Table A1 Physical and chemical properties of metal-modified Y zeolites

Example A.1.1.X	1	2	3	4	5	6	7
Sample	Zr(2)Y	Zr(4)Y	Zr(8)Y	Ti(4)Y	Ti(10)Y	Ti-Zr-Y	Ti(4)Y-1
α0,nm	2.452	2.450	2.449	2.451	2.449	2.449	2.455
crystallinity,%	77.6	73.7	70.3	72.6	69.1	68.8	73.0
Na_2O,wt%	1.0	0.9	0.7	0.9	0.8	1.0	0.9
Al_2O_3,wt%	22.8	22.5	21.8	22.8	21.3	20.9	22.8
SiO_2,wt%	73.6	72.5	69.7	72.1	68.8	70.5	72.0
ZrO_2,wt%	2.1	3.8	7.3	0	0	5.5	0
TiO_2,wt%	0	0	0	3.7	8.6	1.9	3.7
RE_2O_3,wt%	0	0	0	0	0	0	0
specific surface area, m^2/g	676	710	690	726	702	640	722
lattice collapse temperature, °C	1048	1044	1051	1046	1050	1051	1045
the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content	0.05	0.10	0.12	0.08	0.16	0.15	0.10
the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum	0.4	0.3	0.5	0.4	0.6	0.5	0.3
The percent of the secondary pores (pore diameter of 6-20 nm) to the total secondary pores (pore diameter of 2-100 nm)	48.2	50.6	57.8	52.4	62.4	64.5	51.8

Table A1 (continued)

Example A.1.2.X	1	2	3	4	5	
Sample	RE(8)Y	Zr(W)Y	Ti(W)Y	Zr(G)Y	DT2	DT9
α0,nm	2.451	2.450	2.452	2.451	2.458	2.448
crystallinity,%	62.7	50.6	53.9	64.2	69.9	63.0
Na_2O,wt%	1.0	0.8	1.0	0.8	1.1	1.2
Al_2O_3,wt%	21.7	21.9	21.8	20.8	21.2	21.8
SiO_2,wt%	70.5	69.9	72.8	70.7	74.8	67.2
ZrO_2,wt%	0	7.0	0	7.5	0	0
TiO_2,wt%	0	0	3.9	0	2.4	9.1
RE_2O_3,wt%	6.6	0	0	0	0	0
specific surface area, m^2/g	640	548	526	624	535	520
lattice collapse temperature, °C	1043	1028	1015	1030	1036	1036
the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content	-	1.8	1.2	-	1.0	1.3
the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum	-	0.05	0.06	0.02	0.01	0.04

Table A3

	Example A.2.1.8					Example A.2.2.6			
TiO_2,wt%	1.0	2.0	7.0	12.0	15.0	0	0	0	0
RE_2O_3,wt%	0	0	0	0	0	1.0	2.0	12.0	15.0
Na_2O,wt%	1.1	0.9	1.1	0.9	0.9	0.8	1.0	1.0	0.9
Al_2O_3,wt%	23.2	22.8	21.4	19.2	16.5	22.0	21.8	20.2	17.2
SiO_2,wt%	73.3	72.8	68.7	66.9	67.1	74.5	73.5	66.0	66.2
α0, nm	2.449	2.450	2.452	2.455	2.455	2.455	2.457	2.458	2.460
Crystallinity, %	71.2	70.6	72.8	71.1	69.8	70.2	68.4	62.2	60.8
specific surface area , m^2/g	674	680	690	666	645	620	653	560	490
Lattice collapse temperature, °C	1042	1045	1050	1046	1046	1030	1044	1045	1045
the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content	0.02	0.05	0.12	0.15	0.17				
Zeolite No.	Ti(1)Y	Ti(2)Y	Ti(7)Y	Ti(12)Y	Ti(15)Y				
After the hydrothermal aging									
Crystallinity retention,%	62.2	61.2	63.6	66.0	64.5	60.0	63.4	66.2	65.0
Specific surface area retention, %	61.9	63.8	63.4	67.7	66.6	62.2	64.5	67.0	65.9
800°C/8h, activity	82	85	87	85	85	80	82	83	83

