

Changes induced by metal oxide promoters in the performance of Rh–Mo/ZrO₂ catalysts during CO and CO₂ hydrogenation

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Abstract

The effect of promoter M (M (0.5%) = Li, K, Ce, Re, Co) on the surface and catalytic properties of Rh–Mo/ZrO₂ catalysts containing 1 wt% Rh and 2.5 wt% Mo is studied. Chemisorption results show a decrease in the metal dispersion on K and Li promoted catalysts, whereas it remained unchanged for the samples with the other promoters. The same trend was observed with the Rh/Zr atomic surface ratios obtained from XPS. Moreover, XPS also showed that in all catalysts Mo is mainly present as Mo⁶⁺, but there is also an important contribution (approx 25%) of partially reduced Mo^{δ+} species. On the other hand, XPS spectra show that Rh is partially oxidized with the exception of the catalyst promoted with Li in which Rh is completely reduced. TPR and XPS results indicate that the MoO₃ particles are partially reduced. The catalytic activity results in CO hydrogenation which indicates that the turnover number may be affected by the addition of promoters. In fact, Re increases both the activity to methanol and also the TON corresponding to total transformation. Additionally, the selectivity to methanol is slightly affected. With respect to the hydrogenation of CO₂, under the conditions used all catalysts only produced methane and no oxygenated products were detected. When the CO hydrogenation is studied in the presence of CO₂, changes in selectivity and catalytic activity can be detected, and the turnover number to methanol is lower than that obtained in CO hydrogenation, indicating that CO₂ may partially block the sites required for the hydrogenation of CO. © 1998 Elsevier Science B.V.

Keywords: Rhodium; Molybdenum; XPS; Hydrogenation

1. Introduction

The hydrogenation of CO to form hydrocarbon and oxygenated products over supported rhodium catalysts has been investigated for many years, because these catalysts are very

well known for their ability to produce oxygenated compounds from syngas [1–8]. It has been reported that the chemical state of rhodium significantly affects not only the conversion but also the product distribution. Thus, if rhodium is in metallic state, only oxygen-free hydrocarbons are obtained [8] but if rhodium is partially oxidized, i.e. Rh⁺, the selectivity to methanol is strongly enhanced [9].

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In order to induce an electronic effect on the metal function, different changes have been made in the catalysts formulation. The different approaches found in the literature to achieve this objective include the selection of carriers [2,10,11], metal precursors [1,2] and promoters [12–17]. All these factors can affect the electronic state of rhodium supported catalysts and also the selectivity for carbon monoxide hydrogenation. The effect of promoters has been associated with electronic effect, involving charge transfer from the promoter to the metal, or producing the blockage of surface sites or changing the reaction intermediates by interaction between the promoters with reactant molecules [18–20]. The addition of Ce [21], Ti [22,23], V [24], alkali [14] and Mo [11,22] oxides have been found to enhance the rate of CO hydrogenation. Among the studied promoters, Mo has received special attention [1,20,25–27]. Bhore et al. [28] reported an unusually high selectivity to oxygenated compounds and consequently proposed a dual mechanism. It was suggested that hydrogen is activated on Mo^{5+} , where it is not inhibited by CO and then migrates and reacts with CO on Rh. Sachtler et al. [6] and Reyes et al. [29,30] suggested that molybdenum oxides partly cover the surface of rhodium crystallites, thereby forming mixed oxides containing Mo–O–Rh bonds. The presence of positive rhodium ions under the reaction conditions appears to be responsible for the formation of oxygen-containing products. CO_2 hydrogenation has also been investigated on supported Rh [31–34] and significant differences in activity and selectivity compared with CO hydrogenation have been reported. In particular, the selectivity to CH_4 is close to 100% in CO_2 hydrogenation, with the almost complete absence of oxygenates.

In this paper the effect of the promoter on a series of Rh–Mo/ ZrO_2 catalysts is investigated. The catalysts were characterized by hydrogen chemisorption, temperature programmed reduction, X-ray diffraction and X-ray photoelectron spectroscopy. The characterization re-

sults are correlated to the activity results in the CO and CO_2 hydrogenation.

