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(54) METHANOL CATALYST

(54) CATALYSEUR DE METHANOL

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ABSTRACT:

CLAIMS: [Show all claims](#)

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The invention relates to the production of methanol by the catalytic hydrogenation of carbon oxides. The invention also includes new catalysts for use in making methanol from carbon oxides and hydrogen, and methods of making the novel catalyst.

It is known that methanol and other oxygenated organic compounds can be produced by catalytically hydrogenating carbon oxides, and many processes employing various catalysts and conditions for accomplishing this hydrogenation have been proposed. The several catalysts and conditions previously suggested represent such variety as to admit of few generalizations, but it has been generally regarded essential to exclude iron, nickel and related metals from the zone of reaction both because of the detrimental catalytic effect of these metals, and because of their reactivity with carbon monoxide. Also, it has been generally considered essential to avoid subjecting the catalysts to temperatures above those at which it was intended to operate the process, since such higher temperatures were presumed to be injurious to the life and activity of the catalysts.

A principal object of this invention is to provide an improved process for making methanol by catalytically hydrogenating carbon oxides. Another object is to provide a novel catalyst for use in my improved process, and to provide methods of making the new catalyst. Another object is to

provide a process which will operate satisfactorily with iron, nickel and related metals present in the zone of reaction.

In general, my improved process comprises passing mixtures of carbon oxides, predominating in carbon monoxide, together with a larger quantity of hydrogen over my new catalytic material. I prefer to employ active pressures (by which is meant the sum of the partial pressures of the reactive gases in the mixture) in excess of about 2000 pounds per square inch of gage pressure, and to pass the gases over the catalyst with a space velocity (volumes of gas per unit volume of catalyst per hour) at the outlet of about 5,000 to 30,000. The reaction is exothermic and will proceed at a temperature of about 300° to 450° C., dependent somewhat upon the conditions of pressure and velocity and upon the catalyst used. I prefer to operate the process in a reaction vessel constructed of an iron alloy containing both chromium and nickel and which is preferably austenitic in character. However, the nature of the reaction vessel is not a controlling feature of the process.

The new catalyst which I prefer to employ is composed essentially of zinc, copper and chromium which may exist in various forms in the finished catalyst, and the catalyst preferably contains an additional inert metallic diluent of high heat capacity and conductivity. Throughout this specification and the claims, zinc, copper and chromium will be understood to refer to these metals or their compounds however present in the catalyst. This novel catalyst is

peculiar in that it may contain sufficient metallic iron to be magnetic, and it may be reduced at temperatures far above the intended operating temperatures without materially affecting its activity. It is further characterized by exceptional resistance to the usual catalyst poisons, sulfur, for example, and by a remarkable activity and long life.

In the prior art, U. S. patents 1,201,850 (Canadian patent 204,628), 1,558,359 (Canadian patents 251,483 and 251,484), 1,569,775 (Canadian patent 273,685), British patents 227,147 and 247,178 (Canadian patents 264,600 and 264,601); British patent 247,932 (Canadian patents 273,983 and 273,984); and British patents 254,760 and 253,603 propose zinc chromate as a methanol catalyst, but these disclosures supply little information as to the preparation and reduction of the catalysts, and apparently consider such factors, which I have found to be important, of little consequence. In addition, U. S. patent 1,569,775 and British patent 240,955 specify the use of copper chromate.

U. S. patent 1,562,480 (Canadian patent 251,485) mentions a catalyst containing zinc chromate, copper and potassium carbonate, but contrary to this proposal, my researches have shown that alkaline additions are not desirable in methanol catalysts. Patents 1,625,924 (Canadian patents 274,911, 274,912 and 274,913) and 1,625,929 (Canadian patents 274,914, 274,915 and 274,916) describe catalysts comprising one or more non-reducible oxides, such as those of zinc and chromium, one or more easily reducible oxide, such as that of copper, together with a metallic halide. These catalysts are quite essentially different from my new catalysts, and apparently require no reduction before use. In addition to the above, British patents 229,714 and 229,715 mention a long list of metals useful as methanol catalysts and including zinc,

copper and chromium, but do not suggest the particular combination of these three elements. British patent 240,955 separately mentions copper chromium and zinc chromium combinations as catalysts, but does not mention the combination which I have found to be useful.

