

(19)  
(12)

(KR)  
(A)

(51) 。 Int. Cl.<sup>7</sup>  
B01J 29/85  
B01J 23/83  
B01J 35/00  
B01J 37/08

(11)  
(43)

10-2004-0089680  
2004 10 21

(21)  
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(86)  
(86)

10-2004-7013384  
2004 08 26  
2004 08 26  
PCT/US2003/004153  
2003 02 10

(87)  
(87)

WO 2003/074176  
2003 09 11

(30)

60/360,963  
60/366,012  
60/374,697  
10/215,511

2002 02 28  
2002 03 20  
2002 04 22  
2002 08 09

(US)  
(US)  
(US)  
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(71)

77520

5200

(72)

08801

88

19473

89

(74)

:

(54)

,

4 / 1 , 2 3 1 .

( ),

(light) ( ), / .

(oxygenate), ( ) 가 ( ), /

1 ( ) 가

5,367,100 , ZSM-5 ( )

4,062,905 , T, ZK5,

4,079,095 ZSM-34 (  $\text{AlPO}_4$  )

4,310,440 ( )

( ) 가 (SAPO)

[ $\text{SiO}_2$ ], [ $\text{AlO}_2$ ] [ $\text{PO}_2$ ] 4 3

. SAPO ( 가 )

4,499,327 , 4,677,242 , 4,677,243 , 4,873,390

5,095,163 , 5,714,662 6,166,282 가

, SAPO (coking)

가

4,465,889 , -C<sub>4</sub>

6,180,828

1 , , ,

5,417,949 (effluent)

EP-A-312981 (refractory) 1 , -

(Kang) (Inui) [ *Effects of decrease in number of acid sites located on the external surface of Ni-SAPO-34 crystalline catalyst by the mechanochemical method* , Catalysis Letters 53, pages 171-176(1998)]

가 Ni-SAPO-34

MgO, CaO, BaO Cs<sub>2</sub>O, 가 BaO

WO 98/29370 , , , 4 , 5

, 100  
)/m<sup>2</sup>( )  
0.03mg( )/m<sup>2</sup>( )<sup>1</sup>, 0.035mg( )

, 1

2 3  
, 2 / 3  
1

, .

, 4 2 / 3 , ,

4 , , 100 2 , 0.03mg( )/m<sup>2</sup>( )  
1

, 80 4 10 (hydrothermally) , 400 900 ,  
2

4 , , 100 0.03mg( )/m<sup>2</sup>( )  
1 ( ) ( ) , ,

, , , 1

, 1 , 1.5 (LEI) . LEI

, ( )  
1 , ,  
( )

[CRC Handbook of Chemistry and Physics, 78th Edition, CRC Press, Boca Raton, Florida(1997)] IUPAC 4 ( : )

2 / 3 1  
가

IUPAC  
가 3 가  
[the Atlas of Zeolite Framework Types, 5th edition, Elsevier, London, England (2001)]

( ) A  
EL, AFY, AEI, BEA, CHA, EDI, FAU, FER, GIS, LTA, LTL, MER, MFI, MOR, MTT, MWW, TAM TON  
AEI (topology) CHA  
, 가 CHA

[illegible]

SAPO AIPO SAPO-5, SAPO-8, SAPO-11, SAPO-16, SAPO-17, SAPO-18, SAPO-20, SAPO-31, SAPO-34, SAPO-35, SAPO-36, SAPO-37, SAPO-40, SAPO-41, SAPO-42, SAPO-44 ( 6,162,415 ), SAPO-47, SAPO-56, A1PO-5, AIPO-11, AIPO-18, A1PO-31, A1PO-34, A1PO-36, A1PO-37, AIPO-46, SAPO-18, SAPO-34, SAPO-35, SAPO-44, SAPO-56, A1PO-18 A1PO-34, SAPO-18, SAPO-34, AIPO-34 A1PO-18, SAPO-34 A1PO-18

(intergrowth)

2002-0165089 1998 4

16 WO 98/15496

, SAPO-18, AIPO-18 RUW-18 AEI

2-0165089 CHA DIFFaX CHA AEI 가 1:1 , AEI CHA 200

0.40 0.10, 0.32 0.10, 가 0.65 0.65 0.10, 0.32 0.15 Si/Al

(LEI) : .

