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Optimization of nanopores and acidity of USY zeolite by citric modification

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Abstract

To meet the challenges of the crude oil becoming heavier and poorer quality, and the tendency of the increasing liquefied petroleum gas (LPG) and diesel in fluid catalytic cracking (FCC) process, the ultrastable Y (USY) zeolites were further modified by citric acid to optimize their nanopores and acid sites. The nanopores and acid sites of modified zeolites were extensively investigated by N_2 adsorption, XRD and in situ IR methods. The micro-activities of modified samples were also evaluated. The results showed that the nanopore volume of the modified samples is rather more developed than that of the parent zeolite. It indicated that micropores and mesopores might be generated by skeletal reconstruction. The dealumination process might be occurred gradually from the upmost surface to subsurface, then to bulk sites of the USY framework because of the larger volume of citric acid molecules. It resulted in the gradient distribution of nanopores and acid sites in modified zeolites. The hydroxyls with IR bands of 3610 and 3575 cm^{-1} in the micropores or small cages bears the stronger acidity and much more sites than those in mesopores or larger cavities. This gradient acid distribution was rather preferable to produce preferably LPG and diesel in FCC process. MAT evaluations indicated that the LPG and diesel yields of citric modified samples were effectively improved. Optimization of nanopores and acid sites of ultrastabilized USY zeolites modified with citric acid in unbuffered system might result in an industrial process to design novel FCC catalysts. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Nanopores; Dealumination process; Ultrastable Y zeolite; Citric modification

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1. Introduction

Catalytic cracking is a process for the conversion of vacuum distillates and residues into liquefied petroleum gas (LPG), gasoline and diesel oils. Ultrastable Y is a highly acidic zeolite (IZA structure type FAU) commonly used in hydrocracking and fluid catalytic cracking (FCC) catalysts. The FAU structure is characterized by large, essentially spherical, internal cavities (supercages) linked tetrahedrally through pore openings of about 0.8 nm, defined by rings of 12 oxygen atoms (12-rings). The protons are associated with aluminum atoms that, along with silicon atoms, occupy sites at the centers of apex-linked tetrahedra of oxygen atoms that form the three-dimensional framework of the zeolite. Aluminum atoms cannot occupy sites in adjacent tetrahedra (Lowenstein's rule) [1]. There is evidence that Bronsted acid strength is inversely proportion to the number of aluminum atoms in the next nearest neighbor tetrahedron. Some investigators have concluded that only the strongest Bronsted acid sites are active for catalytic cracking. It means the good performances for the heavy oils cracking activity and products selectivity resulted from optimum number and strength of acid sites and suitable pore structure. With the feedstocks of FCC

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being heavier and poorer quality and the tendency of the increasing LPG and diesel, the features of the mesopores and acid sites of USY zeolite will not meet the variation of materials in the future [2].

To increase quality fuel selectivity and decrease coke formation, dealumination in the manufacturing process of zeolite material is conducted by controlling hydrothermal or chemical stabilization, resulting in removal of framework aluminum. Present octane–barrel catalysts consist of ultrastable, steam dealuminated Y zeolites on an active matrix, although the LPG and diesel yields are still rather low. Thus the modification of USY zeolite have been further paid much attention [3].

There are different ways to modify the Y zeolite, such as hydrothermal treatment, extraction by acid complexation or a novel process named secondary synthesis using $SiCl_4$ and $(NH_4)_2SiF_6$ [4]. Here the USY zeolites were treated with citric acid in unbuffered system to optimize their acidity and nanopore distribution [6]. In the aqueous solution of citric acid, the skeletal aluminum atom might be coordinately extruded by the form of $Al(Cit)_n$ complex from the skeleton of zeolite. The effect of the various factors on the USY zeolites was tentatively investigated.

Furthermore, the crystal structure, physical adsorption property, stability, catalytic cracking property of the modified zeolites and structure design mechanism were also investigated by XRD, N_2 adsorption, FT-IR, DTA and micro-activity test (MAT). In this paper, the nanopore volume and distribution of citric-modified USY zeolites were extensively investigated and correlations of nanopore features with MAT and acid sites were also conducted.

