

Preparation of Pt/CeL Reforming Catalyst and Its Naphtha Aromatization Performance

Weizhi Li

Tianjin Yongding Energy Chemical Co., Ltd., liwz@piscomed.com

Abstract: In order to overcome the problems of chloride ion loss and corrosion of equipment in conventional alumina reforming catalysts, Ce³⁺ modified L molecular sieves were prepared by ion exchange method, and Pt/CeL reforming catalysts were prepared by impregnation method; XRD, the carrier and catalyst were characterized by N₂ adsorption-desorption, NH₃-TPD and Py-FTIR. The industrial refined naphtha with sulfur content of 0.50 μg/mL was used as raw material to evaluate on the fixed bed microreactor. The reforming aromatization performance of the Pt/CeL catalyst. The results show that Ce³⁺ ion exchange can increase the acidity and acid strength of the carrier without destroying the skeleton structure of the L molecular sieve. The reforming aromatization performance of the Ce³⁺ modified Pt/CeL catalyst is obviously improved, and the activity and selectivity are achieved. The level of the alumina type commercial reforming catalyst indicates that the appropriate acidity has a significant effect on the aromatization reaction of the reforming catalyst.

Keywords: Catalytic reforming; Cerium; Molecular sieve I; Ion exchange; Aromatization

Catalytic reforming is a secondary process for the production of high-octane gasoline and light aromatic hydrocarbons from naphtha. The commercial reforming catalyst is supported by high-dispersion Pt supported on alumina carriers containing Cl ions. 70 years of development has reached a very mature stage, especially in terms of increasing aromatization activity and C₅₊ liquid yield [1-3]. However, Cl ions are easily lost on this catalyst [4, 5], and it is necessary to continuously replenish chlorine in the raw materials, which inevitably causes corrosion of equipment pipelines and clogging of pump valves by crystals, which brings great safety hazards to production. Therefore, it is of great practical significance to study reforming catalysts without Cl ions. The literature believes that Pt/KL catalyst [6-11] with KL molecular sieve as carrier, and Pt/BaL catalyst [12-17] modified by Ba ion have higher aromatization in linear alkane reforming reaction. Activity, but there are few reports on the use of Ce ion-modified L molecular sieves as reforming catalyst carriers.

In this study, Ce³⁺ modified L molecular sieves were prepared by ion exchange method, and Pt/CeL reforming catalysts containing no chloride ions with Pt content of 0.3% and 0.8% (mass fraction) were prepared by impregnation method. Industrial refining naphtha with a sulfur content of 0.50 μg/mL was used as a raw material to examine the reforming aromatization reaction of the catalyst in a fixed-bed micro-reverse evaluation apparatus, and compared with a commercial alumina catalyst.

1. Experimental Part

1.1 Preparation of CeL Molecular Sieve

KL molecular sieve is synthesized according to the literature [18,19], and its composition is: K₂O·Al₂O₃·6.2SiO₂·xH₂O. The ion exchange modification of KL molecular sieve was carried out by using Ce(NO₃)₃ solution. Firstly, a Ce(NO₃)₃ solution with a concentration of 0.2 mol/L was prepared, and then the ratio of 600 mL of Ce(NO₃)₃ solution was added per 50 g of KL molecular sieve raw powder. It was exchanged at 80 °C for 8 h, then filtered, washed, dried at 120 °C for 8 h, and calcined at 600 °C for 5 h to obtain a modified CeL molecular sieve. The content of the elements was analyzed by inductively coupled plasma spectrometer (ICP) and X-ray fluorescence spectrometer (XRF). It was comprehensively judged that about 30% of the K⁺ in the molecular sieve was exchanged by Ce³⁺, that is,

the ion exchange degree was about 30%.

