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An Investigation of the Thermodynamic Constraints in Higher Alcohol Synthesis over Cs-Promoted ZnCr-Oxide Catalyst[1]

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A thermodynamic analysis of the oxygenate products of the higher alcohol synthesis (HAS) over an alkali promoted high-temperature methanol synthesis catalyst is performed for a wide range of operating conditions. By comparing actual fugacity ratios with equilibrium constants it is found that a number of reactions approach chemical equilibrium under typical synthesis conditions, namely: (a) formation of methanol; (b) water–gas shift reaction; (c) formation of methyl formate and possibly of higher methyl esters; (d) hydrogenation of aldehydes to primary alcohols; (e) hydrogenation of ketones to secondary alcohols; (f) ketonization reactions. The prevailing thermodynamic constraints determine the relative amounts of primary and secondary alcohols, aldehydes, ketones, esters, and acids. They also explain the experimental effects of temperature, pressure, and feed composition on the same products, as well as some of the differences in product composition observed between the HAS over modified high-temperature and low-temperature methanol catalysts. The observed departures from equilibrium provide insight into the reaction network and information on the mechanism of the synthesis. It is also found that the reactions under thermodynamic control are related to some of the major catalytic functions of ZnCr-oxide systems identified by an independent temperature-programmed surface reaction investigation. © 1990 Academic Press, Inc.

INTRODUCTION

The so-called "modified methanol synthesis catalysts" provide a class of potential industrial catalytic systems for the higher alcohol synthesis (HAS), i.e., the synthesis of mixtures of methanol and higher aliphatic alcohols by direct hydrogenation of carbon monoxide.

It has been known for many years that addition of alkali promoters to the original catalyst formulation is suitable for steering the behavior of methanol catalysts toward production of C_{2+} alcohols in addition to CH_3OH. For the same purpose, adoption of higher reaction temperatures and lower space velocities is also helpful (*1, 2*).

Both Cu-based low-temperature methanol catalysts (*3–6*) and high-temperature methanol catalysts based on mixed oxides of Cr, Zn, and/or Mn (*1, 2, 7–12*) have been modified successfully in this way. Catalysts belonging to the former class are typically operated in the HAS at temperatures below or around 300°C, whereas the reaction temperature is about 400°C for modified high-T methanol catalysts.

Modified low-T and high-T methanol catalysts yield alcohol products containing mainly methanol, 2-methyl-1-propanol (isobutanol), and 1-propanol, with smaller amounts of ethanol and linear or monomethyl branched C_{5+} alcohols. The formation of carbon dioxide, water, and of a number of side products including hydrocarbons, aldehydes, esters, ketones, and secondary alcohols also occurs over both systems. However, when typical product distributions generated by catalysts of the two families are compared, differences become apparent in the relative quantities

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of several compounds. Cu-based catalysts are associated with greater concentrations of methanol and of methyl esters; ZnCr-oxide (or MnCr-oxide and ZnMnCr-oxide) catalysts yield greater amounts of aldehydes and ketones.

The role of thermodynamics in explaining such differences has never been fully investigated. Indeed, a complete analysis of chemical equilibrium limitations affecting the experimental product distributions of the HAS is lacking.

The thermodynamic background of the HAS has been studied in the past on an a priori basis (*2, 13*). Inspection of the changes in Gibbs free energies associated with the major classes of reactions indicates that hydrocarbons are more favored than alcohols. Since alcohols are the main products and only small amounts of olefins and paraffins are formed in the synthesis when a suitable catalyst is used, it can be concluded that the reaction is kinetically controlled and that selectivity is an essential requirement for a HAS catalyst. Nevertheless, a number of reactions occurring in the complex reacting system do approach chemical equilibrium over alkali-promoted methanol synthesis catalysts. This is already known to occur, e.g., for the formation of methanol and for the water–gas shift (WGS) reaction over both low-T (*5, 14*) and high-T (*8*) alkali-promoted methanol synthesis catalysts. However, other reactions are also under thermodynamic control over modified methanol catalysts (*15*).

In this paper a thermodynamic analysis of the HAS over a Cs-doped ZnCr-oxide catalyst is presented. In order to determine whether a specific chemical reaction is limited by chemical equilibrium, the corresponding fugacity ratio, K_f, evaluated from the experimental concentrations of reactants and products measured at the reactor exit, is compared with the equilibrium constant, K_{eq}, estimated from thermodynamic relationships. Such an a posteriori approach does not require any assumptions on the number and the nature of the reactions limited by equilibrium. A thermodynamic analysis along these lines has already been reported in the literature for the Fischer-Tropsch synthesis (*16, 17*).

This approach is applied in the present work to a large spectrum of reactions, involving both main and side products of the HAS, the goal being the identification of all the classes of reactions limited by thermodynamic constraints under synthesis conditions. In this respect, a particular effort has been devoted to ensure the accurate separation, identification, and quantification of as many reaction products as possible. This has led us to show that the equilibrium controlled reactions are more numerous than previously reported.

The identification of the chemical equilibria affecting the formation of reaction products contributes to the rationalization of the overall composition of the HAS product mixture. It also allows one to check the consistency of proposed reaction paths and to predict the effects of reaction conditions on the concentrations of several classes of products. Moreover, the temperature dependence of the prevailing thermodynamic constraints explains the differences in the product compositions generated by low-T and high-T modified methanol catalysts.

The relevance of chemical equilibria to the selection of appropriate operating conditions and process configurations is also briefly addressed.

METHODS

Experimental

The ZnCr-oxide catalyst with a Zn/Cr atomic ratio of 1/1 used in this study was prepared by neutralization with $(NH_4)CO_3$ of a solution of $Zn(NO_3)_2$ and $Cr(NO_3)_3$ (final pH 8), followed by filtering of the precipitate, washing, and drying at 110°C. The catalyst precursor was activated in N_2 at 400°C and then impregnated with 15% of Cs_2O (w/w) by the wet impregnation technique.

Before the activity runs, the catalyst was prereduced in the reactor at atmospheric pressure in a flowing H_2–N_2 stream, with H_2 content and temperature progressively increased from 2 to 100% and from room temperature to 400°C, respectively.