So far as I am aware, none of the previous investigators have suggested the use of inert metallic diluents in methanol catalysts. My novel catalyst may include this departure from the art.

My new catalyst is particularly active in promoting the synthesis of methanol, and produces better yields with less total hydrogenation to form hydrocarbons than other catalysts upon which published results of their use is available or which I have tested. It is characterized by unique thermal properties which permit it to be readily reduced under a variety of conditions. It is long-lived and comparatively immune to the usual catalyst poisons, and it is readily prepared in mechanical form which is strong and permits ease of handling.

In a preferred form, the catalyst prior to reduction comprises substantially constant proportions of chromium trioxide, and ferrochromium (containing about 70% to 75% chromium and not more than about 2% carbon) together with varying proportions of zinc oxide and copper oxide. In its active state after reduction the catalyst may contain metallic zinc reduced from the oxide by the copper, or unreduced zinc oxide and reduced copper, or both of these oxides may be

partly or wholly reduced. The precise form in which the components exist in the finished catalyst is unknown to me.

The ferrochromium content is preferably about 13%, the chromium trioxide about 25%, and the zinc oxide and copper oxides constitute the balance within the ranges of about 20% to about 65% zinc oxide; with copper oxide in an amount not less than the least amount which renders possible a violent and highly exothermic reduction of the catalyst in the presence of a concentrated reducing gas and not greater than about 36%. Practically, the range of copper oxide may be from a lower limit to about 1.5% to 2.5% to the upper limit of about 36%. In any event the combined zinc, copper and chromium content of the catalyst is preferably greater than about 50% by weight of the total catalyst. Within these ranges a preferred catalyst is composed of 54.9% ZnO, 6.72% CuO, 25.3% CrO<sub>3</sub>, and 13.1% Fe-Cr.

The catalyst prior to use is formed into pellets or tablets of uniform size, and my catalyst compositions when so formed are characterized by a lack of tendency to crumble or disintegrate. This is an important advantage, since the gas distribution over and contact with the catalyst is dependent upon the formation of a bed of uniformly shaped pellets which will not crumble or disintegrate to permit channelling and uneven gas flow.

The method of making the catalyst will be apparent from the following illustrative description of one method of its preparation:

Metallic zinc was reacted with nitric acid (formed from C. P. synthetic nitric acid diluted with two volumes of water), and the resulting zinc nitrate solution was diluted to form a 10% solution. To this solution copper nitrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ) crystals were added in an amount equal to 12.7% by weight of the zinc nitrate in the solution, and the whole was agitated.

Zinc and copper carbonates were simultaneously precipitated from the solution of the nitrates by slowly adding with agitation a 5% solution of ammonium carbonate. Near the end of the precipitation care must be used to avoid excess ammonium carbonate which will cause the zinc and copper to redissolve.

The precipitate was floccular and gelatinous and settled rapidly. It was filtered immediately after precipitation, and washed free of ammonium nitrate and blown with steam. The press cake was then removed, placed in trays and calcined in an oven. The temperature in the oven was maintained at about 300° C. until the loss in ignition was less than 2%.

The roasted oxides were then placed in a ball mill together with zinc chromate and ferrochromium metal. The proportions charged to the mill were:

calcined oxides	41% by weight
zinc chromate	45% " "
ferrochromium	13% " "

The ferrochromium was crushed to between 20 and 40 mesh size. It contained 72.5% Cr and 1.99% C. The zinc chromate was chemically pure and in powder form.

The mix discharged from the mill was very fine and uniform. It was placed in pans and moistened with water to granulate it, dried and brushed and fed to a mechanical tablet press and formed into 1/2 inch pellets.

The catalyst was then ready for use.

