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Hydrogenation of CO over ZrO_2-Supported Rh Catalysts: Role of Experimental Parameters in Modifying the C_2H_5OH/CH_4 Product Ratio

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The hydrogenation of CO over ZrO_2-supported rhodium catalyst has been extensively investigated in an attempt to increase the C_2H_5OH/CH_4 ratio while minimizing CH_3OH. Only one scheme has been found to account satisfactorily for the experimental rate equation determined by using CO and H_2 partial pressure dependence. This scheme assumes the formation of a CH_x moiety on the catalyst surface as the rate-determining step. Furthermore, in agreement with earlier findings, it is also consistent with the intermediate formation of acetaldehyde. Finally, the role of the support has been emphasized, as it has been found that ZrO_2 significantly affects ethanol selectivity.

INTRODUCTION

Hydrocarbons and oxygenated compounds can be produced catalytically using synthesis gas (CO + H_2) as the starting material. Products are affected by the choice of the catalyst among the Group VIII metals, which all share the ability to hydrogenate carbon monoxide with ultimate hydrogenolysis of the C–O bond and varying extents of C–C bond formation. A screening of the lesser known metals of Group VIII has already provided evidence that rhodium has a unique ability to produce two-carbon (C_2) chemicals selectively (*1*). There is particular interest in understanding the mechanism by which Rh-containing catalysts convert CO/H_2 into C_2-oxygenated products (ethanol, acetaldehyde) rather than hydrocarbons.

Interesting results for ethanol formation have been observed for rhodium supported on TiO_2 (*2*), La_2O_3 (*3, 4*), ThO_2 (*5*), and V_2O_3 (*6*), while conflicting data have been reported for rhodium supported on SiO_2 (*7, 8*) and ZrO_2 (*9, 10*).

The purpose of the present investigation was to establish the role of experimental parameters in modifying the C_2H_5OH/CH_4 ratio while possibly eliminating methanol formation. As for the support, ZrO_2 seemed most appropriate (*11*) since it is known as a metal oxide with intriguing characteristics (*12*), displaying acidic and basic properties on the surface together with oxidizing and reducing properties (*13*).

Another purpose of the present investigation was to shed some light on the mechanism by which the main reaction products are formed. In this regard some authors, on the basis of the proximity of the activation energies, proposed the same intermediate species for hydrocarbon (CH_4) and C_2-oxygenated (C_2H_5OH, CH_3CHO) product formation (*3, 14*). Accordingly, rate data have been acquired over a broad range of reaction conditions and the obtained information has been discussed in the context of reaction mechanism.

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EXPERIMENTAL

Catalyst. The catalyst was prepared as described in Ref. (*15*). $Rh_4(CO)_{12}$ was dissolved in pentane and chemisorbed on suspended ZrO_2 (99.9% from Strem Chemicals). The oxide (70–140 mesh with a surface area of 70 m^2/g) was first treated for 10 h in inert gas at 450°C to obtain a tetragonal/monoclinic phase ratio corresponding to an X-ray diffraction peak intensity ratio of $I_t/I_m = 100/95$ (diffraction peaks at maximum intensity). The catalyst, whose characteristics were reported previously (*11*), was charged into the reactor under inert gas and activated with H_2 at 250°C for 12 h. The treatment was repeated for 2 h before each catalytic test.

Apparatus and procedure. Runs were performed in a stainless-steel (AISI 316) tubular reactor (length 45 cm, i.d. 0.8 cm) heated in a ventilated oven. A thermocouple was placed in the middle of the catalytic bed which was a solid blending (1 : 30) of catalyst and carborundum greater than 200 mesh to obtain better control of the temperature. Carborundum was also added to fill the reactor. A temperature interval of 200–280°C and pressure range of 1–25 atm were investigated using H_2/CO gas-mixture ratios of 2, 3, and 5. Integral and differential runs were performed by varying the space velocity (SV) of the feed. Premixed CO/H_2 mixtures and 99.99% pure H_2 (to activate the catalyst) were supplied through two independent lines, from cylinders equipped with pressure control valves. Flow was maintained at the desired level by two electrically heated fine metering valves at the outlet of the reactor and checked by a flowmeter. When acetaldehyde was supplied to the catalytic bed, the CO/H_2 flowed through a saturator kept at −50°C.