1.2 Preparation of Catalyst

First, a tetraammine platinum nitrate $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ impregnation solution having a Pt content of 5.17 mg/mL was prepared, and the amount of the impregnation liquid was calculated based on 10 g of KL or CeL molecular sieve, and the impregnation liquid was diluted to 50 mL with deionized water. The molecular sieve was added to the diluted Pt-containing immersion liquid, stirred at 40 ° C for 4 h, then dried at 120 ° C for 4 h, and calcined at 600 ° C for 4 h to obtain Pt loadings of 0.3% and 0.8%, respectively. Mass fraction) catalysts, designated as: Pt0.3/KL, Pt0.8/KL, Pt0.3/CeL, and Pt0.8/CeL, respectively. The reforming reaction evaluation contrast agent was a conventional commercial reforming catalyst and was named Pt0.3/Al₂O₃-Cl.

1.3 Characterization Method

XRD phase analysis was performed using a PANalytical X'pertPro diffracto meter, CuK α radiation (wavelength $\lambda = 0.141618$ nm), tube voltage 40 kV, tube current 40 mA, and sample scanning step length 0.017°.

The N₂ adsorption desorption characterization was used to determine the specific surface area and pore volume of the sample. The instrument was a Quantachrome Autosorb 6B physical adsorber. The sample was first degassed and then subjected to isothermal adsorption and desorption of nitrogen at a temperature of 77.3 K.

The NH₃-TPD characterization was used to determine the acidity and acid strength of the molecular sieve. The Tianjin TP-5079 adsorption instrument was used to dehydrate and degas the sample, then saturate the ammonia gas, and then remove the physically adsorbed ammonia with helium gas. The gas was finally heated from 100 ° C to 600 ° C at a rate of 10 ° C / min to obtain a temperature programmed desorption curve.

Using pyridine as the probe molecule, Py-FTIR was used to identify the acid type of each molecular sieve. The characterization instrument was a Nicolet 6700 Fourier infrared spectrometer containing a quartz infrared absorption cell vacuum system. The sample was purified under vacuum and the background was preserved. The pyridine desorption was carried out by heating to 200 and 350 ° C, and the difference spectrum with the background was a Py-FTIR spectrum.

1.4 Evaluation of Reforming Reaction

Catalyst evaluation was carried out on Unitec's YN-CZ-10 fixed-bed micro-reverse device. 5 mL of the catalyst was placed in a stainless steel reaction tube with an inner diameter of 10 mm. After purging the system with N₂, the raw materials and hydrogen were placed in front of the reactor inlet. After mixing, it passes through the catalyst bed from top to bottom. The evaluation process parameters were: reaction temperature 490 ° C, reaction pressure 0.7 MPa (G), liquid hour volume space velocity 2 h⁻¹, and the ratio of feed hydrogen oil substances was 9:1. The product was cooled to zero and then collected and analyzed by an Agilent Model 7890B Gas Chromatograph. The column was HP-PONA capillary column (50 m × 0.20 mm × 0.50 μm) and detected by FID. The PONA group composition is calculated by the chromatograph's own software to obtain the aromatics mass percentage.

The aromatization activity of the reforming catalyst is measured by the aromatic content (abbreviated as aromatic content) in the liquid product. The selectivity of the reforming catalyst is based on the liquid product yield (liquid receiving), and the product value of the two represents the comprehensive performance of the catalyst. For the aromatics).

2. Results and discussion

2.1 XRD Analysis of KL and CeL Molecular Sieves

Figure 1 is an XRD spectrum of KL and CeL molecular sieves. It was found by crystal phase analysis that it matched

the standard card PDF#22-0773 and proved to have the same crystal phase structure as Linde Type L molecular sieve [20]. It shows that Ce³⁺ modification has no effect on the skeleton structure of L molecular sieve. According to the Scherrer equation, the average grain size of the KL and CeL molecular sieves was calculated to be about 100 nm by the full width at half maximum of the diffraction peak of 22.7°.

