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(54) Title: PROCESS FOR PREPARING FISCHER-TROPSCH CATALYST

(57) **Abstract:** Disclosed herein is a process for preparing a Fischer-Tropsch catalyst. The process comprises the steps of: a) impregnating a particulate carrier with an alpha-hydroxy carboxylic acid; b) impregnating the acid impregnated carrier with and active metal selected from cobalt, iron, manganese, and nickel; c) and then calcining the thus impregnated carrier to produce the catalyst.

PROCESS FOR PREPARING FISCHER-TROPSCH CATALYST

BACKGROUND OF THE INVENTION

This invention relates to Fischer-Tropsch catalysts, and more particularly to a process for preparing a Fischer-Tropsch catalyst.

Synthesis gas (typically a mixture of carbon monoxide and hydrogen) can be converted into hydrocarbons in the presence of a Fischer-Tropsch catalyst under suitable pressure and temperature conditions. In preparation of a Fischer-Tropsch catalyst, a particulate carrier is typically impregnated with an active metal, particularly cobalt, iron, manganese, or nickel.

SUMMARY OF THE INVENTION

The invention provides a novel process for preparing a Fischer-Tropsch catalyst comprising the steps of: impregnating a particulate carrier with an alpha-hydroxy carboxylic acid; impregnating the acid impregnated carrier with an active metal, preferably selected from cobalt, iron, manganese, nickel and mixtures thereof; and then calcining the thus impregnated carrier to produce the catalyst.

As demonstrated in the subsequent examples, the process of the invention produces a Fischer-Tropsch catalyst in which there is substantially uniform distribution of the active metal in the carrier particles. As compared to a more typical profile in which the active metal is concentrated on the outer surfaces of the carrier particles, the substantially uniform distribution of active metal achieved by the inventive process will generally enhance selectivity and/or activity, and will also minimize attrition or loss of active metal from the carrier particles and consequent contamination of the hydrocarbon product.

DETAILED DESCRIPTION OF THE INVENTION

Now describing preferred details of the inventive process, the particulate carrier can be an oxide of silicon, aluminum, titanium, zinc, zirconium, or magnesium; zeolites; or a mixture thereof. Alumina is most preferred.

Suitable alpha-hydroxy carboxylic acids include citric, glycolic, malic, glyceric, and tartaric acids. Citric acid is most preferred. The particulate carrier can be impregnated with the acid by using a solution having the acid dissolved in a suitable solvent, preferably water. According to an incipient wetness technique, the particulate carrier can be sprayed with the solution while agitating the particulate carrier with an inclined rotary apparatus, as was used in the subsequently described examples. Alternatively, slurry impregnation could be employed. The acid impregnated carrier is then dried, preferably in air, at a temperature of at least about 80°C for a time of about 0.5-4 hours. When citric acid is used, the drying temperature is preferably about 100-275°C. The acid present in the acid impregnated carrier is preferably in the range of about 2-20 wt.%, as based on the weight of the particulate carrier.

The acid impregnated and dried carrier can be impregnated with the active metal by using a solution with a suitable active metal compound dissolved in a solvent, preferably water. The impregnation techniques described above could be employed. Suitable active metal compounds soluble in water include halides, nitrates, sulfates, acetates, and thiocyanates of the active metal. The most preferred active metal is cobalt, and cobalt(II) nitrate hexahydrate is a preferred cobalt compound. Optionally, the particulate carrier can also be impregnated with a promoter metal. Useful promoter metals are potassium, chromium, magnesium, zirconium, ruthenium, thorium, hafnium cerium, rhenium, uranium, vanadium, titanium, manganese, nickel, molybdenum, wolfram, lanthanum, palladium, praseodymium, neodymium or other elements from groups IA or IIA of the periodic table of the elements. Preferred promoters are selected from platinum, rhodium, ruthenium, and palladium. Impregnation of the particulate carrier with the promoter metals is typically carried out by using a promoter metal containing compound. Preferably the promoter metal compound is soluble in the above mentioned solution containing the active metal compound. Suitable compounds include halides, nitrates, sulfates, acetates and thiocyanates of the promoter metal. The thus impregnated carrier is preferably dried in flowing air at a temperature of about 60-150°C for a time of about 0.1-4 hours. The dried, impregnated carrier is then calcined at a suitable temperature, typically in the range of about 200-800°C. Calcination is preferably carried out in a flowing air environment for a time of about 0.5-8 hours.

