TABLE IV
ACTIVITY COEFFICIENTS

m	γ'_{60}	γ'_{70}	γ'_{80}	γ'_{90}	γ'_{100}
0.05	0.811	0.807	0.803	0.799	0.794
.079	.782	.777	.773	.768	.763
.10	.766(0)	.762(+1)	.757(0)	.752(0)	.746(0)
.14	.744(0)	.739(+1)	.734(0)	.729(+1)	.722(0)
.20	.721(0)	.717(+1)	.711(0)	.705(0)	.698(0)
.30	.697(0)	.691(0)	.686(0)	.679(−1)	.672(−1)
.40	.682(0)	.676(+1)	.671(+1)	.663(−1)	.655(−1)
.50	.672(0)	.667(+2)	.660(0)	.653(−1)	.644(−2)
.60	.665(0)	.659(+2)	.653(+1)	.645(0)	.636(−1)
.70	.661(+1)	.654(+1)	.648(+1)	.640(0)	.631(−1)
.80	.657(0)	.651(+1)	.644(+1)	.636(0)	.627(−1)
1.00	.655(+1)	.648(+1)	.641(+1)	.632(−1)	.622(−2)

the activity coefficients of sodium chloride determined from the boiling point elevation and from electromotive force measurements,[1] are plotted against the temperature. To save space each curve has a different reference point, the ordinate figures give the values of γ at 0° for the corresponding curve. The diameter of each circle represents a variation in γ of ±0.001. An inspection of Fig. 2 shows an excellent agreement between the results obtained by the two methods. While the values of γ at 60° appear to be too high by 0.001 to 0.002 at concentrations above 0.2 M, these deviations are not greater than the expected experimental error. However, the fact that they are all in the same direction would indicate that the observed values of Θ at 60° were slightly too high. This is quite reasonable in view of the greater uncertainty of the measurements at the lower pressures.[13]

Summary

1. The boiling point elevations of aqueous sodium chloride solutions have been measured at reference temperatures of 60, 70, 80, 90, and 100°, and at a number of concentrations between 0.05 and 1.0 M.

2. The activity coefficients of the solute have been calculated.

3. A comparison of the results obtained from the boiling point rise with those obtained from e. m. f. measurements is given.

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The Hydrogenation of Ethane on Cobalt Catalysts

BY ELLISON HALL TAYLOR AND HUGH S. TAYLOR

The immediate precursor of the present study was the work of Morikawa, et al.,[1,2,3] on the activation of the C–H and C–C bonds in hydrocarbons at the surface of a nickel catalyst. By studying two reactions of the same two reactants on the same surface, these authors were able to give to the term "specificity" a concrete meaning. It became immediately a problem of interest to extend the study to other catalysts, in order to see how the factors affecting such reactions would vary from catalyst to catalyst. The hydrogenation-decomposition of ethane gave results of more

interest than the exchange, first because of the abnormally high hydrogen dependence and apparent activation energy, and second because it involved breaking a carbon–carbon bond, a step of more general importance in the transformations of other hydrocarbons than breaking a carbon-hydrogen bond. It was therefore decided to study that reaction on a different catalyst.

Cobalt presented itself as an interesting catalyst for such a study. One reason for the selection of cobalt was its rising industrial importance as a catalyst in the Fischer process.[4] It was therefore decided to use first a catalyst typical of those actually used in that process, one of

(1) Morikawa, Benedict and Taylor, THIS JOURNAL, **58**, 1445 (1936).

(2) Ibid., **58**, 1795 (1936).

(3) Morikawa, Trenner and Taylor, ibid., **59**, 1103 (1937).

(4) Franz Fischer, Brennstoff Chemie, **16**, 1 (1935).

cobalt, thoria, copper and kieselguhr. Work in an entirely different direction led to the choice of a series of cobalt–magnesia catalysts for the other type to be studied. A series of papers by J. R. Lewis,[5,6,7] by Lewis and Taylor[8] and by Taylor, Joris and Verhulst[9,10] had revealed the stability of dilute copper–magnesia catalysts and the high degree of dispersion of the copper as measured by adsorption, reactivity after high temperature treatment and by X-ray studies. Results, as yet unpublished, indicate that cobalt can be similarly very finely dispersed by coprecipitation with magnesium hydroxide.

