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Mechanism of Ethanol Formation from Synthesis Gas over $CuO/ZnO/Al_2O_3$

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The formation of ethanol from CO and H_2 over a CuO/ZnO methanol catalyst was studied in a fixed-bed microreactor by measuring the isotopic distribution of the carbon in the product ethanol when ^{13}C methanol was added to the feed. The purpose of this work was to determine whether experimental support could be obtained for any of the various mechanisms proposed in the literature for the synthesis of ethanol over methanol catalysts. The methanol was added at six partial pressures so that the ratio of methanol to CO ranged from 1 : 34 to 1 : 250. For each feed ratio the isotopic composition of the reaction products was determined at various contact times from 0.5 to 10 s, and the composition at zero contact time was determined by extrapolation. All four isotopic species possible for ethanol, $^{12}CH_3{}^{12}CH_2OH$, $^{12}CH_3{}^{13}CH_2OH$, $^{13}CH_3{}^{12}CH_2OH$, and $^{13}CH_3{}^{13}CH_2OH$, were observed; there was no scrambling of the carbon atoms of ethanol. Contrary to what is expected for the formation of ethanol either by condensation or by homologation of methanol, the fraction of carbon-13 in the ethanol at zero contact time was a function of the partial pressure of ^{13}C methanol in the feed. Also, at low contact times a large fraction of the product ethanol was doubly labeled which is incompatible with the formation of ethanol by carbonylation of formaldehyde, methoxide, or other C_1 species. The isotopic distribution of the ethanolic carbon was consistent with a mechanism that involves a C_1 species that is an intermediate in the formation of both ethanol and methanol. © 1988 Academic Press, Inc.

INTRODUCTION

The synthesis of methanol from CO and H_2, catalyzed either by classical high-temperature, high-pressure metal oxide systems, or by the more recently developed Cu-based catalysts, often is accompanied by the formation of small amounts of higher alcohols. The selectivity to higher alcohols can be enhanced significantly by promoting the catalysts with alkali and by carrying out the synthesis at higher temperatures and lower H_2/CO ratios than those used for the selective methanol synthesis. This approach to the synthesis of higher alcohols has been studied for nearly 60 years; the early work, before 1957, has been reviewed by Natta *et al.* (*1*); more recent work has been summarized by Pasquon (*2*).

Much of this work has been empirical. Although several hypotheses have been advanced over the years to explain the formation of higher alcohols over methanol synthesis catalysts (*1–4*), little is in fact known about the mechanism of the reaction. It is convenient, for a discussion of the reaction mechanism, to distinguish two steps in the formation of higher alcohols: (a) the initial carbon–carbon bond formation and (b) the subsequent chain growth. This paper deals with the first step and the formation of ethanol; the synthesis of propanol and higher alcohols will be discussed in a subsequent report. Several mechanisms have been proposed for the formation of ethanol over methanol synthesis catalysts. One of the earliest is that of Frolich and Cryder (*5*), who concluded that ethanol is formed mainly by condensation of methanol, and, to a minor degree, by homologation of methanol as proposed by Fischer (*6*). According to Frolich (*7*) the condensation reaction occurs by dehydration of two molecules of methanol to form methyl ether,

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which rearranges to form ethanol. In Fischer's mechanism (*6*), carbon monoxide reacts with methanol to form acetic acid, which is reduced stepwise to acetaldehyde and to ethanol.

Graves (*8*) also assumed that ethanol is formed by condensation of two methanol molecules, but proposed that the synthesis takes place by direct dehydration involving the hydroxyl group of one methanol and a hydrogen on the carbon of the other. Graves developed a chain growth scheme based on the formation of higher alcohols by analogous dehydrocondensation of two lower alcohols. Smith and Anderson (*9*) have used Graves's ideas to derive equations describing the alcohol distributions observed over $CuO/ZnO/Al_2O_3$ (*10*), and have suggested a surface carbinol species as an intermediate in the formation of ethanol.