Analysis. One milliliter of product gas mixture was sampled periodically in a heated (110°C) eight-port valve and analyzed simultaneously by two gas chromatographs equipped with hot-wire detectors (H_2 carrier gas 25 ml/min): (A) analysis of volatile products—Porapak QS column (length 4 m, i.d. 2 mm), isothermal at 30°C; (B) analysis of C_1–C_5 fractions—Porapak R column (length 6 m, i.d. 2 mm), isothermal at 140°C.

Data were obtained on the basis of identified products having a retention time less than 45 min from type B analysis. Carbon efficiency was calculated by the formula $n_iC_i/\Sigma n_iC_i$ where n_i is the carbon atom number of the C_i compound. The analytical results adequately satisfied CO material balance.

RESULTS

Table 1 reports a comparative analysis between the most significant rates of formation of CH_4 and C_2H_5OH observed at low conversions within the frame of this investigation. Our data agree with those in the literature (*3*, *9*). The accumulated data can be described by a power-law rate expression of the form

$$r = k_0 e^{-E/RT} P_{H_2}^x P_{CO}^y.$$

It may be seen (Table 2) that the activation energies are almost unaffected if the total pressure is varied between 1 and 12.5 atm. However, if the composition of the reacting mixture is varied at constant pressure, then only the activation energy for ethanol synthesis seems to be unaltered. As for differences in the partial pressure dependence with respect to CO disappearance and CH_4 formation, it may be seen that they agree fairly well with existing data. In any case the CO dependence is of a weakly negative order, while the H_2 dependence is of a

TABLE 1

Rate of Product Formation[a]

No.	T (°C)	P (atm)	SV (h^{-1})	CO conversion (%)	Rate [mmol $(g\ Rh)^{-1}\ h^{-1}$]		
					CH_4	CH_3OH	C_2H_5OH
1	250	1	7290	4.2	93	8	26
2[b]	200	1	729	4	4	0.5	5
3	220	1	729	12.3	25	9	19
4[c]	250	5	729	7.3	9	0.2	7
5	200[d]	1	350	—	7	2.5	4.5[e]
6	243[d]	10	1200	4	8	1	8.4[e]

[a] Tubular reactor; catalyst, Rh/ZrO_2 (1.4% Rh); $H_2/CO = 3$.

[b] $H_2/CO = 5$.

[c] $H_2/CO = 3/2$.

[d] Ichikawa (*9*).

[e] C_{2ox} total.

TABLE 2

Hydrogenation of CO: Kinetic Parameters over Rh/ZrO_2

P (atm)	H_2/CO ratio	CO conversion			CH_4 formation			C_2H_5OH formation		
		E_{act} (kJ mol^{-1})	x^b	y^b	E_{act} (kJ mol^{-1})	x^b	y^b	E_{act} (kJ mol^{-1})	x^b	y^b
1	3	95.4	+0.34	−0.34	116	+0.45	−0.55	71.5	+1	−1
1	5	183			232			77.4		
12.5	3	101			119			77.4		
1[a]	2	—	—	—	121	+0.8	−0.4	96	+1	+0.3

[a] Data of Ichikawa and Shikakura (*3*).
[b] $v = P^x_{H_2}P^y_{CO}$.

weakly positive order. This seems to imply an inhibiting effect, which may be due to a preferential adsorption of CO with respect to hydrogen (*16–18*). In the case of ethanol synthesis the discrepancies reported in the literature concerning the dependence on H_2 and CO partial pressure (*19*) have not been resolved. However, this effect may be partially due to the intermediate formation of acetaldehyde, as suggested by the data in Table 3.

At higher conversions (>10%) the product distribution has been expressed in terms of carbon efficiencies. The influence of different experimental parameters, such as temperature and space velocity (Table 4), composition of the reacting mixture, and pressure (Table 5), can be directly evaluated.

DISCUSSION

To express the fractional coverage of free catalyst surface in terms of H_2 and CO partial pressure we have considered the data reported in Table 3. These data strongly imply that acetaldehyde is easily hydrogenated to ethanol, probably on the same sites that preside over its formation. Accordingly, in agreement with earlier findings (*20*), it may be assumed "by θ_v we define the fraction of free sites while by $\overline{\theta_{CH_3CHO}\theta}$ we define the diadsorbed acetaldehyde" that ethanol formation occurs through an acyl intermediate:

$$\theta_{CH_3} + \theta_{CO} \rightleftharpoons \theta_{CH_3CO} + \theta_v, \qquad (1)$$

$$\theta_{CH_3CO} + H_2 + \theta_v \rightleftharpoons \theta_{CH_3CHO} + \theta_H, \qquad (2)$$

$$\theta_{CH_3CHO} + \theta_v \rightleftharpoons \overline{\theta_{CH_3CHO}\theta}, \qquad (3)$$

$$\overline{\theta_{CH_3CHO}\theta} + 2\theta_H \rightarrow CH_3CH_2OH. \qquad (4)$$