Experimental Details

Gases.—Hydrogen was prepared by electrolysis of sodium hydroxide solution. Traces of oxygen were removed by passing the gas over a red-hot spiral of platinum wire, the hydrogen being dried before use by slow passage through a trap immersed in liquid air.

The ethane used was prepared by hydrogenation of ethylene on a nickel catalyst followed by combustion of excess hydrogen on copper–copper oxide and by fractional distillation to remove methane and nitrogen. Before use, the ethane was further purified by repeated condensation in liquid air and evacuation of any residual permanent gases.

Catalysts.—The cobalt, copper, thoria catalyst no. 2 was prepared from 0.315, 0.035 and 0.070 mole of the respective nitrates dissolved together in distilled water and diluted to 0.2 molar in total solutes. A 0.2 molar solution of 0.59 mole of sodium carbonate was used for precipitation. To the solution of the nitrates 186 g. of kieselguhr was added and brought into suspension by vigorous stirring. The sodium carbonate solution was then added at the rate of 50–70 drops per minute, with continued stirring. Precipitation was incomplete at the equivalence point and so the whole of the carbonate (supposedly 0.1 mole excess) was added. The precipitate was washed nine times by decantation, filtered with suction and dried at 110°. A weighed portion of the catalyst, in the reaction vessel, was evacuated twelve hours at 255° and reduced in hydrogen at that temperature for 150 hours and then at 350° for thirty hours.

The cobalt–magnesia catalysts, 4A, B, C, D, E, were prepared from stock solutions of cobalt and magnesium nitrates and potassium hydroxide. Five solutions, 500-cc. volume, each containing 0.03 mole of cobalt and 1, 2, 3, 4 and 5 times 0.03 mole of magnesium, respectively, were precipitated by addition of hydroxide at 3 cc. per minute with vigorous stirring continued in each case for one hour after completion of precipitation. The precipitates settled for twenty-four hours, were filtered with suction and washed four times each by stirring the filter cake into

a paste with a little water and then adding one liter of water to form a smooth suspension, finally filtering with suction. After the fourth washing, the supernatant liquids gave only a faint potassium flame comparable with that given by 10^{-6} molar potassium solutions.

The dried catalysts, weighed into the reaction vessels, were reduced in streams of hydrogen, at a rate of 750 cc. per hour, the temperature of the catalyst being raised over a period of four hours to 425° and held there for another four hours of reduction.

Analyses of catalysts nos. 2, 4A and 4E showed 22.7, 38.3 and 14.0% cobalt in close agreement with the expected compositions. Catalyst no. 2 was gray-pink when dried before reduction and yielded a black reduced product. The dried catalysts nos. 4A to 4E varied progessively in color from black through brown to light tan, which color-sequence was maintained after reduction.

Apparatus and Procedure.—The apparatus consisted of the following parts: (1) apparatus for preparing, purifying and storing the gases, (2) apparatus for measuring the gases, (3) a reaction vessel, with necessary auxiliary equipment, (4) an automatic pump of modified Töpler type for removing the gases rapidly from the reaction vessel and handling them during the analysis, (5) apparatus for analyzing the gases and (6) a pumping system for evacuating the catalyst and the rest of the apparatus.

The reaction vessels were Pyrex tubes about 22 mm. in external diameter, 25 cm. long and 115 cc. in volume. The vessel was initially connected, top and bottom, through capillary tubing to a stopcock. After reduction, the bottom tube was sealed off close to the vessel. The catalyst was contained in a small glass cup at the bottom of the vessel. This kept it from being blown about while hydrogen was being passed through for reduction.

The catalyst was protected from mercury vapor by a U-tube filled with copper shot and cooled in a mixture of solid carbon dioxide and acetone placed immediately beyond the inlet stopcock. A manometer and gas reservoir, which consisted of a vertical capillary tube of barometric height attached at the bottom to a 125-cc. bulb served for pressure measurements. During a run, the mercury stood high in the capillary tube. The reservoir was used to hold the gas mixtures before they were put onto the catalyst after an analysis.