Many workers have postulated (*11*) that formaldehyde is an intermediate in the synthesis of higher alcohols, either as a free molecule (*12*) or as a surface bound intermediate (*4, 13*). Morgan (*14*), for example, proposed that two formaldehyde molecules condense to form glycolaldehyde, which, by successive dehydration and hydrogenation, is converted to ethanol. This mechanism has been considered very unlikely (*1*) because the equilibrium partial pressure of formaldehyde is very low at the conditions of higher alcohol synthesis. These thermodynamic limitations are overcome if the formaldehyde remains bound to the catalyst surface. Recently Mazanec (*4*), has postulated that over metal oxide catalysts the primary carbon–carbon bond formation step is a CO insertion into the metal–carbon bond of a bound formaldehyde. Natta (*1*), on the other hand, proposed that the surface species which reacts with CO is a methoxide, and Vedage *et al.* (*3*) have assumed a similar mechanism for the formation of ethanol over Cu/ZnO.

This paper reports a study aimed at establishing the viability of the various mechanisms proposed in the literature. In this study, the formation of ethanol from CO and H_2 over a commercial $CuO/ZnO/Al_2O_3$ methanol synthesis catalyst was measured in the presence of ^{13}C methanol and the incorporation of the labeled carbon into the ethanol was monitored to determine the role played by methanol in the formation of ethanol.

EXPERIMENTAL METHODS

Apparatus. The reaction of methanol with synthesis gas at 20 atm was studied using the apparatus drawn schematically in Fig. 1. The flow rates of hydrogen and of carbon monoxide were measured and controlled individually with Matheson mass flow controllers. Methanol was added to the H_2–CO mixture in a saturator held at constant temperature (±0.5°C), using a water bath. The saturator, which was 2 in. long and 0.20 in. in inside diameter, was filled with one gram of 16-mesh alundum to provide surface area for evaporation of the liquid. All lines downstream of the saturator were maintained at temperatures higher than that of the saturator to avoid condensation of the additive. The reactants were passed continuously through the reactor. The reactor was 2 in. long, and its inside diameter was .085 in.; the catalyst charge was held in place with stainless steel fritted disks. The saturator, the reactor, and all the lines were constructed of 316 stainless steel.

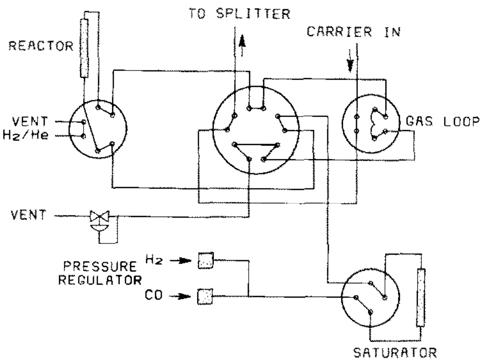


FIG. 1. Apparatus.

Samples of the reactor effluents were taken at reaction pressure using a Valco sampling valve. The samples were passed into the split injector of a Hewlett–Packard chromatograph equipped with an FID detector and a Hewlett–Packard 5970B mass selective detector. Two 50-m cross-linked methyl silicone capillary columns were used, one leading to the FID, the other to the mass selective detector. The mass spectrometer data were obtained using the selected ion monitoring mode of the detector.

Procedure. At the beginning of each day the mass selective detector was tuned with perfluorotributylamine. A charge of fresh catalyst, 100 mg, was loaded into the reactor and purged for 30 min with helium flowing at 20 ml/min while the temperature was raised to 200°C. The catalyst was reduced for 2 h at 200°C with a mixture of 8.5 vol% hydrogen in helium at 20,000 GHSV, then purged with helium at the same space velocity while the temperature was raised to 285°C. The pressure was raised to 20 atm and an equimolar mixture of H_2 and CO was introduced into the system. The H_2/CO mixture was passed over the catalyst at space velocities ranging from 7400 to 148,000 ml/ml catalyst/h. After the activity was measured at several space velocities, the H_2/CO mixture was passed through the saturator and the experiment was repeated with the methanol in the feed. In each experiment the first activity measurement was made 15 min after adjusting the flow rate for the desired space velocity, the others were made after 8 min. At the end of each experiment the reactor was bypassed and the feed mixture containing the additive was analyzed at each flow rate to ensure that liquid–vapor equilibrium had been reached in the saturator. Generally, the saturator was loaded with the methanol while the catalyst was being reduced; it was evacuated briefly to remove air, and its temperature was adjusted as required to obtain the desired vapor pressure. The bath temperatures were calculated from the equation of Yaws (*15*), assuming that there was no isotope effect on the vapor pressure of the liquid. The vapor pressures were 30, 40, 80, 128, 130, 222 Torr, corresponding to methanol : CO ratios of 1 : 253, 1 : 190, 1 : 95, 1 : 59, 1 : 58, and 1 : 34. All experiments were carried out at 285°C and 20 atm with a H_2/CO ratio of 1.