(quantification)

1

$$LEI = \frac{1}{\dots}$$

10% 1g 가 1 LEI / 1.0 LEI

LEI , 1.2 15, 1.3 , 1.5 , 1.7 , 1.5 10 1.1 2

LEI , 1.2 15, 1.3 , 1.5 , 1.7 , 1.5 10 1.1 2

LEI , 1.2 15, 1.3 , 1.5 , 1.7 , 1.5 10 1.1 2

0.035mg( )/m<sup>2</sup>( ) 100 0.03mg( )/m<sup>2</sup>( ) ,

0.035mg( )/m<sup>2</sup>( ) 100 10mg( )/m<sup>2</sup>( )

5mg( )/m<sup>2</sup>( ) 100 0.2mg( )/m<sup>2</sup>( )

0.04 0.2mg( )/m<sup>2</sup>( )

가 200 500 가 가

100 , 가(mg)/ (mg)

(Mettler) TGA/SDTA 851 500

100 10

% 20 ( 12 / ) 가

1mg (Brunauer), (mg) 3 가가 (flushing) 500 ASTM D3663 (mg)/

(m<sup>2</sup>) (Teller)(BET)

( ) 10 m<sup>2</sup>/g , 10 m<sup>2</sup>/g 300 m<sup>2</sup>/g BET

( ) 20 m<sup>2</sup>/g , 20 m<sup>2</sup>/g 250 m<sup>2</sup>/g BET

, 25 m<sup>2</sup>/g , 25 m<sup>2</sup>/g 200 m<sup>2</sup>/g BET

( ) 20 m<sup>2</sup>/g , 25 m<sup>2</sup>/g , 30 m<sup>2</sup>/g BET

( )

. 4 n- 가 . 4 (bridging)

가 가

80 , 100

4

6 , Ca<sup>2+</sup> 8 pH 1 , 8 (NH<sub>4</sub><sup>+</sup> , Na<sup>+</sup> , K<sup>+</sup> , Mg<sup>+</sup> )

Ca<sup>2+</sup> , /

4

7 pH ,

4 2 / 3 , 4 1

2 / 3 2 , 4

, 4 2 / 3

가

200 , 0 200

20 100 80 100 5

3

( )

, 400 , 500 , 600 , 900 , 650

800 48 , 0.5 24 , 1.0 10 , 700

1 3

, 4 2 / 3 , 2 / 3 4

4 3 4 3 1000:1 1:1, 500:1 2:1, 100:1 3:1

, 75:1 5:1 , 3 1 25

%, 4 1 20 %, 1 15 % 3

4 2 4 2 1000:1 1:2, 500:1 2:3, 100:1 1:1

, 50:1 2:1 , 2 1 25 %, 4 1

20 %, 1 15 % 2

( )

1 1

%, 20 % 500 %, 가 800 %, 10 % 600

%, 30 % 400 %

가 가

(glue) . 가 ,

Al<sub>m</sub>O<sub>n</sub>(OH)<sub>x</sub>

)<sub>o</sub>Cl<sub>p</sub> · x(H<sub>2</sub>O){ , m 1 20 , n 1 8 , o 5 40 , p 2 15 , x

0 30 } [G. M. Wolterman, et al., Stud. Surf. Sci. and Catal., 7

6, pages 105- 144 (1993)] Al<sub>13</sub>O<sub>4</sub>(OH)<sub>24</sub>Cl<sub>7</sub> · 12(H<sub>2</sub>O) , 1

1

가 ( )

가 Nalco 8676 ( 가 Nyacol AL20D

W

(densifying), (crush) (thermal sink) 가

1

(Dixie), (McNamee), / /

가 (fresh) ,가

0.1  $\mu\text{m}$  0.6  $\mu\text{m}$  , D<sub>90</sub> 1  $\mu\text{m}$  ,가

1 % 80 %, 5 % 60 %, 5 % 50 %

1:5, 1:10 1:4, 2 % 1:6 1:5 30 %, 5 % 20 %, 7 % 1:15

15 % .