The automatic Töpler pump, which consisted of a vessel of about 600-cc. volume, was operated by electrical contacts and a vacuum tube relay to cause mercury to pump gases at a rate of one or two strokes per minute, introducing them to or removing them from the reaction tube, the burets or the analytical system. During the combustion of hydrogen, in the analytical operation, a slower rate of pumping was used. The pump caused the gases to circulate over a copper oxide tube heated electrically to 300°. The water formed was removed in two traps immersed in a solid carbon dioxide–acetone mixture. The combustion process was repeated until constant volume was obtained. The method of analysis was checked occasionally by fractionation of the residual hydrocarbons, which was fairly satisfactory in mixtures rich in methane.

A two-stage mercury vapor pump backed by a Hyvac oil pump comprised the evacuation system. Catalyst

(5) Lewis, J. Phys. Chem., **32**, 243 (1928).

(6) Ibid., **35**, 915 (1931).

(7) Ibid., **37**, 917 (1933).

(8) Lewis and Taylor, THIS JOURNAL, **60**, 877 (1938).

(9) Taylor and Joris, Bull. soc. chim. Belg., **46**, 241 (1937).

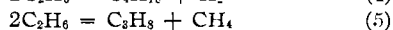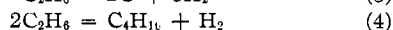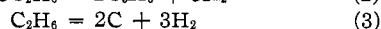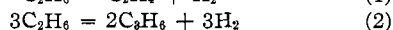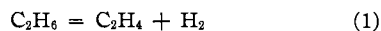(10) Joris, Verhulst and Taylor, ibid., **46**, 393 (1937).

no. 2 was evacuated at 350° and catalysts 4A–4E at 425° between runs for at least eight hours. The reaction temperatures were produced by vapor baths of aniline, 184°, naphthalene, 218°, diphenyl, 255°, and α-bromonaphthalene, 280°.

The experimental procedure was normally as follows: hydrogen and ethane samples to give a desired gas mixture were mixed, introduced to the catalyst and the pressure noted. Adjusting the pressure required from one to two minutes, but the pressure was close to the desired value within about fifteen seconds after the start of the run. At ten-minute intervals throughout the run, the gas was removed partially from the reaction vessel.

At the end of a given interval of reaction, the gas mixture was removed rapidly by expansion into evacuated burets of 500 and 250 cc. volume, respectively, and then into the automatic Töpler pump which was then operated for fifteen minutes. In a typical run 98% of the gas was thus removed within one-half minute. In every case, from 0.1 to 1 cc. of gas could not be removed from the catalyst by this procedure (see later). The gas so collected was analyzed as already described,[2] and, after the analysis, an amount of hydrogen equal to that removed by the combustion was added to the residual hydrocarbons and the reaction procedure repeated. By this method, the pressure at the end of a run could be duplicated to well within 5%.

Calculation of Results.—From the analytical data, corrected to 0° and 760 mm., the amount of ethane decomposed during each reaction stage was calculated by subtracting the initial volume of hydrocarbons from the final volume of hydrocarbons in that stage. The difference between the initial hydrogen volume and the volume of hydrogen burned served as a check, since the hydrogen consumed should be equal to the ethane decomposed. These calculations follow, obviously, from the equation for the assumed reaction $C_2H_6 + H_2 = 2CH_4$.

Two assumptions are involved in the calculations, (a) that the reaction occurring is the hydrogenation of ethane, (b) that all the gas left on the catalyst after removal of the sample in the standard way was hydrogen. The following reactions might conceivably occur in addition to the reaction assumed:

$$C_2H_6 = C_2H_4 + H_2 \tag{1}$$
$$3C_2H_6 = 2C_3H_6 + 3H_2 \tag{2}$$
$$C_2H_6 = 2C + 3H_2 \tag{3}$$
$$2C_2H_6 = C_4H_{10} + H_2 \tag{4}$$
$$2C_2H_6 = C_3H_8 + CH_4 \tag{5}$$

Of these five, the only ones that can take place to an appreciable extent are reactions (3) and (5), all others being eliminated by equilibrium considerations. Reactions (3) and (5) can be eliminated on kinetic grounds. The former results in

a volume increase, which was never observed, and in a deposition of carbon. No large fall in activity was observed as is the case on nickel when carbon deposition occurs. If reaction (5) occurred at an appreciable rate it would yield a larger amount of methane than would be calculated from the combustion analysis. In no case was more methane found by fractionation than was calculated from the combustion analysis. The only remaining reaction is the hydrogenation of ethane to methane and so it is justifiable to base calculations on it as the sole appreciable reaction.