The characterization of the catalyst before and after activity tests has been discussed at length elsewhere (*10, 18*). The catalyst consisted essentially of a spinel-like phase related to zinc chromite and of ZnO.

The catalytic tests were performed in a Cu-lined fixed-bed tubular reactor (1 cm i.d.) loaded with 11 g of catalyst. The temperature profile along the reactor axis was measured by a thermocouple sliding inside a capillary tube immersed in the catalyst bed: deviations from isothermal conditions never exceeded 5–7°C. The following variable space was explored: T = 345 to 430°C, P = 7.1 to 10.1 MPa, GHSV = 8,000 to 25,000 h^{-1}, H_2/CO feed ratios from 1/2 to 4/1, CO_2 feed contents from 0 to 6%.

The experimental setup and the analytical procedures have been described in detail in Refs. (*8, 19*). The effluents from the reactor were cooled to −30°C: the gaseous products escaping from the condenser were analyzed online by a 5750 G Hewlett–Packard GC, using both TC and FI detectors. A Porapak QS column (100–120 mesh, $\frac{1}{8}$-in. diameter, 4.8 m long) operated at 75°C was employed for the analysis of He, CO, CH_4, CO_2, C_2H_4, and C_2H_6. The condensed products were collected during the run (duration ≈4 h) and later analyzed by high-resolution gas chromatography (HRGC) on a Carlo Erba MEGA 5100 GC equipped with fused silica capillary columns (i.d. = 0.32 mm, length = 25 m, stationary phase = SE54, phase thickness = 1 μm) and a FI detector. Several unknown compounds were identified by GC/MS.

Table 1 provides a list of the major reaction products formed in a typical run which are relevant for the present work. Quite a few additional species were also detected, but for many of them identification remained uncertain.

Evaluation of Approach to Equilibrium

For each reaction of interest the equilibrium constant $K_{eq}(T)$ was calculated using thermochemical data (standard Gibbs free energies and heats of formation, polynomial approximations for the specific heats $C_p°(T)$) taken from Ref. (*20*) or estimated by group contribution methods described in the same reference. For the same reaction, the partial pressures ratio K_p was obtained directly from the experimental partial pressures at the reactor exit. The ratio of fugacity coefficients, K_φ, was estimated using the Soave–Redlich–Kwong equation of state (*21*), as recommended in a recent experimental study of chemical equilibria in the methanol synthesis over a commercial Cu-ZnO catalyst (*22*). Only in the case of the reaction of methanol formation, corrections for nonideality were estimated according to a correlation proposed by Klier *et al.* (*23*). Computed K_φ values were in the range 0.9–1.1 for all reactions considered except methanol synthesis, indicating that the assumption of ideal gas behavior is a good approximation compared to the experimental uncertainties of the product distributions.

The degree of approach to equilibrium of the reaction was evaluated by comparing the value of $K_f = K_p \cdot K_\varphi$ with K_{eq}.

RESULTS AND DISCUSSION

In the following, results concerning the relevance of thermodynamic limitations in the HAS over the Cs-promoted ZnCr-oxide catalyst are presented and discussed. The following classes of reactions have been investigated in this respect: (a) methanol synthesis; (b) water–gas shift; (c) hydrogenation of aldehydes to primary alcohols and of ketones to secondary alcohols; (d) formation of methyl esters; (e) ketonization reactions.

1. Methanol Synthesis

The equilibrium of the methanol synthesis reaction

TABLE 1

Concentrations of the Most Significant Compounds Detected in the Product Mixure of a Standard HAS Run over the ZnCr-Oxide + 15% Cs_2O Catalyst

Class of compounds	Species	% Mol fraction at reactor exit
	CO	45.2
	H_2 (from balance)	47.5
	CO_2	0.8544
	H_2O	0.2475
Primary alcohols		
	Methanol	1.0959
	Ethanol	0.0248
	1-Propanol	0.0823
	2-Me-1-propanol	0.2554
	2-Me-2-propen-1-ol	0.0015
	1-Butanol	0.0074
	3-Me-1-Butanol	0.0022
	2-Me-1-butanol	0.0150
	1-Pentanol	0.0045
	2,3-diMe-1-Butanol	0.0020
	2-Me-1-pentanol	0.0142
	4-Me-1-pentanol	0.0019
	2-Et-1-butanol	0.0004
	3-Me-1-pentanol	0.0006
	1-Hexanol	0.0008
	2-Me-1-hexanol	0.0044
	Alcohol C7	0.0014
	2,4-diMe-1-pentanol	0.0076
Secondary alcohols		
	2-Butanol	0.0005
	3-Me-2-butanol	0.0004
	3-Pentanol	0.0018
	2-Me-3-Pentanol	0.0018
	3-Me-2-Pentanol	0.0005
	3-Hexanol	0.0003
	2,4-diMe-3-pentanol	0.0001
	3-Octanol	0.0006
Aldehydes		
	Acetaldehyde	0.0036
	Propanal	0.0119
	2-Me-propanal	0.0285
	n-Butanal	0.0005
	3-Me-butanal	0.0001
	2-Me-butanal	0.0022
	2-Me-Pentanal	0.0038
Ketones		
	2-Butanone	0.0017
	3-Me-2-butanone	0.0011
	3-Pentanone	0.0035
	2-Me-3-pentanone	0.0043
	3-Hexanone	0.0008
	2-Hexanone	0.0014
	2,4-diMe-3-pentanone	0.0009
	2,4-diMe-3-hexanone	0.0002
Esters		
	Methyl formate	0.0049
	Methyl acetate	0.0058
	Methyl-*i*-butanoate	0.0219
Olefins and hydrocarbons		
	Methane	0.2205
	Ethylene	0.0564
	Ethane	0.0178
	Propylene	0.0041
	Propane	0.0005
	Butenes	0.0171
	2-Me-Butane	0.0053
	1-Pentene	0.0016
	C5 olefins	0.0007
	C6 olefins	0.0014
	n-Exhane	0.0007
	2,3-diMe-pentane	0.0002
	n-Octane	0.0006
	n-Decane	0.0015
Ethers		
	Dimethylether	0.0037
	Methyl-*i*-buthyl ether	0.0003

Note. Reaction conditions: $T = 405°C, P = 8.6$ MPa, GHSV $= 8000\ h^{-1}$, $H_2/CO = 1/1$, feed $CO_2 = 0$.

$$CO + 2H_2 \rightleftharpoons CH_3OH \qquad (1)$$

was approached within experimental error during most of our runs, as shown for example in Fig. 1 and Table 2.

