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[54] **IRON ON MIXED ZIRCONIA-TITANIA
SUBSTRATE FISCHER-TROPSCH
CATALYST AND METHOD OF MAKING
SAME**

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[58] Field of Search **502/330, 338, 325; 518/717, 719, 721**

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[57] **ABSTRACT**

A Fischer-Tropsch catalyst comprising iron co-deposited with or deposited on particles comprising a mixture of zirconia and titania, preferably formed by co-precipitation of compounds convertible to zirconia and titania, such as zirconium and titanium alkoxide. The invention also comprises the method of making this catalyst and an improved Fischer-Tropsch reaction process in which the catalyst is utilized.

19 Claims, No Drawings

IRON ON MIXED ZIRCONIA-TITANIA SUBSTRATE FISCHER-TROPSCH CATALYST AND METHOD OF MAKING SAME

This invention was made under DOE contract No. DE-AC22-80PC30021 (DOE) and is subject to government rights arising therefrom.

FIELD OF THE INVENTION

This invention pertains to a catalytic composition and a method of making that composition, as well as the use of that composition in the selective hydrogenation of carbon monoxide in a Fischer-Tropsch process such as the selective catalytic conversion of synthesis gas to liquid hydrocarbons.

Liquid hydrocarbon fuels or chemicals can be produced from coal by indirect liquefaction. This involves the production of synthesis gas by coal gasification. The synthesis gas is then further converted to fuels or chemicals by hydrogenation of the carbon monoxide in the synthesis gas, typically in a Fischer-Tropsch ("F-T") synthesis. New generation coal gasifiers, such as those produced by Westinghouse, Texaco or Shell-Kopper's partial oxidation processes, produce a CO/H₂ mixture that is CO rich (1:1 to 2:1 CO/H₂). To maximize the efficiency of the overall process of indirect liquefaction, a need exists for Fischer-Tropsch catalysts capable of synthesizing hydrocarbons and/or chemicals directly with CO rich synthesis gas, preferably selectively converting the carbon monoxide to hydrocarbons having from 5 to 25 carbons, referred to herein as C₅-C₂₅ hydrocarbons, sometimes referred to as liquid hydrocarbons.

While the Fischer-Tropsch synthesis has been studied extensively, most previous research has involved fixed bed, gas/solid reactors. Early work was reviewed by Storch, Columbic and Anderson (H. H. Storch, N. Columbic, R. B. Anderson, "The Fischer-Tropsch and Related Syntheses", Wiley 1951). Slurry phase F-T synthesis carried out more recently has been reviewed by Kolbel and Ralek (H. Kolbel, M. Ralek, *Catal. Rev. Sci. Eng.*, 1980, 21, 225) and Poutsma (M. L. Poutsma, *ORNL-5635*, 1980, "Assessment of Advanced Process Concepts for the Liquefaction of Low H₂/CO Ratio Synthesis Gas"), where the potential incentives for using high CO/H₂ ratio syngas in liquid phase slurry reactors were pointed out. Satterfield, et al. recently examined literature on product distributions in F-T synthesis, using Fe catalysts (C. N. Satterfield, G. A. Huff, J. P. Longwell, *Ind. Eng. Chem. Proc. Des. Dev.*, 1982, 21, 465).

While the known prior art shows various combinations of catalytic materials, some of which include one or more of the elements iron, titanium and zirconium, none includes the specific combination as disclosed and claimed herein; nor does the prior art disclose a method of making or using a catalytic composition similar to or suggestive of that disclosed and claimed herein.

SUMMARY OF THE INVENTION

The present invention comprises a porous, catalytically active composition comprised of a mixture of zirconium dioxide and titanium dioxide, combined with iron or iron oxide, either as a surface impregnant on the particles or as an interdispersion with the zirconium dioxide and titanium dioxide.

Preferably, the zirconium dioxide/titanium dioxide mixture is produced by co-precipitation of precursor materials convertible by drying and calcining in air or other oxygen-containing atmosphere to zirconium dioxide and titanium dioxide. Similarly, either iron or iron oxide is preferably incorporated with the zirconium dioxide/titanium dioxide combination by impregnation or co-precipitation of an iron precursor; conversion of the iron precursor to iron oxide is accomplished by drying and calcining in air or other oxygen-containing atmosphere; and, in the case of a catalytically active composition with elemental iron, further conversion of the iron oxide to iron by reducing in a reducing atmosphere.