This reaction requires that the ethane decomposed should equal the hydrogen used. If it is assumed that all the gas not recovered is hydrogen, then the calculated amounts of ethane decomposed and hydrogen consumed are equal, in all cases, to well within the experimental error. If it is assumed that part of the gas not recovered is ethane, then the calculated amounts of ethane and hydrogen consumed are not in agreement, thus violating the requirement of the only possible appreciable reaction.

Experimental Results

The experimental results can be presented conveniently in the form of seven diagrams, the first four dealing with the effects of temperature and gas composition on the rate of reaction on the cobalt–copper–thoria catalyst no. 2, the last three the effect of the same variables on three cobalt–magnesia catalysts 4A, 4B and 4E. The experiments were performed in such an order as to repeat, finally, the initial experiment in the group. This procedure would have revealed any marked change in catalyst activity. The initial pressure for each experiment was chosen to give the same partial pressure of ethane, 73 mm., in all the experiments.

Figure 1 shows the effect of temperature, using catalyst no. 2, on a $2H_2 : 1C_2H_6$ mixture at 255 and 280°. Curves 1 and 3 show the reproducibility at 255°. Figure 2 presents, for the same catalyst, the effect of variation in composition at 280°, curves 1 and 4 for a 2:1 mixture and curves 2 and 3 for a 3:1 mixture. Fig. 3 presents data at 255° for variation in gas composition on the same catalyst. Curves 1 and 5 are for a 2:1 mixture, curves 2, 3 and 4 for a 1.25:1 mixture. Figure 4 extends this variable from a 2:1 mixture (curves 1 and 3) to a 3:1 mixture (curve 2). Figures 5, 6
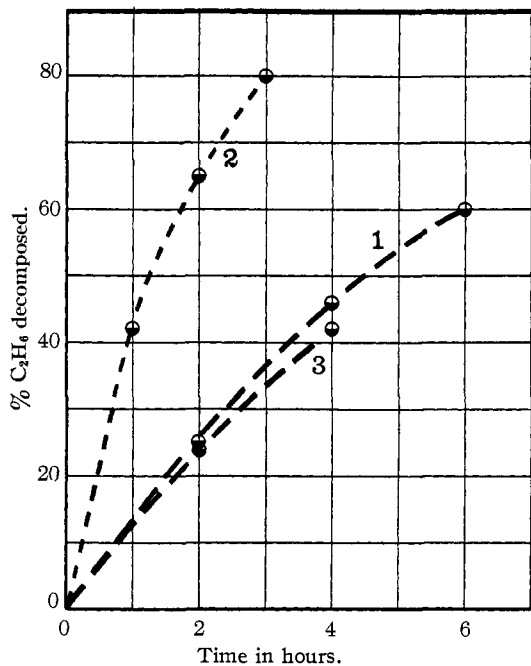
Fig. 1.—Effect of temperature: Co–Cu–ThO$_2$ catalyst; curves 1 and 3 at 255°, curve 2 at 280°.

and 7 present in each case the data for temperature and composition variables for catalysts 4A, 4B and 4E. The mixtures are in each case 2:1 and 3:1, the temperatures are 218 and 255° save
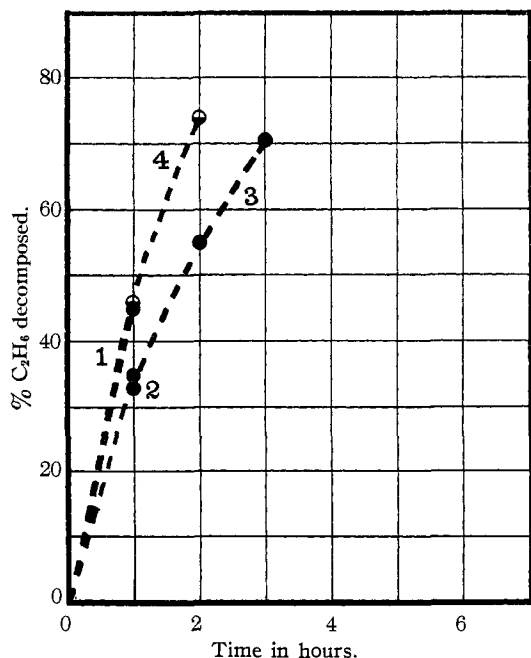

Fig. 2.—Effect of reactant composition at 280° on Co–Cu–ThO$_2$ catalyst: hydrogen–ethane ratio 2:1 in curves 1 and 4, 3:1 in curves 2 and 3.

