SURFACE REACTIVITY OF Rh CLUSTERS ON ZrO$_2$
MODIFIED BY Mn, Fe AND Mo

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Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.

The reactivity of Rh clusters supported on ZrO$_2$ and on ZrO$_2$ modified by chemisorption of Mn, Fe, Mo carbonyls has been studied by various surface techniques such as TPD, TPR, FTIR, and by model reactions: Boudouard reaction, ethylene hydroformylation and CO/H$_2$ reaction. Four CO adsorbed species have been identified and the main effect of the modifiers is to change the distribution of the various CO moieties present on the surface, as shown by TPR and reactivity data. Mn promotes methanol formation, Fe oxygenated compounds and chain growth, Mo increases the CO reactivity, mainly to oxygenates.

Rhodium has a wide spectrum of catalytic applications due to its position in the periodic table, giving it a peculiar reactivity. Indeed Rh is used in homogeneous and heterogeneous catalytic processes like selective hydrogenation, carbonylation, homonuclear recombination of NO to N$_2$, syngas conversion, etc. Of all the catalysts studied till now, Rh supported on oxophylic oxides appears to be the most promising for synthesis gas conversion to oxygenates[1]. Nevertheless its activity and selectivity need to be improved to obtain a catalyst of industrial interest. Efforts to improve its functionality have collided with Rh catalytic mutability. Indeed in syngas conversion, where the reaction is supposed to occur through a sequence of elementary steps including CO dissociation, hydrogenation of surface alkyl species, CO insertion etc., Rh may give a variety of products, such as low or high hydrocarbons, methanol, ethanol, oxygenated compounds etc. The obtained products depend on the support, the rhodium dispersion, the promoters, the impurities, the reaction conditions, etc.[2,3]. In order to deepen knowledge on Rh

functionality, mainly in syngas conversion, it is appropriate to prepare a catalyst with a procedure that guarantees very low impurity contamination, well defined metal dispersion, control of added promoters[3,4] and to follow the evolution of surface reactivity after thermal or chemical treatment, like for instance activation, by surface techniques such as temperature programmed desorption (TPD) and temperature programmed reaction (TPR). These techniques provide information directly related to the catalyst functionality. Furthermore they allow the surface reaction of probe molecules to be described in great detail and with accuracy, and they give information on the evolution of the catalytic surface. Information on reaction intermediates may be obtained by in situ FTIR spectroscopy of the reacting mixture.

Thus we prepared the Rh catalysts under clean conditions using pure "ad hoc" zirconia, and $Rh_4(CO)_{12}$. The catalysts were characterized by TPD and TPR, either of the freshly prepared supported carbonyls (FP) or of CO adsorbed at room temperature after hydrogen activation (HR), and by in situ FTIR spectroscopic experiments of the adsorbed CO/H_2 mixture in the temperature range 298 – 523 K. $Mn_2(CO)_{10}$, $Fe_3(CO)_{12}$, $Mo(CO)_6$ were used as modifiers. The functionality of the catalysts was tested in the Boudouard reaction, ethylene hydroformylation and syngas conversion.

EXPERIMENTAL

Catalyst Preparation

Catalysts were prepared by two step adsorption on ZrO_2, in hydrocarbon suspension under inert atmosphere. In the first step a hydrocarbon (pentane or heptane) solution of the modifier, $Mo(CO)_6$, $Mn_2(CO)_{10}$ or $Fe_3(CO)_{12}$ was added under stirring. Due to the stability of Mo and Mn carbonyls the adsorption was very slow and took more than ten hours. To favour the adsorption the suspension was heated at solvent boiling point. The adsorption was monitored by IR analysis of the solution. When all of the promoter was adsorbed a hydrocarbon solution of $Rh_4(CO)_{12}$ was added, always under stirring. The IR spectra of the solution revealed a partial desorption of the Mn and Mo carbonyls, or $Fe(CO)_5$ in the case of Fe. After a certain time, when the IR bands of the metal carbonyls disappeared, the solvent was siphoned out and the solid dried under vacuum by a mechanical pump. The Rh content of all the samples was 1 % (w/w), and the Rh-promoter atomic ration was 1 : 1. The samples were used as such (FP) or after treatment in hydrogen stream for 2 h at 523 K (HR).