Materials. The catalyst used in this study, a $CuO/ZnO/Al_2O_3$, was a commercial methanol synthesis catalyst supplied by UCI in the form of 0.25-in. tablets. Its UCI designation was C79-2. Before use, the catalyst was crushed, sieved to 16/40 mesh size, and calcined in air at 350°C for 4 h. The carbon-13 labeled methanol (99.6 atom% carbon-13) was obtained from MSD Isotopes, and the unlabeled methanol used in preliminary tests from Fischer (reagent grade); they were used as received. Carbon monoxide and hydrogen were supplied by Matheson Gas Products. The carbon monoxide (Matheson purity, 99.99%) was passed through an activated charcoal trap to remove metal carbonyls, the hydrogen (UHP grade, 99.999%) was used as received. The helium (Linde, Chromatographic Grade, 99.9999%) used as the carrier gas for the GC–MS analyses was passed through an "oxy-trap" filter to remove oxygen and through a 13-X mole sieve trap to remove water.

RESULTS

Addition of ^{13}C methanol to the feed. At the experimental conditions employed in this study (285°C, 20 atm, and $H_2/CO = 1$) the equilibrium partial pressure of methanol was calculated to be 327 Torr, using the equation derived by Cherednichenko (*16*). ^{13}C methanol was added to the feed at six partial pressures, all lower than the equilibrium partial pressure, ranging from 222 to 30 Torr (see Table 1), so that the ratios of methanol to CO were 1 : 34, 1 : 58, 1 : 59, 1 : 95, 1 : 190, 1 : 253. For each of these feed ratios the partial pressures of methanol and ethanol in the reactor effluents were measured at various contact times from 0.5 to 10 s. The experiments were performed at nearly differential reactor conditions with

TABLE 1

Feed Composition

Test no.	P_{MeOH} (Torr)	Percent of feed carbon present as	
		Methanolic carbon	Carbon-13[a]
1	30	0.39	1.5
2	30	0.39	1.5
3	40	0.52	1.6
4	80	1.0	2.1
5	128	1.7	2.8
6	130	1.7	2.8
7	222	2.8	3.9
Control (1a–7a)	0	0	1.1

Note. In all tests $P_{H_2} = P_{CO} = 7600$ Torr.

[a] Includes the methanolic carbon and the naturally occurring carbon-13 (1.1%) in the carbon monoxide.

less than 4% overall conversion of CO. The catalyst was used without alkalization, and the selectivity to methanol was always greater than 95%. In addition to methanol, higher alcohols were formed, among which ethanol was predominant; small amounts of methyl formate were also observed.

Methanol and ethanol yields. The partial pressures of methanol and of ethanol in the reactor effluents are listed as a function of contact time in Table 2 for each of the six methanol to CO feed ratios (tests 1–7) and for the corresponding control tests carried out without methanol in the feed (tests 1a–7a). In the experiments in which methanol was present in the feed the partial pressures of methanol in the effluents were pronouncedly higher than in the control tests only at low contact times; at higher contact times the two became nearly identical as the partial pressure of the product methanol in the control exceeded that of the methanol added to the feed. This behavior is illustrated in Fig. 2, where the partial pressure of methanol in the products is plotted as a function of contact time for the experiment in which the partial pressure of ^{13}C methanol in the feed was 80 Torr (test 4) and for the corresponding control experiment (test 4a).