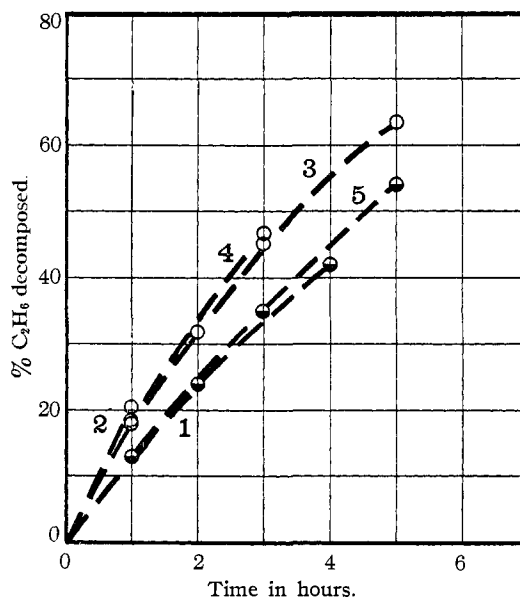in the case of curve 3, Fig. 5, where the temperature is 184° for a 2:1 mixture.[11]

Fig. 3.—Effect of reactant composition at 255° on Co–Cu–ThO$_2$ catalyst: hydrogen–ethane ratio 2:1 in curves 1 and 5, and 1.25:1 in curves 2, 3 and 4.

In Table I is presented a summary of all the experimental results, in which table the initial rate of methane formation per hour is expressed in the fourth column and the derived rates, per
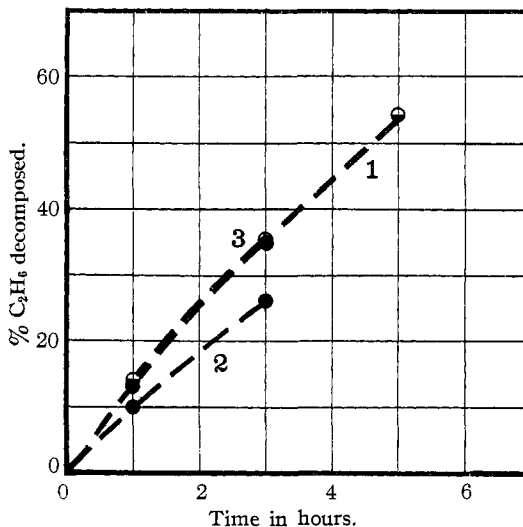

Fig. 4.—Effect of reactant composition at 255° on Co–Cu–ThO$_2$ catalyst: hydrogen–ethane ratio 2:1 in curves 1 and 3, and 3:1 in curve 2.

(11) The actual numerical data from which these curves were constructed are contained in the Ph.D. thesis of Ellison H. Taylor, Princeton University, 1938, a copy of which, in the University Library, may be obtained, on loan, through Inter-library Loan Service.

gram of catalyst and per gram of cobalt in the catalyst, are given in the fifth and sixth columns.

TABLE I

HYDROGENATION OF ETHANE (73 MM.) TO METHANE

Catalyst	Temp., °C.	Initial P_{H_2}, mm.	Average initial rate—% per hour		
			Actual	Per g. cat.	Per g. Co
2	255	92	19	16	70
2	255	147	13	11	48
2	255	220	11	9	40
2	280	147	46	38	167
2	280	220	35	29	130
4A	184	147	4	6	15
4A	218	147	47	66	173
4A	218	220	27	38	99
4B	218	147	14	36	99
4B	218	220	8	20	57
4C	255	147	24	61	200
4E	218	147	2	5	35
4E	255	147	20	49	350