As an alternative to Eq. (1) methane formation may be derived by interacting ad-

TABLE 3

Hydrogenation of Acetaldehyde over Rh/ZrO_2 (Rh = 1.4%)[a]

AcH (m*M*, $\times 10^{-2}$)	CO (conv. %)	Carbon efficiency (%)							
		CH_4	CO_2	CH_3OH	C_2H_5OH	C_{2+4}	C_3	C_5	AcH
0	14.3	60.8	4.7	1.3	16.2	7.2	5.6	2.2	1.6
50	12.1	33.7[b]	2	0.6	42.1	3.9	6.3	4.3	4.2
50	12.1	60.6[c]	4.8	1.1	7.5	6.9	11	7.5	—

[a] Flow reactor; $T = 250°C$; $P = 1$ atm; SV = 3300 h^{-1}; $H_2/CO = 3$; ethyl ether has the same retention time as the C_5 fraction.
[b] Carbon efficiency calculated for comparative purposes on total carbon feed.
[c] Calculated on converted CO only assuming that AcH gives ethanol.

TABLE 4

Effect of Temperature and Spatial Velocity on H_2/CO

No.	T (°C)	P (atm)	SV (h^{-1})	CO (conv.%)	Carbon efficiency (%)					
					CH_4	CO_2	CH_3OH	C_2H_5OH	C_n	AcH
1	250	1	7290	4.2	53	9	0.2	30	6	2
2	220	1	719	16	57	12	2.5	15	10	0.2
3	250	1	719	45	74	10	0.1	5	10	0.4
4	280	1	719	71	88	8	n.v.	0.4	3	n.v.

[a] Tubular reaction: $H_2/CO = 3$; $1 < n \leq 5$.

sorbed hydrogen and the CH_3 moiety on the surface:

$$\theta_{CH_3} + \theta_H \rightarrow \theta_{CH_4}. \tag{5}$$

It should be stressed that this approach involves no assumption regarding the rate-determining step of the whole process. Furthermore, all the steps are in quasi-equilibrium, except Eqs. (4) and (5) where, due to thermodynamic considerations, the reverse reactions have been neglected.

In the first approach, the equations for ethanol and methane formation,

$$\begin{aligned} r_{C_2H_5OH} &= k_4 \overline{\theta_{CH_3CHO}\theta'}\,\theta_H^2 \\ &= k_4 \left(K_1K_2K_3\theta_{CH_3}\theta_{CO}P_{H_2}\frac{\theta_v}{\theta_H} \right) \theta_H^2 \\ &= k'\theta_{CH_3}\theta_{CO}\theta_v\theta_H P_{H_2}, \end{aligned} \tag{6}$$

where $k' = k_4K_1K_2K_3$, and

$$r_{CH_4} = k_5\theta_{CH_3}\theta_H \tag{7}$$

can be used to define the selectivity S

$$\begin{aligned} S = \frac{r_{C_2H_5OH}}{r_{CH_4}} &= \frac{k'\theta_{CH_3}\theta_{CO}\theta_v\theta_H P_{H_2}}{k_5\theta_{CH_3}\theta_H} \\ &= k''\theta_{CO}\theta_v P_{H_2} \end{aligned} \tag{8}$$

where $k'' = k'/k_5$. Equation (8) may be further simplified if (see below) the fractional coverage of catalyst surface by adsorbed CO is defined as

$$\theta_{CO} = K_{CO}P_{CO}\theta_v, \tag{9}$$

"where K_{CO} is the adsorption equilibrium constant as illustrated by Eq. (13)," thus obtaining

TABLE 5

Effect of H_2/CO Ratio and Pressure on Product Distribution[a]