Still other catalytic compounds such as an alkali metal compound, e.g. potassium bicarbonate, may also be included in a concentration of up to 10%, by weight. The additional compound may be incorporated in the catalyst by impregnation or deposition on the particulate material.

The iron content of this catalytic composition may be from 0.1 to 90%, by weight, preferably 5-15%, by weight. The zirconium:titanium atomic ratio generally is in the range 2:1 to 1:2 preferably about 1:1.

This invention further encompasses the process wherein the catalytic composition described above, made as described, is activated (gradually subjected to elevated temperature and pressure over a period of time and in a reducing atmosphere) and then contacted with carbon monoxide in the presence of hydrogen (e.g. synthesis gas with a relatively high CO:H₂ molar ratio—from 1:1 to 2:1) at elevated temperature and pressure, whereby the carbon monoxide is selectively converted to liquid hydrocarbons.

For a better understanding of this invention, reference may be made to the detailed description thereof which follows, taken together with the subjoined claim.

DETAILED DESCRIPTION OF THE INVENTION

The various forms of catalytic composition within the scope of the present invention may best be described by reference to the method of making these catalytic compositions in accordance with the present invention. In all cases, the essential catalytic ingredients in this invention, namely an intimate mixture of zirconium dioxide and titanium dioxide further combined with iron or iron oxide, are produced by coprecipitation or deposition of a precursor material which convert to the desired oxide upon drying and calcining in an oxygen-containing atmosphere, such as air (typically drying at 90°-110° C. and calcining at 500°-550° C. each for times sufficient to effect drying or calcining, typically in the range 1-20 hours) and to elemental metal upon reducing in a reducing atmosphere for sufficient time to convert the metal oxide to the metal. The zirconium dioxide and titanium dioxide precursors typically comprise zirconium and titanium alkoxides, the alkoxides comprising 1 to 5 alkyl carbon atoms. Such alkoxides may be deposited from a solution with a nonreactive solvent therefor, such as propanol or some other alcohol, by the addition of water or a hydroxyl compound, typically ammonium hydroxide. The process may be referred to as hydrolyzing the alkoxide solution and may consist simply of adding water to the solution.

Iron precursor compounds include iron oxide, hydrated iron oxide, iron hydroxide iron acetate, iron benzoate, iron oxalate, iron maleate, iron nitrate, iron

sulfate, iron gluconate, iron citrate, and iron lactate. By definition, iron compounds include both the ferric and ferrous forms and mixtures thereof. Such compounds may be dry blended with the Zr/Ti dioxide particles or deposited from solution by raising the pH of the solution. All convert, upon application of heat, such as by drying and calcining to iron oxide, which in turn may be reduced to iron in the process of activating the catalyst for the F-T reaction.

The co-precipitate formed in accordance with this invention typically is catalytically active, in part because of its high surface area. This may be enhanced by grinding the precipitate. The surface area of the catalytic material is generally at least 100 square meters per gram, preferably 200 square meters per gram for optimum catalytic effectiveness.

The preferred titanium and zirconium alkoxide precursor materials are the butoxides and propoxides of these metals.

The catalytic effectiveness of these materials may also be enhanced by further combination with other catalytic materials, such as co-precipitated cobalt or nickel compound. Preferably, it is impregnated with an alkali metal compound by deposition of a compound such as potassium bicarbonate or potassium carbonate.

The catalytic material of this invention is preferably used in the Fischer-Tropsch selective hydrogenation of carbon monoxide in high CO:H₂ ratio synthesis gas to produce liquid hydrocarbons. For this purpose, the catalytic material is first activated, in a conventional manner, by gradually exposing it to increasing pressures and temperatures up to on the order of 550° C. and 300 psig in a reducing atmosphere, such as a hydrogen containing atmosphere or the synthesis gas itself. The activated catalyst is then exposed to the carbon monoxide-hydrogen reactive mixture, typically synthesis gas, in a tubular fixed bed reactor or in a slurry phase reactor.

In the preferred form of the catalytic material of the present invention, in which the iron is coprecipitated with the zirconium dioxide and titanium dioxide compounds, the iron may produce a more favorable particle size distribution than in the iron impregnated forms of the present invention. The coprecipitated catalyst has higher specific activity than does the impregnated iron-zirconium dioxide-titanium dioxide support.

This invention has been the subject of numerous experimental syntheses and demonstrations, examples of which are set forth below. Those examples referred to as "comparative" are included only for purposes of comparing the invention to typical prior art catalysts and processes outside the scope of the present invention.