Catalyst Characterization

A systematic characterization of the prepared catalysts was performed by TPD and TPR measurements, both on FP- and on HR-samples exposed for 30 min to a flow of pure CO at room temperature.

TPD experiments were performed under vacuum (10^{-4} Pa) in a quartz microreactor connected with a computer controlled quadrupole mass spectrometer (Carlo Erba Instruments) that allows up to eight m/e signals to be simultaneously monitored as a function of temperature. About 30 mg of sample were placed in the quartz holder and heated at a rate of 10 K min^{-1} from room temperature to 800 K.

Desorption of H_2, CH_4, CO, C_2H_6, CO_2 was monitored by m/e = 2, 15, 28, 30 and 44, respectively. Weight factors relative to CO were determined to account for fragmentation, ionization efficiency, and quadrupole transmission in order to evaluate relative desorption rates. TPD experiments were performed on

supported carbonyls (FP), on samples reduced in H$_2$ stream at 523 K (HR) and saturated by CO at room temperature and on samples reduced in H$_2$ stream at 673 K and saturated with H$_2$ at room temperature. TPR experiments were carried out at atmospheric pressure in a stainless steel tubular microreactor equipped with an analytical G C unit (H. P. 5890) and a data logger/controller (Fluke 2280 B (ref.[5])). A sample of freshly prepared catalyst (0.5 – 1 g) was transferred into the reactor under inert atmosphere, and, after cleaning the system with hydrogen, was heated from room temperature to 523 K at a rate of 2 K min^{-1}. The outlet stream was analyzed on-line by periodically sampling with a ten port valve. The same experiments were performed with samples reduced for 2 h in hydrogen stream at 523 K, cooled to room temperature in helium stream and exposed to a flow of pure CO for 30 min.

IR spectra were recorded using an FTIR spectrometer IRF-180 (Centre of Scientific Instrumentation, Berlin). Discs of the samples were mounted in a high pressure cell equipped with CaF$_2$ windows. After reduction in hydrogen (p = 0.1 MPa) for two hours at 523 K a CO/H$_2$ mixture (1 : 1; p = 0.2 MPa) was introduced and the adsorption spectra recorded in the temperature range 298 – 523 K.

Catalytic Tests

Catalytic activity was measured in the same automated reactor used for TPR experiments[5]. All catalysts were reduced in hydrogen stream at 523 K for 2 h before runs. Three kinds of tests were performed: *a*) CO disproportionation, studied by TPR experiments in a stream of pure CO from room temperature to 500 K; *b*) CO hydrogenation, under pressure; *c*) ethylene hydroformylation under conditions in which CO methanation is negligible: T = 433 K; p = 0.1 MPa; C$_2$H$_4$: CO : H$_2$ = 1 : 1 : 1; GHSV = 3 600 h^{-1}.

RESULTS AND DISCUSSION

TPD experiments with supported carbonyls, FP-samples, (Figs 1, 2) and hydrogen-reduced HR-samples (Figs 3, 4), after CO saturation, showed the desorption of CO, CO$_2$, H$_2$; hydrocarbons were observed only on the FP catalysts (not reported in figure for simplicity) and presumably originate from the cracking of the residual solvent adsorbed on the support*. The TPD spectra for each catalyst before and after hydrogen reduction are different, revealing an irreversible evolution of the surface metal species.

The CO-TPD spectra of FP samples (Fig. 1) indicate unambiguously that the supported Rh carbonyls start to decompose already at temperature near 350 K. The T_{max} of CO desorption peak (T_{max} = 480 K) is shifted to high temperature (T_{max} = 500 – 530) on modified catalysts (Fig. 1), where a second peak of CO desorption is present at higher temperature (580 – 650 K) due to the decomposition of the modifier carbonyls.