No.	H_2/CO	P (atm)	SV (h^{-1})	CO (conv.%)	Carbon efficiency (%)					
					CH_4	CO_2	CH_3OH	C_2H_5OH	C_n	AcH
1	3/1	1	719	36.3	72	8	0.2	9	9	0.5
2	3/2	1	729	12.5	51	8	0.3	26	12	2
3	3/1	1	7290	4.2	53	9	0.2	30	6	2
4	5/1	1	7290	34.7	86	2	0.02	4	6	0.3
5	5/1	10.5	7290	7.6	65	5	3	22	4	1
6	3/1	4	719	41	72	6	0.8	15	6.2	0.3
7	3/2	5	729	7.3	37	9	1	41	9	4

[a] Flow reactor; catalyst = Rh/ZrO_2 (1.4%); $T = 250$°C. Runs 1–4 have to be considered two by two, as indicated. Further speculation should be avoided since, with a $H_2/CO = 5$ ratio under the conditions reported for runs 1 and 2, total conversion of CO is observed with almost exclusive formation of CH_4, while with a $H_2/CO = 3/2$ ratio under the conditions reported for runs 3 and 4, very low conversion (<0.5%) of CO is observed, with formation primarily of ethanol.

$$S = k'''P_{CO}P_{H_2}\theta_v^2 \tag{10}$$

where $k''' = k''K_{CO}$. Equation (10) can be equated to the selectivity derived from the experimental rate equation,

$$S = \frac{k_{Et}P_{H_2}P_{CO}^{-1}}{k_{CH_4}P_{H_2}^{0.45}P_{CO}^{-0.55}} = k_{exp}P_{H_2}^{0.55}P_{CO}^{-0.45}, \tag{11}$$

to express the fraction "where $k_{exp} = k_{Et}/k_{CH_4}$ is the ratio of kinetic constants of ethanol and methane formation" of free catalyst surface,

$$\theta_v = A[P_{H_2}^{-0.45}P_{CO}^{-1.45}]^{0.5}, \tag{12}$$

where $A = k_{exp}/k'''$.

It may be seen that θ_v is poorly affected by the hydrogen partial pressure while a stronger dependence on CO partial pressure seems to be operative. With these constraints in mind, a number of kinetic sequences were examined that incorporated the breaking of the carbon–oxygen bond. Only one sequence has been found that is consistent in all respects with the experimental results (*21*).

Carbon monoxide is known to chemisorb strongly on transition metals (*16, 22*) while the more weakly bound hydrogen competes for adsorption on the small number of available metal sites remaining. If the metal surface is preferentially saturated with CO, the rate of reaction might be expected to be dependent upon the strength of metal–adsorbate bond. Accordingly, the following sequence of elementary steps is proposed:

$$CO + \theta_v \rightleftharpoons \theta_{CO} \tag{13}$$

$$H_2 + 2\theta_v \rightleftharpoons 2\theta_H \tag{14}$$

$$\theta_{CO} + \theta_v \rightleftharpoons \theta_C + \theta_O \tag{15}$$

$$\theta_C + \theta_H \rightleftharpoons \theta_{CH} + \theta_v \tag{16}$$

$$\theta_{CH} + \theta_H \rightleftharpoons \theta_{CH_2} + \theta_v \tag{17}$$

$$\theta_{CH_2} + \theta_H \rightleftharpoons \theta_{CH_3} + \theta_v \tag{18}$$

$$\theta_O + H_2 \rightarrow H_2O + \theta_v \tag{19}$$

Here, the last step proceeds very rapidly and does not influence the kinetics of the reaction. This model is similar to that proposed earlier by Wang *et al.* (*23*) while studying the CO hydrogenation to methane on Pd catalysts.

The scheme reported above implies that CO, C, and O are adsorbed on one surface atom whereas H$_2$ is adsorbed on two surface atoms. However, CO may adsorb on metal sites corresponding to three or four atoms as evidenced by CO adsorption on silver–palladium alloys (*24*). Moreover, IR spectroscopy on differently supported Rh crystallites reveals different species. Under CO pressure the formation of *gem*-dicarbonyl species has been shown, while the contributions from linear or bridged CO are negligible (*25*). However, special attention should be focused on the identification of surface species formed during the reaction. By using *in situ* IR spectroscopy it has been shown that above 200°C, only the linearly bonded CO exists on supported Rh catalysts in a detectable concentration on the surface during the reaction (*26*). In addition, the formation of surface C was also detected and its amount increased with increasing temperature. Accordingly, we feel that the assumptions reported above may be justified.