This table immediately reveals the superiority per gram of catalyst or of cobalt, for the conversion of ethane to methane, of cobalt dispersed in magnesia over cobalt dispersed with copper and thoria on kieselguhr.
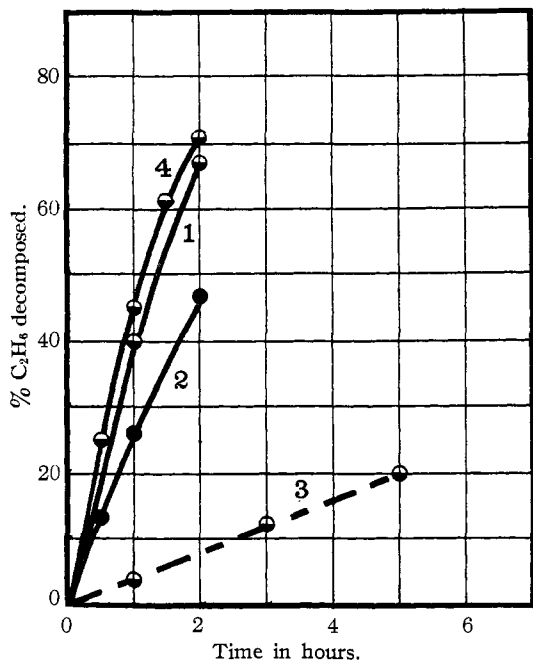

Fig. 5.—Effect of temperature and reactant concentration on 1Co–1MgO catalyst: curves 1 and 4 at 218° and $H_2:C_2H_6$ = 2:1; curve 2 at 218° and 3:1 ratio; curve 3 at 184° and 2:1 ratio.

The apparent activation energy for each catalyst on which sufficient data were available was calculated by applying the Arrhenius equation
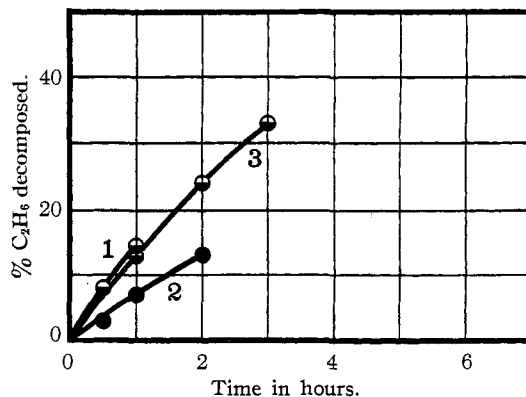

Fig. 6.—Effect of temperature and reactant concentration on 1Co–2MgO catalyst: curves 1 and 3 at 218° and $H_2:C_2H_6$ = 2:1; curve 2 at 218° and 3:1 ratio.

to the initial rates of runs made at different temperatures but with the same partial pressures of reactants. Also, the dependence of the reaction rate on hydrogen concentration was calculated by applying the equation: rate = $k\ p_{H_2}^x p_{C_2H_6}^y p_{CH_4}^z$ to the initial rates of runs with different initial partial pressures of hydrogen, but with constant partial pressure of ethane and at the same temperature. The reaction was assumed to be first-order with respect to ethane (y = 1) and unaffected by methane (z = 0).
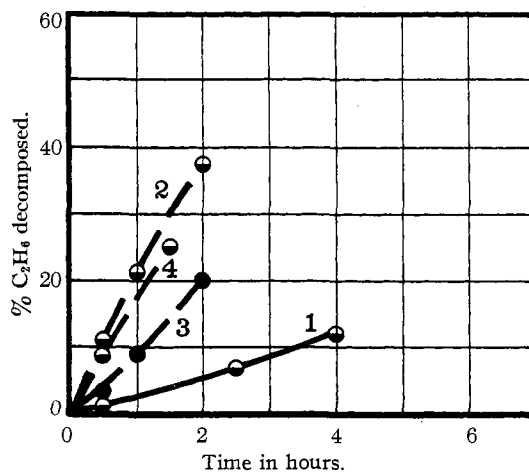

Fig. 7.—Effect of temperature and reactant concentration on 1Co–5MgO catalyst: curve 1 at 218° and $H_2:C_2H_6$ = 2:1; curves 2 and 4 at 255° and 2:1 ratio; curve 3 at 255° and 3:1 ratio.

With the aid of the calculated activation energies the initial rates at a single temperature, 255°, on the different catalysts have been calculated to facilitate comparison. These derived data are presented in Table II.