2. Experimental section

2.1. *Preparation of modified USY zeolites*

The USY parent zeolite supplied by Zhoucun Work of Catalyst, Qilu Petrochemical, Sinopec, whereas USY is already in its hydronium form, in which Si/Al ratio is 8.6 and the unit cell constant is 24.528. Four gram of USY zeolite was placed into a three-necked flask with a certain amount of 0.001 M dilute nitric acid as the solvent and this mixture was stirred and heated to 90°C. Then the 0.5 M citric acid solution was added dropwise with velocity of 10 ml/h. Following addition, the solution was stirred for 4 h at 90°C. After reaction, the gel was filtered, washed, and dried overnight at 120°C.

2.2. *N_2 adsorption*

The nitrogen adsorption of the samples was performed on Micromeritics 2010 analyzer at liquid nitrogen temperature (77.3 K) and the samples were degassed at 673 K for 4 h prior to adsorption analysis. The micropore distribution and mean pore size were calculated from the gas adsorption using the Horvath–Kawazoe equation [5], with relative pressure (P/P^0) below 0.01. *T*-plot calculation was conducted to quantitatively analyze the area and total volume ascribed to micropores. The mesopore volume was determined by subtracting the micropore volume from the total pore volume.

2.3. *MAT evaluation*

The modified sample was powdered, and mixed with kaolin clay matrix (w/w, 30/70) to prepare modified zeolite catalyst, while the average diameter of the catalyst particle is about 60 μm. Prior to catalytic reaction, samples were subsequently steamed at 800°C for 4 h using 95% steam in air in a fixed-bed quartz tubular reactor.

The method to assess modified catalyst activity is in fixed (MAT) using minimum quantities of feed, oil and catalyst. The apparatus is designed according to ASTM D-3907-80 [7], which is simple, quick and easily reproduced. The apparatus was illustrated as in Fig. 1. The feedstock is Shenghua VGO (343–515°C), supplied by Shenghua Oil Refinery Factory, University of Petroleum. The density of feedstock is 0.9165 g/cm^3 (20°C), and Conradson carbon residue (CCR) is 0.25 wt.%. The physical properties of Shenghua VGO feedstock were described as in Table 1. Reaction temperature is 550°C and the catalyst/feedstock is 2.8. The gaseous products were analyzed by HP-5890II GC equipped with a FID and a 50 m fused silicon capillary column. The liquid part was identified from simulated distribution on a HP-5880A with an FID and a 508 mm fused UCW-982 column.

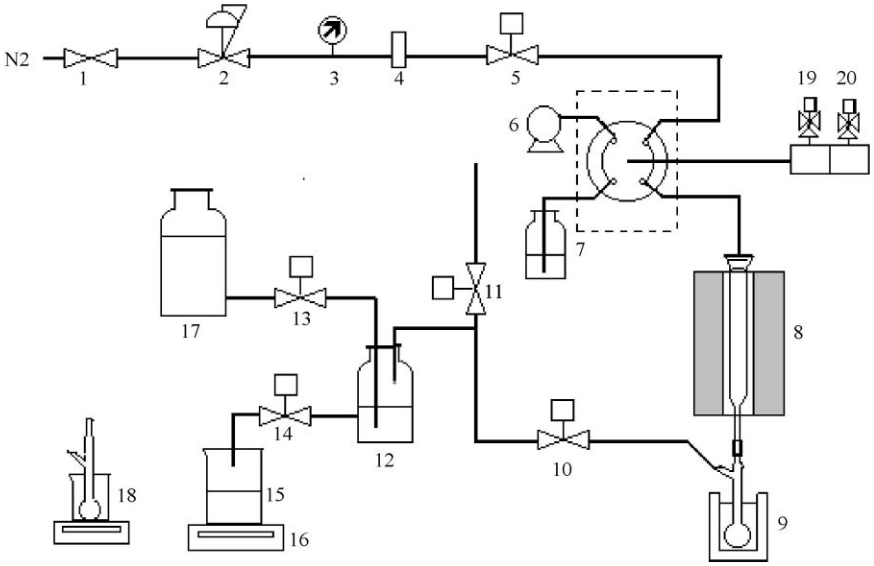

Fig. 1. Schematic of MAT apparatus.