In Fig. 2 the TPD spectra of FP sample Rh–Fe/ZrO$_2$ is reported, those of other samples are not dissimilar[6]. The desorbed CO is the predominant species. A fraction of ligand CO desorbs as carbon dioxide. TPD spectra of FP sample Rh/ZrO$_2$ show[6] only one peak of CO$_2$ desorption with a T_{max} at about 450 K, those of FP modified Rh samples show an additional peak in the 500 – 700 K range, paralleled by an H$_2$

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* In Figs 1 – 5, I denotes intensity in arbitrary units (a.u.).

desorption peak. During TPD the CO is involved in two distinct reactions: below about 500 K there is disproportionation with the formation of surface carbon dioxide; in the 500 – 700 K range water gas shift reaction with surface hydroxyls produces carbon dioxide and hydrogen. The CO-TPD spectra of HR-samples, after CO saturation at room temperature (Fig. 3), underline a significant evolution of the sample surface. The T_{max}'s of the first CO desorption peak decreased by about 100 K on all samples: this indicates that hydrogen reduction weakens the CO chemisorption; moreover the high temperature CO-desorption peak is no longer present and only very small amounts of strongly bonded CO may be assumed on Rh–Fe and Rh–Mo samples. The broadening of the peaks after hydrogen reduction indicates a significant increase in the surface heterogeneity of the samples.

In Fig. 4 the TPD spectra of HR sample Rh–Fe/ZrO$_2$ is reported, those of other samples are not dissimilar for both the Rh and the Rh-modified samples[6].

The main differences with respect to FP samples are the decrease of CO dispro-portionation reaction, as at T < 450 K CO desorption predominates, and a significant increase in the shift reaction, that occurs at a temperature by 100 K lower as compared with FP samples. The hydrogen peak parallels the CO$_2$ peak.

The TPD spectra of hydrogen adsorbed at room temperature on HR-samples are shown in Fig. 5: three types of adsorbed hydrogen are evident. The following tempe-rature ranges can be identified: *a*) from 373 to 473 K: all samples show a small amount of weakly adsorbed hydrogen, the amount being greater on the modified Rh/ZrO$_2$ cata-lysts; *b*) from 473 to 773: a large hydrogen desorption peak with different shape and temperature maximum is present on all catalysts. The peak maximum temperatures are in the following order: Rh–Mn (520 K); Rh–Fe (550 K); Rh (590 K) and Rh–Mo (630 K).
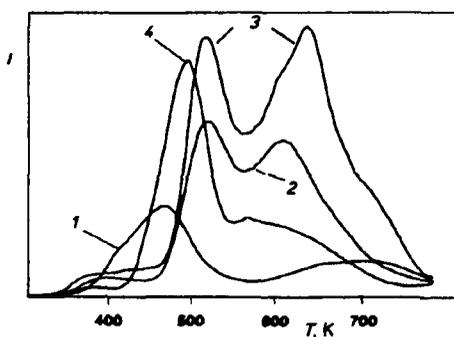

FIG. 1
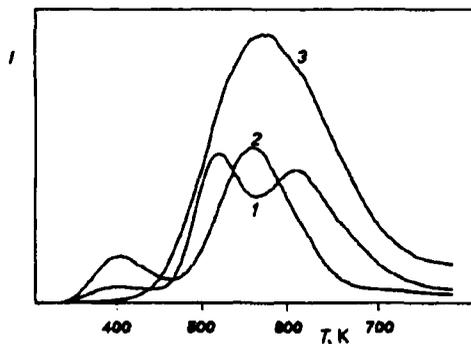TPD profiles of CO from freshly prepared FP-samples. *1* Rh/ZrO$_2$, *2* Rh–Fe/ZrO$_2$, *3* Rh–Mn/ZrO$_2$, *4* Rh–Mo/ZrO$_2$