The catalyst may be reduced under any one of three general conditions. In general, any hydrogen-containing gas may be used for the reduction, but it is usually convenient to employ the regular methanol gas containing carbon oxides as well as hydrogen. The reduction may be conducted on a large scale in the regular methanol converters which may be the usual upright pressure cylinders with gas inlet at the top and outlet at the bottom. The catalyst chamber is preferably formed of austenitic alloy steel containing about 18% chromium and 8% nickel, and may be provided with perforate trays to support the charge of catalyst pellets in several successive beds.

One condition of reduction may consist in passing methanol gas containing, for example, about 4.0% CO<sub>2</sub>, about 22.5% CO, about 64.0% H<sub>2</sub>, and about 9.5% N<sub>2</sub>, through the catalyst under regular operating pressure or about 4000 pounds per square inch. The gas is circulated while being heated in one portion of the cycle until it is at a temperature of about 250° C. Thereafter the reduction will occur quickly and the



temperature is allowed to rise without control. Temperatures in excess of about 1300° C. are probably reached in this process, and the catalyst mass becomes incandescent. After reduction, the temperature will decrease and operation of the hydrogenation may then begin.

This violent reduction occurs only when sufficient copper oxide is present, as before set forth. However, because of the extreme violence of this reduction it is hazardous to use, and should not be employed except upon a small scale. It is possible to use this drastic reduction with my new catalyst primarily because of its metallic content (ferrochromium) which imparts high heat capacity and conductivity thereto, and permits it to assimilate and dissipate larger amounts of heat rapidly presumably without sintering the active surfaces of the catalyst. This method of reduction will be hereinafter referred to as Method I.

A second condition of reduction may be reduction under medium pressures and with controlled temperatures. This method is preferred for reducing catalysts on full scale in the methanol converters. The catalyst to be reduced is placed in the catalyst chamber of the converters and the system is charged with nitrogen at a pressure of 500 to 800, and preferably at 500 to 600, pounds per square inch. The nitrogen is circulated through the catalyst and heated in one portion of the cycle until the temperature of the catalyst is about 220° C. Substantially pure hydrogen under pressure is then admitted in successive quantities of about 500 cubic feet each. By

this procedure the hydrogen in the cycle gas was maintained at about 0.5% to about 1.5%. It was found that for each addition of hydrogen admitted an equivalent quantity of water was withdrawn from the cycle. This relation held true until the reduction was practically complete. Thereafter the hydrogen content of the cycle gas and the temperature of the catalyst were slowly increased to complete the reduction of the catalyst. This preferred method of reduction will be referred to as Method II.

The third method of reduction is a modification of Method II. In this method, reduction is carried out at atmospheric pressure with a diluted reducing gas to maintain the temperature below about 300° C. during the entire reduction. This will be referred to as Method III and is convenient for work on a minor scale.

The operation of the process will be shown by the following tabulated data:

In the tables and throughout this specification and claims the following definition of the terms used will be observed:

Catalyst analyses indicate percentage composition by weight prior to reduction.

Pressures refer to active pressure or the sum of the partial pressures of the reactive gases in the inlet gas in pounds per square inch of gage pressure. Thus, gas containing 4% CO<sub>2</sub>, 22% CO, 64% H<sub>2</sub> and 10% N<sub>2</sub> at a total gage

pressure of 4500 lbs. per sq. in. would have an active pressure of  $\frac{4500 \times (4 + 22 + 64)}{100} = 4050$  lbs. per sq. in.

Space velocity refers to volumes of gas (at standard conditions) per unit volume of catalyst per hour measured at the outlet of the pressure apparatus.

Per cent carbon monoxide converted indicates that portion of the total carbon oxides in the gas converted to methanol in a single pass through the catalyst. Both carbon monoxide and carbon dioxide are included in this calculation since portions of both appear as methanol.

Production ratio indicates grams of refined methanol produced by one liter of catalyst in one hour.