The active metal in the finished catalyst can be, by way of example, in the range of about 1-30 wt.%. The promoter metal in the catalyst can be in the range of about 0.01-5 wt.%. Weight percentages are based upon the total weight of the catalyst. If desired, the particulate carrier could also be impregnated with a carrier stabilizer such as barium or lanthanum.

All steps of the inventive process can be conveniently carried out at atmospheric pressure; as was the case in the specific examples which are described below to further illustrate the invention. These examples should not be construed to limit the invention in any manner.

EXAMPLES

A. Example I

50.0 g of a particulate alumina carrier (obtained from Condea Chemie, Hamburg, Germany, under the designation "Puralox SCCa") was placed in a beaker, and the beaker was positioned on an inclined rotary apparatus. A citric acid solution was prepared by dissolving 5.0 g citric acid in 25 ml of distilled water. The citric acid solution was sprayed on the alumina while the beaker was rotated by the inclined rotary apparatus. The resulting acid impregnated alumina was dried at 250°C for 2 hours in an oven. The acid impregnated alumina was then removed from the oven and allowed to cool.

A cobalt and platinum containing solution was prepared by dissolving 27.8 g of cobalt(II) nitrate hexahydrate in 13 ml of distilled water, and then adding 1.4 g of tetraammine platinum nitrate solution (containing 2.0

wt.% platinum). A beaker containing the acid impregnated alumina was rotated by the inclined rotary apparatus while the cobalt-platinum solution was sprayed on the alumina with an ultrasonic atomizing nozzle. The alumina, as now impregnated with cobalt and platinum, was loaded into a 2 inch diameter quartz tube. The temperature of the tube and its contents was ramped from ambient temperature at 3°C/min to 80°C, and then held at such temperature for 2 hours while flowing air through the tube at 80 cc/min. The temperature was ramped at 3°C/min to 240°C, and then held at this temperature for 2 hours while flowing air through the tube at 300 cc/min. After cooling, the impregnated alumina was further impregnated with cobalt and platinum and then heated a second time using the same procedure as described above, with the exception that 28.4 g of cobalt(II) nitrate hexahydrate and 12 ml of distilled water were used in preparing the cobalt-platinum solution. A third impregnation and heating procedure, identical to the second, was performed to result in the finished catalyst (Catalyst A).

Scanning Electron Microprobe analysis was performed on particles of the catalyst. The weight percentage of cobalt was measured at 2.63 micron increments, starting at the edge (0.0) and ending at an increment close to the center of the particle. Platinum was not measured. Table 1 provides data for ten particles (where "P" stands for "Particle"). This data clearly shows the effectiveness of the inventive process in achieving substantially uniform distribution of cobalt in the particles.

TABLE 1

Cobalt (wt.%)

P	0.00	2.63	5.26	7.89	10.52	13.15	15.78	18.41	21.04	23.67	26.30	28.93	31.56	34.19	36.82	39.45	42.08	44.71	47.34	49.97
1	22.10	22.37	22.53	21.38	21.79	20.87	22.61	19.90	21.85	21.61	21.99	21.10	25.70	26.55	23.01	23.41	27.33	26.95	23.81	20.74
2	22.82	24.55	25.58	22.03	22.82	23.73	24.17	21.79	21.84	23.42	20.84	21.77	17.94	18.95	17.53	19.90	19.29	20.18	24.50	21.80
3	24.09	25.34	25.54	27.26	24.60	22.87	22.34	27.00	21.59	21.08	24.05	19.06	20.28	20.81	21.23	20.60	20.29	15.23	13.51	12.75
4	18.39	18.67	19.95	21.24	20.77	18.70	19.08	19.84	21.37	22.73	20.43	19.39	20.14	21.84	19.07	17.83	19.20	19.09	19.27	19.24
5	20.24	17.53	19.33	19.65	15.10	18.78	24.41	15.26	14.57	15.15	18.29	20.06	20.67	19.92	22.20	17.25	18.23	15.82	16.48	19.18
6	22.62	23.47	23.69	22.24	20.82	25.22	19.86	23.14	22.44	21.86	19.97	20.26	19.59	19.65	19.31	20.09	21.80	23.96	19.24	19.07
7	21.20	24.62	21.01	21.09	18.56	19.86	19.09	23.35	18.85	14.85	27.97	19.72	20.39	23.66	20.45	16.63	16.04	16.20	16.84	15.84
8	22.93	21.84	17.35	17.13	17.83	21.35	21.76	22.25	21.44	19.61	20.04	19.25	20.23	20.94	21.61	22.12	21.80	21.40	20.63	22.89
9	26.30	20.92	24.34	27.24	24.18	17.63	17.88	18.07	19.58	21.17	20.08	19.90	20.57	18.96	18.46	19.44	19.12	19.16	17.13	17.26
10	21.12	27.19	19.76	22.50	16.87	17.31	17.51	18.17	16.10	15.57	25.25	19.03	27.21	23.90	27.45	21.35	20.54	20.13	21.70	18.01