FIG. 2
Fully recorded TPD profiles of FP-sample (Rh$_4$(CO)$_{12}$ + Fe$_3$(CO)$_{12}$) / ZrO$_2$. *1* CO, *2* CO$_2$, *3* H$_2$

We attribute these peaks to atomic hydrogen adsorbed on Rh. The variation of the maximum peak temperature of the different samples with respect to Rh/ZrO_2 may be indicative of the Rh–H bond strength and of the interaction among the promoters and rhodium: while Mn and Fe decrease the Rh–H bond strength, Mo increases it; c) peak with the maximum at the same temperature (850 K) for all samples. The hight of the peak was in the following order: Rh and Rh–Mn (very low); Rh–Mo (medium); Rh–Fe (very high). The invariance of peak maximum temperature with catalyst composition indicates the presence of a species that becomes reactive only at this temperature, evolving hydrogen as a reaction product. It is known from the literature that at this temperature the hydroxyl groups present on zirconia surfaces become reactive, therefore this hydrogen peak was attributed to the reaction of the surface metal moieties with ZrO_2 hydroxyls[7], according to the scheme:

$$M + \sigma\text{-OH} \rightarrow \sigma\text{-O–M} + \tfrac{1}{2} H_2 \; .$$

On Rh and Rh–Mn samples the reaction between Rh^0 and σ-OH with the formation of Rh^+ takes place only to a small extent; Mn has no role in this reaction as it is probably present in some stable oxidized form. On the Rh–Mo sample the increase of the peak may be attributed to either an increase of Rh dispersion, favoured by Mo, or to an oxidation of reduced Mo-species. Furthermore, the very large peak present with the Rh–Fe sample clearly indicates and oxidation of metallic Fe. In fact the Fe/ZrO_2 sample shows the same peak.
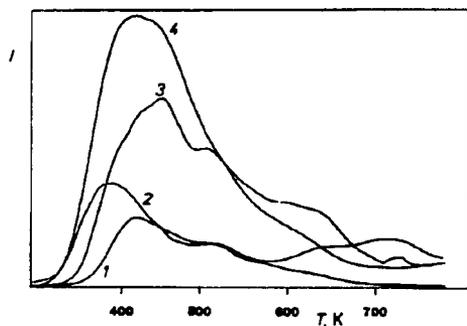

FIG. 3
TPR profiles of CO after saturation coverage by CO of samples reduced in H₂ at 523 K (HR). 1 Rh/ZrO₂, 2 Rh–Mn/ZrO₂, 3 Rh–Fe/ZrO₂, 4 Rh–Mo/ZrO₂
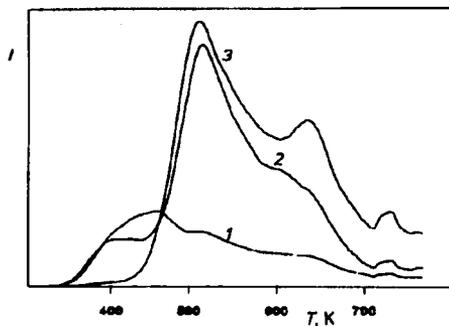
FIG. 4
Fully recorded TPR profiles of Rh–Fe/ZrO₂ after saturation coverage by CO of sample reduced in H₂ at 523 K (HR). 1 CO, 2 CO₂, 3 H₂

TPR experiments of FP-samples in continuous hydrogen flow show that in a narrow temperature range the ligand CO in supported metal carbonyls was converted mostly to methane for all samples; CO, CO_2 and water were also detected in the effluent gas but their signals were weak and did not appear significantly different; C_2–C_3 hydrocarbons were also detected probably coming from hydrocracking of the residual solvent. The main affect of promoters is to increase the maximum peak temperature of methane formation (Table I). HR-samples showed only broad desorption peak of CO in the 300 – 370 K range and a well defined TPR peak of CH_4 in the 370 – 473 range with maximum peak temperatures shifted to lower values (Table I). In any case the profiles of Rh–Fe (a shoulder at 400 K) and Rh–Mo (formation of CH_4 already at 373 K) were a little more complex, suggesting the presence of different sites of CO methanation. The temperature difference for methane T_{max} of FP and HR samples is about 30 K for Rh and Rh–Fe catalysts and 20 K for Rh–Mn and Rh–Mo. We think that this decrease in T_{max} should not be ascribed to some morphological modification of Rh particles but to a lower adsorption of CO on the Rh surface after reduction, and therefore to the presence of sites available for hydrogen adsorption.