For these same experiments the partial pressures of ethanol are also plotted in Fig. 2. There is no indication in the plot that the addition of methanol to the feed influenced strongly the formation of ethanol. However, at the two lowest contact times the partial pressure of ethanol in the experiment in which methanol was added to the feed was significantly higher than in the control experiment. A similar increase in the ethanol partial pressure, in the range of contact times where the partial pressure of the effluent methanol was much higher than in the control test, was observed for other methanol to CO feed ratios (see Table 2). These results appear to be in accord with Smith and Anderson's observation (*9*) that over an alkalized $CuO/ZnO/Al_2O_3$ at 285°C and 100 atm the yield of ethanol doubled when large amounts of methanol (methanol : CO = 1 : 5.6) were added to a feed with a H_2/CO ratio of 0.9.

Isotopic composition. The fractions of

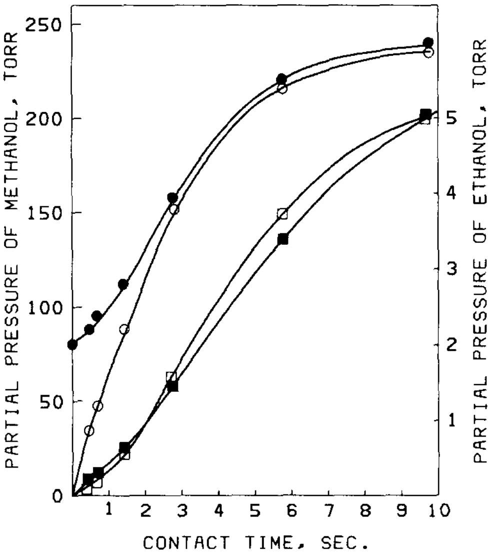


FIG. 2. Outlet partial pressures of methanol (○,●) and of ethanol (□,■) as a function of contact time, when no methanol was present at the inlet (○,□), and when the inlet partial pressure of methanol was 80 Torr (●,■) (tests 4 and 4a).

TABLE 2

Partial Pressures of Methanol and Ethanol in the Reactor Effluent

	Flow rate (cc/min)	200	135	68	34	17	10	
	Contact time (sec)	0.49	0.72	1.4	2.9	5.8	9.7	
	Inlet P_{MeOH}(Torr)	Outlet partial pressures of methanol and ethanol (Torr)						Test No.
Methanol	0	35	52	93	145	209	216	1a
	30	45	53	84	136	219	221	1
Ethanol	0	0.13	0.18	0.56	1.27	3.20	4.22	1a
	30	0.10	0.16	0.32	0.94	2.42	3.02	1
Methanol	0	27	43	86	151	211	216	2a
	30	45	55	85	148	216	223	2
Ethanol	0	0.06	0.15	0.45	1.20	3.27	4.66	2a
	30	0.09	0.17	0.18	0.99	2.71	3.98	2
Methanol	0	35	52	102	155	213	231	3a
	40	54	62	96	143	214	225	3
Ethanol	0	0.09	0.19	0.67	1.44	3.38	4.79	3a
	40	0.12	0.19	0.48	1.15	3.03	4.54	3
Methanol	0	33	47	87	151	216	236	4a
	80	83	93	112	158	221	239	4
Ethanol	0	0.08	0.17	0.53	1.55	3.73	5.00	4a
	80	0.17	0.28	0.62	1.43	3.39	5.05	4
Methanol	0	33	49	90	145	189		5a
	128	129	134	151	185	208		5
Ethanol	0	0.11	0.22	0.80	1.88	3.74		5a
	128	0.30	0.51	1.13	2.04	4.07		5
Methanol	0	24	46	91	150	234		6a
	130	132	138	150	183	239		6
Ethanol	0	0.05	0.13	0.45	1.21	3.72		6a
	130	0.22	0.28	0.70	1.26	3.18		6
Methanol	0	26	49	95	139	193	186	7a
	222	215	218	216	226	214		7
Ethanol	0	0.07	0.17	0.53	1.24	3.55	4.53	7a
	222	0.20	0.36	1.04	1.44	3.39		7

carbon-13 in the product methanol and ethanol are listed in Table 3 for all seven tests and are plotted in Fig. 3 for test 4. The content of labeled carbon in the product methanol was a function of the initial partial pressure of methanol in the feed and of the contact time. The fraction of labeled methanol in the effluent decreased from essentially 100% at zero contact time and approached the concentration of the labeled carbon in the feed, as the contact time increased (see Fig. 3), reflecting increases in both the decomposition of the added methanol and the formation of unlabeled methanol from syngas.