Examples 1-2 pertain to the making of an impregnated zirconia/titania support catalyst in accordance with the present invention. Analyses of these catalysts are summarized in Table 1.

EXAMPLE 1

ZrO₂.TiO₂ was prepared by co-precipitation of equimolar mixtures of Zr(OC₃H₇)₄ and Ti(OC₃H₇)₄ in propanol with water. 50 g Ti(OC₃H₇)₄ and 57.5 g of Zr(OC₃H₇)₄ were dissolved in 200 ml of dry degassed 1-propanol at room temperature. To this was added, with stirring, 200 ml of 50% isopropanol in water to precipitate the hydroxides. The resultant precipitate was washed with water, dried at 110° C. in air, and calcined at 550° C. in air for 2 hours to produce ZrO₂

and TiO₂, intimately mixed in a particulate material with a surface area of 200 m²/gram.

Iron was added by impregnation of the support with an aqueous solution of Fe(N₃)₃. 25.5 g of calcined ZrO₂.TiO₂ was impregnated with 32.54 g of Fe(NO₃)₃.9H₂O dissolved in 30 ml of water. To this solution was added ammonium hydroxide to precipitate iron nitrate. The product was dried in air at 110° C. for 16 hours, and then calcined at 510° C. in air for 2 hours to convert the iron nitrate to Fe₂O₃.

EXAMPLE 2

Ferrous oxalate was supported on another sample of the mixed ZrO₂.TiO₂ precipitate described above (before Fe(NO₃)₃ addition). Specifically 14.49 g of Fe(C₂O₄).2H₂O was dry blended with 22.5 g of ZrO₂.TiO₂. This material was then calcined in air at 550° C. for 2.5 hours, to convert the iron oxalate to iron oxide, and then "promoted" with 0.2% potassium by addition of K₂CO₃ in H₂O to incipient wetness followed by drying at 110° C. for 2 hours.

The following examples (3-6) illustrate the preparation of co-precipitated Fe₂O₃.ZrO₂.TiO₂ catalysts. The analyses of these catalysts are summarized in Table 2.

EXAMPLE 3

Fe(CH₃COO)₂ (ferrous acetate) was hydrated by exposing it to water saturated air for 3 days at 20° C. Fifty-six grams of hydrated Fe(CH₃COO)₂, 91.4 g of Ti(OC₃H₇)₄ and 105.4 g of Zr(OC₃H₇)₄ were dissolved in 1300 ml of dry 1-propanol. To this solution was added with stirring a solution containing 47.0 ml H₂O, 100 ml 1-propanol, and 20 g of 28.9% aqueous NH₃. The resulting precipitate was washed with water and dried in air for 16 hours at 110° C. to produce a co-precipitated mixture of iron oxide and zirconium and titanium dioxides in particle form. This catalyst was promoted with 0.29% K by incipient wetness addition of K₂CO₃ and again dried in air at 110° C. for 5 hours.

EXAMPLE 4

Another sample of the co-precipitated iron oxide, titanium dioxide, zirconium dioxide mixture described above in Example 3 was promoted with 8.0% K by incipient wetness addition of K₂CO₃ and dried in air at 110° C. for 5 hours. It was then calcined in air at 550° C. for 2 hours.

EXAMPLE 5

Twenty-eight grams of hydrated iron acetate, 91.4 g of Ti(OC₃H₇)₄ and 105.4 g of Zr(OC₃H₇)₄ were dissolved in 1300 ml of dry 1-propanol. To this solution was added, with stirring, a solution containing 47.0 ml H₂O, 100 ml 1-propanol and 20 g of 28.9% aqueous NH₃. The resulting precipitate was washed with water and dried in air for 16 hours at 110° C.

This catalyst was promoted with 0.2% K by incipient wetness addition of K₂CO₃. After air drying at 110° C. for 16 hours, the catalyst was calcined at 500° C. for 2 hours.

EXAMPLE 6

A separate sample of the above-described catalyst (Example 5) was promoted with 9.4% K, dried and calcined as in Example 5.

The following examples illustrate the utility of the Fe/ZrO₂.TiO₂ catalyst of this invention for the produc-

tion of diesel range hydrocarbons. Results are shown in Tables 3 and 4.