B. Example II

A particulate alumina carrier (obtained from Condea Chemie, Hamburg, Germany, under the designation “Pural SCF”) was first heated in a muffle furnace at 750°C for 16 hours. After cooling, a sample was analyzed and found to have a surface area of 148 m^2/g. 50.0 g of the alumina was placed in a beaker, and the beaker was positioned on an inclined rotary apparatus. A citric acid solution was prepared by dissolving 5.0 g citric acid in 25 ml of distilled water. The citric acid solution was sprayed on the alumina while the beaker was rotated by the inclined rotary apparatus. The resulting acid impregnated alumina was dried at 250°C for 2 hours in an oven. The acid impregnated alumina was then removed from the oven and allowed to cool.

A cobalt and platinum containing solution was prepared by dissolving 27.8 g of cobalt(II) nitrate hexahydrate in 13 ml of distilled water, and then adding 1.4 g of tetra ammine platinum nitrate solution (containing 2.0 wt.% platinum). A beaker containing the acid impregnated alumina was rotated by the inclined rotary apparatus while the cobalt-platinum solution was sprayed on the alumina with an ultrasonic atomizing nozzle. The alumina, as now impregnated with cobalt and platinum, was loaded into a 2 inch diameter quartz tube. The temperature of the tube and its contents was ramped from ambient temperature at 3°C/min to 80°C, and then held at such temperature for 2 hours while flowing air through the tube at 80 cc/min. The temperature was ramped at 3°C/min to 240°C, and then held at this temperature for 2 hours while flowing air through the tube at 300 cc/min. After cooling, the impregnated alumina was further impregnated with cobalt and platinum and then heated a second time using the same procedure as described above, with the exception that 28.4 g of cobalt(II) nitrate hexahydrate and 12 ml of distilled water were used in preparing the cobalt-platinum solution. A third impregnation and heating procedure, identical to the second, was performed to result in the finished catalyst (Catalyst B).

Scanning Electron Microprobe analysis was performed on particles of the catalyst. The weight percentage of cobalt was measured in 2.0 micron increments, starting at the edge (0.0) and ending at an increment close to the center of the particle. Platinum was not measured. Table 2 provides data for ten particles (where "P" stands for "Particle"). This data clearly shows the effectiveness of the inventive process in achieving substantially uniform distribution of cobalt in the particles.

TABLE 2

	Cobalt (wt.%)									
P	0.0	2.0	4.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0
1	12.1	11.8	13.5	12.9	8.9	11.1	13.1			
2	15.6	15.1	12.3	13.2	13.1	13.7	14.3	13.3	13.5	
3	9.4	10.1	10.7	9.1	9.3	12.8				
4	15.1	13.2	12.0	10.9	9.9	12.4	12.6	10.6	12.7	
5	14.5	9.6	9.5	11.0	9.4	7.7	8.1	9.7	11.3	
6	13.1	13.8	16.1	13.0	13.3	18.1	13.5			
7	19.9	9.9	21.4	19.7	19.8	19.2	11.2	7.1	7.0	9.1
8	18.7	20.2	14.9	18.7	13.8	9.8	19.4	18.3	14.1	
9	8.8	10.2	10.2	8.7	8.8	9.2	9.9	9.0	9.3	
10	11.6	10.0	9.9	16.6	15.8	11.0	13.0	12.1	14.0	8.3