The activity of a modified catalyst is a quantitative measure of the ability of a compound to catalyze hydrocarbon cracking. The activity of each modified zeolite was calculated as in the following equation:

$$\text{MAT\%} = 100 - \frac{m_1(100 - (A_1/(A_1 + A_2)) \times 100)}{m}$$

here MAT means the micro-activity of the catalyst, m_1 and m refers to the mass of liquid part (products) and of feedstock, respectively. A_1 and A_2 mean the amount of gasoline and of diesel by simulated distillation, respectively. The distillates <204°C was distributed to gasoline part, and the distillates between 205 and 350°C was assigned as diesel part. The distillates >350°C referred to heavy oil part, which might be assigned as the not converted feed part.

The selectivity describes the ability of a catalyst to favor one reaction pathway over all other possibilities. Herein, the selectivity was calculated as in the following equation:

$$\text{Selectivity} = \frac{m_i \times 100}{\sum m_i}$$

in which m_i means the mass of product i and $\sum m_i$ refers to the mass of all products, such as dry gas, gasoline, diesel and coke.

A direct measurement of the amount of deposited coke on catalysts was made by an extensive oxidation of the coke deposition to carbon dioxide. The coke amount tests were conducted in a self-made carbon content analyzer. The schematic of the coke

Table 1
Physical properties of Shenghua VGO feedstock

Tests	Shenghua VGO
Density (20°C)	0.9165 g/cm^3
Viscosity (50°C)	23.74
CCR	0.25 wt.%
Distillation range (°C)	
10%	343
30%	416
50%	448
70%	462
90%	500
95%	515
Hydrocarbon composition (wt.%)	
Saturated paraffin content	71.29
Asphaltene content	23.01
Gummy oil content	5.7
Heavy metal content (ppm)	
Ni	0.5
V	1.0
Fe	0.3
Cu	0.1

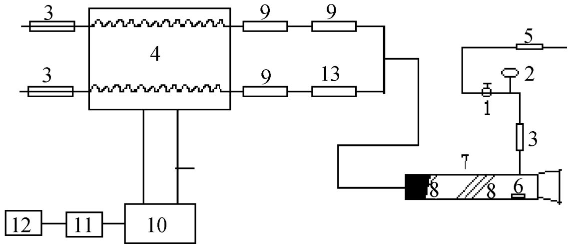

Fig. 2. Schematic of coke determination apparatus.

determination apparatus was illustrated as in Fig. 2. The used catalyst was firstly placed in a long quartz tube, then the heating coil of the hottest temperature zone, which twined round the tube, was quickly shifted to the location of the catalyst. Coke deposition on the catalyst was oxidized to most carbon dioxide and minority carbon monoxide in the oxygen atmosphere. The small quantity of carbon monoxide was stepwise catalytically oxidized by the CuO catalyst. The trace of water of the effluent gas was removed by dehydrate agents, subsequently the amount of produced carbon dioxide was monitored by a gas chromatograph equipped with TCD detector. The coke amount deposited on the catalyst can be obtained by comparison of CO_2 response of basic magnesium carbonate standard material.

The degree of coke deposition was calculated by the following equation:

$$\text{Coke} = \frac{m_\mathrm{r} A_\mathrm{s}}{m_\mathrm{s} A_\mathrm{r}} \times 12\%$$

in which m_s and m_r means the mass of coke catalyst and of reference sample, $CaCO_3$, respectively and A_s and A_r refers to the GC peak area of coke catalyst and of reference sample, $CaCO_3$, respectively.