Negative deviations from equilibrium were observed only at low temperature when using a space velocity of 8000 h^{-1} or at high space velocities with $T = 385°C$. High CO_2 feed contents appeared to adversely affect the methanol concentration in the products. However, this effect is related to a parallel reduction in the equilibrium concentration of methanol. In fact, equilib-

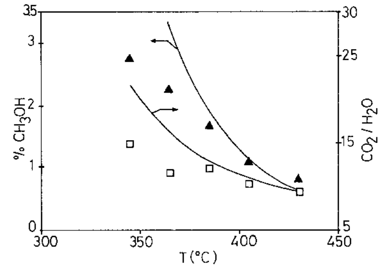

FIG. 1. Effect of reaction temperature on CH_3OH concentration (▲) and on CO_2/H_2O ratio (□). Reaction conditions: $P = 8.6$ MPa, GHSV $= 8000\ h^{-1}$, $H_2/CO = 1/1$, feed $CO_2 = 0$. The solid lines represent interpolation of equilibrium values calculated using actual partial pressures of CO and H_2.

TABLE 2

Effect of Reaction Pressure on the Equilibrium of Reactions (1) and (2)

		Pressure (MPa)		
		7.1	8.6	10.1
CH_3OH	Exper.	0.67	1.07	1.51
% mol fr.	Equil.[a]	0.66	0.99	1.51
CO_2/H_2O	Exper.	11.2	10.4	11.1
	Equil.[a]	11.3	11.4	11.4

[a] Calculated from actual CO and H_2 partial pressures.

Note. Reaction conditions: $T = 405°C$, GHSV = 20,000 h^{-1}, $H_2/CO = 1/1$, feed $CO_2 = 0$.

rium was still approached also with 6% CO_2 in the feed.

Equilibrium methanol concentrations in the gas product mixture have already been reported for both high-T modified methanol catalysts (*8–11, 15*) and for low-T Cu-based modified methanol catalysts (*14*) when operated in the HAS. In fact, higher temperatures and lower space velocities are used in the HAS with respect to typical conditions of the methanol synthesis, both modifications favoring the approach to equilibrium. Since the equilibrium concentrations of methanol grows with decreasing temperature, the greater methanol concentrations in the products observed over Cu-based catalysts are simply related to the thermodynamic limitations of reaction (*1*).

Equilibrium of reaction (*1*) also explains why addition of methanol to the reactor feed during the HAS did not affect significantly the product distribution obtained over a K-doped ZnCr-oxide catalyst (*12*), CH_3OH behaving essentially as CO + H_2.

Since methanol is at equilibrium in the HAS, the effects of the reaction variables on the methanol concentrations can be readily predicted. For example, high methanol-to-C_{2^+} alcohols ratios are undesired in the HAS product mixture: in order to depress the formation of methanol low H_2/CO feed ratios are used. Also, because of equilibrium the content of methanol in the products grows quadratically with total pressure, while the concentrations of higher alcohols exhibit a weaker dependence (*10*). Thus, high pressures adversely affect the ratio of higher alcohols to methanol.

2. *Water–Gas Shift (WGS) Reaction*

From a comparison between experimental values of the CO_2/H_2O molar ratio in the HAS products and corresponding calculated equilibrium values for the direct WGS reaction,

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad (2)$$

as given for example in Fig. 1 and Table 2, it appears that equilibrium of the WGS reaction is closely approached for all of the conditions investigated, except at low temperatures and low H_2/CO feed ratios. In these cases negative deviations become apparent, suggesting that the reaction proceeds from left to right under our experimental conditions.

It is well known that catalysts for the methanol synthesis are usually excellent catalysts for the WGS reaction as well. Thus, it is hardly surprising that reaction (*2*) is under thermodynamic control over the Cs-promoted ZnCr-oxide system. In fact reaction (*2*) has been reported to approach chemical equilibrium in the HAS over both high-T (*8–11, 15*) and low-T (*24*) modified methanol catalysts, and CO_2 has been named a "fatal" by-product of the HAS (*24*).

The equilibrium of reaction (*2*) affects several important aspects of the alcohol synthesis, as detailed in the following.

(a) Its equilibrium constant is about 12 at 400°C and grows with decreasing temperature. This implies large effects of reaction (*2*) on the overall carbon selectivity. Significant amounts of CO are converted to CO_2, especially if CO_2-free feeds with low H_2/CO ratios are used and the HAS is operated at low temperatures.

(b) Reaction (*2*) controls the amount of water in the HAS products, CO_2-rich feed streams resulting in greater H_2O contents which may then require more expensive

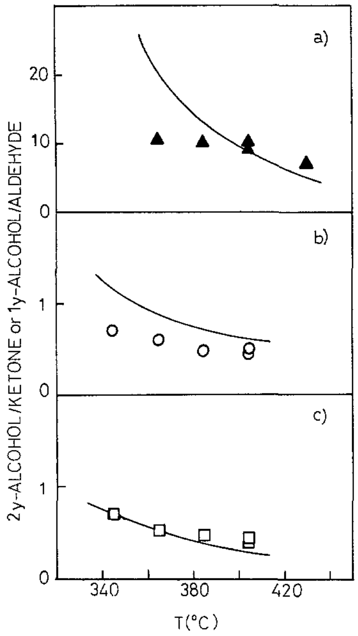

FIG. 2. Effect of reaction temperature on the molar ratios: (a) *i*-butanol/*i*-butanal; (b) 3-pentanol/3-pentanone; (c) 3- hexanol/3-hexanone. Reaction conditions: $P = 8.6$ MPa, GHSV $= 8000\ h^{-1}$, $H_2/CO = 1/1$, feed $CO_2 = 0$. Solid lines are interpolations of equilibrium values based on actual H_2 partial pressures. Thermochemical data for 3-pentanone, 3-pentanol, 3-hexanone, and 3-hexanol were estimated by Benson's group contribution method (*20*).

drying treatments. In this respect, operation with lower temperatures and lower H_2/CO ratios is more favorable.

