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Isotopic Equilibration of Carbon Monoxide Catalyzed by Supported Ruthenium

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The rate of isotopic equilibration of CO has been studied at 373 K on a ruthenium/Al_2O_3 catalyst. CO partial pressures from 5×10^2 to 15×10^3 Pa were used, and the effect of H_2 (0–10% vol) was studied. The analysis of kinetic data and the absence of CO_2 or CH_4 in the reaction products show that CO is present on the catalyst surface in an undissociated and reactive form. Hydrogen has a strong inhibiting effect on the exchange reaction, and does not react with CO under these conditions. It is argued that carbon monoxide can be adsorbed as a single carbonyl or in geminal dicarbonyl form, on metallic or partially oxidized ruthenium sites. This latter form displays a lower back-donation effect and with a contiguous similar group can form a square planar transition complex, by means of which the exchange reaction occurs. The inhibiting effect of H_2 is two-fold, namely, competitive adsorption against CO and stabilization of the carbonyl bond. *Ab initio* molecular calculations on a simplified model (H instead of Ru) seem to support this mechanism.

INTRODUCTION

The reaction between CO and H_2 is attracting renewed attention because of the possibility of achieving new synthesis routes, alternative to the classical petrochemical processes. Ruthenium is among the transition metals being studied as catalysts, but unlike metals such as Ni or Fe, the interaction mechanism of H_2 and CO with the surface of ruthenium and the factors influencing the reaction selectivity have not been well clarified (*1–4*). On ruthenium, a low gas pressure of the reactants favors the formation of methane, whereas at high pressures heavy hydrocarbons are synthetized (*1–3, 5*). For several transition metal catalysts, experimental results agree with a reaction mechanism which implies the breakage of C–O and H–H bonds and the subsequent hydrogenation of the carbon atom present on the metal surface as active carbon or carbide (*6, 7*). In the case of Ru, no evidence for the formation of such carbon forms occurs at the usual reaction conditions. Some available CO decomposition data indicate that this reaction occurs at high temperature (773 K) giving rise to graphitic carbon, which is completely inert in the hydrogenation reaction (*8*). Very recent TPD data confirmed that CO_2 is formed at relatively high temperatures ($\gtrsim$420 K) with a maximum at 740 K. Carbon deposited on the surface due to the CO decomposition was found to be reactive by TPR forming methane and ethane, with a tendency to lose activity upon thermal aging (*9*).

The hypothesis of a CO dissociation on Ru, followed by the formation of carbenes in an H_2 atmosphere, has been suggested by

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analogy with its behavior on other metal catalysts, e.g., Fe, Co, and Ni, where surface defects were found to be the active centers for the CO dissociation process (*7, 8, 10*). On the other hand, experimental evidence for a nondissociative interaction between CO and Ru has been reported. Infrared spectroscopy studies carried out on supported Ru by Dalla Betta *et al.* (*11*) and Brown *et al.* (*12*) show the formation of surface carbonyl-like species, strongly depending on the previous history of the catalyst, particularly on the activation treatment. By thermal desorption and LEED–AES experiments, Reed *et al.* (*13*) showed the existence of two carbon monoxide species on the (101) surface of single crystal Ru, the high-coverage α-form and the more stable low-coverage β-form. On oxygen-contaminated surfaces two other very stable forms are observed, γ and δ. In all cases, at the operation temperature of 300 K, neither the formation of oxygen or carbon dioxide coming from the disproportionation of CO nor the exchange reaction between preadsorbed $^{18}O_2$ and the oxygen atoms of CO was observed.

The above observations are confirmed by the results of Ku and Gjostein (*14*) on the Ru(100) surface in the temperature range 400–495 K. Two molecular species were again identified by flash desorption spectroscopy, with an adsorption energy of 23 and 29 kcal/mole, respectively. Two species were also found by Madey and Menzel (*15*) on Ru(001). A theoretical interpretation of the existence of two different chemisorbed states of CO is not yet available.