2.4. *In situ FT-IR investigation*

The in situ FT-IR spectra of OH groups and pyridine adsorption were run on a Nicolet 750 Fourier transform IR spectrometer using self supporting zeolite plates. Samples were dehydrated at 400°C and 10^{-3} Pa for 4 h. The interaction with pyridine was then carried out at room temperature for 0.5 h, and weakly adsorbed species were removed by evacuation at 100°C for 2 h. The number of pyridinium ions (PyH^+) and pyridine–aluminium complexes (PyAl) were evaluated from the heights of the 1549–1540 and 1450–1455 cm^{-1} bands, respectively, with the assumption that the extinction coefficients remain constant. Herein, the number of PyH^+ and PyAl actually mean the numbers of Bronsted acid sites and Lewis acid sites in the modified zeolites, which originated from that one pyridine molecule can only reacted with one acid site of the zeolite. For the characterization of the stability of pyridine complexes, temperature programmed desorption in the evacuation at different temperature were conducted.

3. Results and discussion

USY zeolite is a typical and feature active component for hydrocarbon cracking, which has special nanopore and acid sites. The special nanopores insure the product selectivity and the acid sites hold out the high conversion of heavy hydrocarbons. It means that the optimization of the nanopore and acid sites of zeolites might be the key to design the effective catalyst for catalytic cracking of hydrocarbons. The current ultrastabilization method of Y type zeolites that has been employed industrially is the hydrothermal method under high temperature. The hydrothermal treatment (stabilization) results in the dealumination of the skeleton with total content of Al, Si and Na remaining unchanged [8]. However, its dealuminum degree is rather limited and the non-framework aluminum formed during the steam treatment may affect the catalytic performance of the zeolites in FCC process. Here the unbuffered system of the citric acid was first used to modify the USY zeolite further under moderate condition to explore a new modification method that has the prospect of industrial application [6]. The modification results indicate that it is a new effective modification method to treat USY zeolite with citric acid in the unbuffered system. Special modified zeolite samples with higher silicon to aluminum ratio can be prepared by this way, which shows higher yields of LPG and diesel in traditional FCC process. The pH value and the amount of the citric acid show great influence on the modification. The drop velocity of the citric acid has little influence on the modification. XRD results indicated that chemical dealumination of USY zeolite is believed to result in framework reconstruction with the USY zeolite skeleton. Aluminum is subsequently removed from the zeolite crystal as a soluble citric aluminum complex. Simultaneously, some extra framework silica fills the skeleton vacancies left by aluminum. Thus, structural differences exist between USY and modified samples because of the presence of extra framework aluminum and formation of mesopores. A great difference in IR spectra followed and XRD pattern [6] provides clear evidence of the essential influence of the modification process on the properties of skeletal and surface structure.

3.1. N_2 adsorption isotherm analysis

The isotherms of nitrogen adsorption on the representative modified USY samples (Cit-3) and untreated sample are shown in Fig. 3. The isotherms of N_2 adsorption and desorption of the modified USY zeolites are similar to type IV which posses a distinct hysteresis loop. The hysteresis loop exhibits at a relative pressure of 0.45 which is in good agreement with the threshold pressure reported in the literature [9] and it closes at a point equal saturation. It has also been found that the relative pressure (P/P^0) at which the adsorption reaches the last plateau shifts to the right for samples with larger pore diameter. This characteristic relative pressure (P/P^0) has been used to qualitatively compare the pore dimensions of different samples [10]. A higher value of the characteristic (P/P^0) indicates a larger pore size. De Boer's *t*-plot can provide very useful information on pore structures in which *t* is the statistical thickness of nitrogen film adsorbed on a non-porous solid. The adsorption amount on a sample, V_a, is plotted as a function of *t* at the same relative pressure. Furthermore, it is noted that the upward swing region of isotherm is prior to the lower closure point of the hysteresis loop, which means that the capillary condensation is not hysteresis at this region. The relative pressure of upward swing is at 0.05 and therefore wells below the closure point (0.45). This enhanced adsorption may be occurring in pores narrow enough for the whole of the adsorbate to be within the range of the surface forces emanating from the solid surface. The capillary condensed liquid in such narrow pores would show micropore property of modified samples [11]. Fig. 3 indicated that the nanopore volumes of modified sample are much higher than that of untreated sample, both for micropores and mesopores. It means that the micropore and mesopore all are effectively generated in the citric modification procedure. It resulted in the skeletal reconstruction of SiO_4 or AlO_4 tetrahedrons.