The fraction of labeled carbon in the ethanol also decreased with increasing contact time, but less rapidly than that in the methanol. Unlike methanol, ethanol does not undergo appreciable decomposition over this catalyst (*17*), so that there is not a rapid equilibration of the labeled carbon in the product with that in the feed. In all experiments the abundance of labeled carbon in the product ethanol (5–68%) was always significantly higher than in the feed (1.50–4%). In the feed essentially all of the unlabeled carbon was in the carbon monoxide; the methanol, which was nearly completely (99.6%) labeled, never contributed more

TABLE 3

Carbon-13 Content of the Product Methanol and Ethanol

Contact time (sec)	0	0.49	0.72	1.4	2.9	5.8	9.7	
			% ^{13}C					Test no.
Methanol	100	64	52	29	14	4	1.4	1
Ethanol	(40)[a]	32	39	23	18	11	7	1
Methanol	100	61	47	26	12	4	2	2
Ethanol	(35)	30	28	24	18	9	6	2
Methanol	100	71	58	32	16	4	0.5	3
Ethanol	(46)	39	36	23	19	11	6	3
Methanol	100	86	78	57	29	7	2	4
Ethanol	(60)	56	54	47	32	15	9	4
Methanol	100	91	85	67	37	7		5
Ethanol	(65)	61	60	55	38	19		5
Methanol	100	92	87	70	47	18		6
Ethanol	(63)	58	59	52	44	28		6
Methanol	100	94	91	81	62	21		7
Ethanol	(70)	64	69	61	56	32		7

[a] Values in parentheses were determined by extrapolation (see text).

than 3% of the total carbon in the feed. Because the conversion of carbon monoxide was very low, the partial pressure of carbon monoxide remained essentially constant throughout the tests, so that the abundance of labeled carbon in the carbon monoxide could not be significantly higher than in the feed, even if all the labeled methanol decomposed into carbon monoxide and hydrogen. Therefore, it must be concluded that labeled methanol was incorporated into ethanol without first undergoing decomposition into carbon monoxide and hydrogen.

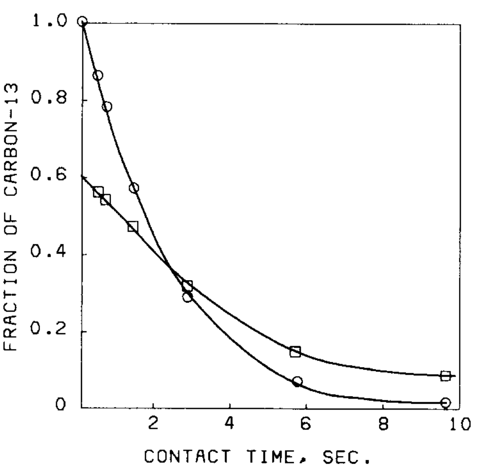


FIG. 3. Fraction of carbon-13 in the methanolic (○) and ethanolic (□) carbon in the product when the partial pressure in the feed was 80 Torr (test 4).

The methanol was not the sole source of the carbon in the ethanol; extrapolation of the curve for ethanol in Fig. 3 to zero contact time shows a significant amount of the ethanolic carbon (40%) to be unlabeled even when essentially all of the methanol was labeled. The percentages of labeled carbon in the ethanol at zero contact time are given in parentheses in Table 3 for all experiments; there is a clear dependence of these values on the partial pressure of the labeled methanol in the feed, contrary to what is expected for the synthesis of ethanol either by condensation or by reductive carbonylation of methanol.

The isotopic distribution of the carbon in the product ethanol is reported in Table 4. All four possible isotopic species were observed, $^{12}CH_3{}^{12}CH_2OH$, $^{12}CH_3{}^{13}CH_2OH$,