The tendency of Ru to give methane at low pressures and heavy hydrocarbons at high pressures in the presence of CO and H_2 mixtures could be explained either by a strong hydrogenation power which makes the hydroxycarbene radicals unstable, or by dissociative adsorption followed by hydrogenation with formation of methyl and hydroxyl radicals. The aim of this work is to confirm the existence of undissociated CO species on Ru at 373 K and to study the reactivity of such adsorbed molecular species. We carried out equilibration experiments of the isotopic mixture $^{12}C^{18}O$ + $^{13}C^{16}O$ at 373 K on a commercial Ru/Al_2O_3 catalyst with and without the presence of H_2 in the gas atmosphere. From the experimental equilibration rate of the isotopic mixture it is possible to obtain information on the reactivity of chemisorbed CO and to verify the validity of a nondissociative model on the basis of the analysis of the reaction products. For instance, if carbon dioxide is found to be absent after equilibration, a significant dissociative CO adsorption can be excluded.

EXPERIMENTAL

A commercial catalyst was used, containing 0.5% (by weight) of Ru supported on alumina, with a total specific surface area of 134 $m^2\ g^{-1}$ and a metal specific surface area of 1.1 $m^2\ g^{-1}$ determined by oxygen adsorption. CO isotopic mixtures were obtained by diluting with pure He (Carlo Erba R. P. E.) the proper amounts of $^{13}C^{16}O$ (denoted henceforth as C29) at 90.5% (Merck, Sharp & Dohme) and $^{12}C^{18}O$ (denoted as C30) at 99.8% (Gesellschaft fur Kernforschung M. B. H., Karlsruhe). The ratio of the unreacted species was maintained constant for the whole set of experiments (C29/C30 = 0.95) while partial pressures were changed in the range 5–150 × 10^2 Pa. The experimental set-up consisted essentially of a recirculating discontinuous reactor (Temkin type), magnetically pumped. The total volume of the system was 330 cm^3. Gas analyses were made by means of a quadrupole mass analyzer (QMA, E.A.I. Mod. 250-B) connected to the reactor equipment. The equilibration reaction

$$\begin{array}{ccccccc} ^{12}C^{18}O & + & ^{13}C^{16}C & \rightleftarrows & ^{12}C^{16}O & + & ^{13}C^{18}O \\ (C30) & & (C29) & & (C28) & & (C31) \end{array} \qquad (1)$$

was followed by sampling the gas phase and measuring at time intervals the mass ratio

C30/C31. After sampling, all operations were automatically carried out by a PDP 11/50 computer connected to the QMA, which measures mass intensities and background level, evaluates the data, and finally presents a C30/C31 vs time plot complete with a linear regression analysis (*16*).

The experiments were carried out as follows: 0.5 g of fresh catalyst was installed in the reactor, degassed to 0.1 Pa, and heated at 673 K. When this temperature was reached, 0.67 × 10^5 Pa of pure H_2 was injected into the reactor chamber and recirculated for 2 hr. Any products and impurities coming from the catalyst were condensed in dry ice/ethanol traps at 193 K. After activation, the system was degassed and cooled to 373 K. To obtain good reproducibility in the equilibration experiments carried out in the presence of CO species alone, it was found necessary to submit the catalyst to a conditioning procedure in a CO atmosphere at a pressure of 1.3 × 10^4 Pa for 2 hr. After degassing, the system was ready for isotopic equilibration experiments. About 10 gas samplings were made for each experiment, in a quantity (0.25 cm^3) which is likely to influence only very slightly the total pressure of the system.

Blank experiments carried out without catalyst in the reactor showed no reactivity.