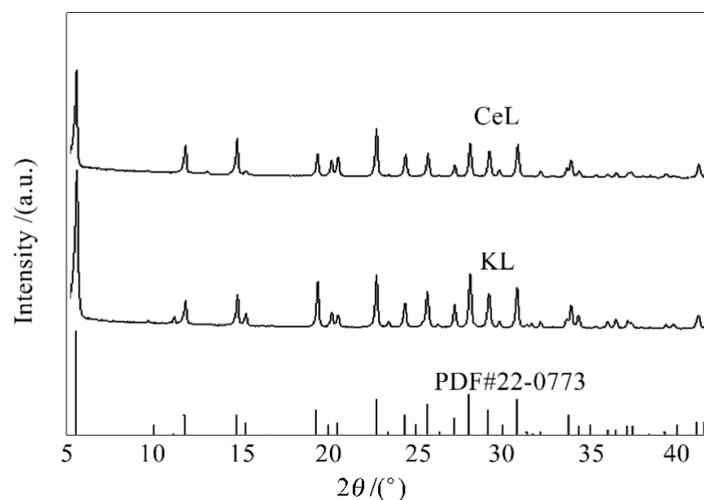


Fig. 1 XRD patterns of KL and CeL molecular sieves

2.2 Texture Properties of KL and CeL Molecular Sieves

Table 1 shows the texture properties of KL and CeL calculated from the N₂ adsorption-desorption results. The total specific surface area is calculated by the MultiPointBET method. The mesoporous specific surface area and pore volume are calculated by the BJH method, and the specific pore surface area is determined by the t-method method. The micropore volume was calculated using the SF method. It can be seen from Table 1 that the specific pore surface area of the L molecular sieve before and after the Ce³⁺ ion exchange is 220 m²/g, the mesoporous specific surface area is 46 m²/g, and the micropore volume is 0.12 and 0.11 mL/g, respectively. The mesoporous pore volumes were 0.14 and 0.13 mL/g, respectively. The parameters of these pores showed that although the exchange degree of Ce³⁺ ions reached 30%, the ion exchanged CeL molecular sieve remained as rich as the original KL molecular sieve. Microporous structure. Since the specific surface area and pore volume of the L molecular sieve before and after Ce³⁺ ion exchange did not change significantly, it was further inferred from the XRD results that the skeleton structure of the L molecular sieve after Ce³⁺ ion exchange remained intact. It is speculated that the Ce³⁺ ion did not enter the skeleton of the L molecular sieve, but was balanced. The form of charge exists.

Table 1 Textural properties of the KL and CeL zeolites

Sample	Surface area $A / (\text{m}^2 \cdot \text{g}^{-1})$			Pore volume $v / (\text{mL} \cdot \text{g}^{-1})$		
	total	micropore	mesopore	total	micropore	mesopore
KL	266	220	46	0.26	0.12	0.14
CeL	266	220	46	0.24	0.11	0.13

2.3 Acidity Analysis of KL and CeL Molecular Sieves

Figure 2 is a NH₃-TPD spectrum of KL, CeL molecular sieve and commercial reforming catalyst support Al₂O₃-Cl. By comparison, it is found that the NH₃ desorption peak temperature of KL molecular sieve is smaller than that of CeL molecular sieve and Al₂O₃-Cl. The NH₃ desorption peak area of CeL molecular sieve and Al₂O₃-Cl is obviously larger than that of KL molecular sieve, indicating that the acid amount and acid strength of CeL and Al₂O₃-Cl are obvious. Greater than KL. In the high temperature range of 400-600 °C, the CeL curve and Al₂O₃-Cl basically coincide and

intersect twice, indicating that the strong acid content of the two is about the same. According to the NH₃-TPD spectrum, the acid number and total acid amount of weak acid, medium acid and strong acid of KL, CeL molecular sieve and Al₂O₃-Cl were calculated by simulated integral. The results are shown in Table 2. The ratio of total acid amount of CeL to KL and strong acid The ratio of the amount of 6.5 and 22.9 respectively indicates that the total acid amount and the strong acid amount of CeL are significantly larger than KL, which proves that the monovalent K⁺ cation in the L molecular sieve is more acidic after being exchanged by the trivalent Ce³⁺ ion, and The laws reported in [21] are consistent.