C. Control I

A Catalyst was prepared in accordance with the process described in US 5,733,839. 50 g of Puralox SCCa Alumina was added to a solution of 40.0 g of $Co(NO_3)_2 \cdot 6H_2O$ dissolved in 50 ml distilled water. The resultant slurry was treated for 2.5 hours at 75°C and 3.4 kPa in a rotary evaporator to impregnate the alumina carrier and to dry the impregnated carrier. The dried impregnated carrier was calcined at 230°C for 2 hours in an air flow of 1.5

l_n/min. The resultant calcined sample was re-slurried in a solution that was made up by dissolving 35.0 g $Co(NO_3)_2 \cdot 6H_2O$ and 53 mg $Pt(NH_3)_4(NO_3)_2$ in 50 ml of distilled water. This slurry was again vacuum treated for 2.5 hours at 75°C and 3.4 kPa until free flowing in rotary evaporator. The dried impregnated carrier was calcined at 230°C for 2 hours in an air flow of 1.5 l_n/min to produce the finished catalyst (Catalyst C).

D. Control II

A particulate alumina carrier (obtained from Condea Chemie, Hamburg, Germany, under the designation "Puralox SCCa") was first heated in a muffle furnace at 120°C for 4 hours. After cooling, 50.0g of the alumina was placed in a beaker. An aqueous solution was prepared containing 70g of water, 75 g $Co(NO_3)_2 \cdot 6H_2O$, and 0.68 g of a platinum chloride (10 wt.%) solution. 90 g of this solution was added to the beaker containing the alumina and stirred at room temperature for 1 hour. The mixture was next heated on a hot plate to dryness while stirring. The resulting material was further dried overnight in air at a temperature of 120°C followed by calcining at a temperature of 350°C for 3 hours. After cooling to room temperature the resulting material was further impregnated with the remaining solution (55.68g) using the same procedure to produce the finished catalyst (Catalyst D).

E. Catalyst Test Procedure

The reactor used in this catalyst test was a 300 cc stirred tank reactor (purchased from Autoclave Engineers). For each catalyst tested, 10 grams of catalyst were loaded into the reactor and reduced with pure hydrogen at 300 C, atmospheric pressure and 100 cc/min of hydrogen for approximately 6 hours with slow stirring. After the hydrogen reduction, the catalyst was cooled to room temperature in hydrogen atmospheric environment. After cooling, approximately 90 g of octadecane were injected into the reactor as solvent. Then the system was pressurized to 300 psig with a mixture of CO and H_2 and the temperature was increased to 220°C for reaction. The feed gas (CO and H_2) flow rate and feed ratio were controlled using two calibrated mass flow controllers. The stirring speed was maintained at 1200 rpm during all tests, which was sufficient to minimize mass transfer effects between the gas and slurry phases. The outlet gas from the reactor passed through a high-pressure trap (same pressure as the reaction), then to a low-pressure ice trap (atmospheric pressure) to collect the liquid products. The outlet gas was sent to an on-line gas chromatograph for compositional analysis. A wet test meter was used to measure the flow rate of the outlet gas. The tests were conducted for three days. The liquid product was measured and analyzed every day. At the end of the run, the mixture of catalyst, octadecane and wax product accumulated in the reactor was discharged from the reactor. The catalyst was separated by hot filtration through a Whatmans 42 filter paper. The wax mixture was analyzed by gas chromatography. The final product distribution was determined by combining gas phase, liquid product from the two condensers, and product in the octadecane solvent. The results for each catalyst are shown in Table 3.

TABLE 3

Catalyst	**Catalyst A**	**Catalyst B**[1]	**Catalyst C**	**Catalyst D**
Day 1 run				
CO conversion (%)	68.96	31.67	31.33	25.49
Selectivity to HC	68.78	95.17	95.63	94.70
Selectivity to CO_2	31.22	4.83	4.37	5.30
Day 2 run				
CO conversion (%)	39.94	17.02	30.84	32.37
Selectivity to HC	92.69	94.98	96.40	96.56
Selectivity to CO_2	7.31	5.10	3.60	3.44
Day 3 run				
CO conversion (%)	39.91	18.01	28.00	22.69
Selectivity to HC	96.26	97.55	96.86	99.19
Selectivity to CO_2	3.74	2.45	3.14	0.81

TABLE 3 (Cont.)