RESULTS

According to Winter (*17*) the total exchange rate r of a gas mixture in dynamic equilibrium can be calculated from equilibration changes by means of the equation

$$\frac{\tilde{N}V}{wA}\,\frac{P}{RT}\ln\frac{1}{1-F} = rt \qquad (2)$$

where $\tilde{N}$ is the Avogadro number, V the system volume, P the total CO pressure, w the catalyst weight, A the total specific surface area, and t the reaction time. F represents the reaction conversion, calculated from the ratio γ between C30 and C31 mass intensities, as measured by the QMA, by means of the equation

$$1 - F = 1 - \frac{C31 - C31^0}{C31^\infty - C31^0} = \frac{\gamma - \gamma^\infty}{\gamma + 1}\,\frac{\gamma^0 + 1}{\gamma^0 - \gamma^\infty}.$$

Plotting the left term of (2) as a function of t, a straight line, the slope of which is the rate r (molecules m^{-2} min^{-1}), is expected. Equation (2) is valid if the total number of molecules is maintained constant during the reaction, so excluding exchanges with the solid. Furthermore, the number of adsorbed molecules must be a small fraction of the total number. Experimental data of isotopic equilibration of CO fit Eq. (2) very well, as shown in Fig. 1. In Fig. 2 the total exchange rate vs CO pressure is reported.

The presence of hydrogen strongly inhibits Reaction (1). Using gas mixtures with a H_2/CO ratio equal to 1 no exchange was observed. By reducing H_2 : CO to 10 : 90 it was possible to measure an equilibration rate. When hydrogen was present in the gas mixture, even in traces, the linear dependence on t of conversion was observed only after an induction period. Initially, the equilibration rate is always higher than in the steady state. Some experiments carried out after injecting H_2 and degassing to 0.13

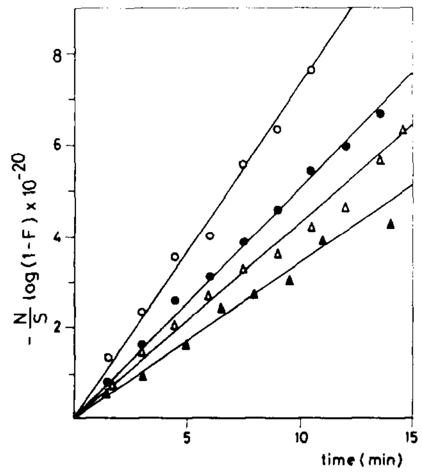


FIG. 1. Conversion vs. time for Reaction (1) at 373 K; p_{CO} (Pa): (▲) 1600; (△) 3200; (●) 6500; (○) 13100.

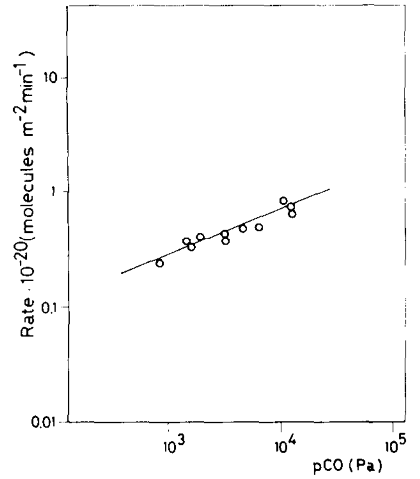


FIG. 2. Rate for Reaction (1) vs p_{CO} at 373 K in the absence of H_2.

Pa at the reaction temperature showed a decrease of the system reactivity. The initial activity of a catalyst contacted with hydrogen at 373 K can be restored by a vacuum treatment (0.13 Pa) for 2 hr at 673 K.

Since a high H_2 concentration reduces the equilibration rates to negligible values, experiments were carried out using the following hydrogen concentrations in the CO isotopic mixtures: 0.5, 2.5, 5, and 10%. Results are reported in Fig. 3.

