon Monoxide

Fourier-transform infrared spectroscopy is a powerful tool for the study of carbon monoxide adsorption. The pioneering work of Yang and Garland³ in i.r. spectroscopy showed different adsorbed species on rhodium; the absorption bands were attributed as follows: 2070 cm⁻¹ to linear carbonyls, 1920 cm⁻¹ to bridged carbonyls and 2100 cm⁻¹ and 2030 cm⁻¹ to gem dicarbonyls.

Our infrared spectra were obtained under 60 Torr of carbon monoxide at room temperature on reduced catalysts (375 °C, 4 h, 700 Torr, H₂). With a 5% Rh/SiO₂ catalyst the absorption spectra showed two bands at 2070 and 1914 cm⁻¹ corresponding to linear and bridged carbonyls, respectively. No other bands in the region of carbon monoxide absorption could be observed.

With a 5% Rh–5% Ce/SiO₂ catalyst additional bands were observed during carbon monoxide adsorption. Twin bands at 2100 and 2030 cm⁻¹ attributed to the symmetrical and antisymmetrical modes of gem dicarbonyls, respectively. It is generally accepted that linearly and bridge-bonded CO species are located on metal crystallites.^{4, 5} The formation

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of gem dicarbonyls species is associated with isolated oxidized rhodium atoms.⁴⁻¹³ Furthermore, on catalysts containing cerium oxide a new band was also observed at 1725 cm⁻¹.

This band can be ascribed to a particular type of chemisorbed CO where the oxygen interacts with a Lewis acid site of the support.¹⁴ Such a carbon monoxide bonded through both the carbon and the oxygen ends of this molecule has been observed during the reaction of $(Me_5C_5)_2$ Yb with $Co_2(CO)_8$, the divalent metallocene acting as a one-electron reducing agent resulting in a bridging-carbonyl-bonded product (Me_5C_5) YbCo(CO)₄(THF).¹⁵ The bridged carbonyl accounts for the low CO adsorptions at 1798 and 1761 cm⁻¹. We may therefore represent this chemisorbed carbon monoxide by the following scheme:



For these C- and O-bonded species, the lowering of the adsorption frequency $(100-200 \text{ cm}^{-1})$ is attributed to an increase of the back-donation of metal electrons to the π -antibonding orbital of CO resulting from a delocalization on the Lewis-acid centre.¹⁴ These electronic factors also affect the bond lengths; the CO distance is lengthened and the M—C distance shortened.

Such an interaction between the support and the carbon monoxide may have two consequences, either favouring the carbon monoxide dissociation by diminishing the carbon–oxygen bond order^{16–18} or promoting the migratory carbon monoxide insertion by modification of the electron density in the vicinity of the carbon end.¹⁴

In homogeneous catalysis, it is widely admitted that both the metal and the oxygen of metal carbonyls are basic.¹⁴ The site of interaction is partly sterically controlled; thus a proton will attack at the metallic site whereas a much bulkier Lewis acid attacks at the oxygen end. In the case of alkalines or alkaline earths (M^+ or M^{2+}) it depends on the bulk of the ligand attached to M^+ or M^{2+} . In surface reactions the cation is involved in the surface structure, and therefore the interaction will be easier on the carbonyl oxygen, which is more exposed than the metal centre.

Formation of the First C₁-Intermediates

The sharp drop in activity by addition of cerium oxide shows that the sites responsible for the formation of hydrocarbons are blocked by CeO_2 . This was attributed to the suppression of the carbon monoxide dissociation.¹⁹ To investigate the possible intermediates in the $CO+H_2$ reaction chemical trapping experiments were performed on catalysts containing different amounts of cerium. Chemical trapping was described in details elsewhere.²⁰ Our experiments aimed to reveal the presence of formyl species on the catalytic surface. We used a methylating agent which gives, after reaction with the formyl entity, acetaldehyde.²¹ In order to be sure that the detected acetaldehyde does not result from the $CO+H_2$ reaction, the chemical trapping was performed with labelled methyliodide (CD_3I). The results of the chemical trapping on catalysts with different amounts of cerium oxide are given in table 4.

From the activity experiments at atmospheric pressure, and from the corresponding formyl concentration for the different catalysts studied, we concluded that formyl species could be intermediates for both hydrocarbons and oxygenates.²¹ In addition to the formyl species, formates and acetates were detected by reaction with dimethylsulphate. No direct correlation was found between these species and the catalytic activity. The concentration of acetate increased with time on stream, whereas the activity decreased.