2. Experimental

The ZrO_2 ($S_{\text{BET}} = 52 \text{ m}^2 \text{ g}^{-1}$) was prepared by precipitation at room temperature of zirconium oxychloride solution, with an excess of ammonia solution. The obtained solid was filtered, washed with distilled water until the chlorine was removed. Then it was dried at 393 K overnight and calcined in air at 823 K for 2 h. Rh–Mo supported catalysts containing 1 wt% Rh, 2.5 wt% Mo and 0.5 wt% of promoter, were prepared by successive impregnation of the support. Firstly, the carrier was impregnated with an aqueous solution of ammonium heptamolybdate (Merck) and the excess water removed in a rotary evaporator. Then the impregnated solids were dried overnight in air at 393 K and subsequently calcined in air at 673 K. The Mo/ ZrO_2 samples were impregnated with an aqueous solution of rhodium trichloride (Aldrich), dried at 393 K and calcined at 573 K. Finally, the promoter was impregnated with an aqueous solution of lithium, potassium, cerium and cobalt nitrates or ammonium perrhenate. The solid was then dried and calcined at 573 K. The solids were reduced in situ before the characterization experiments or the catalytic runs by flowing hydrogen (40 cc/min) at 573 K for 30 min at atmospheric pressure.

The adsorption measurements were carried out in a greaseless volumetric system. The specific surface area was evaluated by the BET method from the nitrogen adsorption at 77 K and metal dispersion from hydrogen adsorption isotherm at 298 K. The method of Benson and Boudart [35] and Wilson and Hall [36], in which the linear part of the isotherm between 50 and 250 Torr is extrapolated to zero pressure was used to determine the hydrogen uptake. Temperature programmed reduction (TPR) experiments were carried out in a TPR/TPD Micromeritics 2900 system provided with a ther-

mal conductivity detector. The reducing gas is a mixture of 5% H₂/Ar (40 cm³ min⁻¹) and a heating rate of 10 K min⁻¹ was used. X ray diffraction (XRD) patterns were obtained using a Rigaku powder diffractometer using nickel-filtered Cu K α radiation. Photoelectron (XPS) spectra were obtained using a Fisons Escalab 200 R spectrometer with a hemispherical analyzer operated in the constant pass energy mode. Unmonochromatized Mg K α X-ray radiation ($h\nu = 1253.6$ eV) operated at 10 mA and 12 kV was used as exciting source. The spectrometer was equipped with a high-pressure reaction cell to carry out pretreatments at high temperatures. The samples were pressed in a hydraulic die to form thin smooth discs and placed in the high pretreatment chamber of the spectrometer. Afterwards, the samples were reduced in H₂ at 573 K for 30 min. Then they were transported to the analysis chamber without contact with air. The C 1s line at a binding energy of 284.9 eV was used as an internal standard. The intensity of various XPS peaks was determined using S-shaped background subtraction and integration of peak areas. Rhodium and molybdenum peaks were decomposed into several components assuming that the peaks had Gaussian–Lorentzian shapes. The Rh/Zr and Mo/Zr ratios were estimated from the integrated intensities of Rh 3d, Mo 3d and Zr 3d peaks, using the Wagner et al. sensitivity factors [37].

The hydrogenation of CO was investigated in a stainless steel (coated with gold) reactor. For the standard catalytic tests, the experiments were run for 8 h at 493 K and 15 atm. After the reduction in situ of the catalysts (200 mg), as described previously, the reactor was cooled to the reaction temperature, 493 K, and the reactant mixture at 15 atm was fed into the reactor. The mixtures used consisted of: (a) H₂ = 75%, CO = 25%; (b) H₂ = 80%, CO₂ = 20%; and (c) H₂ = 77.3%, CO = 18.7% CO₂ = 4%. The reactants and products were analyzed by an on-line GOW-MAC gas chromatograph. Steady state activity and product distribution were achieved after 180 min on stream.