DISCUSSION

CO isotopic equilibration experiments carried out without H_2 require a conditioning time interval of almost 2 hr after the reduction treatment in the hydrogen stream. This treatment must be repeated every time the catalyst sample comes into contact with H_2. In this interval the catalyst activity vs equilibration time continuously increases until a steady value is reached. Excluding a further reducing effect at the relatively low temperature of experiments, some assumptions can be formulated to explain such behavior, such as the removal of surface poisoning due to atomic hydrogen dissolved in Ru during reduction (*18*) or the decomposition of CO giving rise to adsorbed carbon and oxygen active in the equilibration reaction (*19*). This last hypothesis seems extremely unlikely: if adsorbed carbon is active in the equilibration reaction, it should then be active in the competitive methanation reaction. If on the contrary it is inactive, it should inhibit Reaction (1). One can conclude, according to Dalla Betta and Shelef (*11*), that at the operating temperature CO is stable in the presence of Ru, which is moreover a poor catalyst for the CO disproportionation (*20*). However, the activity increase is attributable to the decrease of the surface poisoning induced by dissolved hydrogen, which has a quite low desorption rate (*21*).

Reaction rates obtained in the presence or not of H_2 were related to a pseudo-homogeneous kinetic model:

$$r = k' P_{CO}{}^{m} P_{H_2}{}^{n}. \tag{3}$$

The obtained parameters are reported in Table 1. The parameter values indicate that the reaction order with respect to CO increases when hydrogen is present. This fact can be interpreted as due to a competitive adsorption of hydrogen on reaction sites of carbon monoxide. The negative reaction order with respect to H_2 confirms this interpretation.

The absence of reaction products such as

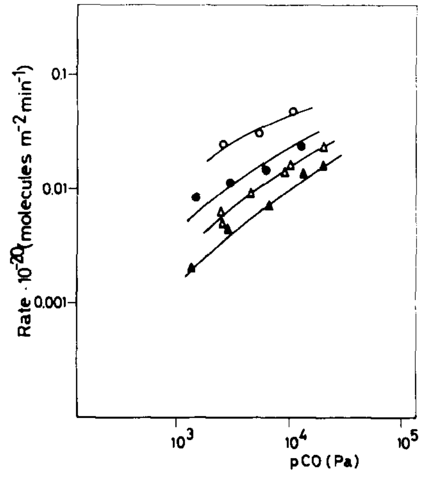


FIG. 3. Rate for Reaction (1) vs p_{CO} at 373 K in the presence of different H_2 amounts: (○) 0.5% (v/v); (●) 2.5% (v/v); (△) 5.0% (v/v); (▲) 10.0% (v/v).

TABLE 1

Calculated Parameters from a Nonlinear Regression on a Pseudo-Homogeneous Model

H_2	$k' \times 10^{-19}$	m	n	Number of runs	$\bar{\epsilon}\%$
No	1.42 ± 0.12	0.34 ± 0.03	—	12	7.6
Yes	$(2.9 \pm 1) \times 10^{-3}$	1.07 ± 0.08	-0.488 ± 0.044	19	11.3

CO_2 and CH_4 (in case formed H_2O should be removed by traps) indicates that a nondissociative adsorption of CO occurs. Thus, the oxygen exchange reaction must occur between two adsorbed CO molecules. Assuming a Langmuir-type isotherm for CO and H_2 adsorption, the reaction rate can be expressed as:

$$r = k''\left(\frac{b_{CO}P_{CO}}{1 + b_{CO}P_{CO} + (b_H P_H)^{1/2} + b_{COH}P_{CO}{P_H}^{1/2}}\right)^2. \tag{4}$$

Equation (4) is consistent with a nondissociative adsorption for CO and a dissociative adsorption of H_2. Furthermore, hydrogen adsorption is competitive with CO adsorption and/or H_2 can adsorb on sites where CO is already present (*5*, *22*). Calculated parameters are reported in Table 2 for the two series of data. Examination of the values obtained suggests that the quantity of hydrogen coadsorbed with CO on the same sites does not markedly influence the reaction rate (that is, $b_{COH} \simeq 0$). The most surprising result is the very high value of the H_2 adsorption constant, four orders of magnitude higher than that of CO. Such a strong inhibiting effect of hydrogen on the reaction rate cannot simply be interpreted as a competitive adsorption. In fact CO is more easily adsorbed on Ru than H_2 ($V_{CO}/V_{H_2} = 2.3$ at 375 K), while using a $H_2/CO = 1/1$ mixture V_{CO}/V_{H_2} reduces to 0.82, due to a decrease of CO adsorption and an increase of H_2 adsorption (*21*, *22*). Therefore, it is necessary to assume that *the adsorption constant of H_2 is correlated to an inhibiting effect which is not only a competitive adsorption.* Namely, the hydrogen adsorption can induce a chemical change of Ru surface sites. The amount of inhibited sites is a function of H_2 partial pressure. These concepts will be further clarified in the following.