TABLE II

INITIAL RATES AT 255°, APPARENT ACTIVATION ENERGIES AND HYDROGEN DEPENDENCE OF METHANE FORMATION

Catalyst	Per g. cat., %	Per g. Co, %	Apparent activation energy, kcal.	Hydrogen dependence
2	11	48	30	−0.5 to −0.8
4A	660	1730	31–33	−1.1 to −1.6
4B	360	990		−1.2 to −1.6
4C	61	200		
4E	49	350	31–34	−0.7 to −1.2

The table reveals still more forcefully the greater availability of cobalt dispersed in magnesia for this reaction over that in the usual Fischer type catalyst. The apparent activation energy is slightly higher on the magnesia catalysts probably because of the somewhat larger inhibiting effect of the hydrogen.

Discussion of Results

Comparison with Other Catalysts.—One of the purposes of this study was to place cobalt in its proper position among the metallic catalysts with regard to ability in breaking carbon–carbon bonds in this simple reaction. The table below summarizes results, as nearly comparable as possible, taken from Morikawa's work on nickel,[2] that of Taylor and Joris[9] on copper promoted with magnesia, and the present work on cobalt.

TABLE III

Catalyst	Initial ratio $H_2:C_2H_6$	Temp., °C.	Rate—% per hour per g. of metal
Cu-MgO	3:1	450	4
Co-ThO₂, etc.	2:1	255	48
Co-MgO-1:5	2:1	255	350
Co-MgO-5:5	2:1	184	15
Ni	1:1	184	69

It is obvious that cobalt falls between copper and nickel in its ability to catalyze the reaction being studied, and that it is much nearer to nickel than to copper. This would have been expected from the chemical properties of these elements.

Availability of Cobalt for the Fischer Synthesis.—The latter part of the present work, that on the series of cobalt–magnesia catalysts, was undertaken in an attempt partially to elucidate the problem of the availability of cobalt in catalysts for the Fischer synthesis. Because of the relatively high cost of cobalt, it is of economic importance to find catalysts in which the cobalt is more available for that synthesis, that is, in which the same amount of cobalt shows greater

synthesis activity. It was hoped that the hydrogenation-decomposition of ethane might serve as an index for the availability of cobalt in catalysts for the Fischer process, and, since it is a simpler reaction, that it might aid in putting the whole problem of the Fischer synthesis on a less empirical basis. In this, as in all other catalytic reactions, the only sure method for predicting the properties of a catalyst for the reaction is, of course, to try the reaction on the catalyst. However, since the Fischer synthesis is so complex, it was felt that little fundamental information about catalysts for that process could be obtained by studying that process alone, and that it would be highly desirable to find a simple reaction, involving similar bonds, that would either parallel the Fischer reaction in so far as catalytic activity was concerned, or would provide a method of assessing the availability of the cobalt to carbon–carbon bonds. In the latter case, any effect upon the Fischer catalyst of constituents other than the cobalt should be more obvious, since the hydrogenation-decomposition would indicate the availability to carbon–carbon bonds of the cobalt, leaving to be explained on the basis of promoter action variations in activity for the Fischer process itself. Suppose, for example, that two catalysts were tested in the Fischer process, and that one gave good yields of liquid hydrocarbons and the other poor yields. From that observation alone it would not be clear whether the poor yields in the second case were due to inefficiency of the catalyst in reducing the carbon monoxide to hydrocarbon radicals, or to inefficiency of the catalyst in catalyzing the polymerization of such radicals to the desired higher hydrocarbons. Experiments on the two catalysts with the hydrogenation of ethane would distinguish between the two possibilities, by showing whether there was any difference between the two catalysts in availability of the cobalt to carbon–carbon bonds, and hence to reduction of the carbon monoxide to hydrocarbon radicals.

The results summarized in Table II show that the availability of cobalt for the hydrogenation of ethane is indeed enhanced by the substitution of magnesia for thoria. On the most active of the cobalt–magnesia catalysts, the rate of the reaction per gram of cobalt was about 36 times as great as that on the cobalt–thoria catalyst, and even on the poorest it was about four times as great.