3. Results and discussion

The specific surface areas and the H/Rh atomic ratios derived from hydrogen chemisorption and particle sizes evaluated from chemisorption results are compiled in Table 1. To estimate the particle size, it was assumed that the hydrogen is essentially adsorbed by the rhodium atoms with a stoichiometry Rh_s:H = 1:1 and the particle size was calculated from the equation $d = 5/S\rho$ where S is the metal surface area and ρ is the density of the metal.

Specific surface areas of the ternary Rh–Mo/ZrO₂ catalysts are essentially constant and slightly lower than the support surface area. This is reasonable as the formation of layers of molybdenum oxides, partially block the porous structure of the support, therefore leading to a decrease in the surface area. As the Mo loading is 2 wt% in all the catalysts a comparable decrease may be expected. However, in the case of the catalyst promoted with Li the decreases in surface area is higher. The molar amount of lithium is much higher compared with the other promoters, because all catalysts contain the same promoter loading, in wt%, but Li has a low atomic weight and, therefore, a larger amount expressed in moles of promoter per g of catalyst.

The extent of chemisorbed hydrogen expressed by the H/Rh ratio remains almost constant for catalysts promoted with Co and a slight increase is observed for Ce or Re promoted catalysts. In the case of Ce, the observed increase may be explained considering that Ce has

Table 1
Specific surface areas, H/Rh atomic ratios and metal particle size for Rh–Mo–M/ZrO₂ catalysts

Catalyst	S_{BET} (m ² /g)	H/Rh	d (nm)
Rh–Mo	54.0	0.27	4.7
Rh–Mo–Li	46.6	0.18	7.1
Rh–Mo–K	51.3	0.13	9.8
Rh–Mo–Re	52.0	0.29	4.4
Rh–Mo–Co	52.8	0.27	4.7
Rh–Mo–Ce	56.6	0.29	4.4

been recognized as an effective promoter to redispense noble metals [38]. In addition, H_2 adsorption on CeO_2 may take place simultaneously. For the Re promoted samples, it must be considered that this metal may be reduced under the experimental conditions and may promote redispersion of Rh, as has been proposed for Pt–Re and Rh–Re catalysts [39,40]. The addition of Li or K produces an important drop in the H/Rh ratio. This may be assigned to a decrease in metal dispersion, induced by these promoters. It should be born in mind that Li or K deposited on a support can form LiOH or KOH species whose melting points are 723 and 633 K, respectively, thus an important mobility of the mentioned species inducing an agglomeration of Rh particles may be expected during catalyst calcination [41]. It is emphasized that the H/Rh ratio in the studied catalysts does not necessarily correspond to metal dispersion, because molybdenum oxide is highly dispersed and covers not only the support but also rhodium particles as it has been previously reported [29]. For this reason, the particle size may also be over-estimated. In fact, TEM studies of Rh–Mo/ ZrO_2 catalysts give a particle size of 3.5 nm, lower than the value obtained from chemisorption. Moreover, XRD results do not show the presence of lines due to Rh or molybdenum oxide confirming the high dispersion of MoO_3 phase. With respect to Rh, the low metal content makes it difficult to observe the diffraction lines of the metal component.

Fig. 1 displays the TPR profiles in the temperature range 300–550 K of the calcined Rh–Mo samples. All the catalysts show a TPR peak centered approximately at 360 K which moves around this temperature depending on the promoter incorporated. This may be attributed to the reduction of rhodium particles and is in agreement with previous TPR results for different Rh supported catalysts [11,29,30]. The reduction of molybdenum oxide takes place at much higher temperatures. Thus, while the reduction of bulk MoO_3 begins at temperatures above 893 K, for silica supported molybdenum