.8 g/cc 3 g/cc 0.5 g/cc 5 g/cc, 0.6 g/cc 5 g/cc, 0.7 g/cc 4 g/cc, 0

---

.가

(kneader) (muller), ( ) /

/ /

가 가

/ .가

den) / 000 , 500 , 800 , 가 550 700 (flue) (가 가) 가 400 (har 1,

15 , 1 10 600 700 1 5 ,가 30

2 4 가

[illegible]



(WHSV)  $1 \text{ hr}^{-1}$  5000  $\text{hr}^{-1}$ , (  $2 \text{ hr}^{-1}$  3000  $\text{hr}^{-1}$ , 5  $\text{hr}^{-1}$   
 $1500 \text{ hr}^{-1}$ , 가  $10 \text{ hr}^{-1}$  1000  $\text{hr}^{-1}$  , WHSV  $20 \text{ hr}^{-1}$   
 , 가 / 20  $\text{hr}^{-1}$  300  $\text{hr}^{-1}$  .

(fixed bed) , (fluidized bed) (

, 1 ( )  
 (riser) ( )  
 (disengaging vessel) 가 .

(stripping) , , , , , ,  
 , , / , , , , ,

, 가  
 0.5 %  
 50 , 700 , 450 750 , 5

/ ( ) .

( ),

, / ( )  
 1 ,  
 150 450 5 MPa 10 MPa  
 (heterogeneous) ,  
 , ( ), /

EP-B-0 933 345

, ( )

가 .

, LEI ( ) (LEI가 1 )  
 가 ( ) 10% 1 10% 1 ( ) ,

' (prime) '  $C_2 = / C_3 = '$  가  
 .  $C_3$  '  $C_4$  's  $C_5$  +'s  
 ,  $C_5$  's,  $C_6$  's,  $C_7$  's 100%가  
 ,  $C_5$  +'s

A

(templating agent) (R1)

(R2) MSA (Condea Pural) SB, SAPO-34

: 0.2 SiO<sub>2</sub> / Al<sub>2</sub>O<sub>3</sub> / P<sub>2</sub>O<sub>5</sub> / 0.9 R1/ 1.5 R2/ 50 H<sub>2</sub>O.

가 , R1 가 170 40 가 (mother liquor)

가 (85%) 가 Ludox AS40(40% SiO<sub>2</sub>) R2 가 ,

B

(furnace) (1/4 (0.64cm) )

. 475 (WHSV) 25 psig(172.4 kPag) 1

100h<sup>-1</sup> (load) 50 mg , (bed)

1

1000g ZrOCl<sub>2</sub> · 8H<sub>2</sub>O 3.0 . 400g NH<sub>4</sub>OH 3.0

가 60 가 가 pH 9 50ml/

가 72 (100 ) 3 700

85

2

500g ZrOCl<sub>2</sub> · 8H<sub>2</sub>O 84g La(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O 3.0 . 260g

g NH<sub>4</sub>OH 3.0 60 가 ,

50ml/ 가

pH 9 72 (100

) 85

3 700 10 % La(

)

3

50g ZrOCl<sub>2</sub> · 8H<sub>2</sub>O 300ml . 4.2g La(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O 300m

l (28.9g) 가 pH 9

72 (100 ) 3 700

85 5 % La

4

500g ZrOCl<sub>2</sub> · 8H<sub>2</sub>O 70g Y(NO<sub>3</sub>)<sub>3</sub> · 5H<sub>2</sub>O 3.0 . 260g

g NH<sub>4</sub>OH 3.0 60 가 ,

50ml/ 가

pH 9 72 (100 )

85

3 700 , 10 % Y( )

