

	(19) (12)	(KR) (A)	(11) (43)	10-2010-0041782 2010 04 22
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	2009 01 15			
(30)	0704553 2007 06 25	(FR)		
	: 15			

(54) -

(57)

(a) 1 / 1 B /
20 1 1 ;
1 ;

(b) (a) ;

(c) (b)

1

(a) 1 / 1 B /
20 1 1
1 ;

(b) (a) (b)
60 12 340);

(c) (b)

2

1 / 1 B (B) 1 (

3

1 / 1 B (B) 1 (

4

1 3 (a) H_3PO_4 P_2O_5 P_4O_{10}

5

4 (a) H_3PO_4

6

1 5 B ()
P 0.001 3 mol/mol

7

6 B () P 0.01 1
mol/mol

8

1 7 (a)

9

1 8 (a) 24

10

1 9 (a) 24 2

11

1 10
, , , 1,2

12

1 11
, DSC)

13

1 12 (c) 50 200
(furnace)

14

1 13

15

14 , / / / , , , ,

[0001]

[0002]

[0003]

(, , ,) (, ,)
) , , ,

[B S Clausen, HT Topsø e and F E Mørsoth in the work Catalysis Science and Technology, 11 (1996), Springer-Verlag]

[Topsø e et al in number 26 of the Catalysis Review Science and Engineering 1984, 395-420]

[0004]

(European Union Official Journal, L76, 22nd March 2003, Directive 2003/70/CE, L76/10-L76/19)
(2005 1 1 50 ppm(parts per million by weight) 2009 1 1 10 ppm).

[0005]

(refractory) (, $Al_2(MO)_3$ $CoAl_2O_4$
 NAl_2O_4)

: Al^{3+}
 [Carrier et al, Journal of the American Chemical Society 1997, 119, (42) 10137-10146]

$[Al(CH_6M_6O_8)]^3$ (Anderson)

(Raman spectroscopy)

$CoMoO_4$ Co_3O_4

(B S Clausen, HT Topsøe and F E Misseth in the publication Catalysis Science and Technology, 11 (1996), Springer-Verlag).

[0006]

$[Al(CH_6M_6O_8)]^3$

$[Al(CH_6M_6O_8)]^3$

[0007]

$P_{12}M_{12}O_{30}^3$, $P_{11}M_{11}O_{27}^7$

$P_2M_5O_{23}^6$

[Journal of the American Chemical Society 2004, 126 (44), 14548-14556]

$P_2M_5O_{23}^6$

P/M 0.4

[0008]

pH

BET

([Applied Catalysis 56 (1989), 197-206 202])

$CoMoO_4$

$NMoO_4$ Co_3O_4 N_2O

[0009]

[0010]

$CoMoP$

$NMoP$

[0011]

(Intevap)

US 4 743 574

[0012]

1

/

1

B

/

[0013] (1 g m²) , 1 / 1 B

[0014] ; BET

[0015] (a) 1 / 1 B /
20 1 1

[0016] (b) (a) ;

[0017] (c) (b)

[0018]

[0019] (a) , 20 () 1 / B
1 1 , 1 / BET

[0020] (a) 1 / 1 B

[0021] (a)

[0022] 1 / 1 B

[0023]

[0024] 40 %

[0025]

[0026] :

(peptization) , 80 150
0.4 4 mm , 300 600

[0027] 1 B , / /
1

[0028] B / 2.5 %

[0029]

[0030]

B

[0031]

B

% ,

16 29 %

5 35 % ,

15 30

[0032]

[0033]

9 % ,

2 8 %

1 10 % ,

1.5

[0034]

[0035]

[0036]

()

[0037]

B

[0038]

1

1

() B ()

1

250 500

[0039]

)

B /

()

() B

[0040]

Si(OEt)₄

(NH₄)₂SiF₆

Na₂SiF₆

/

[0041]

HPO₃

/

/

[0057] 1 (a) 1 B (B)