CO reacts with ruthenium giving carbonyl-type bonds by donation of an electron pair of carbon to empty d orbitals of the metal, that is by overlapping of an occupied σ orbital of C and an empty σ orbital of Ru. The excess of negative charge which should be localized on the metal is reduced by back-donation of metal elec-

TABLE 2

Calculated Parameters from a Nonlinear Regression Based on a Langmuir–Hinshelwood Model

H_2	$k'' \times 10^{-19}$	b_{CO}(Pa)	b_H(Pa)	b_{COH}(Pa)	Number of runs	$\bar{\epsilon}\%$
No	7.46 ± 1.25	20.6 ± 10.1	—	—	12	14.0
Yes	1.1 ± 0.02	20.6^a	$(12.6 \pm 3.) \times 10^3$	1.3×10^{-6}	19	8.0

[a] In this calculation the equilibration constant b_{CO} was assumed equal to that found in the absence of H_2.

trons from full d orbitals to π^* antibonding orbitals of carbon. This produces a weakening of the C–O bond. The formation of a dative bond between an occupied dπ orbital of Ru and an empty pπ orbital of C gives rise to a synergic mechanism: the back-donation of electrons by the metal to carbon increases the ability of the carbon to be an electron-donor through its σ bond and such displacement favors in turn the metal back-donation power. Owing to the special nature of the bonding, the Ru–C–O group must be linear. This consideration is confirmed by investigations on Ru carbonyls, where the Ru–C–O angle was found to be near 180° (*23*). Angle values different from 180° can be explained only by assuming a weak back-donation of the metal atom.

If two vicinal CO molecules are taken into account, bonded to Ru by means of carbonyl-like bonds, it is extremely difficult to devise an oxygen exchange mechanism between the two adsorbed CO molecules when they have a linear configuration (Fig. 4a). A Ru–Ru length of 2.87 Å is assumed from EXAFS data (*24*), while Ru–C and C–O distances are 2.0 and 1.25 Å, respectively (*22*). Even if the orientations of CO molecules favored the exchange from the point of view of distances, the new bond should originate with a strongly distorted angle (Fig. 4b). An analogous situation arises from the assumption of an exchange between two CO molecules bonded to the same Ru atom.

In conclusion the oxygen exchange reaction between two undissociated CO molecules adsorbed on Ru can be envisaged only supposing that the Ru–C–O sequence is not linear, in such a way that the two oxygen atoms face at the same distance the two C atoms and the Ru–C–O angles have both the same value. In such a hypothesis each carbon atom looks undistinguishably at the two O atoms.

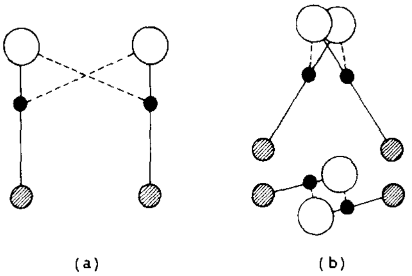
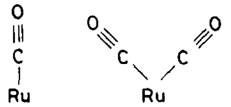
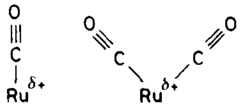


FIG. 4. Models for CO adsorption on Ru. (a) Lateral view of vicinal and unbent CO groups; (b) lateral and top view of bent CO groups forming a regular tetrahedron. Dashed lines are new bonds originated by the exchange reaction. Large open circles represent O, little black circles C, and dashed medium circles Ru.