TABLE 4

Distribution of Carbon-13 and Carbon-12 in the Product Ethanol

	Contact time (sec)	0.49	0.72	1.4	2.9	5.8	9.7	
	Inlet P_{MeOH}(Torr)	Percentage of product ethanol						Test no.
^{12}C-^{12}COH	30	51.4	41.6	63.3	68.6	81.3	88.0	1
^{13}C-^{12}COH	30	8.2	25.8	12.5	13.7	7.7	4.5	1
^{12}C-^{13}COH	30	26.2	13.4	15.9	13.3	7.9	5.1	1
^{13}C-^{13}COH	30	14.2	19.2	8.3	4.4	3.1	2.4	1
^{12}C-^{12}COH	30	51.1	54.8	61.7	69.2	85.6	91.9	2
^{13}C-^{12}COH	30	15.8	19.0	16.8	13.2	5.0	2.6	2
^{12}C-^{13}COH	30	21.7	15.4	12.9	12.4	5.7	2.7	2
^{13}C-^{13}COH	30	11.5	9.3	8.6	5.3	3.7	2.8	2
^{12}C-^{12}COH	40	42.4	43.9	60.6	66.9	80.9	89.6	3
^{13}C-^{12}COH	40	20.9	24.4	15.3	15.0	7.6	4.0	3
^{12}C-^{13}COH	40	15.8	16.3	16.7	12.8	8.2	4.7	3
^{13}C-^{13}COH	40	20.9	15.4	7.4	5.3	3.4	1.8	3
^{12}C-^{12}COH	80	24.2	26.6	32.7	49.0	75.5	85.0	4
^{13}C-^{12}COH	80	22.9	22.2	22.2	19.7	10.0	6.2	4
^{12}C-^{13}COH	80	15.7	17.6	18.1	18.4	9.9	6.1	4
^{13}C-^{13}COH	80	36.4	33.7	27.0	12.9	4.7	2.7	4
^{12}C-^{12}COH	128	22.9	22.2	24.2	42.0	68.9		5
^{13}C-^{12}COH	128	16.2	15.2	19.7	19.2	10.4		5
^{12}C-^{13}COH	128	15.6	21.1	22.5	20.5	13.3		5
^{13}C-^{13}COH	128	45.4	41.5	33.7	18.2	7.4		5
^{12}C-^{12}COH	130	25.9	24.2	29.5	36.9	55.1		6
^{13}C-^{12}COH	130	15.9	16.9	19.6	19.9	17.9		6
^{12}C-^{13}COH	130	16.2	16.6	16.9	19.1	16.4		6
^{13}C-^{13}COH	130	42.0	42.3	34.0	24.1	10.7		6
^{12}C-^{12}COH	222	24.0	16.8	22.9	25.3	50.5		7
^{13}C-^{12}COH	222	8.9	13.9	18.2	20.3	17.4		7
^{12}C-^{13}COH	222	15.7	14.5	14.3	21.6	12.1		7
^{13}C-^{13}COH	222	51.5	54.8	44.7	36.4	14.3		7

^{13}CH$_3$^{12}CH$_2$OH, and ^{13}CH$_3$^{13}CH$_2$OH. In a control experiment, no scrambling of the carbon atoms of ethanol was observed when ^{12}CH$_3$^{13}CH$_2$OH was passed over the catalyst. This indicates that the isotopic distribution of the carbon in the ethanol arises during the synthesis of ethanol and is not the consequence of subsequent reactions. The relative abundances of the two singly labeled species varied considerably, particularly at low contact time. However, statistically there was no preference for either species. The average ratio ^{13}CH$_3$^{12}CH$_2$OH/^{12}CH$_3$^{13}CH$_2$OH for all the experiments in Table 3 was unity.

The fractions of the doubly labeled, singly labeled, and unlabeled ethanol (α_{LL}, α_{UL}, and α_{UU}, respectively) in test 4 are plotted in Fig. 4 as functions of the contact time. In this experiment, as the contact time (hence the fraction of unlabeled methanol) increased, the fraction of unlabeled ethanol increased and that of the doubly labeled ethanol decreased; the fraction of singly labeled ethanol went through a maximum. The same behavior was observed in