(c) Carbon dioxide acts as an inhibitor for the formation of C_{2+} oxygenates: in our runs over the Cs-promoted ZnCr-oxide catalyst, increasing the concentration of CO_2 in the feed from 0 to 6% resulted in a threefold reduction of the productivity to higher oxygenates. Quite similar results had been obtained using another ZnCr-oxide catalyst promoted with K (*8*), whereas it has been reported in the patent literature that increasing the CO_2 feed content caused a drop in the productivity to higher alcohols over a K-promoted Cu-based catalyst (*25*). It has been proposed that H_2O is the true inhibitor of the HAS instead of CO_2, because of its competition with C_1 oxygenated intermediates for adsorption on the catalyst active sites (*8, 26*). According to this picture, the direct WGS reaction is beneficial, as it provides a chemical route for removing water from the catalyst surface by evolution of gaseous carbon dioxide. Therefore, conditions favoring smaller H_2O concentrations in the reactor are expected to improve the yield of higher alcohols, too.

Thus, the equilibrium of the WGS reaction has an important bearing on the carbon utilization of industrial processes where CO_2 is washed from reactor feed and only partially recycled to the stage of syngas preparation, for the choice of process configurations and for the kinetic analysis of the synthesis, as detailed elsewhere (*8, 24, 27–29*).

3. Equilibria between Aldehydes and Primary Alcohols

Figure 2a and Table 3 illustrate a comparison between measured and equilibrium values of the molar ratio isobutanol/isobutyraldehyde as a function of temperature and contact time, respectively. Equilibria refer to the general reaction

$$C_{n-1}H_{2n-1}CHO + H_2 \rightleftharpoons C_nH_{2n+1}OH. \quad (3)$$

Equilibrium is clearly established at synthesis conditions. Similar results are obtained with the other aldehyde–primary alcohol pairs. In the case of $n = 1$, the equilibrium of reaction (3) could not be checked, as formaldehyde was never de-

TABLE 3

Effect of Contact Time on the Molar Ratio (*i*-Butanol/*i*-Butanal)

	i-C_4H_9OH/i-C_3H_7CHO				
GHSV (h^{-1}) =	25,000	20,000	15,000	8,000	Equil.[a]
$T = 385$°C	7.5	9.3	10.2	10.1	12.6
$T = 405$°C	8.0	8.9	8.3	8.5 9.0	8.1

Note. Reaction conditions: $P = 8.6$ MPa, $H_2/CO = 1/1$, feed $CO_2 = 0$.

[a] Calculated from actual H_2 partial pressure.

tected in the products. This is however in agreement with its very small calculated equilibrium concentration.

Moreover, the alcohol/aldehyde ratios were equally affected by changing either the total pressure or the H_2/CO feed ratio and were directly proportional to the H_2 partial pressure, as expected from the equilibrium of reactions (3).

Deviations from thermodynamic predictions became apparent at temperatures below 400°C (Fig. 2), and tended to increase with decreasing contact time (Table 3). The negative sign of the departures from equilibrium in both cases suggests that aldehydes act as reactants in hydrogenation reactions.

Due to the characteristics of the hydrogenation equilibria (3), the content of aldehydes in the reaction products is reduced by operating at low temperatures, with high pressures and with high H_2/CO ratios. Notably, under HAS conditions, the equilibria of reactions (3) favor alcohols as compared to aldehydes, so that these compounds are actually by-products of the HAS: under the conditions of Table 1 the molar ratio isobutanol/isobutyraldehyde is about 9 at 405°C.

The effect of temperature on these equilibria is in line with the observation that much smaller amounts of aldehydes are detected among the products of the HAS over modified low-T methanol catalysts. Indirect evidence for the occurrence of primary alcohol–aldehyde equilibria over a Cs-promoted Cu-based catalyst was reported by Vedage *et al.* (*5*), who experienced equal effects on the product distribution upon adding either 1-propanol or propanal to the reactor feed and attributed this result to the onset of a rapid hydrogenation–dehydrogenation equilibrium. Essentially equal modifications of the product distribution in the HAS were also obtained over a K-promoted ZnCr-oxide catalyst when formaldehyde or methanol, acetaldehyde or ethanol, and propanal or 1-propanol were added to the feed (*12*).

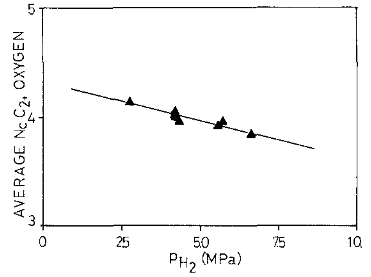

FIG. 3. Effect of H_2 partial pressure on the average carbon number of C_{2^+} oxygenates. Reaction conditions: T = 405°C, P = 8.6 MPa, GHSV = 8000 h^{-1}, feed CO_2 = 0.

The aldehyde/alcohol equilibrium also possibly affects the product distribution in a different respect. Several authors have proposed that the chain growth of alcohols over modified methanol catalysts occurs via condensations of aldehydic intermediates (*5, 12, 30*). Conclusive experimental validations of the aldol-coupling hypothesis have been obtained in very recent years (*31–34*). Thus, conditions reducing the concentrations of aldehydes are also detrimental to the extent of chain growth. Figure 3 shows a plot of the average carbon number of the C_{2^+} oxygenates in the HAS products, N_c, versus the H_2 partial pressure in the feed. The decrease in N_c with growing p_{H_2} is small but significant, considering that N_c is an averaged quantity. The correlation displayed by the data is indeed consistent with a picture where a reduction in the concentration of aldehydic compounds effected by raising the H_2 partial pressure adversely affects the rate of alcohol chain growth.