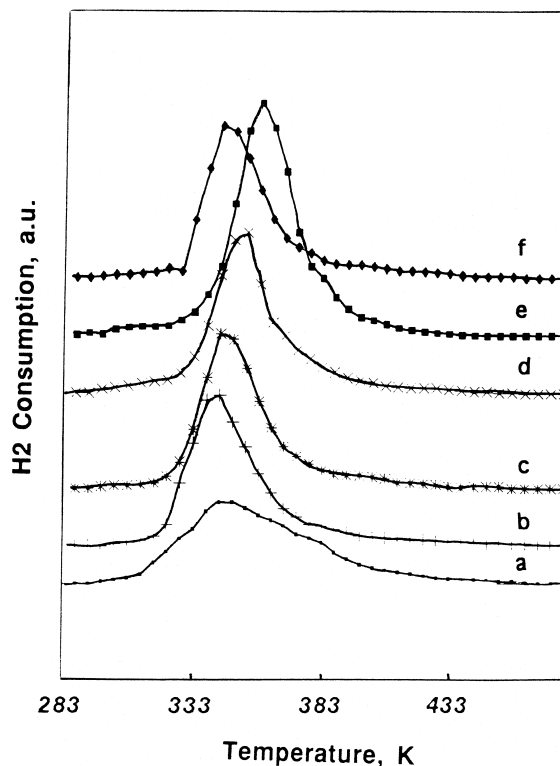


Fig. 1. Temperature programmed reduction profiles of various Rh–Mo/ ZrO_2 catalysts. (a) Rh–Mo, (b) Rh–Mo–Co, (c) Rh–Mo–Re, (d) Rh–Mo–K, (e) Rh–Mo–Li, (f) Rh–Mo–Ce.

oxide this process starts at 753 K. However, in the present work a shoulder at about 380 K overlapping with the principal TPR peak is observed. Such a shoulder may be assigned to a slight reduction of MoO_3 particles produced by H_2 spillover from Rh crystallites. As can be seen below, this partial reduction of MoO_3 particles has also been detected by XPS. In the Co, Re and Ce promoted samples, a partial reduction of the corresponding oxides may also be involved. In the K and Li promoted samples, a slight increase (5 and 10 K) of the maximum of the reduction peak is observed. This behaviour may be explained taking into account that the KOH and LiOH species may partially cover the rhodium species, decreasing the extent of H_2 spillover and therefore, the reduction of rhodium particles occurs at higher temperatures. As it is expected, in the Li promoted catalyst, which

possesses a higher molar concentration compared with that of the K sample, a more significant increase in the reduction temperature is observed. The hydrogen consumption for all the studied catalysts exceeds the amount required for a complete reduction of the Rh_2O_3 particles, confirming that a partial reduction of MoO_3 takes place, as has also been reported previously [29]. Finally, a higher increase in H_2 consumption was detected in Li promoted catalysts, in agreement with XPS results.

The chemical state of the catalyst component and their relative abundance at the surface has been revealed by XPS. Table 2 compiles the binding energy of Mo, Zr, Rh 3d core levels and also Ce 3d, Co 2p, K 2p, Li 1s and Re 4f levels of the promoter. Moreover, the Rh 3d core level spectra of catalysts reduced at 573 K are shown in Fig. 2a. For the sake of clarity, the Mo 3d spectra of a few representative catalysts are displayed in Fig. 2B. The BE of the Rh 3d_{5/2} peak at 307.2 eV suggests that Rh^0 is the major rhodium species [9], although a certain proportion of Rh^+ is present in most of the catalysts and is much higher in the catalyst promoted with K. The exception is the Li promoted Rh–Mo catalyst in which Rh is completely reduced. The Mo 3d profiles for catalysts with different promoters (Fig. 2b) display the characteristic doublet of Mo^{6+} species, however, the curve fitting procedure of the experimental spectra

shows partially reduced molybdenum species in a proportion below 30%, being slightly higher in the catalysts promoted with Li. This is in agreement with the TPR results of the promoted catalysts, which showed higher H_2 consumption, considering a complete reduction of Rh and a higher reduction of MoO_3 particles. After curve fitting, the presence of $\text{Mo}^{\delta+}$ and Mo^{6+} with binding energies of 231.4 and 232.5 eV were observed. In relation to Rh, the same procedure allowed the detection of Rh^+ (BE = 308.5 eV) and Rh^0 (BE = 307.4 eV) (the estimated percentage of each oxidation state species is given in parentheses).