[0058] 1 (a) 1 B (B)

[0059] 1 (a) 1 B (B)

[0060] (a) 20 1

[0061] H_3PO_4 (a) P_2O_5 P_4O_{10} ; H_3PO_4

[0062] (a)

[0063] $NH_4H_2PO_4$ (a) $(NH_4)_2H_2PO_4$ $(NH_4)_4P_2O_7$

[0064] 0.005 2 mol/mol , B () P 0.001 3 mol/mol , 0.005 1 mol/mol , 0.01 1 mol/mol (a)

[0065] (a) 1 /

[0066]

[0067] (a) (a)

[0068] 1 (a) (a) 20 1

[0069] (a) 1 , , 1 20 , 24

[0070] (a) 1 , 20 1

[0071] , 24 1

[0072] (a) 2 , 2 (2 20) 1

[0073] , 2 (2 24

-) 1 , .
- [0074] (a) 3 , 20
1 1 ,
- [0075] 20 1
- [0076] 20 2
- [0077] (a) 3 24
1 1 ,
- [0078] 24 1
- [0079] 24 2
1 ,
- [0080] (a) , 1,2
- [0081] (a) , DMSO)
- [0082]
- [0083] ["Solvents and Solvent Effects in Organic Chemistry", C
Reinhardt, Wiley-VCH 3 , 2003, 472-474]
- [0084] (a) , 1
- [0085] (b) , (a) (b) ,
60 12 340 , 24 170
Cast ai ng , X
(napping) (a)
- [0086] (c) , (b) (b)
- [0087] (c)
(c) 50 200 , 60 190 , 60 150
30 4 , 1 3
- [0088] (c) ,

[0089]

[0090]

[0091]

[0092]

[0093]

[0094]

[0095]

[0096]

[0097]

[0098]

[0099]

[0100]

[0101]

(d) (c) ,
 (d) (c) ,
 H₂S
 ARKEMA TPS-37 n- TPS-54 , t-

(d) ,
 / / / (/
 / / /)
 (d)

(d)
 1

: 180 450 , 250 440 ,
 0.5 30 MPa, 1 18 MPa , 0.1 20 h⁻¹,
 0.2 5 h⁻¹ ,
 / 50 2000 l/l

(d) 1
 2

1: CoMP Cl' Cl' ()
 Condea Chemie GmbH SB3 (tabular)
 66% (1 g 7 %
 15 1.6 mm
 120 1 kg 40 g

2 540 1.2 nm 300 m²/g
 0.70 cm³/g 93 X

[0102] (67.9 g)
 (V=57.3 cm³) (7.47 g) (23.34 g) (5.34 g)
 12 120
 Cl' 2 450 C
 1' Cl Cl' Cl ()
 BET :

[0103] · MoO₃: 23.4 (%);

[0104] · CoO 4.1 (%);

[0105] · P₂O₅: 4.6 (%);

[0106] · (S_{BET}): 180 (m²/g), Cl 273 m²/g;

[0107] · P /M₀ 0.563 mol/mol.

[0108] 2 CoMP C2 C2 ()

[0109] C2 (70.7 g), (24.23 g), (5.21 g) (3.25 g)
 Cl

[0110] 1 C2 C2

[0111] · MoO₃: 23.3 (%);

[0112] · CoO 4.0 (%);

[0113] · P₂O₅: 2.0 (%);

[0114] · (S_{BET}): 203 (m²/g), C2 287 m²/g;

[0115] · P /M₀ 0.174 mol/mol.

[0116] Cl BET C2
 BET g

[0117] 3 CoMP C3 C3 ()

[0118] C3 Cl C2 , Co₂M₁₀O₈₈H₄⁶⁺

EP 1 393 802 A1

1 2 C3
 C3 C3 :

[0119] · MoO₃: 23.0 (%);

[0120] · CoO 5.3 (%);

[0121] · (S_{BET}): 214 (m²/g), C3 298 m²/g;

[0122] · P /M₀ 0 mol/mol.

