

CLAIMS

1. A catalyst precursor comprising:
 - (i) a catalyst support comprising silica and TiO_2 ; and
 - 5 (ii) 35-60 wt% Co present as Co_3O_4 on the catalyst support, wherein the numerical average particle diameter of the Co_3O_4 is less than 12 nm as determined by XRD.

2. A catalyst precursor comprising:
 - 10 (i) a catalyst support comprising silica and TiO_2 ; and
 - (ii) 35-60 wt% Co present as Co_3O_4 on the catalyst support, wherein:
 - (a) the numerical average particle diameter of the Co_3O_4 is less than
12 nm as determined by XRD and the c value of a lognormal
15 particle size distribution of Co_3O_4 is from 0.19 to 0.31; or
 - (b) the D-value of the lognormal particle size distribution is from 19 to 23.5.

3. The catalyst precursor of claim 1 or claim 2, wherein the numerical average
20 particle diameter of the Co_3O_4 is less than 12 nm as determined by XRD and the c value of the lognormal particle size distribution is from 0.19 to 0.31.

4. The catalyst precursor of claim 1 or claim 3, wherein the average particle diameter
of the Co_3O_4 is between 8 and 10 nm.
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5. The catalyst precursor of claim 4, comprising:
 - a TiO_2 -modified silica catalyst support;
 - at least 40 wt% Co, wherein the Co is present in the form of Co_3O_4 , wherein
the numerical average particle diameter of the Co_3O_4 is 8 to 10 nm as determined
30 by XRD; and
 - Pt and optionally Re as promoters;wherein:
 - the mean particle size distribution of the support is between 180 and 300
 μm ;
 - 35 the mean pore volume is less than 1 ml/g;
 - the mean pore diameter is less than 100 Å;

the FTIR spectra band at 950cm^{-1} is 50%-200% of the intensity of the band at 970 cm^{-1} ; and

the catalyst precursor comprises a Co_3O_4 spinel on a titania surface as indicated by Raman spectra.

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6. The catalyst precursor of claim 4, comprising:

a TiO_2 -modified silica catalyst support;

at least 40 wt% Co, wherein the Co is present in the form of Co_3O_4 , wherein the numerical average particle diameter of the Co_3O_4 is 8 to 10 nm as determined by XRD; and

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Pt and optionally Re as promoters;

wherein:

the mean particle size distribution of the support is between 180 and 300 μm ;

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the mean pore volume is less than 1 ml/g;

the mean pore diameter is less than 100 \AA ;

the FTIR spectra band at 950cm^{-1} is 50%-200% of the intensity of the band at 980 cm^{-1} ; and

the catalyst precursor comprises Co_3O_4 as indicated by Raman spectra.

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7. The catalyst precursor of any of claims 4 to 6, wherein the average particle diameter of the Co_3O_4 is about 9 nm.

8. The catalyst precursor of any one of claims 1 or 3 to 7, wherein the c value of the lognormal particle size distribution is from 0.19 to 0.31.

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9. The catalyst precursor of any one of claims 1 or 3 to 8, wherein the c value of the lognormal particle size distribution is from 0.19 to 0.25.

10. The catalyst precursor of claim 2, wherein the D-value of the lognormal particle size distribution is from 19 to 23.5.

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11. The catalyst precursor of claim 10, wherein the D-value of the lognormal particle size distribution is $21 \leq D \leq 23$.

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12. The catalyst precursor of claim 10, wherein the D-value of the lognormal particle size distribution is $21.4 \leq D \leq 22.2$
13. The catalyst precursor of claim 10, wherein the D-value of the lognormal particle size distribution is $21.35 \leq D \leq 22.2$.
14. The catalyst precursor of any one of claims 1 to 13, wherein the catalyst support is a TiO₂-modified silica support.
15. The catalyst precursor of any one of claims 1 to 14, wherein the catalyst support comprises silica and at least 11wt% TiO₂.
16. The catalyst precursor of claim 15, wherein the catalyst support comprises 12-18wt% TiO₂.
17. The catalyst precursor of claim 16, wherein the catalyst support comprises about 16wt% TiO₂.
18. The catalyst precursor of any of claims 14 to 17, wherein the TiO₂ is amorphous.
19. The catalyst precursor of any one of claims 1 to 16 or 18, wherein the catalyst precursor comprises:
40 – 44 wt% Co, 0.1 to 0.3 wt% Re, and 0.01 to 0.05 wt% Pt (each expressed as a percentage of the total weight of the catalyst precursor); and
a TiO₂-modified silica catalyst support, comprising 12-18wt% TiO₂ (expressed as a percentage of the total weight of the catalyst support).
20. A catalyst which is an activated catalyst precursor of any preceding claim.
21. A method of preparing a catalyst precursor according to any one of claims 1-19 comprising
depositing a solution or suspension comprising at least one catalyst metal precursor and a reducing agent onto a catalyst support;
drying the catalyst support onto which the solution or suspension has been deposited; and

calcining the catalyst support onto which the solution or suspension has been deposited in an oxygen-containing atmosphere,

wherein the reducing agent is a carboxylic acid selected from the group consisting of citric acid, ~~tartaric acid, malic acid, maleic acid,~~ lactic acid, glycolic acid, propionic acid, succinic acid, oxalic acid and combinations thereof.

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22. The method of claim 21, wherein the carboxylic acid is citric acid.
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23. The method of claim 21 or claim 22, wherein the catalyst metal precursor is a cobalt-containing precursor.
24. The method of claim 23, wherein the catalyst metal precursor is cobalt nitrate.
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25. The method of any of claims 21 to 24, wherein the catalyst support is a TiO₂-modified silica support.
26. The method of any of claims 21 to 25, wherein the catalyst support comprises silica and at least 11wt% TiO₂.
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27. The method of claim 26, wherein the catalyst support comprises 12-18wt% TiO₂.
28. The method of claim 26, wherein the catalyst support comprises 15-17wt% TiO₂.
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29. The method of claim 28, wherein the catalyst support comprises about 16wt% TiO₂.
30. The method of any of claims 25 to 29, wherein the TiO₂ is amorphous.
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31. The use of a carboxylic acid as the reducing agent to minimise catalyst precursor fracturing in a method of preparing a catalyst precursor as defined in any one of claims 21 to 30.