H<sub>2</sub>/CO ratio indicates the combining ratio of hydrogen with carbon oxides or the ratio of the volume of hydrogen in the inlet <sup>gas</sup> to the combined volume of carbon monoxide and of carbon dioxide corrected on the basis of its combining power with hydrogen in the methanol reaction. Thus, CO + 2H<sub>2</sub> = C H<sub>3</sub>OH and CO<sub>2</sub> + 3H<sub>2</sub> = C H<sub>3</sub>OH + H<sub>2</sub>O, hence, the combining power of carbon dioxide with hydrogen is 1.5 times greater than that of carbon monoxide, and the volume of carbon dioxide in the gas is multiplied by 1.5 in obtaining the H<sub>2</sub>/CO ratio, as in a gas containing 4% CO<sub>2</sub>, 22% CO, 64% H<sub>2</sub> and 10% N<sub>2</sub>, the H<sub>2</sub>/CO ratio is  $\frac{64}{22 + (1.5 \times 4)} = 2.285$ .

TABLE I

In the experiments tabulated below, catalysts were used having a constant content of  $\text{Cr}_2\text{O}_3$  and Fe-Cr, viz. 25.3% and 12.1% respectively, and the proportions of ZnO and CuO therein were varied. In each case the inlet gas contained about 3% to 5%  $\text{CO}_2$ , 60% to 66%  $\text{H}_2$ , 22 to 25% CO and 6% to 10%  $\text{N}_2$ . The significant  $\text{H}_2/\text{CO}$  ratio for each particular gas is shown.

	%	%	$\text{H}_2/\text{CO}$	Space Velocity							
				10,000		20,000		30,000			
				% CO Conv.	Prod. Ratio	% CO Conv.	Prod. Ratio	% CO Conv.	Prod. Ratio		
III	3660	390	51.6	0	2.27	19.2	900	13.11	1345	13.31	1800
III	4100	360	56.3	4.0	2.10	21.08	1075	16.6	1680	14.52	2300
III	3720	355	56.3	4.0	2.26	20.94	1020	16.9	1585	17.68	2580
I	3080	334	56.3	4.0	1.54	24.32	1194			23.72	2110
III	3985	361	54.9	6.7	1.96					24.5	4320
III	4000	361	49.1	12.6	2.14	24.6	1400			20.1	3080
III	3970	350	39.2	22.4	1.98			19.45	1928	24.7	4445
III	3860	350	32.6	29.0	1.84	22.75	1322	19.32	1768	26.0	4650
III	4020	358	26.4	35.2	2.08	26.75	1220	19.41	1910	20.3	3130

TABLE 2

In these experiments, catalysts were used in which the effect of varying the amount of all four constituents is shown. The inlet gas was similar to that given for Table I

			Space Velocity												
							10,000				30,000				
			% CrO <sub>2</sub>	% FeCr	% ZnO	% CuO	H <sub>2</sub> /CO Ratio	% CO Conv.	% CO Prod. Ratio	% CO Conv.	% CO Prod. Ratio	% CO Conv.	% CO Prod. Ratio		
III	4000	340	0	13.1	76.7	14.2	2.22	15.8	792	17.7	2745				
III	4100	360	8.0	13.0	67.1	11.9	2.08			15.5	2328				
III	4000	370	20.5	10.6	60.4	8.5	2.05	15.7	768	17.5	2470				
III	3985	361	25.3	13.1	54.2	6.7	1.96			21.0	3472				
III	4000	375	29.5	13.0	52.1	5.5	2.15	16.1	834	12.2	1885				
III	3800	420	45.5	13.2	40.6	0.68	2.20	12.1	601	8.1	1022				
III	3300	370	47.9	13.1	39.0	0	2.04	11.9	574	15.5	2104				
III	3600	440	49.1	11.7	0	39.2	2.18	4.9	210	3.6	455				

The foregoing tables clearly indicate the characteristics of my new catalysts and the process employing them. The quantity of metallic inclusion, ferrochromium, may be varied if desired. Decreasing the amount detracts from the heat capacity of the catalyst, while increasing amounts have no particular benefit, and serve to reduce the yields by reducing the quantity of active material in the catalyst. Other

metallic additions may be substituted for ferrochromium. For example, I have successfully employed zinc dust, pure iron and tool steel turnings. I have employed up to 75% of inert metallic additions, but I prefer to use less than about 50%.