Table A6 Evaluation Result

Example	A.3.1.2	A.3.1.3	A.3.1.4	A.3.1.5	A.3.1.6	A.3.1.7	A.3.1.8	A.3.1.9	A.3.2.3	A.3.2.4	A.3.2.5
Catalysts	C11	C21	C31	C41	C41-1	C41-2	C51	C61	DC11	DC21	DC31
Zeolites	Zr(6)Y	Zr(10)Y	Ti(2)Y	Ti(4)Y	Ti(4)Y-1	Ti(4)Y REY	Ti(8)Y	Ti-Zr-Y	RE(8)Y	Ti(W)Y	Zr(W)Y
Reaction Temp, °C	500	500	500	500	500	500	500	500	500	500	500
Catalyst-to-oil weight ratio	8.04	8.04	8.04	8.04	8.04	8.04	8.04	8.04	8.04	8.04	8.04
WHSV, h^{-1}	16	16	16	16	16	16	16	16	16	16	16
Production Distribution, wt%											
Dry gas	1.35	1.32	1.33	1.34	1.33	1.3	1.32	1.35	1.34	1.34	1.35
liquefied gas	14.04	13.61	13.30	14.43	14.21	13.96	14.52	14.26	13.58	13.35	13.72
coke	6.71	6.86	7.52	7.05	7.13	7.42	6.76	6.71	8.02	7.29	7.12
gasoline	54.11	53.52	52.98	53.44	53.25	53.51	53.24	53.87	52.22	49.87	50.55
diesel	16.76	16.84	16.96	16.65	16.94	16.71	16.94	16.84	16.89	17.19	17.37
Heavy oil	7.03	7.85	7.91	7.09	7.14	7.1	7.22	6.97	7.95	10.96	9.89
Total	100	100	100	100	100	100	100	100	100	100	100
Conversion, wt%	76.21	75.31	75.13	76.26	75.92	76.19	75.84	76.19	75.16	71.85	72.74
coke /conversion	0.08805	0.09109	0.10009	0.09245	0.09391	0.09739	0.08914	0.08807	0.10671	0.10146	0.09788

Table B1

Raw Material	NaY	DASY(0.0)	Once-exchanged-once-calcined
Elemental composition, wt%			
Na_2O	12.8	1.2	3.7
Al_2O_3	21.9	23.6	23.4
SiO_2	64.4	71.7	72.0
Unit cell size, nm	2.466	2.448	2.453
crystallinity, %	81.6	65.6	78.0
Total specific surface area , m^2/g	762	620	644
Total pore volume, ml/g	0.377	0.353	0.352

Table B2

	Example	B.1.1.1	B.1.1.2	B.1.1.3	B.1.1.4	B.1.1.5
Step (1)	Y zeolite raw material	NaY	DASY(0.0)	Once-exchanged-once-calcined	Once-exchanged-once-calcined	NaY
	Acid solution concentration, mol/L	0.5	0.1	1.0	0.2	0.5
	Acid	Hydrochloric acid	hydrochloric acid	Oxalic acid	Sulfuric acid	Hydrochloric acid
	Acid solution:zeolite weight ratio	10	10	10	10	10
	The content of Na_2O after treatment, wt%	3.5	0.6	1.2	0.8	3.5
Step (2)	Calcination Temperature, °C	300	300	350	350	300
	Calcination time, hours	3	3	3	3	3
	Water content, wt%	4	3	1.5	1.5	4
Step (3)	Compound containing IVB group metal	zirconium nitrate	zirconium oxychloride	zirconium isopropoxide	zirconium isopropoxide	titanium tetrachloride
	Solvent	ethanol	ethanol	n-hexane	n-hexane	butanone
	Water content in solvent, wt%	0.1	0.1	0.2	0.2	0.3
	Solvent:Zeolite weight ratio	1.3	1.5	1.5	1.2	1.3
	Metal salt (as oxide):zeolite weight ratio	0.01	0.03	0.06	0.10	0.02
Step (4)	Used solvent	ethanol	ethanol	n-hexane	n-hexane	butanone
	Solvent:Zeolite weight ratio	5.1	10.0	10.0	10.0	5.1
	Introduced Inert Gas	nitrogen	nitrogen	nitrogen	nitrogen	nitrogen
	Pressure, MPa	0.5	1.0	0.5	0.8	0.5
	Temperature, °C	26	25	60	25	25
	Time, hour	12	8	5	8	5
	Manner	By standing	Being stirred	Being stirred	By standing	being stirred