- [0123] C2 C1
- [0124] 4 C1 C1' C4 C4' ()
- [0125] C4(C4') 0.05 (P nml)/(C1 C1')
 Ml nml) (a) CoMlP C1(C1'
 C1') 50/50 /
 20 (78.4
 24.5). 48 , 100 nbar 120 2
 , C4 C4' C4 C4'
 P /Ml :
- [0126] · MoO₃: 23.3 (%);
- [0127] · CoO 4.1 (%);
- [0128] · P₂O₅: 5.1 (%);
- [0129] · (S_{BET}): 179 (m²/g), , C4 273 m²/g;
- [0130] · P /Ml 0.613 nml/nml.
- [0131] BET (a) C1 C1'
- [0132] 5 C2 C2' C5 C5' ()
- [0133] C5(C5') 0.44 (P nml)/(C2 C2')
 Ml nml) (a) CoMlP C2(C2'
 C2') , C4 C5 C4' C5'
 P /Ml , , 0.613 (P nml)/(Ml nml) . 50/50
 /
 20 (78.4 24.5). 48 , 100
 nbar 120 2 , C5 C5'
 C4 C4' P /Ml :
- [0134] · MoO₃: 22.6 (%);
- [0135] · CoO 3.9 (%);
- [0136] · P₂O₅: 5.0 (%);
- [0137] · (S_{BET}): 193 (m²/g), , C5 287 m²/g;
- [0138] · P /Ml 0.614 nml/nml.
- [0139] C4 C4' , (a)
 g
 C4
- [0140] 6 C3 C3' C6 C6' ()
- [0141] C6(C6') 0.613 (P nml)/(C3 C3')
 Ml nml) (a) CoMl C3(C3')
 C6 C6' P /Ml C4 C5

C4' C5' , , 0.613 (P nol)/(
M6 nol) . 50/50 /
, 20 (78.4
24.5). 48 , 100 nbar 120 2 .
C6 C6 :

- [0142] . MO₃: 21.9 (%);
- [0143] . CoO 5.0 (%);
- [0144] . P₂O₅: 4.8 (%);
- [0145] . (S_{BET}): 200 (m²/g), , C6 298 m²/g;
- [0146] . P /M6 0.613 nol/nol.
- [0147] C6 C6' C4 C4', C5 C5' P /M6
(a) . C5 C5',
C4 C4' .
- [0148] ()
- [0149] C6 C6' 450 2 C9 C9' (BET C9 C9')
- [0150] . MO₃: 21.4 (%);
- [0151] . CoO 4.9 (%);
- [0152] . P₂O₅: 4.8 (%);
- [0153] . (S_{BET}): 185 (m²/g), , C9 276 m²/g;
- [0154] . P /M6 0.613 nol/nol.
- [0155] C6 C6' C9 C9' C9 C9' C1 C1' C6 C6'
- [0156] 7. C1, C2, C3, C1', C2',
C3', C4, C4', C5, C5', C6 C6', C9 C9'
- [0157] Cat at est (Geometric) ()
- [0158] (DMS) 5.8 % 20 % 74.2 %
- [0159] :
- [0160] . : 6.0 MPa;
- [0161] . : 0.38 MPa;
- [0162] . : 1.55 MPa;
- [0163] . : 3.64 MPa;

[0164] · H₂S : 0.22 MPa;

[0165] · : 40 cm³

[0166] · : 80 cm³/h

[0167] · : 2 h⁻¹;

[0168] · : 36 l/h

[0169] · & : 350 .