Catalyst	**Catalyst A**		**Catalyst B**[1]		**Catalyst C**		**Catalyst D**	
Product distribution (wt%)		Olefin to paraffin ratio		Olefin to paraffin ratio		Olefin to paraffin ratio		Olefin to paraffin ratio
C1	8.85		12.04		9.45		10.25	
C2-C4	9.82	0.85	10.46	0.83	10.28	1.51	10.47	1.20
C5-C11	29.30	0.42	24.24	0.39	23.64	0.72	27.59	0.56
C12-C18	23.02	0.01	21.41	0.01	22.95	0.02	20.97	0.02
C19+	29.01		31.85		33.70		30.72	
Co Content[2] (ppm)	3.1		1.4		13.3		1.9	

[1] The data for Catalyst B is an average of two runs except for the Co content where only one of the two runs was analyzed for Co content.

[2] Cobalt content of the wax product and solvent measured using x-ray fluorescence.

The results from Table 3 indicate that the inventive method of producing a Fischer-Tropsch catalyst results in a catalyst with favorable selectivity, conversion and product distribution. Also, the inventive catalyst shows a favorable attrition as shown by the Co content. Additionally, Table 3 indicates better olefin to paraffin ratios than the control methods.

Obviously, many modifications and variations of the present invention are possible in light of the above teachings. It is, therefore, to be understood that the invention may be practiced otherwise than as specifically described.

THAT WHICH IS CLAIMED IS:

1. A process for preparing a Fischer-Tropsch catalyst comprising the steps of:

impregnating a particulate carrier with an alpha-hydroxy carboxylic acid to produce an acid impregnated carrier;

impregnating the acid impregnated carrier with an active metal to produce a metal impregnated carrier; and

calcining the metal impregnated carrier to produce the catalyst.

2. A process according to claim 1 wherein the alpha-hydroxy carboxylic acid is chosen from citric, glycolic, malic, glyceric, tartaric acids and mixtures thereof.

3. A process according to claim 2 wherein the alpha-hydroxy carboxylic acid is citric acid.

4. A process according to claim 1 wherein the acid impregnated carrier is impregnated with the active metal by exposing the acid impregnated carrier to a solution of an active metal compound.

5. A process according to claim 4 wherein the active metal compound is a halide, nitrate, sulfate, acetate or thiocyanate of the active metal or a mixture thereof.

6. A process according to claim 5 wherein the active metal is selected from cobalt, iron, manganese, nickel and mixtures thereof.

7. A process according to claim 6 wherein the active metal is cobalt.

8. A process according to claim 1 further comprising impregnating the acid impregnated carrier with a promoter.

9. A process according to claim 8 wherein the promoter is selected from platinum, rhodium and palladium.

10. A process according to claim 9 wherein the promoter is platinum.

11. A process for preparing a Fischer-Tropsch catalyst comprising the steps of:

impregnating a particulate carrier with citric acid to produce an acid impregnated carrier;

impregnating the acid impregnated carrier with a promoter and with cobalt by exposing the acid impregnated carrier to a solution of a cobalt compound selected from halides, nitrates, sulfates, acetates and thiocyanates of cobalt and mixtures thereof; and

calcining the thus formed cobalt impregnated carrier to produce the catalyst.

12. A process according to claim 11 wherein the promoter is selected from platinum, rhodium and palladium.

13. A process according to claim 12 wherein the promoter is platinum.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US00/10457

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) :Please See Extra Sheet.
US CL :502/325, 326, 327, 332, 335, 336, 337, 338
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/325, 326, 327, 332, 335, 336, 337, 338

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,856,365 A (ZENNARO et al) 05 January 1999, SEE COLUMN 2, LINES 28-35.	1-13
Y	US 5,783,607 A (CHAUMETTE et al.) 21 July 1998, SEE COLUMN 3, LINES 19-31	1-13
X	US 5,863,856 A (MAULDIN) 26 January 1999, SEE COLUMNS 2 AND 3.	1-13
Y	US 4,568,450 A (TING et al) 04 February 1986, SEE COLUMN 3.	1-13
Y	US 4,409,131 A (FETCHIN) 11 October 1983, SEE COLUMNS 1-2.	1-13
Y	US 4,568,449 A (ANGMORTER et al) 04 Febuary 1986, SEE COLUMN 4.	1-13

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:
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A. CLASSIFICATION OF SUBJECT MATTER:
IPC (7):

B01J 23/38, 23/40, 23/42, 23/44, 23/46, 23/74, 23/745, 23/75, 23/755