Step (4)	Drying Temperature, °C	100	120	120	120	100
	Drying Time, hour	24	6	6	6	12
Step (5)	Inert Gas	nitrogen	nitrogen	nitrogen	nitrogen	nitrogen
	Calcination Temperature, °C	500	550	550	550	500
	Calcination Time, hour	4	2	3	3	3
Metal-modified Y zeolite, No.		ZrY(1)	ZrY(3)	ZrY(6)	ZrY(10)	TiY(2)
Na_2O,wt%		1.0	0.5	0.8	0.6	1.2
Al_2O_3,wt%		23.3	23.5	22.2	20.5	22.8
SiO_2,wt%		73.8	72.8	70.5	67.8	73.1
ZrO_2,wt%		0.9	2.8	6.1	10.5	
TiO_2,wt%						2.2
α0, nm		2.456	2.448	2.450	2.452	2.451
Crystallinity, %		78.8	64.7	70.6	72.2	76.9
Specific surface area ,m^2/g		710	616	624	635	702
lattice collapse temperature, °C		1048	1050	1045	1047	1044
The ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum		0.2	0.3	0.5	0.6	0.2
The percent of the secondary pores (pore diameter of 6-20 nm) to the total secondary pores (pore diameter of 2-100 nm)		32.5	42.8	48.7	50.3	38.6

Table B2 (continued)

	Example	B.1.1.6	B.1.1.7	B.1.1.8	B.1.1.9
Step (1)	Y zeolite raw material	Once-exchanged once-calcined	Once-exchanged- once-calcined	NaY	NaY
	Acid solution concentration, mol/L	1.0	1.0	0.5	0.5
	Acid	acetic acid	oxalic acid	hydrochloric acid	EDTA
	Acid solution:zeolite weight ratio	10	10	10	10
	The content of Na_2O after treatment, wt%	1.0	1.0	3.5	3.5
Step (2)	Calcination Temperature, °C	350	350	300	300
	Calcination time, hours	3	3	3	3
	Water content, wt%	1.8	1.5	4	4
Step (3)	Compound containing IVB group metal	butyl titanate	butyl titanate+zirconium nitrate	zirconium nitrate	zirconium nitrate
	Solvent	cyclohexane	ethanol	ethanol	ethanol
	Water content in solvent,wt%	0.2	0.1	0.1	0.1
	Solvent:Zeolite weight ratio	1.5	1.5	1.3	1.3
	Metal salt (as oxide):zeolite weight ratio	0.10	0.08	0.01	0.01
Step (4)	Used solvent	cyclohexane	Ethanol	ethanol	ethanol
	Solvent:Zeolite weight ratio	10.0	8.0	5.1	5.1
	Introduced Inert Gas	nitrogen	nitrogen	nitrogen	nitrogen
	Pressure, MPa	0.5	1.5	0.0	0.5
	Temperature, °C	25	80	26	26
	Time, hour	10	24	12	12
	Manner	Being stirred	Being stirred	By standing	By standing
Step (4)	Drying Temperature, °C	120	120	100	100
	Drying Time, hour	6	24	24	24

Step (5)	Inert Gas	nitrogen	nitrogen	nitrogen	nitrogen
	Calcination Temperature, °C	550	550	500	500
	Calcination Time, hour	2	3	4	4
	Metal-modified Y zeolite, No.	TiY(10)	Ti-Zr-Y	ZrY(1)-1	ZrY(1)-2
	Na_2O,wt%	1.0	0.8	1.0	0.9
	Al_2O_3,wt%	21.5	21.9	23.2	23.4
	SiO_2,wt%	67.1	69.0	73.9	73.6
	ZrO_2,wt%		3.8	0.9	0.9
	TiO_2,wt%	9.8	4.0		
	α0, nm	2.455	2.455	2.454	2.455
	crystallinity, %	73.5	72.9	71.5	77.7
	specific surface area ,m^2/g	642	639	700	699
	lattice collapse temperature, °C	1045	1050	1045	1048
	the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum	0.5	0.5	0.2	0.2
	The percent of the secondary pores (pore diameter of 6-20 nm) to the total secondary pores (pore diameter of 2-100 nm)	49.8	44.4	35.4	33.9

Table B3

Example	B.1.2.1	B.1.2.2	B.1.2.3	B.1.2.4	B.1.2.5
Y zeolite No.	REY	Zr(W)Y	Zr(J)Y	Zr(G)Y	Ti(D)Y
Na_2O,wt%	1.2	0.8	0.6	0.5	1
Al_2O_3,wt%	21.4	20.6	21.8	20.8	21.5
SiO_2,wt%	70.5	70.2	71	70.7	69.3
ZrO_2,wt%		8	6.2	7.5	
TiO_2,wt%					7.9
RE_2O_3,wt%	6.6				
α0, nm	2.451	2.45	2.452	2.451	2.453
crystallinity, %	62.7	51.9	55.7	60.2	59.6
specific surface area ,m^2/g	640	536	548	624	610
lattice collapse temperature, °C	1043	1027	1028	1041	1033
the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum		0.05	0.01	0.02	0.01

B.2 Stability of the modified zeolite

Modified Y zeolites prepared according to Example B.2.1.1-B.2.1.9 and B.2.2.1-B.2.2.5 were aged at 800°C under a 100% steam condition for 8 hours and 17hours respectively to determine the crystallinity and the specific surface area, and the crystallinity retention and the specific surface area retention were calculated. The aged zeolites were subjected to the light oil micro-activity (MA) test. The results were listed in Table B4.