4. Equilibria between Ketones and Secondary Alcohols

Inspection of Table 4 shows a strict correspondence between the ketones and the secondary alcohols identified in the product mixtures of our runs. Such a correspondence is similar to that existing between aldehydes and primary alcohols. Indeed, the same conclusions concerning the equilibria between aldehydes and primary alcohols apply to the hydrogenation equilibria involving ketones and secondary alcohols, according to the stoichiometry

TABLE 4

Ketones and Secondary Alcohols Detected in the Products of the HAS over the ZnCr-Oxide + 15% Cs_2O Catalyst

Ketone	Secondary alcohol	Primary alcohols involved in the related ketonization reaction
2-Butanone	2-Butanol	Ethanol + 1-propanol
3-Pentanone	3-Pentanol	1-Propanol + 1-propanol
3-Hexanone	3-Hexanol	1-Butanol + 1-propanol
3-Methyl-2-butanone	3-Methyl-2-butanol	*i*-Butanol + ethanol
2-Methyl-3-pentanone	2-Methyl-3-pentanol	*i*-Butanol + 1-propanol
2,4-Dimethyl-3-pentanone	2,4-Dimethyl-3-pentanol	*i*-Butanol + *i*-butanol

$$RCOR' + H_2 \rightleftharpoons RCH(OH)R'. \quad (4)$$

The approach to equilibrium at different temperatures for two ketone–secondary alcohol pairs is shown as an example in Figs. 2b and 2c. The very small concentrations of ketones and particularly of secondary alcohols prevented achieving sufficient accuracy to discuss possible departures from equilibrium.

The existence of ketone–secondary alcohol equilibria in the HAS is supported by "chemical enrichment" experiments over a ZnCr-oxide + K catalysts, where equal results were obtained upon addition to the feed of acetone or 2-propanol (*12, 35*). The yields of ketones and secondary alcohols obtained in the HAS over Cs/Cu/ZnO catalysts were also close to equilibria (4) (*31*).

The influence of the operating variables on the concentrations of ketones and secondary alcohols, and the role of these compounds in the reaction pathways of the HAS, are discussed in Section 6. It should be noted that, contrary to the case of primary alcohols with respect to aldehydes, secondary alcohols are less favored than ketones. Under the conditions of Table 1 the equilibrium ratio (3-hexanol/3-hexanone) is estimated to be about 0.3.

5. *Reactions Involving Esters*

Methyl formate, methyl acetate, and methyl-*i*-butanoate were the only esters that could be identified certainly among the products of our runs. High-resolution gas chromatographic analysis indicated that also methyl-*n*-propanoate was possibly formed, but it could not be separated from *i*-butanol.

Figure 4 illustrates the effects of the H_2/CO feed ratio on the approach to equilibrium of the methanol carbonylation reaction,

$$CH_3OH + CO \rightleftharpoons HCOOCH_3. \quad (5)$$

Reaction (5) is clearly limited by thermodynamics. Since methanol has been shown already to tend to equilibrium with CO and H_2, methyl formate approaches equilibrium also according to the stoichiometry

$$2CO + 2H_2 \rightleftharpoons HCOOCH_3. \quad (6)$$

Interestingly, negative deviations from equilibrium were detected not only at low temperatures but also in the case of CO_2-rich feeds. This seems to indicate that addition of CO_2 to the feed inhibits the formation of $HCOOCH_3$ over the Cs-promoted ZnCr-oxide catalyst. As mentioned above, addition of CO_2 was found to depress the formation of C_{2^+} oxygenates, too.

Methyl formate formation is reportedly limited by thermodynamics also over modified Cu-based low-T methanol catalysts (*14*). Since the equilibrium constant of reac-

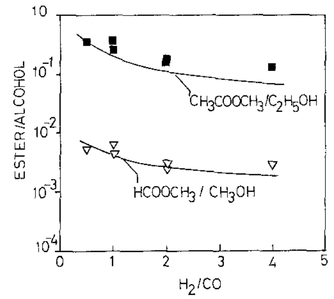

FIG. 4. Effect of H_2/CO feed ratio on the molar ratios $HCOOCH_3/CH_3OH$ and CH_3COOCH_3/C_2H_5OH. Reaction conditions: T = 405°C, P = 8.6 MPa, GHSV = 8000 h^{-1}, feed CO_2 = 0. The solid lines interpolate equilibrium values calculated using estimates of K_{eq} for reactions (5) and (7), respectively, and actual partial pressures of methanol, CO, and H_2.

tion (6) at 400°C is about 50 times smaller than that at 310°C, this clarifies why much greater selectivities to this ester are observed in the HAS over Cu-based catalysts.

Recently, Nunan *et al.* (*14*) have published an exhaustive study concerning the mechanism of formation of $HCOOCH_3$ and C_2H_5OH from $CO+H_2$ over Cs-promoted Cu/ZnO catalysts. Primarily on the basis of isotopic labeling experiments, the authors provide evidence supporting the hypothesis that methyl formate originates from the direct carbonylation of a methoxy anion, although they do not exclude the possibility of a direct esterification of adsorbed formate species by methanol. Due to fast equilibration of the reverse water–gas shift reaction over modified methanol catalysts, the addition of CO_2 to the reactor feed results in greater H_2O contents in the reaction product mixture; water is expected to displace methanol from Cs cations. Thus, the mechanism of Nunan *et al.* is able to explain the inhibiting action of CO_2 on the formation of methyl formate observed in our runs. However, greater water concentrations would probably reduce the yield of $HCOOCH_3$ also in the case of a direct esterification route.

It is of interest to assess whether higher methyl esters are also limited by thermodynamics over the Cs-doped ZnCr-oxide catalyst, particularly in respect to the possible mechanisms for ester formation. In fact, Klier and co-workers have suggested that over Cu/ZnO catalysts distinct mechanisms govern the formation of methyl formate and of higher methyl esters (*14, 31*).