EXAMPLE 7

The calcined, iron nitrate impregnated catalyst of Example 1 was activated and used for CO hydrogenation in a tubular fixed bed reactor. It was activated by raising the temperature of the catalyst by 50° C./hour from ambient to 275° C. under 1 atm of a 1:1 molar ratio H₂/CO blend flowing at 1160 h⁻¹ followed by increasing the pressure to 300 psig by 50 psi/hour. At 275° C. and 300 psi the CO conversion was 31.8%, the product contained 33.6 wt % hydrocarbons in the diesel range, and the CO/H₂ usage ratio was 0.96. At 700 psi at 281° C. the CO conversion increased to 40.6% (see Table 3).

EXAMPLE 8

The same catalyst used in Example 7 was activated by reducing in H₂ at 450° C. for 2 hours and used for CO hydrogenation at 270° C. and 300 psig in a tubular fixed bed reactor. Results of CO hydrogenation are in Table 3.

EXAMPLE 9

The same catalyst used in Example 7 was activated by reducing in H₂ followed by carburizing in CO for 2 hours at 250° C. It was used for CO hydrogenation at 264° C. and 300 psig in a tubular fixed bed reactor. The results are shown in Table 3.

EXAMPLE 10

The potassium promoted, calcined oxalate catalyst of Example 2 was activated by heating in He at 500° C. for 2 hours. Results of CO hydrogenation in gas phase testing are in Table 3.

EXAMPLE 11

The calcined, ferric nitrate impregnated catalyst of Example 1 was first ground to <325 mesh and then loaded into a tubular reactor. Under 1:1 molar ratio CO/H₂ at 1 atm pressure and GHSV (Gas Hourly Space

Velocity)=277 h⁻¹, the catalyst was heated from ambient to 275° C. over a period of 5 hours, raising the temperature at 50° C./hour. At 275° C., the pressure was then increased at 50 psi/hour to 300 psig over a further 6 hour period. After cooling under N₂, the catalyst was unloaded in a N₂ purge box and slurried in deoxygenated paraffin oil (a commercial product of

Fisher Scientific), before being transferred to a 300 ml continuous stirred tank reactor (CSTR) under N₂. The final loading of the reactor was 160 mls of 19.4 wt % slurry, containing 29.31 g of reduced catalyst. The CO hydrogenation activity was determined with stirring at 1200 RPM, over 300 hours of testing.

Results of testing are shown in Table 4. The activity in the liquid phase was lower than in the gas phase, but the CO/H₂ usage ratio increased to 2.00. The C₉-C₂₅ (diesel range) product was 66% at the beginning of the run.

The following examples illustrate the utility of Fe₂O₃.ZrO₂.TiO₂ for the production of diesel range hydrocarbons from synthesis gas. Results are given in Tables 5 and 6.

EXAMPLE 12

The catalyst in Example 5 was activated as in Example 7. Results of CO hydrogenation are shown in Table 5. The hydrocarbon distribution favored hydrocarbons in the C₉-C₂₅ range; the C₂₆+ yield was only 1.74%.

EXAMPLE 13

The catalyst in Example 5 was activated by reduction in 1 atm H₂ at 294 h⁻¹ at 450° C. for 5.5 hours. The activated catalyst was then slurried in paraffin oil in the absence of air to produce 160 ml of a 13.0 wt % suspension. Results of CO hydrogenation in a 300 cc CSTR autoclave operating at 1200 RPM are shown in Table 6.

TABLES

TABLE 1

Example	Fe Source	Calcination	Fe/ZrO ₂ .TiO ₂ Catalysts (impregnated)			
			Composition (wt %)			
			Fe	Zr	Ti	K
1	Nitrate	510° C.-2 h	14.70	34.88	17.51	—
2	Oxalate	550° C.-2.5 h	5.46	19.82	34.30	0.2

TABLE 2

Example	Calcination	Fe ₂ O ₃ /ZrO ₂ /TiO ₂ Catalysts (co-precipitated)			
		Fe	Zr	Ti	K
3	—	17.84	22.56	21.78	0.29
4	550° C.-2 h	18.23	19.14	21.88	7.98
5	500° C.-2 h	8.45	29.90	16.37	0.20
6	500° C.-2 h	9.93	27.88	17.71	9.38