In Table 3, the Rh/Zr, Mo/Zr and M/Zr (M = Li, K, Co, Ce, Re) surface atomic ratios are given. For comparison Rh/Zr, Mo/Zr and M/Zr bulk ratios are also included. It can be seen that Mo/Zr surface ratios are three times higher than bulk ratios, indicating high dispersion of Mo. It can also be observed that $(\text{Mo}/\text{Zr})_s$ does not change significantly in the promoted catalyst. This implies that the promoters do not affect either the dispersion or the sintering of molybdenum oxide on the ZrO_2 surface. It should be emphasized at this point that an important fraction of the ZrO_2 surface can be covered by the MoO_3 phase. This is illustrated by considering that an MoO_3 entity covers approximately 0.20 nm², therefore, a 2.5 wt% Mo dispersed as a monolayer will cover

Table 2
Binding energies (eV) of core electrons of Rh–Mo/ZrO₂ catalysts

Catalyst	Mo 3d _{5/2} (eV)	Zr 3d _{5/2} (eV)	Rh 3d _{5/2} (eV)	Promoter (eV)
Rh–Mo	231.4 (25) 232.5 (75)	182.2	307.3 (69) 308.5 (31)	
Rh–Mo–Li	231.4 (34) 232.5 (66)	182.2	307.3 (100)	Li 1s 56.1
Rh–Mo–K	231.4 (22) 232.5 (78)	182.2	307.3 (28) 308.5 (72)	K 2p _{3/2} 293.1
Rh–Mo–Re	231.4 (22) 232.5 (78)	182.2	307.4 (85) 308.5 (15)	Re 4f _{7/2} 42.5
Rh–Mo–Co	231.4 (32) 232.5 (68)	182.2	307.4 (82) 309.1 (18)	Co 2p _{3/2} 781.7
Rh–Mo–Ce	231.4 (26) 232.5 (74)	182.2	307.4 (82) 308.7 (18)	Ce 3d _{5/2} 882.6