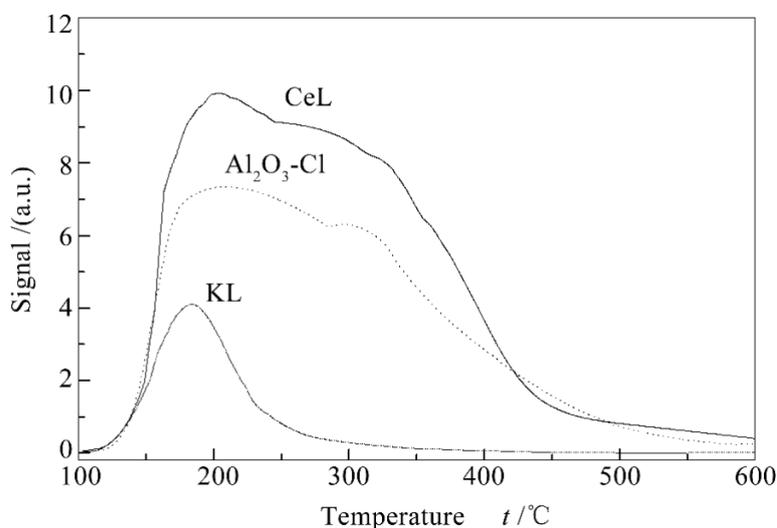


Fig. 2 NH₃-TPD spectra of KL, CeL and Al₂O₃-Cl

Table 2 Acid distribution of zeolite KL, zeolite CeL and Al₂O₃-Cl

Sample	Acid amount determined by NH ₃ -TPD/(a. u.)			
	weak (100–200 °C)	medium (200–400 °C)	strong (400–600 °C)	total (100–600 °C)
KL	199.5	130.5	9.6	339.6
CeL	414.6	1585.4	219.6	2219.6
Al ₂ O ₃ -Cl	333.3	1150.8	203.9	1688.0

The acid types of total acid and strong acid in KL, CeL molecular sieve and Al₂O₃-Cl were studied by Py-FTIR characterization. The relevant data are shown in Table 3.

Table 3 Lewis (L) and Brönsted (B) acid distribution of KL, CeL and Al₂O₃-Cl

Sample	Total acid amount measured by Py-FTIR at 200 °C / (μmol·g ⁻¹)				Strong acid amount measured by Py-FTIR at 350 °C / (μmol·g ⁻¹)			
	L	B	B+L	B/L	L	B	B+L	B/L
KL	93.2	0	93.2	0	8.9	0	8.9	0
CeL	466.0	130.5	596.5	0.28	200.2	14.0	214.2	0.07
Al ₂ O ₃ -Cl	340.3	0	340.3	0	196.5	0	196.5	0

As can be seen from Table 3, there is no Br nsted acid (abbreviated as B acid) in the KL molecular sieve and Al₂O₃-Cl, and only Lewis acid (abbreviated as L acid). B acid appeared in the CeL molecular sieve modified by Ce³⁺ ion exchange, but the strong acid was mainly L acid. For the amount of L acid in strong acid, CeL is almost equal to Al₂O₃-Cl, which is significantly larger than KL.

2.4 Reforming Aromatization Performance

The performance of catalytic reforming reaction was evaluated by reforming the pre-hydrogenated refined naphtha on the 1.4×109kg/year continuous reforming unit of Petro China Liaoyang Petrochemical Company. The properties of the raw materials are shown in Table 4, which is a representative conventional reforming feed stock oil.