[0170] (T)

(MOC6), (Et CC5) (DMOC5)
 X_{HD} :

[0171] $X_{HD}(\%) = 100 \times (MOC6 + Et CC5 + DMOC5) / (T + MOC6 + Et CC5 + DMOC5)$

[0172] 1

A_{HD} :

[0173] $A_{HD} = 1 \ln(100 / (100 - X_{HD}))$

[0174] 1 (100%) C3

1

[0175]

	CoO/MO ₃ /P ₂ O ₅	P (a)	S _{BET} (m ² /g)	S _{BET} (m ² /g)	C3 A _{HD}	
C1	4 1/23 4/4 6	0	180	273	130	-
C2	4 0/23 3/2 0	0	203	287	112	-
C3	5 3/23	0	214	298	100 ()	-
C4	4 1/23 3/5 1	8%	179	273	138	C1 6%
C5	3 9/22 6/5 0	71%	193	287	144	C2 29%
C6	5 0/21 9/4 8	100%	200	298	145	C3 45%
C9	4 9/21 4/4 8	100%	185	276	109	C3 9% C6 25%

[0176] 1

[0177] 1 g m²

[0178] C6 C9

[0179] 2 (100%) C3

[0180] 2

[0181] C6 () (, C9)

2

[0182]

	CoO/MO ₃ /P ₂ O ₅	C3	A _{MD}	
C1'	4 1/23 4/4 6		123	-
C2'	4 0/23 3/2 0		105	-
C3'	5 2/23		100()	-
C4'	4 1/23 3/5 1		148	C1' 12%
C5'	3 9/22 6/5 0		154	C2' 46%
C6'	5 0/21 9/4 8		153	C3' 53%
C9'	4 9/21 4/4 8		105	C3' 5% C6' 31%

[0183] 8 NMP C7 C7 ()

[0184] C7 C7 C1' C1 ,
24.02 g 11.19 g 7.47 g : 68.2 g

[0185] C7 C7 : 292 m²/g

[0186] · MO₃: 23.1 (%);

[0187] · NO: 4.1 (%);

[0188] · P₂O₅: 4.6 (%);

[0189] · (S_{BET}): 191 (m²/g), , C7 292 m²/g

[0190] 9 C7 C7 NMP C8 C8
()

[0191] C8(C8') (a) 0.05 (P
mol)/(M6 mol) NMP C7(C7)
["Solvents and Solvent Effect in Organic Chemistry", C Reichardt, Wiley-
VCH 3, 2003, 472-474] 46 DMSO . 48
, 100 mbar 120 2 C8 C8'
:

[0192] · MO₃: 23.0 (%);

[0193] · CoO: 4.1 (%);

[0194] · P₂O₅: 5.1 (%);

[0195] · (S_{BET}): 190 (m²/g), , C8 282 m²/g

[0196] 10 C7, C8 C7, C8

[0197] C7, C7, C8 C8
:

[0198] · 15 : 0.8522

[0199] . : 1.44 %
 [0200] .
 [0201] IP : 155
 [0202] 10% : 247
 [0203] 50% : 315
 [0204] 90% : 392
 [0205] EP : 444
 [0206] 2 % 350

[0207] . : 7 MPa
 [0208] . : 30 cm³
 [0209] . : 340
 [0210] . : 24 l/h
 [0211] . : 60 cm³/h

[0212] 3 , C7
 100 (HDS) 1.5

[0213] $A_{HDS} = 100 / ([(100 - \%HDS)]^{0.5}) - 1$

3

[0214]

	C7		C8
	S _{BET} (² m ² /g)	S _{BET} (² m ² /g)	C7 A _{HDS}
C7	191	282	100
C8	190	282	145

[0215] 3 HDS CoM6 NM6
 . C7 C8 4 , C7

[0216] , 3 1 g m² C7
 C8

4

[0217]

C8	C7
	C7 A _{HDS}
C7	100
C8	155

[0218] 4 HDS CoM6 NM6

[0219] **11:**

[0220] C7 C8

[0221] . 20 : 0.9365

[0222] . : 2.92 %

[0223] . : 1400 ppm

[0224] .