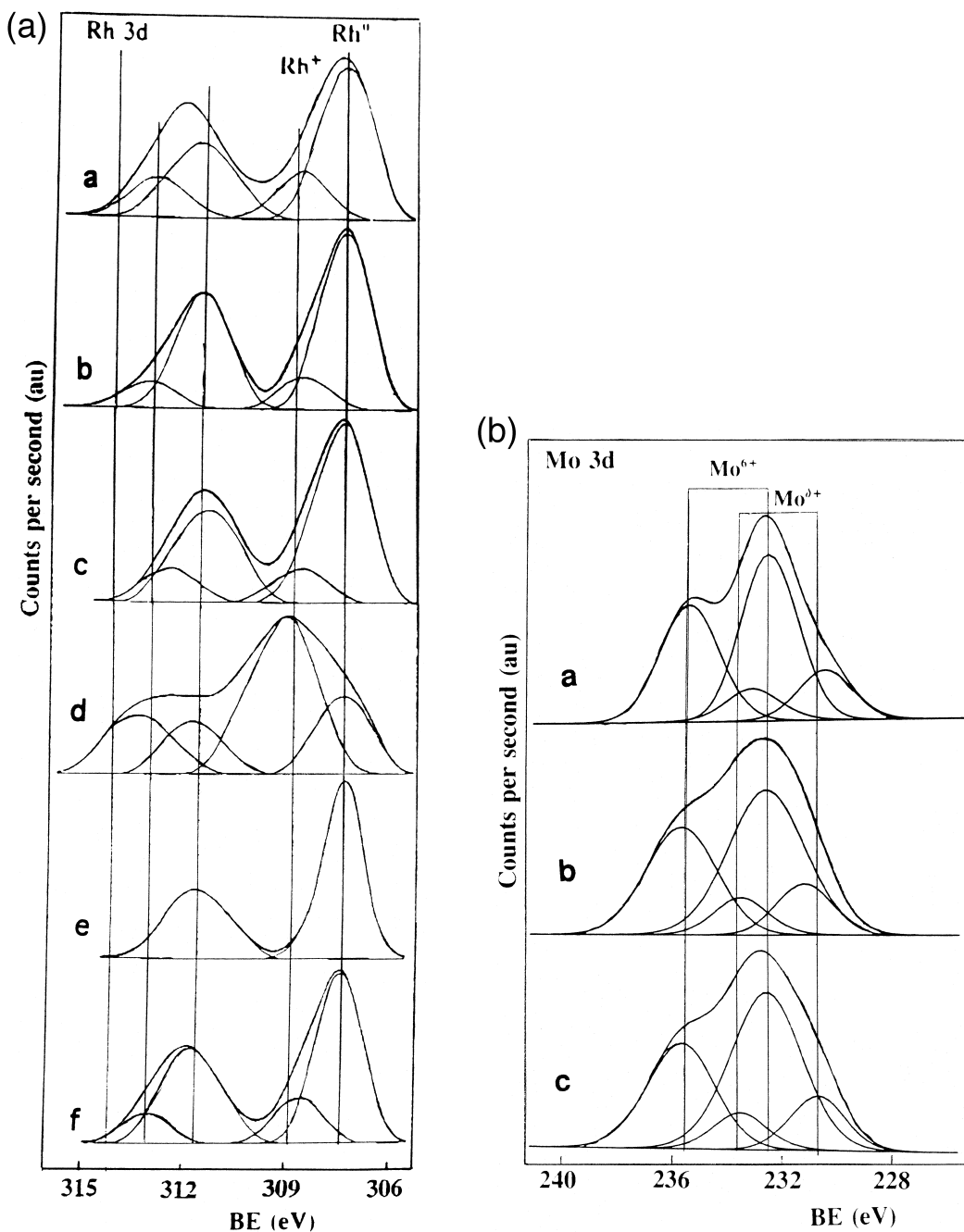


Fig. 2. XP spectra for (a) Rh and (b) Mo 3d core level of different Rh–Mo/ZrO₂ prerduced in H₂ at 573 K. (a) Rh–Mo, (b) Rh–Mo–Ce, (c) Rh–Mo–Co, (d) Rh–Mo–K, (e) Rh–Mo–Li, (f) Rh–Mo–Re.

60% of the support surface area. On the other hand, (Rh/Zr)_s remains almost constant, in Co, Re and Ce promoted catalysts, as compared with the Rh–Mo counterpart, but it drops in the

case of Li and K. The same trends were also observed by hydrogen chemisorption. The BE of Li 1s and K 2p_{3/2} are close to the expected for their respective hydroxides. On the other

Table 3
XPS atomic ratios for Rh–Mo–M/ZrO₂ catalysts

Catalyst	(Rh/Zr) _s	(Mo/Zr) _s	(M/Zr) _s	(M/Zr) _b ^a
Rh–Mo	0.015	0.094	—	—
Rh–Mo–Li	0.010	0.101	0.357	0.0931
Rh–Mo–K	0.007	0.097	0.060	0.0164
Rh–Mo–Re	0.015	0.094	0.067	0.0345
Rh–Mo–Co	0.016	0.088	0.032	0.0109
Rh–Mo–Ce	0.016	0.095	0.017	0.0458

^aM = Li, K, Re, Co, Ce; s = surface; b = bulk; (Rh/Zr)_b = 0.0125; (Mo/Zr)_b = 0.0335.

hand, the BE of Co 2p_{3/2} corresponds to Co₃O₄ while the BE of Ce 3d_{5/2} and Re 4f_{7/2} suggests a slight reduction of CeO₂ and ReO₃ species. Concerning the M/Zr ratios, the results suggest that the promoters remain highly dispersed in all catalysts.