Unfortunately, a completely reliable comparison between measured and equilibrium concentrations of CH_3COOCH_3 and of $(CH_3)_2CHCOOCH_3$ was not possible. We could not trace experimental data for the standard Gibbs energy of formation of these compounds. On the other hand, the estimates of the equilibrium constants obtained by different group contribution methods were found to differ by over an order of magnitude. Within this accuracy, however, our data for CH_3COOCH_3 are apparently consistent with the equilibrium of the reaction

$$C_2H_5OH + CH_3OH \rightleftharpoons CH_3COOCH_3 + 2H_2 \quad (7)$$

as calculated from the average value of the Gibbs free energy of formation of CH_3COOCH_3 obtained from two of the most reliable group contribution methods, namely Benson's and Joback's method (*20*). In fact, the effects of reaction temperature, contact time, total pressure, and feed composition have been found to be in line with those expected on the basis of chemical equilibrium of reaction (7), as shown for example in Fig. 4. In addition, the observed magnitudes of the (ester/alcohol) ratios were in the order

$$\frac{HCOOCH_3}{CH_3OH} \ll \frac{(CH_3)_2CHCOOCH_3}{(CH_3)_2CHCH_2OH} \approx \frac{CH_3COOCH_3}{C_2H_5OH}$$

which is consistent with thermodynamic predictions and also with published data on the formation of methyl esters in the HAS over Cs-promoted Cu-based methanol catalysts (*31*). For such esters, yields close to the equilibrium of the reaction $RCHO + CH_3OH \rightleftharpoons RCOOCH_3 + H_2$ have been reported.

Notably, when methanol reaches equilibrium with $CO + H_2$, equilibrium (7) is equivalent to the equilibrium of

$$C_2H_5OH + CO \rightleftharpoons CH_3COOCH_3 \quad (8)$$

Of course, reaction (8) is not suggestive of a carbonylation mechanism for CH_3COOCH_3, which would result in ethyl formate rather than methyl acetate. The equilibrium of reaction (7) (or (8)), however, is consistent with other reaction paths, including:

(a) a crossed Tischenko reaction between acetaldehyde and formaldehyde, both aldehydes being in equilibrium with the corresponding alcohols;

(b) a reaction between acetaldehyde and a methoxide via a hemiacetal intermediate, acetaldehyde and methoxide being in equilibrium with ethanol and methanol, respectively;

(c) an esterification of adsorbed acetic acid with methanol, CH_3COOH being in equilibrium with ethanol.

Over copper-based catalysts mechanisms equivalent to (a) and (b) for $HCOOCH_3$ have been ruled out by isotopic labeling studies by Klier and co-workers (*14*).

On the other hand, the esterification route (mechanism c), based on the reactions

$$HCOO^- + CH_3OH \rightleftharpoons HCOOCH_3 + OH- \quad (9.a)$$

$$CH_3COO- + CH_3OH \rightleftharpoons CH_3COOCH_3 + OH^- \quad (9.b)$$

with the formation of the carboxylic species occurring for example via

$$CO + OH^- \rightleftharpoons HCOO^- \quad (10.a)$$

$$C_2H_5OH \rightleftharpoons CH_3CHO + H_2 \quad (10.b)$$

$$CH_3CHO + OH^- \rightleftharpoons CH_3COO^- + H_2 \quad (10.c)$$

appears feasible for the generation of both methyl formate and methyl acetate, and generally of all methyl esters, and is consistent with the thermodynamic constraints on the concentrations of these products. In fact, the sum of reactions (9.a) and (10.a), and the sum of reactions (9.b), (10.b), and (10.c) have the same stoichiometry as that of reactions (5) and (7), respectively.

Acids were not detected in the reaction products of our runs. However, their calculated equilibrium concentrations are very small, indicating that carboxylic compounds might indeed be present in the reacting system, although in trace amounts. The existence of salts of carboxylic acids on the catalyst surface during the HAS has been documented in the past (*2*). Riva *et al.* (*12*) have published spectroscopic evidence for the presence of surface formate groups on ZnCr-oxide catalysts following methanol adsorption and decomposition, as well as during CO + H_2 reaction at low pressure at 380°C. Temperature-programmed surface reaction (TPSR) experiments with C_4 oxygenates in our laboratory, along with FT-IR measurements, have also demonstrated the formation of carboxylic surface species on ZnO-based catalysts (*34, 36–38*). Adsorbed carboxylic species are probably involved also in ketonization reactions occurring during the HAS. Their role in the reacting system is therefore discussed further in the following section.

The fact that primarily methyl esters are formed in the HAS can also be explained on thermodynamic grounds. For example, the estimated equilibrium concentration of ethyl formate is considerably smaller than that of methyl acetate and is below the limit of detection of our analytical facilities.

6. *Ketonization Reactions*

As mentioned in Section 4, small amounts of ketones (≈2% w/w) were present in the product mixture obtained over the ZnCrO + Cs_2O catalyst. The existence of equilibria involving ketones and primary alcohols was investigated with respect to the following stoichiometries:

$$C_2H_5OH + n\text{-}C_3H_7OH \rightleftharpoons CH_3(CO)CH_2CH_3 + CO + 3H_2 \quad (11)$$

$$n\text{-}C_3H_7OH + n\text{-}C_4H_9OH \rightleftharpoons CH_3(CH_2)_2(CO)CH_2CH_3 + CO + 3H_2 \quad (12)$$

$$n\text{-}C_3H_7OH + i\text{-}C_4H_9OH \rightleftharpoons (CH_3)_2CH(CO)CH_2CH_3 + CO + 3H_2 \quad (13)$$

$$2n\text{-}C_3H_7OH \rightleftharpoons CH_3CH_2(CO)CH_2CH_3 + CO + 3H_2 \quad (14)$$

Figure 5 illustrates the influence of reaction temperature on the approach to equilibrium of reactions (11)–(13). Table 5 presents the effects of contact time and feed composition.