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2	1	2	3

$\operatorname{CeO}_2(\%)$	formyl/10 ⁻⁷ mol (g catalyst) ⁻¹
0	78
0.5	41
2	32
5	47

Table 4. Concentration of formyl species on 5% Rh-x% Ce/SiO₂ catalysts as determined by chemical trapping²¹

How can the formation of formyl species be explained on rhodium-containing catalysts? A survey of the literature shows that the homogeneous formal migratory insertion of CO into metal-carbon or metal-hydrogen bonds can be enhanced by different factors: (i) interaction of the oxygen end of the molecule with a Lewis-acid centre or with an unsaturated cationic metal,^{22, 23} thus forming an acyl ligand bridging two metal centres; (ii) bimetallic reaction inducing an alkyl-CO migratory insertion on a second metal centre concomitant with metal-metal bond formation;²²⁻²⁴ (iii) oxidation of alkylmetal carbonyl complexes by some electrophilic reagents (*e.g.* Ag⁺,^{25, 26} Cu²⁺, Ce^{4+ 25}) or by an electrochemical reaction;²⁷ (iv) the presence of a positive charge on the metal centre.²⁸⁻³⁰

Although the hydride migration induced by alkali metals in order to form metal formyls in an analogous manner to cation-induced alkyl migration has never been observed, *ab initio* calculations have shown its feasability.²³ Even if with homogeneous complexes it has been shown that small metal cations attack at the metal centre and abstract hydrogen from transition metal hydrides,³¹ as already mentioned, the situation may be different on surfaces, since the cations are involved in the structure. In that case the interaction with the oxygen of the carbonyl group could be possible even with small cations.

The promotion of formyl in presence of cerium oxide can readily be explained by the formation of C- and O-bonded carbon monoxide which was observed by Fourier-transform infrared spectroscopy. Furthermore, the basicity of the formyl oxygen is higher than that of the oxygen of carbon monoxide,¹⁴ so that the formyl species is highly stabilized by the presence of a Lewis acid.

In absence of cerium oxide, a process similar to that depicted by Prins *et al.*¹³ and Solymosi *et al.*⁵ could explain the migratory insertion towards formyl on the metal. In the first step a hydridorhodium carbonyl can be formed with rupture of a metal-metal bond; in the second step a bimetallic reaction with reconstruction of the metal-metal bond leads to the formyl species. However, the occurrence of a partial surface oxidation which also favours migratory insertion cannot be excluded. A formyl species located on the metal would have a much more concentrated hydrogen environment and readily be reduced to hydrocarbons.

By introduction of methanol and acetaldehyde on a cerium-containing catalyst at room temperature an i.r. band is observed at 2038 cm⁻¹ after evacuation. Yang and Garland³ noticed that the introduction of H₂ on Rh/Al₂O₃ containing only linearly bonded CO shifted the band from 2062 to 2038 cm⁻¹; this was attributed to the formation of H and Rh CO entities. The formation of Rh has also been assumed to take CO place on the surface decomposition of H CO HCO H CH OH C HO³² CH OH

place on the surface decomposition of H_2CO , HCO_2H , CH_3OH , C_3H_6O ,³² CH_3OH , CH_3CH_2OH and CH_3CHO ,³³ or on the low-temperature interaction of H_2 and CO_2 .³⁴





Fig. 1. Ethylene addition (1.6%) to a CO-H₂ flow. Catalyst 5% Rh/SiO₂; T = 200 °C; flow rate 2 dm³ h⁻¹; catalyst weight 500 mg.



Fig. 2. Ethylene addition (1.6%) to a CO-H₂ flow. Catalyst 5% Rh/CeO₂; T = 200 °C; flow rate 2 dm³ h⁻¹; catalyst weight 500 mg.

Carbon-Carbon Bond Formation

An insight into carbon–carbon bond formation might be obtained by modifying the relative surface concentration of the different species. This can be achieved by the introduction of a third reagent into the $CO-H_2$ flow. The modification of the selectivities can provide information on the reaction pathway or on the importance of a given surface entity.

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Fig. 3. Acetaldehyde addition (0.3%) to a CO-H₂ flow. Catalyst 5% Rh/SiO₂; T = 200 °C; flow rate 2 dm³ h⁻¹; catalyst weight 500 mg.

Ethylene (1.6%) was introduced into the gas flow to change the relative concentration of surface C_1H_x and C_2H_x groups. The results with 5% Rh/SiO₂ and 5% Rh/CeO₂ catalysts are shown on fig. 1 and 2, respectively. The addition of ethylene to the CO-H₂ flow enhances the formation of C_3 oxygenates on both catalysts. However, when oxide is present the selectivity is shifted from the aldehyde to the alcohol. This result is in accordance with our reactivity experiments (tables 1 and 2).