The evaluation reaction results are shown in Table 5. As can be seen from Table 5, when the Pt content in the Pt/KL and Pt/CeL catalysts was increased from 0.3% to 0.8% (mass fraction), both aromatic and aromatic production increased. It can also be found that the aromatization activity of Pt0.3/KL and Pt0.8/KL is significantly lower than that of commercial reference agent, and the aromatization activity of Ce3+ ion exchanged CeL is significantly higher than that of KL molecular sieve catalyst, Pt0.3/ CeL activity is slightly lower than that of commercial reference agents, while Pt0.8/CeL is comparable to commercial reference agents in activity and selectivity. Combined with the texture and acid properties of the catalyst, it is considered that the texture property has little effect on the catalyst. The main influencing factor is the acidity of the catalyst. The amount of strong acid in the CeL molecular sieve after Ce3+ ion exchange is significantly increased, which leads to reforming. An important reason for the high formation activity.

Table 4 Properties of the hydrofining naphtha feedstock

Item	Result
Density(20 °C) / (g • cm ⁻³)	0. 7374
Sulfur content / (μg • mL ⁻¹)	0. 50
Nitrogen content / (μg • mL ⁻¹)	0. 32
PONA w / %	
<i>n</i> -paraffin	10. 9
<i>i</i> -paraffin	43. 5
Olefin	0. 0
Naphthene	41. 4
Aromatic	4. 2
RON	76. 2

Table 5 Catalytic evaluation results of Pt/KL and Pt/CeL for naphtha reforming

Catalyst	Aromatics content	Liquid yield	Total aromatics	Benzene	Toluene	C ₈ aromatics	C ₉₊ aromatics
	in liquid products	w / %	yield w / %	yield w / %	yield w / %	yield w / %	yield w / %
	w / %						
Pt 0. 3 / KL	34. 5	86. 8	30. 0	1. 1	7. 7	10. 7	10. 5
Pt 0. 8 / KL	53. 1	83. 5	44. 3	1. 9	12. 8	15. 8	13. 8
Pt 0. 3 / CeL	65. 4	82. 4	53. 9	2. 7	15. 7	19. 3	16. 2
Pt 0. 8 / CeL	70. 5	79. 9	56. 3	3. 8	17. 9	19. 9	14. 7
Pt 0. 3 / Al ₂ O ₃ -Cl ⁺	71. 0	79. 0	56. 1	2. 4	15. 7	19. 5	18. 5

* : a widely used commercial alumina-type reforming catalyst;

reaction conditions: 490 °C , 0. 7 MPa(G) , LHSV = 2 h⁻¹ , H₂ / hydrocarbon mole ratio = 9

In summary, when the Pt loading is the same, the reforming aromatization activity of the Pt/KL catalyst is significantly lower than that of the Pt/CeL catalyst. For molecular sieve reforming catalysts, the literature holds that "molecular sieve reforming catalysts are metal monofunctional catalysts" [12] or "molecular sieve reforming catalysts should eliminate acidity" [14], and from the results of this study, appropriate strong acidity promotes the aromatization reaction of naphtha, and the reaction mechanism is more inclined to the metal-acid dual function stated by Antos Catalysis [1].

3. Conclusion

The molecular sieve specific surface area, pore volume and XRD diffraction peaks of Ce3+ ion exchange did not

change, indicating that Ce³⁺ ion exchange did not destroy the original L molecular sieve skeleton structure.

The presence of Ce³⁺ increases the acidity and acid strength of the original L molecular sieve. The acid type of CeL molecular sieve is mainly L acid with a small amount of B acid.

The reforming aromatization activity of Ce³⁺ ion-modified Pt/CeL catalyst is obviously improved, and the comprehensive performance level reaches the commercial chlorine-containing alumina type reforming catalyst.