Under stationary conditions the rates of disappearance of adsorbed oxygen and carbon can be equated. Specifically, the rate of water formation may be equated to the rate of methane and ethanol formation from adsorbed CH$_3$, as indicated in Eqs. (7) and (6). If the rate-determining step (RDS) is the hydrogenation of adsorbed carbon [Eqs. (16)–(18) to form a CH$_y$ moiety on the surface (*27*), then (see below) it may be assumed that

$$r_{RDS} = k\theta_C\theta_H^y = k_{19}\theta_O P_{H_2} \tag{20}$$

where y = number of hydrogen atoms involved in the rate-determining step.

The oxygen coverage is thus given by

$$\theta_O = \frac{k}{k_{19}}\frac{\theta_C\theta_H^y}{P_{H_2}} \tag{21}$$

which can be used to obtain the carbon coverage through

$$K_{15}\theta_{CO}\theta_v = \theta_C\frac{k\theta_C\theta_H^y}{k_{19}P_{H_2}} \tag{22}$$

and

$$\theta_C = \left[K_{15} \frac{k_{19}}{k} P_{H_2} \frac{\theta_{CO}\theta_v}{\theta_H^y} \right]^{0.5}. \quad (23)$$

The rate of reaction then is

$$r_{RDS} = [K_{15} k k_{19} P_{H_2} \theta_{CO} \theta_v \theta_H^y]^{0.5}. \quad (24)$$

By substituting Eq. (9), Eq. (12), and

$$\theta_H = (K_{14} P_{H_2})^{0.5} \theta_v \quad (25)$$

in Eq. (24) and by expressing y algebraically, we obtain

$$r = k^{IV} P_{H_2}^{0.34} P_{CO}^{-0.34} \quad (26)$$

where $k^{IV} = [K_{15} k k_{19} K_{CO} K_{14}^{y/2} A^{(y+2)}]^{0.5}$ which satisfactorily confirms the experimental data.

Normally, the number of H atoms interacting in the rate-determining step should be an integer from 1 to 3 if the RDS involves a two-body or a multiple improbable interaction. In this case, considering the nonintegral value of y obtained, it is reasonable to assume as a limiting value $y = 0$ or $y = 1$. If $y = 0$ the H_2 dependence is zero and the rate of reaction necessarily implies a dissociative adsorption of CO:

$$r_{RDS} = K_{15} \theta_{CO} \theta_v. \quad (27)$$

By substituting Eq. (9) and Eq. (12) into Eq. (27), it can be shown that

$$r_{RDS} = k^V P_{H_2}^{-0.45} P_{CO}^{-0.45} \quad (28)$$

with $k^V = k_{15} K_{CO} A$, while we have found that the hydrogen partial pressure positively affects the rate. If $y = 1$, only one hydrogen atom is involved in the RDS and the rate of reaction becomes

$$r_{RDS} = k_{16} \theta_C \theta_H. \quad (29)$$

By substituting Eq. (23) into Eq. (29) and Eqs. (9), (12), and (25) into the result, and simplifying, we obtain

$$r_{RDS} = k^{VI} P_{H_2}^{0.41} P_{CO}^{-0.6} \quad (30)$$

where $k^{VI} = (A^3 K_{CO} K_{14}^{0.5} K_{15} k_{16} k_{19})^{0.5}$ which agrees satisfactorily with the experimental results. It may be seen that the calculated dependence on CO partial pressure is slightly overestimated. However, it should be observed that the CO disappearance is not regulated only by its reaction with H_2 since it is also affected by the formation of ethanol.

Finally, the rates of methane [Eq. (7)] and ethanol [Eq. (6)] formation may be equated to the rate-determining step [Eq. (24)]:

$$k_5 \theta_{CH_3} \theta_H + k' \theta_{CH_3} \theta_{CO} \theta_v \theta_H P_{H_2} = (K_{15} k k_{19} P_{H_2} \theta_{CO} \theta_v \theta_H)^{0.5}. \quad (31)$$

Under stationary conditions θ_{CH_3} may be expressed explicitly from Eq. (31). Assuming that

$$k_5 \gg k' \theta_{CO} \theta_v P_{H_2} \quad (32)$$

we obtain

$$\theta_{CH_3} = \left(\frac{K_{15} k k_{19}}{k_5^2} P_{H_2} \frac{\theta_{CO}\theta_v}{\theta_H} \right)^{0.5}. \quad (33)$$

Thus, by substituting Eq. (33) into Eq. (7) and Eqs. (9), (12), and (25) into the result, and simplifying, we obtain dependences on H_2 and CO partial pressures that agree with the experimental values. Similarly, if we substitute Eq. (33) into Eq. (6) and Eqs. (9), (12), and (25) into the result, after simplification we confirm the data obtained for ethanol and the validity of Eq. (32).