Activity in the hydrogenation of CO was measured at 423 K under pressure of 15 atm using a mixture H₂:CO = 3:1. The experiment was run for 7 h on stream. The obtained products were CH₄, C₂H₆, C₃H₈, CH₃OH, HCHO, CO₂, CH₃CHO and CH₃CH₂OH. Table 4 compiles the conversion as well as the selectivity towards the main products, methanol and methane and the activity per site, expressed as turnover number, TON, molecules of CO converted per Rh surface atom per second. Methanol and methane formation rates (TON) are also included. It can be seen that the precursor can significantly affect the total conversion, which ranges from 0.7 to 6%. The selectivities to methanol are in the range 23 to 33% whereas higher differences are produced in the selectiv-

ity to methane. In fact, selectivity to CH₄ is between one and a half and two and a half times lower in cobalt promoted Rh–Mo catalysts compared with other catalysts. This behaviour is due to the fact that this sample is much more selective to ethanol than all the other catalysts. Additionally, changes in TON by a factor of 5 were detected, indicating a modification of the nature of active sites, due to the presence of the promoters. It should be kept in mind that the proposed active site for this system consists in Rh⁰ species in intimate contact with Rh^{δ+} and partially reduced molybdenum oxide, MoO_{3-x} [29]. It seems that there is a fast spillover/reverse spillover of hydrogen between Rh and MoO_{3-x}. This process allows an increase in hydrogen concentration to the reactive intermediates and therefore produces an enhancement of the rate [22]. Incorporation of Li decreases the conversion level probably because it produces a decrease in H₂ uptake and a suppression in hydrogenation [16], observed by the drop in selectivity to CH₄. On the contrary, selectivity to CH₃OH and CH₃CHO are increased. As expected, similar activity patterns are observed in K promoted catalysts, although showing a lower conversion level. Incorporation of Re produces a drastic reduction in the catalytic activity, improving the selectivity to methanol and decreasing the selectivity to methane. This may be due to Rh–Re interactions which produce a change in the Rh^{δ+}/Rh⁰ ratio. With respect to Ce incorporation, a decrease in the conversion level, a slight increase in the

Table 4
CO hydrogenation at 493 K and 15 atm on Rh–Mo/ZrO₂ catalysts. Reactant mixture: H₂ = 75%, CO = 25%

Catalyst	Conversion X (%)	Selectivity S (%)		TON (× 10 ² s ⁻¹)	TON (× 10 ² s ⁻¹)	
		CH ₃ OH	CH ₄		CH ₃ OH	CH ₄
Rh–Mo	5.89	26.4	29.1	7.66	1.41	1.55
Rh–Mo–Li	2.05	33.2	19.4	4.00	0.91	0.53
Rh–Mo–K	0.75	30.6	29.1	2.00	0.44	0.42
Rh–Mo–Re	1.23	32.3	23.6	1.49	0.33	0.24
Rh–Mo–Co	6.13	22.7	12.0	7.98	1.82	0.62
Rh–Mo–Ce	3.13	31.3	26.4	3.79	0.83	0.70

TON, turnover number.

Table 5
CO₂ hydrogenation at 493 K and 15 atm on Rh–Mo/ZrO₂ catalysts. Reactant mixture: H₂ = 75%, CO₂ = 25%

Catalyst	Conversion <i>X</i> (%)	TON ^a ($\times 10^2$ s ⁻¹)
Rh–Mo	1.74	2.26
Rh–Mo–Li	0.36	0.70
Rh–Mo–K	0.50	1.38
Rh–Mo–Re	2.58	3.10
Rh–Mo–Co	1.08	1.40
Rh–Mo–Ce	0.76	0.92

^aAll samples exhibit 100% selectivity to CH₄.

selectivity to methanol and a decrease in the selectivity to CH₄ are observed. It has been reported that the addition of Ce [42] to Rh catalysts may contribute to redispersion of the metallic phase, a change in the coordination number of Rh and, therefore, a decrease in the selectivity to CH₄, which is in agreement with our results. Also, the coordination number of Rh may be modified by the promoter affecting both activity and selectivity [43].