Table B4

Example B.2.1.X	1	2	3	4	5	6	7	8	9
Y zeolite	ZrY(1)	ZrY(3)	ZrY(6)	ZrY(10)	TiY(2)	TiY(10)	Ti-Zr-Y	ZrY(1)-1	ZrY(1)-2
800°C/8h crystallinity retention, %	61.2	62.8	63.7	68.4	63.1	67.5	68.6	62.0	61.8
800°C/17h crystallinity retention, %	55.5	57.0	56.7	62.5	57.6	60.1	60	56.5	56.1
800°C/8h specific surface area retention,%	62.0	61.3	62.9	69.6	66.1	68	69.6	62.8	61.0
800°C/17h specific surface area retention,%	57.2	56.7	57.6	63.9	59.6	62.2	62.8	57.0	56.4
800°C/8h activity,%	80	82	84	87	85	86	87	80	80
800°C/17h activity,%	76	77	79	82	79	80	81	75	77

Table B4 (continued)

Example B.2.2.X	1	2	3	4	5
Y zeolite	REY	Zr(W)Y	Zr(J)Y	Zr(G)Y	Ti(D)Y
800°C/8h crystallinity retention, %	63.2	50.4	50.5	60.8	61.6
800°C/17h crystallinity retention, %	56.5	45.8	42.5	52.9	53
800°C/8h specific surface area retention,%	67.1	58	54.2	64.9	62.4
800°C/17h specific surface area retention,%	61.2	52.6	49.8	58.2	59.1
800°C/8h activity,%	85	75	72	80	72
800°C/17h activity,%	79	68	65	75	66

Table B8 Evaluation Result

Example	B.3.1.3	B.3.1.4	B.3.1.5	B.3.1.6	B.3.1.7	B.3.1.8	B.3.1.9
Catalyst No.	C17	C18	C19	C20	C21	C22	C23
Modified Y Zeolite No.	ZrY(2)	ZrY(6)	ZrY(10)	TiY(8)	TiY(4)	HfY(6)	Ti-Zr-Y
Reaction Temp,°C	500	500	500	500	500	500	500
Catalyst-To-Oil Ratio (Weight)	5	5	5	5	5	5	5
WHSV, h^{-1}	16	16	16	16	16	16	16
Production Distribution,wt%							
Dry Gas	1.25	1.12	1.29	1.22	1.10	1.18	1.20
Liquefied Gas	12.04	13.05	11.53	12.09	12.41	12.48	12.35
Coke	5.09	4.26	4.95	4.96	5.01	4.85	4.99
Gasoline	53.99	54.61	54.59	54.44	54.07	53.95	54.11
Diesel	21.41	20.98	21.58	21.34	21.84	21.69	21.36
Heavy Oil	6.22	5.98	6.06	5.95	5.57	5.85	5.99
Total	100	100	100	100	100	100	100
Conversion, wt %	72.37	73.04	72.36	72.71	72.59	72.46	72.65
Coke /Conversion	0.07033	0.05832	0.06841	0.06822	0.06902	0.06693	0.06869

Table B8: Evaluation Result (continued)

Example	B.3.1.10	B.3.1.11	B.3.1.12	B.3.2.4	B.3.2.5	B.3.2.6
Catalyst No.	C24	C25	C26	DC14	DC15	DC16
Modified Y Zeolite No.	ZrY(1)	ZrY(1)-1	ZrY(1)-2	Zr(W)Y	Ti(J)Y	RE(8)Y
Reaction Temp, °C	500	500	500	500	500	500
Catalyst-To-Oil Ratio (Weight)	5	5	5	5	5	5
WHSV, h^{-1}	16	16	16	16	16	16
Production Distribution, wt%						
Dry Gas	1.21	1.22	1.23	1.32	1.18	1.10
Liquefied Gas	11.81	11.79	11.89	11.78	12.03	11.66
Coke	4.62	4.52	4.71	5.88	5.25	5.45
Gasoline	54.15	54.21	54.48	50.57	50.30	53.08
Diesel	21.88	21.91	21.28	22.01	22.12	21.46
Heavy Oil	6.33	6.35	6.41	8.44	9.12	7.25
Total	100	100	100	100	100	100
Conversion,wt%	71.79	71.74	72.31	69.55	68.76	71.29
Coke/Conversion	0.06435	0.06301	0.06514	0.08454	0.07635	0.0764