Equation (30) is consistent with the selectivities obtained by using the data reported in Table 2 since it increases or decreases on increasing the H_2 or CO partial pressures. On an increase in the CO partial pressure the CO dissociation is emphasized and this beneficially affects the formation of methane, whereas the rate of ethanol formation is more affected by an increase in the H_2 partial pressure. From what has been discussed above it is clear that no definite conclusion can be drawn yet because of the limited and contradicting information found in previous studies on the dependence on H_2 and CO partial pressure. The rate parameters determined from the present measurements disagree with those given by Ichikawa and Shikakura (*13*); moreover, the rate data obtained by the latter authors differ from those reported by Underwood and Bell (*19*) in the case of Rh/La_2O_3. In this respect it should be noted, however, that the role of the support cannot be disregarded. We have already anticipated that a number of basic oxides having weak acidity, such as La_2O_3, CeO_2, TiO_2, ZrO_2, and ThO_2, act as promoters for the formation of C_2-oxygenated products when used as carriers for dispersing Rh clusters. In contrast, the same Rh precursors impregnated on acidic oxides, such as SiO_2, γ-Al_2O_3, Zeolite 13X, V_2O_5, and WO_3, produce largely methane and higher hydrocarbons. Since Rh clusters supported on basic oxides are known to be active for olefin hydroformylation, while when supported on acidic supports they are virtually inactive (*28, 29*), it may be provisionally assumed in agreement with our kinetic assumptions that ethanol formation may be rationalized in terms of a base-promoted CO insertion into the surface CH_x moiety. This, however, does not explain the conflicting evidence found when using the same support ZrO_2: contrary to Ichikawa's data (*9*) and to our results, Tiruka *et al.* (*10*) do not report the formation of C_2-oxygenated products. Rather, these differences can be attributed to different activating conditions. Indeed, it has been reported (*30*) that the strength of the acidic and basic properties of the active sites depend on the temperature. For ZrO_2, the basic properties are more pronounced at 500°C rather than 700°C, whereas for the acidic properties the opposite is true. Furthermore, it has been reported that at 600–700°C, the low-temperature metastable tetragonal form of zirconia (*31*) is converted into the monoclinic form. At 500, 600, and 700°C we have found 14, 60, and 94% of the monoclinic form, respectively (unpublished); accordingly, under our experimental conditions for the ZrO_2 activation, we never excluded 600°C in order to optimize the basic and acidic requirements. References (*9, 10*) do not report the phase composition used.

When dealing with higher conversions, it may be observed that on increasing the space velocity (see Table 4, runs 1 and 3), in agreement with Kuznetsov *et al.* (*4*), the C_2H_5OH/CH_4 ratio increases in terms of carbon efficiency while the ethanol yield decreases. On increasing the reaction temperature (see Table 4, runs 2–4) while the yield of methane increases, the yield of ethanol decreases specifically between 250 and 280°C. Based on the activation energies it is reasonable that methane formation is more affected by the temperature than ethanol formation; it may also be assumed that an increase in space velocity inhibits any further evolution of ethanol (*4*).

As for the effect of the reaction mixture, on increasing the CO partial pressure (Table 5, runs 1, 2 and 3, 4) the CO conversion decreases; furthermore, while the yield of ethanol seems unaffected, the C_2H_5OH/CH_4 ratio increases in terms of carbon efficiency. It may also be seen that with three different H_2/CO ratios, on increasing the total pressure (Table 5, runs 2–7, and Table 4, run 3) the ethanol-to-methane carbon efficiency ratio sharply increases in agreement with a few indications given by Ichikawa (*9*).

CONCLUSION

The present results demonstrate that under appropriate experimental conditions it is possible to obtain, at low conversions, much smaller amounts of methanol than with other catalysts (*4, 5*); the results can thus be discussed mainly in terms of the C_2H_5OH/CH_4 ratio. At higher conversions the same trend for methanol is confirmed, but a clearer interpretation of the results, which are intriguing and sometimes unexpected, must await the development of a better understanding of metal–support interactions and their influence on catalyst activity and selectivity. Comparison of the obtained rate expressions seems to suggest that the hydrogenation of acetaldehyde may indeed be a major pathway to ethanol.

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