[0225] IP : 361

[0226] 10% : 430

[0227] 50% : 492

[0228] 90% : 567

[0229] EP : 598

[0230] 2 % 350

[0231] . : 12 MPa

[0232] . : 40 cm³

[0233] . : 380

[0234] . : 40 l/h

[0235] . : 40 cm³/h

[0236] 5 , C7

100 1.5

(%HD) :

[0237] $A_{HD} = 100 / ((100 - \%HD)^{0.5}) - 1$

[0238] (%DN A_{DN})

[0239] , 380

(ASTMD86) :

[0240] = (%380⁺ - %380⁻) / %380⁺

5

[0241]

	C7		C8
	C7	A _{HD}	C7 A _{DN} 380 ⁻ (%)
C7		100	100 25
C8		135	145 29

[0242] 6

[0243] **12 CoM** C9 ()

[0244] C9 C3 , 1.35 (factor)

C9

:

[0245] · MoO₃ 17.0 (%);

[0246] · CoO 3.9 (%);

[0247] · (S_{BET}): 231 (m²/g).

[0248] 13 C9 CoMo C10 ()

[0249] C10 0.015 (P mol)/(M mol)

C9 ["Solvents and Solvent Effect in Organic Chemistry", C Reichardt, Wiley-VCH 3, 2003, 472-474]

33 96 100 nbar 120 2

C10 :

[0250] · MoO₃ 16.8 (%);

[0251] · CoO 3.8 (%);

[0252] · P₂O₅ 1.0 (%);[0253] · (S_{BET}): 228 (m²/g).

[0254] 14 FCC

[0255] C9() C10() FCC
3.5 MPa 200 Grignard ()
3- 1000 ppm n- 2,3- - -2- 10 %210 cm³ ; 4 g () .H₂S/H₂(4 l/h, H₂S 15 %) 400 2 (5 /)200 H₂ 2 Grignard[0256] (1 g) (k_{HIS}) 1 (k_{HIO}) 0
k_{HIS}/k_{HIO} C9 C10

6

6

	C9()	C10()	
	K _{HIS}	K _{HIO}	K _{HIS} /K _{HIO}
C9	1.0	2.32	0.43
C10	1.3	2.34	0.56

[0258] C10 C9()

[0259] 15 C11' C11

[0260] C11'

C2 ["Solvents and Solvent Effect in Organic Chemistry", C Reichardt, Wiley-VCH 3, 2003, 472-474] 38 1,2

[0261] C11 C2

[0262] 15 C2 C2 () C12

C12

[0263] C12 C2 1 mol 0.275 mol
 ["Solvents and Solvent Effect in
 Organic Chemistry", C Reichardt, Wiley-VCH 3, 2003, 472-474]
 38 1, 2- C12 :

[0264] · MgO : 22.6 (%);

[0265] · CoO : 3.9 (%);

[0266] · P_2O_5 : 5.0 (%);

[0267] · (S_{BET}): $197 \text{ m}^2/\text{g}$, C12 $288 \text{ m}^2/\text{g}$

[0268] **16** **C13**

[0269] C13 C2 1 mol 0.275 mol
 ["Solvents and Solvent Effect in Organic
 Chemistry", C Reichardt, Wiley-VCH 3, 2003, 472-474] 5.7

[0270] · MgO : 22.5 (%);

[0271] · CoO : 3.8 (%);

[0272] · P_2O_5 : 5.1 (%).

[0273] **17**: C2(C2')(), C11(C11')(), C12(C12')() C13(C13')()

[0274] C2, C2' (), C11, C11' (), C12, C12' (), C13 () 10

7

	C2	A_{HS}
C11,		115
C12,		145

[0276] 7 CoMP (a)

[0277] C11', C12 C13 8, C7

8

	C11', C12 C13	
	C7	A_{HS}
C11',		135
C12',		175
C13',		97

[0279] , 5
 (a) 20, 1, 2

[0280]

C11'