In the Boudouard reaction with TPR experiments in flow of pure CO, the CO activation was evaluated from the CO_2 formation rate (Fig. 6) (r_{CO_2} given in μmol g^{-1} s^{-1}). By increasing the temperature, the activity of CO_2 formation is in the order: Rh–Mo > Rh–Fe > Rh–Mn > Rh.

In the investigated temperature range the Arrhenius plot for the rate of CO_2 formation is a straight line for Rh while for Rh–Mn, Rh–Fe and Rh–Mo samples the line bends downwards. This anomalous behaviour of the CO_2 formation rate with temperature can be explained by the fouling of the catalysts due to carbon formation in the Boudouard reaction.

If only the values in the low temperature region are considered, the apparent activation energies for all the modified Rh catalysts are in the range 100 – 120 kJ mol^{-1}, this value being consistent with the theoretical evaluation for activation energy of CO

TABLE I
T_{max} of methane in TPR profile for FP- and HR-samples

Catalyst	T_{max}, K		ΔT
	FP-samples	HR-samples	
Rh	453	423	30
Rh–Fe	468	435	33
Rh–Mn	458	440	18
Rh–Mo	463	443	20

dissociation over Rh[2], while that for the unmodified Rh catalyst was lower (about 70 kJ mol^{-1})[8]. This suggests that fouling occurs on Rh catalyst at lower temperatures than investigated.

FTIR spectra were performed with HR samples Rh/ZrO$_2$ and Rh–Mo/ZrO$_2$ in synthesis gas atmosphere (CO/H$_2$ = 1/2; p = 0.2 MPa) and a temperature range 300 – 523 K (ref.[9]). At room temperature Rh/ZrO$_2$ shows bands at 2 048, 1 813, 1 631, 1 430, and 1 337 cm^{-1}. After heating at 423 K the bands at 1 430 and 1 337 cm^{-1} disappear and the region 1 700 – 1 200 cm^{-1} is dominated by bands at 1 575, 1 388, and 1 359. New bands appear at 2 977 and 2 878 cm^{-1}. After heating at 523 K new bands appear at 1 550 and 1 440 cm^{-1} while bands at 1 575, 1 388, and 1 359 cm^{-1} decrease. Similar bands were observed also with Rh–Mo/ZrO$_2$, with the only significant difference being that distinct bands 2 087 and 2 019 cm^{-1} appear at room temperature. All bands were recently reported in the literature and correspond to carbon monoxide present in linear (ca 2 050 cm^{-1}), bridge-bonded (ca 1 800 cm^{-1}) and twin (2 087 and 2 019 cm^{-1}) form, and to formate species (1 575, 1 388, 1 359 cm^{-1}), bidentate acetate (1 550, 1 440 cm^{-1}), and C–H stretching (2 978, 2 921, 2886 cm^{-1}). The band in the 1 700 – 1 500 cm^{-1} region can be assigned to dual site CO interaction at metal/support boundary which can develop to a weak carboxylate complex[10,11].