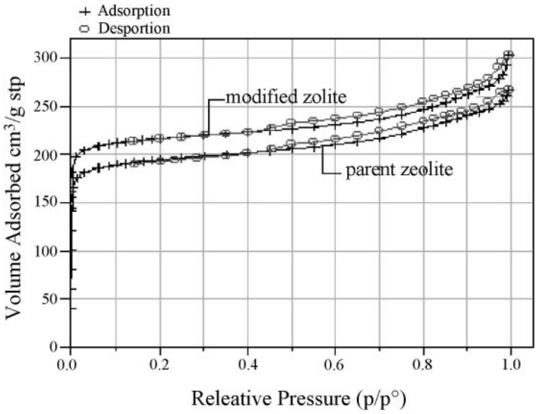

Fig. 3. The isotherms of the modified and untreated USY samples.

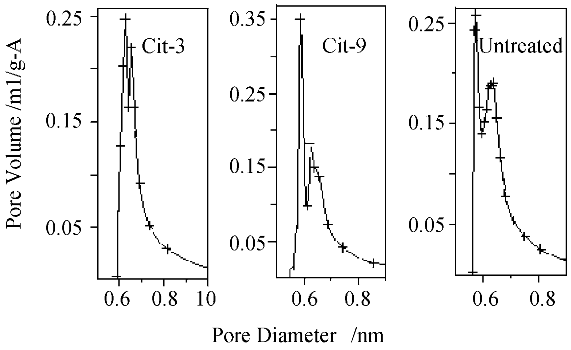

Fig. 4. Diagram of micropore distribution of modified zeolites.

Figs. 3 and 4 illustrated that the nitrogen adsorption amount of the modified samples is increased, but the shape of the isotherm is not change. It means that the pore volume of the modified samples is rather more developed than that of the parent zeolite and the pore distribution gradient is not obviously changed. The increase of micropores may be beneficial not only to the rebuilding of the framework, which leads to the transformation of larger mesopores into several micropores, but also to the enlarging tendency of the existing micropores (such as hexagonal column cages), which cannot be measured by nitrogen adsorption. Micropore, in charge of LPG formation in FCC process, is the major nanopore in modified zeolite. It means that the USY modification with citric acid can generate micropores. This process is actually not an amorphous substitution and just a partial dealumination by coordination pathway. It indicated that the generation of micropores might come from the acid clearups of amorphous or non-skeleton alumina formed in steam ultrastabilization. To increase the micropore volume might be favor the deep cracking reactions to produce much more LPG or lighter olefins, which can be used to synthesize MTBE, mixed esters in reformulated gasoline.

Simultaneously, the isotherms of nitrogen adsorption and mesopore distribution (described as in Fig. 5) also indicate that the secondary mesopore volume is positively improved in the modification with citric acid. Furthermore, the secondary mesopore diameters of modified samples were concentrated at ±3.8 nm, which might be desirable for FCC processes of residual oil or heavy feedstocks which average van der Waal radius is 25 Å. It is also positive for the production of diesel fraction in FCC process (as shown in Table 4). The pores with 3.8 nm diameter match the three supercage's diameter. It is possible that the supercages are formed while neighboring micropores of parent zeolite were inter-connected and mingled each other. It means that the microcages that encircle the supercage are preferably destroyed. The effective destruction of supercage of USY samples in the modification makes the supercages reciprocally link-up and formed mesopore of 3.8 nm.