\_\_\_\_\_ 5

500g  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  56g  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  3000ml . 260  
 g  $\text{NH}_4\text{OH}$  3000ml  
 (160g) 가 pH 9  
 72 (100 ) , , 85  
 3 700 ,  
 5 % Ca( )

\_\_\_\_\_ 6

70g  $\text{TiOSO}_4 \cdot x\text{H}_2\text{O}$   $\text{SO}_4 \cdot x\text{H}_2\text{O}(x=1)$  400ml . 12.8g  $\text{CeSO}_4$   
 300ml 가 pH 8 . (64.3g)  
 (100 ) , , 85  
 3 700 ,  
 5 % Ce

\_\_\_\_\_ 7

5g  $\text{HfOCl}_2 \cdot x\text{H}_2\text{O}$  100ml . (4.5g) 가  
 pH 9 72 (100 )  
 3 700 , , 85

\_\_\_\_\_ 8

5g  $\text{HfOCl}_2 \cdot x\text{H}_2\text{O}$  0.62g  $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  100ml .  
 (3.5g) 가 pH 9  
 72 (100 ) , , 85  
 3 700 ,  
 5 % La

\_\_\_\_\_ 9

(Mettler) TGA/SDTA 851

1 1 8  
 (Brunauer), 500 , 100  
 (mg)/ (m<sup>2</sup>) (Emmett) (Teller)(BET)  
 1

[ 1 ]

실시에	축매 건조 중량 (mg)	CO <sub>2</sub> (mg)	표면적 (m <sup>2</sup> /g)	CO <sub>2</sub> 흡착량 (CO <sub>2</sub> (mg)/m <sup>2</sup> )
1	76	0.0980	29	0.045
2	115	0.7781	80	0.085
3	73	0.4243	89	0.065
4	97	0.3808	100	0.039
5	78	0.5399	85	0.081
6	43	0.1035	50	0.048
7	158	0.3704	25	0.094
8	164	0.7359	60	0.075

10( )

3 50mg B , , A , MSA 2

11

, A MSA 40mg 1 10mg (bed) B  
2 3 ,  
가 ,

12

, 10mg A MSA 40mg 2 10 % La  
B , 2 3 , 2 3  
10 % La 20% LEI 2  
et gain) , 1.07% 1.7% (n  
가 , 39% 37% 2.76%

13

, 20mg A MSA 30mg 2 10 % La  
B , 2 3 , 2 3  
10 % La B 40% SAPO-34 440% 가  
8

14

, 10mg A MSA 40mg 4 10 % Y  
B , 2 3 ,  
LEI 가 가 1.2%

15

, 10mg A MSA 40mg 3 5 % La  
B , 2 3 , 5 %  
8 10 % La LEI 가

16

16 , 10mg A MSA 40mg 5 5 % Ca  
B , 2 3  
. 5 % 223% 가

17( )

10mg 16 , A MSA 40mg /

- 11 B LEI가 1.0 2 3 17 ,  
1.07% , 가 .
- 18
- 10mg A MSA 40mg 6 Ce  
B 2 3  
134% 가 .
- 19
- 10mg A MSA 40mg 7  
2 3 2 3 126% 가  
20% 40% 46% B
- 20
- 10mg A MSA 40mg 8 5 % La  
B 2 3  
5 % La 20% 51%  
51% ,

## [ 2 ]

실시예	반응기 상 조성물 (중량%)	LEI	프라임 올레핀 (%)	$C_2^*/C_3^*$	$C_3$ 순도 (%)
10 (비교예)	100% MSA	1	74.65	0.92	92.7
11	80% MSA/20%ZrO <sub>2</sub>	2.64	74.79	0.82	96.1
12	10% La/ZrO <sub>2</sub> 의 80% MSA / 20%	2.03	76.34	0.84	95.6
13	10% La/ZrO <sub>2</sub> 의 60% MSA / 40%	5.41	75.50	0.85	94.6
14	10% Y/ZrO <sub>2</sub> 의 80% MSA / 20%	2.79	75.81	0.85	94.9
15	5% La/ZrO <sub>2</sub> 의 80% MSA / 20%	4.85	75.84	0.84	94.8
16	5% Ca/ZrO <sub>2</sub> 의 80% MSA / 20%	3.23	73.85	0.79	96.7
17 (비교예)	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> 의 80% MSA / 20%	0.79	73.58	0.93	93.3
18	Ce/TiO <sub>2</sub> 의 80% MSA / 20%	2.34	65.65	0.87	95.1
19	HfO <sub>2</sub> 의 80% MSA / 20%	2.26	72.98	0.71	96.2
20	5% La/HfO <sub>2</sub> 의 80% MSA / 20%	2.50	72.75	0.76	96.5