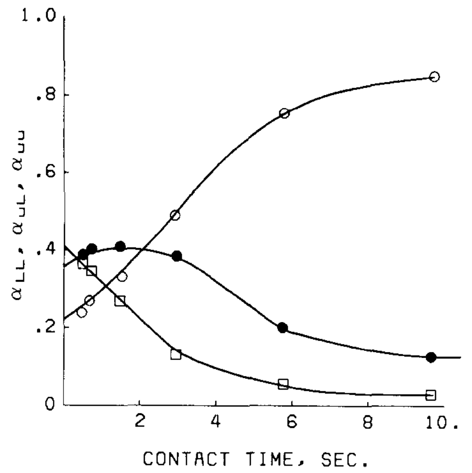


FIG. 4. Fraction of unlabeled, α_{UU} (○), singly labeled, α_{UL} (●), and doubly labeled, α_{LL} (□), ethanol as a function of the contact time in test 4.

all four experiments in which the fraction of carbon-13 in the ethanol, α_L, at zero contact time was greater than that of carbon-12, α_U. In the other three experiments the fraction of the singly labeled ethanol decreased with contact time without going through a maximum. A better illustration of this behavior is provided by Fig. 5, where α_{LL}, α_{UL}, and α_{UU} are plotted as functions of α_U for all seven experiments.

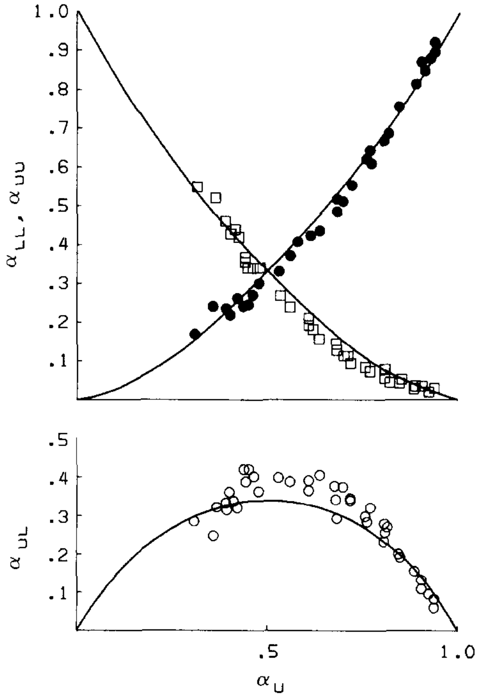


FIG. 5. Predicted (solid lines) and experimental (points) values of α_{LL} (□), α_{UU} (●), and α_{UL} (○) as a function of α_U.

DISCUSSION

As outlined in Fig. 6, the formation of ethanol from CO and H_2 over methanol synthesis catalysts may proceed by one of three main paths: (1) it may occur by a mechanism completely independent of methanol formation, (2) it may involve methanol as an intermediate, or (3) it may involve an intermediate that is common to the synthesis of both methanol and ethanol.

If the synthesis of ethanol is unrelated to that of methanol (path a), the content of labeled carbon in the product ethanol depends solely on the content of labeled carbon in the CO, so that in all the experiments described in this report the fraction of labeled ethanolic carbon at zero conversion should equal the natural abundance of carbon-13 (1.1%). The much larger fraction of labeled ethanolic carbon observed when labeled methanol was present in the feed is incompatible with this route and indicates that the synthesis of ethanol and that of methanol are related. However, the presence of substantial amounts of unlabeled ethanol at zero conversion excludes the participation of methanol as an intermediate in the synthesis of ethanol from CO and H_2. The ethanol should be essentially all doubly labeled if formed by self-condensation of methanol (path e), and at least singly labeled if formed by condensation of metha-

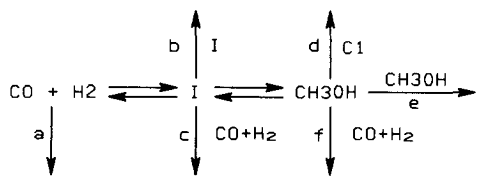
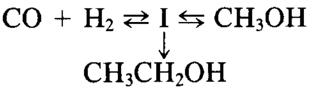


FIG. 6. Potential paths for the formation of ethanol from synthesis gas.

nol with another C_1 species (path d) or by reductive carbonylation of methanol path f). On the other hand, the observation that a large fraction of the ethanol is doubly labeled cannot be reconciled with a mechanism involving the carbonylation of any C_1 species, including I (path c). If ethanol were formed by a carbonylation reaction, no more than 1.1% of the ethanol should be doubly labeled at zero conversion and no more than 4% at higher conversions.