TABLE 3

Example	Activation	Temp °C.	Activity mole CO/ kg · h	CO Conversion %	Fe/ZrO ₂ .TiO ₂ Tubular Fixed Bed Testing				CO/H ₂ Usage Ratio
					Hydrocarbon Distribution				
					C ₁	C ₅ -C ₁₁	C ₉ -C ₂₅	C ₂₆ ⁺	
7	H ₂ /CO to 275° C.	275	7.89	31.8	8.39	27.63	33.60	7.14	0.956
7*	H ₂ /CO to 275° C.	281	10.36	40.6	9.71	29.66	28.03	4.14	0.649
8	H ₂ - 450° C.	270	10.28	18.4	15.07	36.63	13.08	0	0.754
9	H ₂ - 450° C. CO - 250° C.	264	6.60	26.9	10.55	27.93	38.08	2.98	0.954
10	He - 500° C.	287	6.58	22.0	6.33	43.37	35.34	0	0.564

*700 psi

Conditions: GHSV = 1000, pressure = 300 psig, H₂/CO = 1

TABLE 4

Fe/ZrO ₂ /TiO ₂ Slurry Phase Testing - Example 11														
Time h	P psig	T °C.	GHSV h ⁻¹	CO		H ₂		CO/H ₂		Selectivity wt %				CO/H ₂ Usage Ratio
				Conversion %	Conversion %	Conversion %	Conversion %	Feed Ratio	mol CO/ kg cat/h	C ₁	C ₅ -C ₁₁	C ₉ -C ₂₅	C ₂₆ ⁺	
165.9	497	280.9	289.8	9.2	5.8	1.01	3.29	17.6	2.2	65.6	4.9	1.61		
190.4	680	280.1	282.9	8.4	4.1	0.96	2.86	26.1	0.2	58.4	0.5	2.00		
238.9	710	312.1	281.1	9.5	4.5	0.95	3.15	35.6	6.4	18.8	4.1	2.00		
335.0	711	312.1	281.4	8.2	5.8	0.94	3.39	34.5	2.5	17.8	3.6	1.67		
394.1	710	331.5	281.8	10.9	9.0	0.95	3.66	41.4	5.6	12.5	1.7	1.16		
419.6	719	331.7	282.0	12.2	7.2	0.95	4.10	46.7	5.0	6.5	0.2	1.61		
514.6	713	329.6	132.6	13.2	15.5	0.89	2.01	37.5	5.6	27.5	1.6	0.76		
538.6	714	329.3	139.3	18.7	11.7	1.92	4.16	36.0	7.0	21.1	1.4	3.03		
562.6	313	279.6	343.4	3.6	3.9	0.97	1.48	33.0	7.8	41.0	0.0	0.90		

TABLE 5

Fe ₂ O ₃ /ZrO ₂ /TiO ₂ Gas Phase Testing - Example 12										
Temp °C.	GHSV h ⁻¹	CO		H ₂		Hydrocarbon Distribution				CO/H ₂ Usage Ratio
		Conv %	Conv %	Conv %	Conv %	Activity mole CO/kg · h	C ₁	C ₅ -C ₁₁	C ₉ -C ₂₅	
258	1205	25.3	37.8	5.35	12.90	28.82	27.36	0	0.67	
257	554	40.8	32.6	3.64	5.37	18.80	58.35	1.74	1.06	

Condition: pressure = 300 psig, H₂/CO = 1

TABLE 6

Fe ₂ O ₃ /ZrO ₂ /TiO ₂ Slurry Phase Testing - Example 13														
Time h	P psig	T °C.	GHSV h ⁻¹	CO		H ₂		CO/H ₂		Selectivity wt %				CO/H ₂ Usage Ratio
				Conversion %	Conversion %	Conversion %	Conversion %	Feed Ratio	mol CO/ kg cat/h	C ₁	C ₅ -C ₁₁	C ₉ -C ₂₅	C ₂₆ ⁺	
96.8	302	260.8	322.1	1.5	6.0	1.08	0.94	16.7	19.5	37.4	3.2	0.26		
120.3	498	281.7	314.5	2.9	6.1	1.04	1.79	15.9	26.0	32.2	1.7	0.49		
143.9	498	309.6	314.0	8.3	14.2	1.03	5.15	19.8	29.5	12.4	0.0	0.60		
167.6	498	309.6	318.6	5.6	9.7	2.07	4.68	15.8	33.3	12.0	0.2	1.19		
240.3	502	312.2	320.0	9.2	9.7	1.55	7.01	16.2	21.6	30.5	0.6	1.48		
263.4	698	344.0	343.1	19.8	28.2	1.47	15.74	21.9	24.1	13.9	0.1	1.03		
387.8	708	340.2	267.4	15.4	21.8	1.77	10.24	22.1	23.6	12.2	0.0	1.25		
312.0	708	343.6	311.7	13.5	19.1	0.987	8.15	36.7	14.6	9.4	0.0	0.70		

While this invention has been described with respect to specific embodiments thereof, it is not limited thereto. It is intended therefore that the appended claims be construed to encompass not only those forms and embodiments of the invention described above, but to such other forms and embodiments as may be devised by those skilled in the art without departure from the true spirit and scope of the invention.