[ 3 ]

실시예	반응기 상 (중량%)	생성물 선택도 (%)						
		CH <sub>4</sub>	C <sub>2</sub> <sup>=</sup>	C <sub>2</sub> <sup>o</sup>	C <sub>3</sub> <sup>=</sup>	C <sub>3</sub> <sup>o</sup>	C <sub>4</sub> 's	C <sub>5</sub> +
10 (비교예)	100% MSA	1.51	35.82	0.95	38.83	3.05	14.50	2.12
11	80% MSA / 20% ZrO <sub>2</sub>	1.50	33.74	0.53	41.05	1.68	14.79	3.31
12	10% La/ZrO <sub>2</sub> 의 80% MSA / 20%	1.31	34.75	0.58	41.59	1.93	14.96	2.46
13	10% La/ZrO <sub>2</sub> 의 60% MSA / 40%	1.47	34.75	0.66	40.75	2.32	14.76	2.52
14	10% Y/ZrO <sub>2</sub> 의 80% MSA / 20%	1.32	34.92	0.66	40.88	2.20	14.41	3.07
15	5% La/ZrO <sub>2</sub> 의 80% MSA / 20%	1.26	34.59	0.64	41.25	2.28	14.96	2.52
16	5% Ca/ZrO <sub>2</sub> 의 80% MSA / 20%	1.50	32.65	0.42	41.20	1.43	14.84	5.34
17 (비교예)	SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> 의 80% MSA / 20%	2.17	35.46	0.89	38.12	2.72	14.21	2.65
18	Ce/TiO <sub>2</sub> 의 80% MSA / 20%	6.79	30.57	0.75	35.09	1.80	12.72	3.97
19	HfO <sub>2</sub> 의 80% MSA / 20%	1.98	31.62	0.52	41.36	1.65	14.64	4.93
20	5% La/HfO <sub>2</sub> 의 80% MSA / 20%	1.98	31.58	0.47	41.18	1.49	14.53	5.52

(57)

1. 0.03mg( )/m<sup>2</sup>( ) 100
2. 100 0.035mg( )/m<sup>2</sup>( )
3. 100 10mg( )/m<sup>2</sup>( )
4. 1 2 3 가
- 5.

- 4 ,
- 4 , 2 / 3 , , , , 1 .
6. 1 5 , 10m<sup>2</sup>/g .
7. 1 6 , 1 가 .
8. 4 2 / 3 , , .
9. 8 , 가 .
10. 8 9 , 4 , 2 / 3 , , 1 .
11. 1 10 , 가 .
12. 11 , 가 CHA / AEI .
13. 4 100 0.03mg( )/m<sup>2</sup>( ) 2 , 1 .
14. 13 , 2 가 10 m<sup>2</sup>/g .
15. 13 14 , 1 가 , , .
16. 13 15 ,

2 가 2 / 3 가 .

17.

13 16 ,  
4 10 (hydrothermally) , 400 900 , 80  
2 .

18.

100 , 1 0.03mg( )/m<sup>2</sup>( ) 4  
,

19.

18 ,  
1 (LEI) .

20.

18 19 ,  
가 .

21.

18 20 ,  
2 / 3 가 .

22.

18 21 ,  
가 / .

23.

, , , 1 ( ) .

24.

23 ,  
2 / 3 4 .

25.

13 17 , 1  
( ) .