The occurrence of both unlabeled ethanol and doubly labeled ethanol at zero conversion is consistent with the formation of a surface bound C_1 precursor that can be formed either from methanol (labeled carbon) or from syngas (unlabeled carbon):



$$\begin{array}{c} CO + H_2 \rightleftarrows \mathrm{I} \leftrightarrows CH_3OH \\ \downarrow \\ CH_3CH_2OH \end{array} \qquad (1)$$

According to this mechanism the ethanol is formed by a series of parallel reactions,

$$\begin{array}{ll} I_L + I_L \rightarrow & {}^{13}CH_3\text{-}{}^{13}CH_2OH \\ I_L + I_U \rightarrow & \begin{cases} {}^{13}CH_3\text{-}{}^{12}CH_2OH \\ {}^{12}CH_3\text{-}{}^{13}CH_2OH \end{cases} \\ I_U + I_U \rightarrow & {}^{12}CH_3\text{-}{}^{12}CH_2OH, \end{array}$$

where I_L is the C_1 precursor containing carbon-13 and I_U that containing carbon-12.

The fractions of the labeled and of the unlabeled C_1 precursor can be determined from the isotopic distribution of the ethanolic carbon. In the absence of significant isotopic effects in the synthesis of ethanol, the fraction of ethanol that is doubly labeled, α_{LL}, is given by

$$\alpha_{LL} = \mathrm{Rate}_{LL}/(\mathrm{Rate}_{UU} + \mathrm{Rate}_{UL} + \mathrm{Rate}_{LL}), \qquad (2)$$

where Rate_{UU}, Rate_{UL}, and Rate_{LL} are the rates of formation of the unlabeled, singly labeled, and doubly labeled, respectively, two-carbon intermediate from which ethanol is formed. For a reaction occurring by the Langmuir–Hinshelwood mechanism, i.e., with both C_1 precursors in the adsorbed state, the rate expressions are given by

$$\begin{aligned} \mathrm{Rate}_{UU} &= k\theta_U^2 = k\theta^2 x_U^2 \\ \mathrm{Rate}_{UL} &= k\theta_U\theta_L = k\theta^2 x_U x_L \\ \mathrm{Rate}_{LL} &= k\theta_L^2 = k\theta^2 x_L^2 \end{aligned}$$

where k is the reaction constant, θ is the fraction of active surface sites occupied by the C_1 precursor, θ_U that occupied by the unlabeled C_1 precursor, and θ_L that occupied by the labeled C_1 precursor; x_L and x_U are the labeled and unlabeled fractions, respectively, of the adsorbed C_1 precursor so that

$$\theta_U = \theta x_U \quad \text{and} \quad \theta_L = \theta x_L.$$

Therefore, Eq. (2) can be written as

$$\alpha_{LL} = x_L^2/[x_L^2 + x_U x_L + x_U^2].$$

Similar expressions can be written for α_{UL} and α_{LL}. The values of α_{LL}, α_{UL}, and α_{UU} calculated for the entire range of isotopic composition of I, from 0 to 100% labeling, are plotted in Fig. 5 as functions of α_U, the fraction of unlabeled ethanolic carbon. As α_U increases, α_{LL} decreases, α_{UU} increases, and α_{UL} goes through a maximum at a_U = 0.5. The experimental data show a similar behavior. The values of α_{LL}, α_{UL}, and α_{UU} determined in tests 1 through 7 (see Table 4 are also plotted in Fig. 5. There is sufficient agreement between predicted and experimental values to conclude that the formation of ethanol occurs according to Eq. (1), i.e., through an intermediate that is common to the formation of both methanol and ethanol. The nature of this intermediate will be discussed in a subsequent report.

CONCLUSIONS

Many of the mechanisms proposed in the literature over the past 60 years for the synthesis of ethanol from CO and H_2 are not supported by the results of this study. These are mechanisms that either propose the participation of methanol in the synthesis of ethanol, e.g., by condensation of methanol (*5, 6*), or propose that ethanol is formed by carbonylation of a C_1 species such as methanol (*6*), methoxide (*1, 3*), and formaldehyde (*4*). The results instead indicate that the formation of ethanol involves a C_1 species which is also a precursor of methanol.

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