References

1. ANTOSG J, AITANIAM. Catalytic Naphtha Reforming: Second Editio, Revised and Expanded [M] . New York: Marcel Dekker Inc. 2004: 335–349.
2. Xu Chengen. Catalytic reforming process and engineering [M]. Beijing: China Petrochemical Press, 2006: 1-26.
3. Ma Aizeng. Progress in catalytic reforming technology in China [J]. Chinese Science: Chemistry, 2014, 44(1): 25-39.
4. Guo Chunlei, direction morning, Jia Liming, Liu Quanjie, Zhang Xiwen, Zhao Xiaodong. Research progress in molecular sieve reforming catalysts [J]. Chemical Industry Progress, 2012, 31(4): 825-832.
5. ARENAF, FRUSTERIF, MONDELLON, GIORDANON, PARMALIANAA. Interaction pathway with γ -Al₂O₃: surface acidity and thermal stability of Cl / γ -Al₂O₃ system [J]. Chemistry, Faraday transformation
6. BESOUKHANOVAC, BARTHOMEUFD, BREYSSEM, BERNARDJR. Irregular properties of platinum chlorobenzothio phenehexanede hydro cyclization and benzene hydrogenation reaction [J]. Stud Surf Sci Catal, 1981, 7: 1410-1411.
7. LANECS, MODICAFS, MILLERJT. Platinum/zeolite catalyst reforming hexane: kinetic and mechanical considerations [J]. J Catal, 1991, 129(1): 145-158.
8. JACOBSG, ALVAREZWE, REMASCODE. Preparation of non-hexane aromatization by powder and acrylated Pt / KL catalyst [J]. Appl Catal A: Root, 2001, 206(2): 267-282.
9. KUMARM, SAXENAAK, NEGIBS, VISWANADHAMN. Responsible for the analysis and development of the role of zeolite reforming cocatalyst [J]. Catal Today, 2008, 130(2): 501-508.
10. Jiang Xian, Zhai Zhinong, Qi Zhenkui, Huang Jiasheng, Xu Yude, Guo Yuxian, Luo Xihui, He Jinhai. The role of basicity in Pt / L molecular sieve catalyst [J]. Journal of Fuel Chemistry, 1994, 22(1): 9-15.
11. Zhang Yuhong, Xue Lian, Ma Aizeng. The role of carrier acidity and alkalinity in Pt/KL aromatization catalyst [J]. Petroleum Refining and Chemical Industry, 2009, 40(3): 1-5.
12. HUGHESTR, BUWSSC, TAMMPW, JACOBSONRL. Aromatization of hydrocarbon superplatic soil zeolite [J]. Stud Surf Sci Catal, 1986, 28: 725-732.
13. HONGSB, MIELCZARSKIE, DAVISME. The n-hexane aromatization of the platinum-containing molecule. part 1. Catalyst prepared by gas phase impregnation [J]. J Catal, 1992, 134: 349-358.
14. MIELCZARSKIE, HONGSB, DAVISRJ, DAVISME. Aromatization of n-hexane of a platinum-containing molecule II. Hexane reactivity [J]. J Catal, 1992, 134: 359-369.
15. ARCOYAA, SEOANEXL, GRAUJM. Dehydrocyclization reaction mechanism of n-heptane-PtBa / KL catalyst [J]. Appl Catal A: Gen, 2005, 284(1): 85-95.
16. Dong Jialu, Jin Changtai, Xu Yuhua. Study on a new type of reforming catalyst - the role of ruthenium in Pt/BaKL zeolite [J]. Journal of Fuel Chemistry, 1992, 20 (3): 244-251.
17. Shi Yingwei, Jiang Xian, Zhang Yong, Yan Zhenkui, Zhang Yang, Guo Yuxian. Mechanism of aromatization of alkane in platinum/L molecular sieve reforming catalyst [J]. Journal of Catalysis, 1993, 14(4): 312-316.
18. MINTOVAS, BARRIERN. Proven synthesis of zeolitic materials, third edition [M]. Published in the Comprehensive Committee of the International Zeolite Association (ISBN: 978-0-692-68539-6), 2016: 271-273.
19. Huo Quan. L-zeolite pilot-scale amplification synthesis and its application in hydrocarbon
20. TREACYMMJ, HIGGINSJB. Simulated XRD Powder Model Zeolite, Revision 4 [M]. Netherlands: Elsevier, 2001: 220-221.
21. Molecular sieve group of Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Zeolite molecular sieve [M]. Beijing: Science Press, 1978: 298-313.