Inspection of Fig. 5 and Table 5 leads to the following remarks:

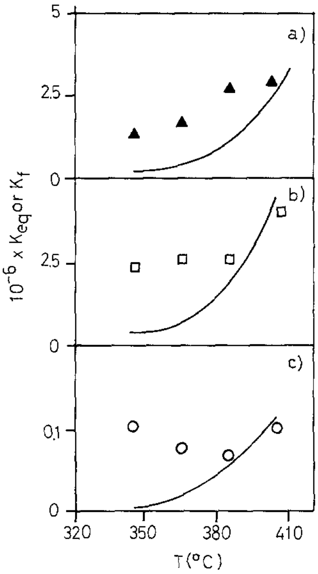

FIG. 5. Effect of reaction temperature on the fugacity ratios of reactions (11) (△), (12) (□), and (13) (○). Reaction conditions: $P = 8.6$ MPa, GHSV = 8000 h^{-1}, $H_2/CO = 1/1$, feed $CO_2 = 0$. The solid lines represent calculated equilibrium values. Thermochemical data for 3-hexanone and 2-methyl-3-pentanone were estimated by Benson's group contribution method (*20*).

(a) within experimental error, reactions (11)–(14) are at equilibrium at high temperatures and contact times;

(b) positive departures from equilibrium are apparent at low temperatures, low contact times, high H_2/CO ratios, and with CO_2-rich feeds, indicating that reactions (11)–(14) proceed from right to left, with ketones acting as reactants.

Similar considerations apply to all of the ketones identified in the products of our runs. As shown in the third column of Table 4, these included all those expected from the possible equilibria involving the main primary alcohols in the products, namely ethanol, 1-propanol, isobutanol and 1-butanol, with the exceptions of acetone and 2-pentanone, which were not detected. However, the concentrations of these ketones, calculated on the basis of their equilibria with ethanol and with ethanol + 1-butanol, respectively, were below the sensitivity threshold of our analytical procedures (≈0.02% w/w of the liquid product). It is possible therefore to conclude that both the concentrations of the observed ketones and the lack of detection of acetone and 2-pentanone support the existence of chemical equilibria associated with ketonization reactions such as (11)–(14). Only the concentration of 2,4-dimethyl-3-pentanone was found about two orders of magnitude lower than that expected from equilibrium with two molecules of isobutanol. This point will be addressed in the following.

Thermodynamics dictate that the equilibrium concentrations of ketones have an inverse cubic dependence on the reaction pressure. This explains why small concentrations of ketones are obtained under HAS conditions over modified methanol catalysts, with typical pressures ranging from 7 to 15 MPa. Smaller contents of ketones relative to primary alcohols are also expected when the HAS is operated at lower temperatures (see Fig. 5). Indeed, only traces of ketones are reported in the products of the HAS over low-T modified methanol catalysts: as discussed below, thermodynamic constraints possibly affect the concentrations of these compounds over such catalytic systems as well.

Additional evidence for the reversible nature of reactions similar to (11)–(14) under HAS conditions is provided by the results of two independent chemical enrichment studies over modified methanol catalysts. 2-Propanol was added to the $CO + H_2$ feed during HAS runs over a ZnCr-oxide + K_2O catalyst (*12, 35*) and over a Cu/ZnO + NaOH catalyst (*5*). In both cases a significant increase in the yield of ethanol (and also of acetaldehyde over the ZnCr-oxide catalyst) was observed. These results are easily interpreted by assuming that the equilibrium between 2-propanol and acetone, and the equilibrium of reaction (15),

$$2C_2H_5OH \rightleftharpoons CH_3(CO)CH_3 + CO + 3H_2 \quad (15)$$

are established over both catalysts, in agree-

TABLE 5

Comparison between Experimental Fugacity Ratios K_f and Calculated Equilibrium Constants K_{eq} for Ketonization Reactions

Reaction	K_f				K_{eq}
GHSV (h^{-1}) =	25,000	20,000	15,000	8,000	
Effect of contact time[a]					
(11)	4.0*E* + 6	3.4*E* + 6	3.0*E* + 6	2.7*E* + 6	1.0*E* + 6
(12)	3.9*E* + 6	3.0*E* + 6	2.9*E* + 6	2.6*E* + 6	1.9*E* + 6
(13)	12.0*E* + 5	8.3*E* + 5	7.3*E* + 5	6.6*E* + 5	4.2*E* + 5

Reaction	K_f				K_{eq}
H_2/CO =	0.5	1	2	4	
Effect of H_2/CO feed ratio[b]					
(11)	2.7*E* + 6	2.7*E* + 6	4.6*E* + 6	3.9*E* + 6	2.6*E* + 6
(14)	0.8*E* + 6	1.5*E* + 6	2.0*E* + 6	2.3*E* + 6	0.7*E* + 6

Reaction	K_f			K_{eq}
% CO_2 feed =	0	3	6	
Effect of CO_2 feed content[c]				
(11)	2.7*E* + 6	4.7*E* + 6	5.1*E* + 6	2.6*E* + 6
(12)	4.1*E* + 6	4.7*E* + 6	6.8*E* + 6	4.4*E* + 6

[a] Reaction conditions: $T = 385°C$, $P = 8.6$ MPa, $H_2/CO = 1/1$, feed $CO_2 = 0$.
[b] Reactions conditions: $T = 405°C$, $P = 8.6$ MPa, GHSV $= 8000\ h^{-1}$, feed $CO_2 = 0$.
[c] Reaction conditions: $T = 405°C$, $P = 8.6$ MPa, GHSV $= 8000\ h^{-1}$, $H_2/CO = 1/1$.

ment with our findings reported in Section 4 and in the present section.

The rapid equilibrium of reactions involving primary alcohols and ketones over an alkali-promoted ZnCr-oxide catalyst is not surprising. A ZnO-Cr_2O_3-K_2O catalyst operated at 400°C and 1 atm with an ethanol-H_2O-N_2 feed gave 100% conversion of ethanol with 88% selectivity to acetone (*39*); chromia was reportedly an efficient catalyst in the condensation of linear C_6–C_8 alcohols to symmetrical ketones (*40*); high activities and selectivities in related aldehyde decarbonylation reactions have been claimed also for alkali-promoted ZnMnCr-oxide catalysts (*41*). Furthermore, the capability of a K-doped ZnCr-oxide catalyst to promote the formation of C_7-ketones by condensation of C_4-aldehydes and/or acids has been demonstrated recently in our laboratory by the TPSR technique and by flow microreactor experiments (*34, 36–38*). A comparison between the results obtained with linear and branched C_4-oxygenated molecules has pointed out a much lower reactivity of the iso- compounds toward formation of ketones compared to that of the corresponding linear molecules, which is probably correlated with the unique behavior of isobutanol under HAS conditions. As mentioned before, in fact, the reaction involving two molecules of isobutanol to give 2,4-dimethyl-3-pentanone is the only ketonization reaction removed from equilibrium.