In a previous work on the surface characterization of Ru catalysts supported on various oxides (*25*), we found that even after a reduction treatment in an H_2 stream at 873 K, ruthenium remained in an oxidized form. The nature of such a form is not at all well clarified, but it is likely that it depends on the nature of the support. In fact this effect was not observed on silica whereas on alumina the existence of such oxidized sites is experimentally consolidated. Assuming that CO can adsorb on such sites in a formally analogous way as on Ru° sites, the following species can be present on the surface:

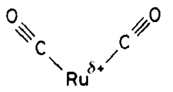


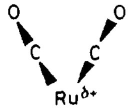


where $Ru^{\delta+}$ indicates the oxidized metal form. Geminal species will be dominant at high coverages, while single-carbonyl species will prevail at low coverages. On the oxidized form of Ru, where less back-donation is present, the Ru–C bond will be weaker. Consequently, the bending of Ru–C–O angle will be easier.

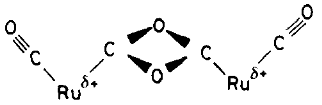
An enhancement of CO equilibration rates on partly oxidized metals, in comparison with oxides, has been observed due to oxygen vacancies in the oxide lattice and a heteromolecular exchange mechanism was suggested (*17*). In our case, an enhancement in comparison with the metal is present and a homomolecular exchange mechanism is working.

Let us now consider two $Ru^{\delta+}$ atoms in a vicinal position, each of them with two geminal CO adsorbed molecules:





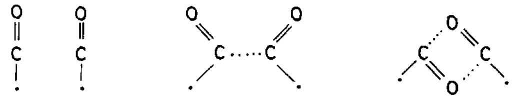
CO molecules which face one another can strongly interact, and due to this interaction a further distortion of the Ru–C–O bond and angle cannot be excluded. Such a strong distortion could bring to the formation of the following active complex (where C has a sp^3 hybridization) containing a cyclic C–O species:



The formation of such a complex could justify the low temperature isotopic exchange reaction, with the breakdown of the cycle and the restoration of the initial form, while at higher temperature the disproportionation reaction could occur. The equilibration rate on a Ru single crystal slice or on Ru/SiO_2 was found to be two orders of magnitude lower than on Ru/Al_2O_3. Such results on samples where Ru is completely reduced to the metal state further support the proposed mechanism. The strong inhibiting effect of hydrogen on the exchange reaction, pointed out in kinetics experiments, can be explained by an increase of the electron charge density on Ru atoms surrounding the adsorption site. As a consequence, the change of the chemical properties of oxidized ruthenium sites is to be expected. The increase of the electron charge density inhibits the bending vibration of the Ru–C–O angle so hindering the formation of the cyclic complex.

The proposed interpretation justifies both the existence of more stable surface carbonyl species, as observed by IRS and TDS experiments, and the complete lack of the CO_2 formation reaction. As the experimental evidence presented by this and previous papers agree but are not sufficient to confirm the proposed mechanism, "ab initio" calculations were made with the LCAO-MO-SCF method on some simplified models which reasonably simulate the real situation. The aim of this effort was to test the non-contradictoriness of the proposed model from the physical point of view rather than to test its full validity. In the model we substituted ruthenium atoms with hydrogen atoms so reducing the number of integrals. As we assumed that the active center for the CO isotopic exchange is the oxidized Ru, this substitution is not irrealistic, and represents the extreme limit of a metallic center devoid of the charge back-donation.

With respect to these metallic centers, CO chemisorbed molecules can assume a linear or bent configuration:

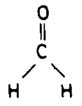


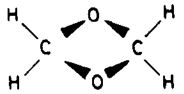
A B1 B2

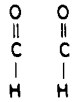
Noninteracting Interacting

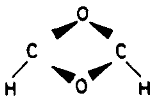
In the first case (A) a pair of noninteracting carbonyl groups results, whereas in the second case an interaction is possible in several forms (B1 and B2). In B1 the sp^2 hybridization is maintained for C atoms; in B2 the hybridization becomes sp^3.