Carbon dioxide hydrogenation was studied on catalysts at 493 K and 15 atm using a mixture H₂ = 75% CO₂ = 25%. After 4 h on-stream, the system reached a steady state. In all catalysts the only detected products were CH₄ and H₂O. Table 5 summarizes the results, expressed as conversion level, and TON. In all catalysts, the conversion is below 3%, but important differences can be observed in the conversion of carbon dioxide on Rh–Mo–M/ZrO₂ catalysts. The fact that the rate of CO₂ hydrogenation is higher than for CO hydrogenation and that in the former reaction only CH₄ is obtained in agreement with findings reported in

the literature [34]. The C–O bond cleavage in the CO₂ molecule is easier than in the CO, hence the extent of CH₄ formation should be expected to be higher. In most of the promoted catalysts the conversion to methane is much lower than on the Rh–Mo/ZrO₂ sample. This could be attributed to a decrease in the concentration of hydrogen as explained previously. On the contrary, on Re promoted catalyst, an important enhancement in the turnover to methanol as well as to methane is observed. This behaviour could be related to the additional sites for hydrogenation provided by the Re particles.

Additionally, the simultaneous hydrogenation of CO and CO₂ was also studied. The experiments were run under similar experimental conditions, but using a mixture H₂ = 77.3%, CO = 18.7% and CO₂ = 4%. The results are compiled in Table 6. Significant differences with respect to the hydrogenation of pure CO or CO₂ can be observed. Thus, the conversion level, selectivity and turnover numbers show values between those found for the hydrogenation of pure components. This suggests that the mechanism of CO and CO₂ hydrogenation and the active sites for their adsorption are the same. In fact, Bell et al. [34] have recently reported that the FTIR spectra of the adsorbed CO and CO₂ were similar and the only differences were a higher surface coverage in the case of CO. The dissociation of H₂CO produced by the hydrogenation of CO seems to be the step limiting the formation of CH₄. Hence, the higher rate of CH₄ formation is achieved in the catalysts with higher ability to hydrogenate, i.e., that promoted with

Table 6
CO and CO₂ hydrogenation at 493 K and 15 atm on Rh–Mo/ZrO₂ catalysts. Reactant mixture: H₂ = 77.3%, CO = 18.7%, CO₂ = 4%

Catalyst	Conversion <i>X</i> (%)	Selectivity <i>S</i> (%)		TON ($\times 10^2$ s ⁻¹)	TON ($\times 10^2$ s ⁻¹)	
		CH ₃ OH	CH ₄		CH ₃ OH	CH ₄
Rh–Mo	4.42	17.1	33.8	5.22	0.64	1.76
Rh–Mo–Li	2.12	26.8	15.0	3.75	0.66	0.56
Rh–Mo–K	2.19	23.7	22.4	5.37	0.87	1.20
Rh–Mo–Re	8.95	24.1	25.6	9.84	1.67	2.51
Rh–Mo–Co	4.04	30.3	23.5	4.77	1.04	1.12
Rh–Mo–Ce	2.41	17.4	28.5	2.65	0.32	0.75

TON, turnover number.

Re. On the other hand, even the rate of formation of CH_3OH does not change drastically with the addition of promoter, the Re-promoted catalyst is the most active.

4. Conclusions

Both the surface properties and the catalytic activity in the hydrogenation of CO and CO_2 are affected by the incorporation of a promoter to Rh–Mo/ZrO₂ catalysts. The main effect of the promoter is to modify the ability to insert hydrogen on the adsorbed CO molecule. Decreasing this ability, an enhancement of the selectivity to oxygenated products may be produced. All the promoters used increase the selectivity to methanol in CO hydrogenation. However, due to changes in the conversion level and in the surface properties, the change in the rate of methanol formation does not vary markedly. On the other hand, the rate of CO_2 hydrogenation to methane is higher than for CO hydrogenation under similar conditions in all the catalysts studied

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