Mechanisms proposed in the literature to account for the formation of ketones over oxide catalysts involve decarboxylative condensations of a carboxylate species and a molecularly adsorbed aldehyde or acid molecule (*42–44*). The detection of equilibria between ketones and primary alcohols suggests that at the conditions of the synthesis the reactants in such condensations approach equilibrium with the corresponding alcohols. The equilibria between alcohols and aldehydes have been actually demonstrated in Section 3. As for acids, their equilibria with aldehydes and alcohols could not be checked directly, but are however consistent with the equilibria for alcohol esterification discussed in Section 5. The overall resulting picture, therefore, suggests that local equilibria are established between the primary oxygenated compounds (primary alcohols, aldehydes, acids), and also with the related species (ketones, secondary alcohols, esters). Notably, equilibrium between acetic acid, acetaldehyde, and ethanol was documented directly by Weitkamp and Frye (*16*) in the FT synthesis performed over a fluidized iron catalyst bed under conditions where detection of acetic acid was possible.

Natta *et al.* (*2*) reported the presence of alkali salts of fatty acids on alkali-doped ZnO base catalysts for the HAS, and explained it by their direct participation in the mechanism of the synthesis. They noted that the temperature of 400°C corresponds to effective equilibrium conditions between the formation and decomposition of fatty acid salts on the surface of the catalysts: this agrees with the results of the present thermodynamic analysis. The same authors further proposed that decomposition of alkali salts of fatty acids is responsible for the formation of ketones according to reactions like (11)–(14), while secondary alcohols would result from successive hydrogenation of ketones. However, an interesting indication of the data in Fig. 5 and Table 5 is that the ketonization reactions (11)–(14) are not apparently associated with the formation of ketones, but rather with their consumption. Therefore, an alternative route leading directly to the formation of ketones seems to exist during the HAS. This may involve aldol-type condensations of aldehydes with retention of the anionic oxygen in the condensation intermediate. Such a path represents a reversal of the usual aldol synthesis mechanism. Evidence for its occurrence in the HAS over alkali-promoted Cu/ZnO catalysts has been recently obtained by isotopic-labeling studies under HAS conditions (*14, 45*) and by direct observation of the reaction products in microreactor experiments (*32*). The formation of C_8 ketones from *n*-butyraldehyde in the temperature range 250–350°C had also been detected during TPSR experiments over a ZnCr-oxide + K_2O catalyst (*36*). Thus, on the basis of these data it is possible to envisage a pathway for formation of ketones in the HAS which parallels the main route for alcohol chain growth, the two routes being both based on aldol condensations and involving oxygenates whose concentrations are related through multiple chemical equilibria.

CONCLUSIONS

The a posteriori thermodynamic analysis of the HAS over a Cs-promoted ZnCr-oxide catalyst has been shown to be an informative tool for the rationalization of this very complex reacting system. Our results show that the following classes of reactions are subject to thermodynamic constraints under the typical conditions of the synthesis: (a) formation of methanol; (b) water–gas shift reaction; (c) formation of $HCOOCH_3$ and possibly of higher methyl esters; (d) hydrogenation reactions of aldehydes to primary alcohols; (e) hydrogenation reactions of ketones to secondary alcohols; (f) ketonization reactions.

Such equilibria determine the contribution of many classes of reactions to the spectrum of products of the HAS by introducing upper or lower bounds on the concentrations of several primary products, namely methanol, carbon dioxide, and water, and secondary products, including aldehydes, ketones, secondary alcohols, esters, and acids. The identification of the thermodynamic limitations prevailing in the HAS is also helpful in understanding (and predicting) the effects of temperature, pressure, and feed composition on the selectivities to these products.

The data available in the literature further suggest that such thermodynamic constraints affect the HAS also when operated over other modified high-T methanol catalysts and over alkali-doped low-T methanol catalysts as well. In the latter case the temperature dependence of the relevant equilibria has been shown to be consistent with the observed differences in product composition compared to the HAS over high-T methanol catalysts.

The identified equilibrium constraints also have considerable practical impact on the design of industrial processes. This is especially true in the case of the equilibria governing the formation of methanol and the water–gas shift reaction, which can influence significantly the productivity and selectivity to higher alcohols, and the overall carbon utilization of the process.

Thermodynamics cannot establish the individual steps of the HAS mechanism. However, the observed departures from equilibrium have provided mechanistic insight into the formation of esters and ketones among other products. With respect to this point, it is worth noting the existence of a route to the formation of ketones which is distinct from the pathway for alcohol chain growth, but interlinked with it through the prevailing equilibria between oxygenates (alcohols, aldehydes, acids). Furthermore, we have found that many of the reactions under thermodynamic control in the HAS are associated with some of the major catalytic functions pointed out by an independent TPSR study (e.g., decarboxylation, ketonization, hydrogenation–dehydrogenation).

While in this paper we have focused on reactions limited by thermodynamics, it should be recognized that several reactions in the HAS are not constrained by equilibrium. Among these, the alcohol chain growth is certainly the most important. Indeed, the existence of local equilibria between acids, aldehydes, alcohols, and the related species (esters, ketones) is clearly a consequence of the fact that C–C bond formation is a slow reaction compared, for example, with hydrogenation of carbonyl compounds.

Thus, rationalization of the alcohol distribution calls for a kinetic rather than a thermodynamic treatment. Nevertheless, a necessary requirement is that the proposed pathways for chain growth should be consistent with the articulate thermodynamic background of the synthesis. In this respect, the present work is preliminary to future kinetic modeling approaches and complements information available from independent chemical, physical, and spectroscopic evidence. Development of a kinetic model for the alcohol chain growth according to this strategy is currently in progress.

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