The assignment of formate and acetate bands has been confirmed by adsorption of formic and acetic acids. No formate was observed on ZrO$_2$ alone when it was pretreated under the same conditions as the catalysts. The presence of significant amounts of twin CO at room temperature on Rh–Mo/ZrO$_2$ indicates that the main role of Mo is to inhibit Rh particle sintering[12]. At increasing temperature (> 424 K) the bands due to the dicarbonyl disappear indicating that these surface species are not stable at reaction conditions.
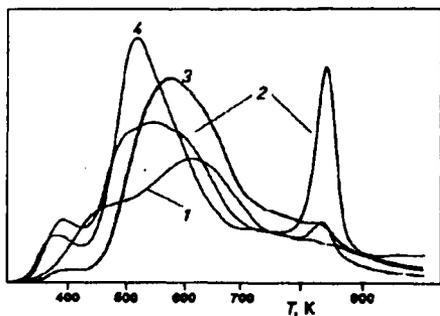

FIG. 5
TPD profiles of H$_2$ adsorbed at room temperature from samples reduced at 673 K. *1* Rh–Mo/ZrO$_2$, *2* Rh–Fe/ZrO$_2$, *3* Rh/ZrO$_2$, *4* Rh–Mn/ZrO$_2$
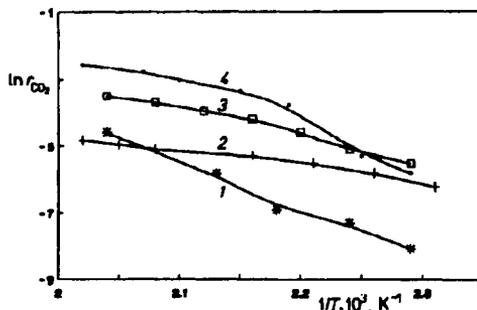
FIG. 6
Arrhenius plot of Boudouard reaction data (r_{CO_2} stands for rate of CO$_2$ formation in µmol g^{-1} s^{-1}. *1* Rh–Mn, *2* Rh, *3* Rh–Fe, *4* Rh–Mo

Formate bands disappear after purging with H_2 and no formyl or methoxyl species were detected. By increasing the temperature of thermal treatments the formate band decreases while the acetate band increases.

To investigate the effect of promoters on hydrogenation activity vs the CO insertion reaction of Rh, the ethylene hydroformylation was used as test reaction. The reaction products are: ethane, propionaldehyde, and propanol. The product yields are reported in Table II. Mn inhibits both the ethylene hydrogenation and CO insertion. Fe does not change the total conversion of ethylene: the decrease in ethylene hydrogenation is balanced by an increase in CO insertion reaction. The global effect is to double the selectivity to C_3 products. Mo increases the total conversion more than three times by increasing both reactions, but mainly the CO insertion, as the selectivity to C_3 increases.

As an example of the performed runs, the syngas reaction rates on the various catalysts are reported in Table III. Measurements under continuous H_2–CO flow showed a gradual decrease in catalytic activity during the first 10 h, with a significant rise in selectivity to oxygenates; data reported were obtained after 20 h on the stream.

TABLE II
Ethylene conversion (%) in hydroformylation reaction

Catalyst	C_2H_6	C_3H_5CHO	C_3H_7OH	Σ^a	S^b
Rh	1.8	0.61	0.16	2.6	0.4
Rh–Fe	1.5	1.22	0.11	2.8	0.9
Rh–Mn	0.86	0.06	0.10	1.0	0.2
Rh–Mo	6.1	2.7	0.80	9.6	0.6

[a] Total ethylene conversion (%). [b] Total C_3 compounds/C_2H_6.

TABLE III
Rate of CO conversion (mmol CO per g_{cat} h) to various products. Conditions: T 503 K, p = 3 MPa, H_2/CO= 1, GHSV = 2 400 1 per kg_{cat} h

Catalyst	CO_2	CH_4	C_{2+}	$MeOH^a$	$EtOH^a$	PrOH	$C_{4+}Ox$	$Other^b$	S^c
Rh/ZrO_2	0.052	0.26	0.026	0.017	0.077	0.0	0.0	0.0	0.37
$Rh–Mn/ZrO_2$	0.018	0.29	0.05	0.079	0.11	0.0	0.0	0.083	0.66
$Rh–Fe/ZrO_2$	0.10	0.35	0.18	0.16	0.41	0.07	0.085	0.036	1.5
$Rh–Mo/ZrO_2$	0.18	0.68	0.19	0.26	0.51	0.062	0.0	0.12	0.94

[a] Including the amount present as esters. [b] Aldehydes and acids. [c] $S = (C_{2+}$ compounds$)/(CH_4 + CH_3OH)$.