All the published information indicates, however, that cobalt–magnesia catalysts do not measure up to the cobalt–thoria catalysts in yield of liquid hydrocarbons. Yields of 150 cc. per cubic meter of gas are now normal in the latter case whereas with cobalt–magnesia catalysts the yields reported are less than 100 cc. of liquid per meter cube.

It appears, therefore, that the thoria in a Fischer catalyst exerts a promoter action more specific than that of merely dispersing the cobalt. In other words, good availability of cobalt to carbon–carbon bonds, associated in the Fischer process with the reduction of the carbon monoxide to hydrocarbon radicals, is not a sufficient condition for a good Fischer catalyst. There must be present a promoter, such as thoria, which will give to the catalyst suitable properties, presumably for catalyzing the polymerization of the hydrocarbon radicals to the desired products. More evidence for the specific action of the promoter is found in the type of hydrocarbon product resulting from cobalt catalysts with different promoters. The data in the literature indicate that alumina as a promoter gives rise to a light spirit, thoria to the normal Fischer spirit, and manganese oxide to paraffin wax. In these cases, obviously, the promoter is exercising an influence upon the extent of polymerization that takes place.

This suggests that, although it is a better dispersing agent for the cobalt (which undoubtedly initiates the reduction of carbon monoxide to hydrocarbon radicals), the magnesia is less efficient than thoria in bringing such radicals into the polymerizing reactions which ultimately yield the Fischer spirit.

Summary

1. The rate of the hydrogenation-decomposition of ethane has been studied on a cobalt–thoria–copper–kieselguhr catalyst, and upon four cobalt–magnesia catalysts containing varying proportions of the components.

2. The results indicate that, for this reaction, cobalt is somewhat less active than nickel, but much more active than copper.

3. This reaction on cobalt is inhibited by hydrogen, but to a less extent than the same reaction on nickel. The dependence of the rate on hydrogen concentration varies with the nature of the second component of the catalyst.

4. The cobalt–magnesia catalysts are markedly more active in this reaction than the cobalt–thoria–copper catalyst. In the range of composition studied, the activity of the catalysts of the cobalt–magnesia series increased with increasing cobalt content.

5. These results have been discussed in connection with the work of previous investigators on nickel and copper.

6. The use of the hydrogenation-decomposition of ethane as an index to the availability of cobalt in catalysts for the Fischer synthesis of higher hydrocarbons from water gas has been discussed.

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, McGILL UNIVERSITY]

Studies on Lignin and Related Compounds. XXXV. The Ethanolysis of Spruce Wood

BY A. B. CRAMER,[1] M. J. HUNTER[2] AND HAROLD HIBBERT

The isolation from extracted lignins of various aromatic products[3a] such as veratric, dehydrodiveratric and isohemipinic acids[3b]; protocatechuic acid and gallic acid[3c]; catechol, phenol, o-cresol, guaiacol, creosol, 1-vinyl-3-methoxy-4-hydroxy-

benzene, 1-n-propyl-3-methoxy-4-hydroxybenzene[3d] has led to the formation of certain theories of lignin structure, which would seem to be based on unsatisfactory and very incomplete experimental evidence. Up to quite recently there has been a general tendency to ascribe a highly complex structure, or series of closely related structures, to lignin, but there is now a growing opinion[4] that lignin may possibly exist in the wood

(1) Post-graduate student and holder of Hibbert–Cole Fellowship.

(2) Post-graduate student and holder of Dow Chemical Company Fellowship.

(3) (a) For review see "Chemistry of Lignin," M. Phillips, *Chem. Rev.*, **14**, 103 (1934); (b) Freudenberg and co-workers, *Ber.*, **71**, 1821 (1938); **69**, 1415 (1936); (c) Hibbert and co-workers, THIS JOURNAL, **58**, 345, 348 (1936); **59**, 2447 (1937); **60**, 565 (1938); *Can. J. Research*, **16B**, 54, 68 (1938); (d) Phillips and Goss, *Ind. Eng. Chem.*, **24**, 1436 (1932).

(4) Hilpert and co-workers, *Ber.*, **67**, 1157 (1934); **68**, 16, 371, 380, 1575 (1935); **69**, 680 (1936); **70**, 108, 413, 514 (1937); *Z. angew. Chem.*, **49**, 54 (1936); *Cellulosechemie*, **16**, 92 (1935); **17**, 124 (1936).