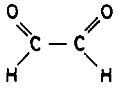
With the aim of evaluating the relative stability of B1 and B2 species and to compare their energy with that of the A configuration, we calculated the total energy of the following molecular systems, varying some structural parameters (bonds and angles): H_2CO, $(H_2CO)_2$, 2(HCO), and $(HCO)_2$.


(1)


(2)


(3)


(4b)


(4a)

The calculations were made using the IBMOLH program (*26*) and describing the one-electron states in terms of a minimal basis set of gaussian functions using an optimized exponent (*27*). Results obtained for the various molecular models are reported in Table 3.

The comparison of the monomeric and dimeric forms of formaldehyde (1 and 2, respectively) indicate that the dimeric form, where C and O atoms are arranged at the vertices of a square is more stable by about 27 kcal/mole with respect to the monomeric form.

By analogy with this result, we assumed in the model (4b) a square arrangement of C and O atoms, with HCO angles and C–H bond lengths equal to those found in the previous calculations.

For the models 3, 4a, and 4b, which simulate the possible configurations of CO chemisorption (A, B1, and B2, respectively) a H–H length of 5.72 a.u. was assumed, equal to the average metal–metal length on the various low index surfaces of Ru.

The comparison between the total energy calculated for the above models clearly indicates that the lack of back-donation from the metal induces an attractive interaction between two CO molecules adsorbed in a vicinal position. The form 4a, which is connected to a sp^2 hybridization, is more stable than the square complex 4b, which in turn has a lower total energy than the linear carbonyl situation. The simplified model assumed, with H instead of Ru, can play a determinant role on this result. However, the lower energy value obtained for 4b with respect to 3 is noticeable. Since species such as 3 were experimentally found on Ru, the existence of different biradical forms, such as 4a and 4b, with only the second of them active in the exchange reaction, can be envisaged.

CONCLUSIONS

Kinetic measurements of the equilibration reaction of CO and the analysis of the reaction products show that carbon monoxide is present in an undissociated and reactive form on supported Ru catalysts at 373 K.

The remarkable inhibiting effect of hydrogen, too strong to be attributed to simple coadsorption, indicates that hydrogen

TABLE 3

Molecular Parameters Used and Total Energy Results of *ab Initio* Calculations

		R(CO) (Å)	R(C–H) (Å)	R(H–H) (Å)	$\alpha(H\hat{C}O)$	E_{tot}(a.u.)
1	H_2CO calc.	1.28	1.1	—	121.0°	−113.50259
	exp.	1.22	1.1	—	119.5°	—
2	$(H_2CO)_2$ calc.	1.52	1.1	3.23 *	115.0°	−227.04877
3	2(HCO) calc.	1.27	1.1	3.02[a]	180.0°	−225.56849
4a	$(HCO)_2$ calc.	1.27	1.1	3.02[a]	120.5°	−225.81281
4b	$(HCO)_2$ calc.	1.45	1.1	3.02[a]	124.0°	−225.69007

[a] Assumed value. Other values have been optimized.

has a specific influence on the catalytic properties of Ru. Carbon monoxide can be adsorbed as a single carbonyl or geminal dicarbonyl form on metallic or partially oxidized Ru. The bond between the CO group and this last form of Ru is weak and can be easily modified through an interaction with a contiguous carbonyl group, giving a square planar transition complex.

Ab initio calculations seem to support this mechanism. The dimeric species is the active intermediate form in the CO exchange reaction, under the adopted experimental conditions. It is known from the literature that at higher temperatures CO_2 is formed by disproportionation of CO; also in this case it is possible to match the nondissociative mechanism with the high-temperature breakage of the square complex, with formation of C and CO_2.

A double inhibiting effect of hydrogen was evidenced, namely, competitive adsorption against CO and stabilization of the carbonyl bond, owing to an increase of the metal electron density. The strong hydrogen adsorption observed by McKee (*22*) is not in disagreement with the proposed model, bearing in mind that the square complex is a biradical group which tends to saturate by hydrogen adsorption.

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