The activity in CO conversion and the rate of formation of the products is enhanced on all modified catalysts. The increase is in the order Mo > Fe > Mn. The rate of formation of methane, and of other hydrocarbons on Rh–Mn catalysts is similar to that on Rh catalysts, the rate of methanol and ethanol formation increases, the latter only moderately. The main changes occur with Fe and Mo modified catalysts. The rates of CO_2 and hydrocarbon formation are doubled on Rh–Fe and tripled on Rh–Mo catalyst; methanol formation increases nine times on Rh–Fe and fifteen times on Rh–Mo. The rate of ethanol formation increases five to six times on both these catalysts.

In conclusion the main effect of Mn is to increase methanol formation, that of Fe to increase oxygenates and that of molybdenum to increase oxygenates, mainly methanol. All modifiers favour chain growth, or CO insertion, to a greater extend than C_1 compounds.

The hydrogen desorption spectra (Fig. 5) suggest an increase in hydrogen binding energy in the order: Rh–Mn < Rh–Fe < Rh–Mo: on Rh–Mo catalysts hydrogen can compete more favourably with strongly adsorbing CO. The variations in the hydrogen binding energy are not enough to explain the promoter effect of the modifiers so one can infer that the main effect must be on CO adsorption and activation. TPD and TPR data of HR catalysts suggest that there is an intimate contact between Rh and promoter after hydrogen activation, as only one CO desorption peak is evidenced (Fig. 3). The T_{max} of the CO desorption peak (Table I), and consequently the binding energy, increase in the order Rh < Rh–Mn < Rh–Fe < Rh–Mo.

The apparent energy of activation for CO disproportionation in the Boudouard reaction (Fig. 6) is greater on modified catalysts but this increase is compensated by a strong increase in the number of sites where CO is activated: probably new CO adsorption sites are available in the presence of the modifiers. This increase in activity in the presence of modifiers must be ascribed to the increase in the number of active sites. It could be due to the reduction in Rh particle sintering, promoted by the modifiers, and/or to the formation of new adsorption sites at the boundary of the Rh particles. It may be hypothesized that the sites for CO activation in the Boudouard reaction are the same as in the hydrogen atmosphere but in this case the reaction path is different.

By considering the selectivity S (Table II) for CO insertion vs ethylene hydrogenation in the hydroformylation reaction, and the chain growth in CO hydrogenation vs C_1 compounds (Table III), a quite similar trend is obtained, with the exception of Rh–Mn, where there is probably some uncertainty in the evaluation of S due to the low conversion data.

CONCLUSIONS

The experimental results on the studied catalysts can be summarized as follows:

a) in the presence of hydrogen at least four types of adsorbed CO moieties are present at room temperature;

b) $Rh(CO)_2$ and Σ-CO bonded at the boundary of metal particles are not stable under reaction condition;

c) formate is formed under a CO/H_2 mixture at 423 K: this surface species is unstable under hydrogen flow at 473 K, or by heating under the CO/H_2 mixture at 523 K. No formyl or methoxyl peak was detected after the disappearance of the formate. It has been suggested that formate is a precursor of methane[13];

d) surface acetate moiety appears at a temperature where formate is no longer stable; it is quite stable in hydrogen flow;

e) CO dissociation occurs at relatively low temperature (420 – 450 K);

f) CO_2 under reaction condition is formed mainly by water gas shift reaction;

g) the role of the modifiers is to change the surface CO moiety distribution: Mn promotes the methanol formation, Fe the oxygenate products and the CO insertion reaction, Mo enhances CO reactivity mainly to oxygenates.

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