The long active life of my new catalyst is made apparent by the fact that various batches thereof have operated continuously without appreciable decrease in activity in the production of methanol for periods in excess of eighteen months. The resistance of the catalysts which I have discovered to poisons, such as sulfur, is demonstrated by the fact that these catalysts have continued to operate satisfactorily in producing good yields of methanol after they have become contaminated with sulfur to the extent of 10% or more of the weight of the catalyst.

Within the ranges of conditions for the new process which I have given, I prefer to operate with active pressures of about 3000 pounds per square inch, and with an outlet space velocity of about 18,000 to about 20,000 volumes per volume per hour. Under these conditions, temperatures of about 300° to about 375° C. are preferred.

## I CLAIM:

1. Methanol catalyst initially comprising as the sole essential ingredients zinc oxide, chromium trioxide, and copper oxide at least in an amount which renders possible a violent and highly exothermic reduction in the presence of concentrated reducing gas.
2. Methanol catalyst initially comprising as the sole essential ingredients zinc oxide, chromium trioxide and at least about 1.5% by weight of copper oxide, the combined content of zinc oxide, chromium trioxide, and copper oxide, being greater than about 50% by weight of the total.
3. Methanol catalyst initially comprising essentially zinc oxide, chromium trioxide, copper oxide at least in an amount which renders possible a violent and highly exothermic reduction in the presence of concentrated reducing gas and an inert metallic addition.
4. Methanol catalyst initially comprising as the sole essential ingredients from about 25% to about 65% zinc oxide, from about 8% to about 50% chromium trioxide, and from about 1.5% to about 35% copper oxide, all by weight; the amount of zinc oxide being greater than that required to form a chromate with the chromium oxide present.
5. Methanol catalyst initially comprising essentially from about 25% to about 65% zinc oxide, from about 8% to about 50% chromium trioxide, from about 1.5% to about 35% copper oxide and up to about 50% of an inert metallic addition, all by weight.

6. Methanol catalyst initially comprising essentially from about 25% to about 65% zinc oxide, from about 2% to about 50% chromium trioxide, from about 1.5% to about 35% copper oxide, and up to about 50% ferrochromium, all by weight.
7. Methanol catalyst initially comprising essentially from about 25% to about 65% zinc oxide, about 25% chromium trioxide, from about 1.5% to about 35% copper oxide, and about 13% ferrochromium, all by weight.
8. Methanol catalyst initially comprising essentially about 55% zinc oxide, about 25% chromium trioxide, about 7% copper oxide and about 13% ferrochromium which contains about 70% to 75% chromium and less than about 2% carbon, all by weight.
9. Methanol catalyst substantially identical with a catalyst resulting from the reduction by means of a hydrogen-containing gas at pressures less than 800 pounds per square inch and at temperatures between about 200° and about 300° C. of a catalyst initially comprising as the sole essential ingredients zinc oxide, chromium trioxide, and a substantial amount of copper oxide, the combined weight of zinc oxide, chromium trioxide, and copper oxide being more than 50% of the total.
10. Methanol catalyst substantially identical with a catalyst resulting from the reduction by means of a hydrogen-containing gas at pressures less than 800 pounds per square inch and at temperatures between about 200° and 300° C. of a catalyst initially comprising essentially zinc oxide; chromium trioxide, copper oxide at least in an amount which renders possible a violent and highly exothermic reduction in the presence of concentrated reducing gas and an inert metallic addition.



11. Methanol catalyst substantially identical with a catalyst resulting from the reduction by means of a hydrogen-containing gas at pressures less than 600 pounds per square inch and at temperatures between about 200° and about 300° C. of a catalyst initially comprising essentially zinc oxide, chromium trioxide, at least about 1.5% by weight of copper oxide and an inert metallic addition.

12. Methanol catalyst substantially identical with a catalyst resulting from the reduction by means of a hydrogen-containing gas at pressures less than 600 pounds per square inch and at temperatures between about 200° and about 300° C. of a catalyst initially comprising as the sole essential ingredient from about 26% to about 65% zinc oxide, from about 8% to about 50% chromium trioxide, and from about 1.5% to about 35% copper oxide, all by weight; the amount of zinc oxide being greater than that required to form a chromate with the chromium oxide present.