INDUSTRIAL UTILITY

The industrial utility of this invention is in the conversion of carbon monoxide, together with hydrogen, to liquid hydrocarbon fuels. This utility may be particularly important in the conversion of synthesis gas, such as that produced in coal gasification processes, thereby to effect conversion of the coal gasification product into liquid hydrocarbon fuels.

We claim:

1. A composition comprising porous, solid particles, said particles containing a mixture of zirconium and titanium dioxides, said particles further containing, at least on the surfaces thereof, iron or iron oxide, and said particles still further containing up to 10%, by weight, of an alkali metal compound.
2. A composition comprising porous, solid particles, said particles containing a mixture of zirconium and titanium dioxides, said particles further containing, interdispersed with said zirconium and titanium dioxides, iron or iron oxide, and said particles still further con-

taining up to 10%, by weight, of an alkali metal compound.

3. The composition according to claim 1, comprising, by weight, 5-15% iron with an atomic ratio of zirconium to titanium in the range of 2:1 to 1:2.

4. The composition according to claim 2, comprising, by weight, 5-15% iron with an atomic ratio of zirconium to titanium in the range of 2:1 to 1:2.

5. The composition according to claim 1, comprising, by weight, 5-15% iron with an atomic ratio of zirconium to titanium on the order of 1:1.

6. The composition according to claim 2, comprising, by weight, 5-15% iron with an atomic ratio of zirconium to titanium on the order of 1:1.

7. The composition according to claim 1, wherein said iron oxide is ferric oxide.

8. The composition according to claim 1, having a surface area of at least 100 square meters per gram.

9. A method of making a catalytically active material wherein said method comprises:

- (a) co-precipitating zirconium dioxide and titanium dioxide precursors, convertible upon drying and calcining in air or an oxygen-containing atmosphere to zirconium dioxide and titanium dioxide;
- (b) drying and calcining said co-precipitate in an oxygen-containing atmosphere to form porous solid particles comprising a mixture of zirconium dioxide and titanium dioxide;
- (c) combining with said co-precipitate, at least on the surface of said co-precipitate, an iron precursor,

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convertible upon drying and calcining in air or an oxygen-containing atmosphere to iron oxide; and (d) drying and calcining said deposit in an oxygen-containing atmosphere or air to convert said precursor to iron oxide.

10. The method according to claim 9, which comprises the further step of reducing in a reducing atmosphere for a sufficient time to convert said iron oxide to elemental iron.

11. Method, as recited in claim 9, wherein an iron precursor is combined by co-precipitation with said zirconium dioxide and titanium dioxide precursors.

12. Method, as recited in claim 9, wherein said zirconium dioxide and titanium dioxide precursors are co-precipitated by hydrolyzing a solution of zirconium alkoxide and titanium alkoxide in an anhydrous, non-reactive solvent.

13. Method, as recited in claim 12, wherein said alkoxides comprise from 1 to 5 alkyl carbon atoms.

14. A method, as recited in claim 12, wherein said resultant catalytically active material is further en-

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hanced, with respect to its catalytic activity by deposition thereon of an alkali metal compound.

15. A method, as recited in claim 14, wherein said alkali compound is potassium bicarbonate or carbonate.

5 16. A method, as recited in claim 9, wherein said convertible iron precursor is selected from the group consisting of iron oxide, hydrated iron oxide, iron hydroxide, iron acetate, iron benzoate, iron maleate, iron nitrate, iron gluconate, iron citrate, iron lactate and iron sulfate.

17. A method, as recited in claim 16, wherein said iron precursor is soluble and is deposited from solution onto said co-precipitated and dried zirconium dioxide-titanium dioxide porous material.

18. Method, as recited in claim 11, wherein said iron precursor is ferric oxide produced by neutralizing a solution including ferric acetate.

19. Method, as recited in claim 9, wherein said iron precursor is soluble and is co-precipitated with said zirconium dioxide and titanium dioxide precursors.

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