The enhancement of the formation of C_3 oxygenates on both catalysts can be explained in two different ways: either cerium oxide plays no role in carbon-carbon bond formation or, in the case of the catalyst containing no cerium, the introduction of ethylene reduces the hydrogen concentration and consequently the hydrogenation rates of C_1H_x and C_2H_x , thus allowing the formation of C_2 and C_3 oxygenates.

Our results on the correlation of the formyl concentration and the total activity on cerium-containing catalysts suggest that an alternative to carbon monoxide insertion for the formation of C_2 oxygenates could be the reaction of a C_1H_x species with the formyl species. Such a reaction would be favoured by the presence of cerium oxide if we assume that there is an interaction between a Lewis acid site and the oxygen of the formyl species:

$$\begin{array}{c} CH_3 + CHO \rightarrow CH_3 CHO. \\ \bot \qquad \qquad \bot \end{array}$$

A similar reaction pathway was proposed by Keim et al.³⁵ and by Van den Berg et al.³⁶

Role of Cerium Oxide in the Reduction of Acetaldehyde to Ethanol

The behaviour of acetaldehyde on 5% Rh/SiO₂ and 5% Rh/CeO₂ catalysts was studied with a pulse reactor. As can be seen in fig. 3, on a Rh/SiO₂ catalyst the addition of acetaldehyde (0.3%) to the CO-H₂ flow does not modify the conversion into the different hydrocarbons (C₁, C₂, C₃) and no ethanol is detected. On the other hand, on Rh/CeO₂ (fig. 4) we have an increase in ethanol when acetaldehyde is introduced. The hydrocarbons are not affected.

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Fig. 4. Acetaldehyde addition (0.3%) to a CO-H₂ flow. Catalyst 5% Rh/CeO₂; T = 200 °C; flow rate 2 dm³ h⁻¹; catalyst weight 500 mg.



Fig. 5. Acetaldehyde addition (0.8%) to a helium flow. Catalyst CeO₂; T = 200 °C; flow rate $2 \text{ dm}^3 \text{ h}^{-1}$; catalyst weight 500 mg.

The reduction of acetaldehyde to ethanol can be related to the presence of cerium oxide, as can be seen in fig. 5. In fact, even when acetaldehyde is introduced with a helium flow on the support alone, we have formation of ethanol, which passes through a maximum after 60 min and then diminishes slowly. It is also obvious that the acetaldehyde is strongly adsorbed on cerium oxide. The same experiment with silica showed that acetaldehyde is not chemisorbed and no other products were detected.

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Fig. 6. Acetaldehyde addition (0.8%) to a helium flow. Catalyst 5% Rh/CeO₂; T = 200 °C; flow rate 2 dm³ h⁻¹; catalyst weight 500 mg.

From chemical trapping and Fourier-transform infrared experiments we detected acetate species on cerium oxide after exposure to acetaldehyde. These acetate species may be formed by reaction of the acetaldehyde with a surface basic site (O_s^-) as proposed by Bowker *et al.*:^{37, 38}

$$CH_{3}CHO + O_{s}^{-} \rightarrow CH_{3}CHOO_{s}^{-}$$
$$CH_{3}CHOO_{s}^{-} \rightarrow CH_{3}COO^{-} + H_{a}$$

The hydrogen liberated by their formation could explain how the ethanol is obtained, since it can migrate on the surface and reduce the acetaldehyde chemisorbed on different sites. When rhodium is present on the cerium oxide, similar results are obtained as far as the ethanol is concerned, but we also have decomposition of the acetaldehyde and formation of methane (fig. 6).

The strong chemisorption of the acetaldehyde when cerium oxide is present can explain why ethanol is obtained even if acetaldehyde is the primary product of the synthesis. Once the acetaldehyde is chemisorbed on the surface, spilt-over hydrogen can reduce it to ethanol. However, on silica, even if acetaldehyde is a minor product, in the absence of chemisorption it is not reduced.

Conclusions

This study shows that rhodium catalysts containing cerium oxide, deposited or not on silica, are very active and selective for the $CO-H_2$ ethanol synthesis. Fourier-transform infrared spectroscopy, chemical trapping and probe molecules have been used and lead to a mechanistic proposition in which acetaldehyde is a primary product of the synthesis.

Formyl species are involved in the formation of both CH_x groups and oxygenates. When formyl groups are formed on large rhodium ensembles, they lead to CH_x species. At the metal-support interface the stabilization of the formyl by interaction of the oxygen with a Lewis-acid site of the support favours the formation of oxygenates.

The presence of oxygen vacancies on the surface would be responsible for the

formation and the stabilization of the formyl species by an interaction with the oxygen of the CO. Cerium oxide is also responsible for the reduction of acetaldehyde to ethanol.

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