13. Methanol catalyst substantially identical with a catalyst resulting from the reduction by means of a hydrogen-containing gas at pressures less than 600 pounds per square inch and at temperatures between about 200° and about 300° C. of a catalyst initially comprising from about 26% to about 65% zinc oxide, from about 8% to about 50% chromium trioxide, and from about 1.5% to about 35% copper oxide, together with less than about 50% of an inert metallic addition, all by weight.

14. Methanol catalyst substantially identical with a catalyst resulting from the reduction by means of a hydrogen-containing gas at pressures of about 500 to about 600 pounds per square inch and at temperatures between about 200° and about 300° C. of a catalyst initially comprising from about 25% to about 85% zinc oxide, about 25% chromium trioxide, from about 4% to about 35% copper oxide, and about 13% ferrochromium, all by weight.

15. Process of making methanol which comprises passing carbon oxides together with hydrogen at a temperature of about 300° to about 450° C. with an active pressure of at least 2000 pounds per square inch and at a space velocity of 5000 to about 30,000 volumes per volume per hour over a catalyst initially comprising zinc oxide, chromium trioxide, and a substantial amount of copper oxide.

16. Process of making methanol which comprises passing carbon oxides together with hydrogen at a temperature of about 300° to about 450° C. with an active pressure of at least 2000 pounds per square inch and at a space velocity of about 10,000 to about 30,000 volumes per volume per hour over a catalyst initially comprising as the sole essential ingredients zinc oxide, chromium trioxide, and copper oxide at least in an amount which renders possible a violent and highly exothermic reduction; the amount of zinc oxide being greater than that required to form a chromate with the chromium oxide present.

17. Process of making methanol which comprises passing carbon oxides together with hydrogen at a temperature of about 300° to about 450° C. with an active pressure of at least 2000 pounds per square inch and at a space velocity of about 10,000 to about 30,000 volumes per volume per hour over a catalyst initially comprising essentially zinc oxide, chromium trioxide and at least about 1.5% of copper oxide, together with an inert metallic addition.

18. Process of making methanol which comprises passing carbon oxides together with hydrogen at a temperature of about 300° to about 375° C. with an active pressure of about 3000 to about 4000 pounds per square inch and at a space velocity of about 18,000 to about 30,000 volumes per volume per hour over a catalyst initially comprising essentially from about 26% to about 65% zinc oxide, about 25% chromium oxide, from about 1.5% to about 35% copper oxide, and about 13% ferrenchromium.

19. Process of making methanol which comprises passing carbon oxides together with hydrogen at a temperature of about 300° to about 450° C. with an active pressure of at least 2000 pounds per square inch and at a space velocity of 5000 to about 30,000 volumes per volume per hour over a catalyst initially comprising essentially zinc oxide, chromium trioxide and a substantial amount of copper oxide, said catalyst being contained within a vessel having inner surfaces composed of an austenitic alloy steel containing both chromium and nickel.

20. Process of making methanol which comprises passing carbon oxides together with hydrogen at a temperature of about 300° to about 450° C. with an active pressure of at least 2000 pounds per square inch and at a space velocity of about 10,000 to about 30,000 volumes per volume per hour over a catalyst initially comprising essentially zinc oxide, chromium trioxide and at least about 1.5% of copper oxide, said catalyst being contained within a vessel having inner surfaces composed of an austenitic alloy steel containing both chromium and nickel.

21. Process of making methanol which comprises passing carbon oxides together with hydrogen at a temperature of about 300° to about 375° C. with an active pressure of about 3000 to about 4000 pounds per square inch and at a space velocity of about 18,000 to about 30,000 volumes per volume per hour over a catalyst initially comprising essentially from about 26% to about 65% zinc oxide, about 25% chromium oxide, from about 1.5% to about 35% copper oxide and about 13% ferrochromium, said catalyst being contained within a vessel having inner surfaces composed of an austenitic alloy steel containing both chromium and nickel.