The nanopore distribution (Fig. 5 and Table 2) and isotherm of nitrogen adsorption (Fig. 3) indicated that the skeletal reconstruction of USY zeolite is positively occurred. The dealumination process might be occurred gradually from the utmost surface to inner surface, then to bulk skeleton of the USY framework because of the larger volume of citric acid molecules. It will result in the gradient distribution of nanopores in modified USY zeolites. XRD characterization showed that the XRD pattern of modified sample bear the same crystalline structure with parent zeolite [6]. Simultaneously, the crystalline degree and micro-crystallite

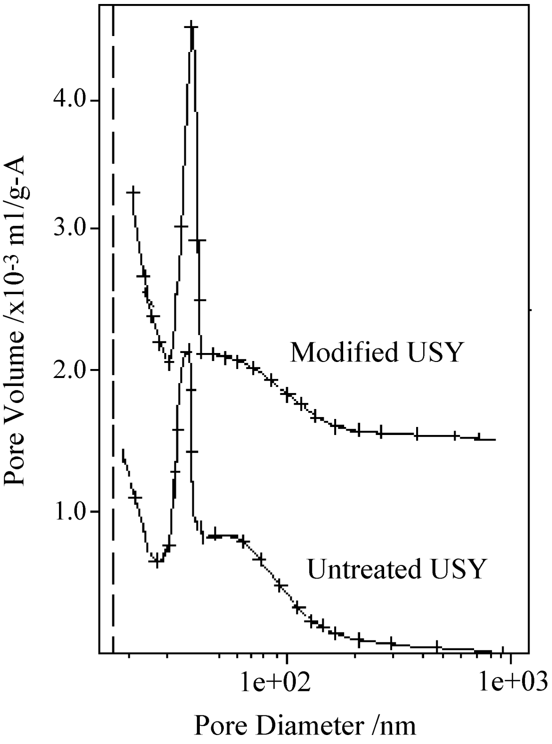

Fig. 5. Profile of the mesopore distribution of modified zeolites.

Table 2
Surface area and pore distribution of modified USY zeolites

Samples	External area (m^2/g)	Mesopore area (m^2/g)	Micopore area (m^2/g)	Mespore volume (cm^3/g)	Micropore volume (cm^3/g)
Cit-1	80.58	78.47	326.60	0.1383	0.2441
Cit-2	96.56	94.42	396.60	0.1549	0.2435
Cit-3	86.47	84.79	337.48	0.1352	0.2095
Cit-4	102.27	89.93	414.57	0.1527	0.2492
Cit-5	84.31	78.84	342.51	0.1448	0.2335
Cit-6	77.12	66.86	334.60	0.1504	0.2721
Cit-7	85.93	71.86	386.29	0.1426	0.2406
Cit-8	85.02	71.00	339.06	0.1248	0.2036
Untreated	102.37	78.50	318.12	0.1176	0.2016

particle sizes of modified samples are positively improved in the modification process. Of special is that the unit cell of modified sample is effectively reduced. It means that the dealumination of USY zeolite is actually occurred and that the modification with citric acid induces and accelerates the skeletal reconstruction.

3.2. Acidity characterization

In catalytic cracking, zeolite USY is the dominant source of activity in commercial FCC catalysts. In the case of a series of parallel and subsequent reactions [15] in FCC process where each requires a different level of acid strength, it could be possible to control the overall selectivity by design of the acid strength distribution of the catalyst. The crystalline structure of zeolite is convenient for defining the number of potential acid sites, which equals to the number of aluminum atoms present in framework [3]. However, the strength of the acid site associated with aluminum atom will depend on the chemical composition and crystalline structure. The key to design the effective FCC catalyst is to optimize the number and the distribution of aluminum atoms in the framework to achieve the best acid strength and acid site numbers.

It is difficult to accept the framework Al distribution throughout a dealuminated zeolite crystal will be uniform. In such cases, it is likely that there will be a higher concentration of framework Al at or near the internal surface of dealuminated USY zeolite and, therefore, an aluminum gradient throughout the structure. The preferential dealumination in citric modification might be outer surface of the USY crystal because of the huge bulk volume of citric molecule. Table 3 indicates that the numbers of the acid sites PyH^+ ions on the original and modified USY zeolites decrease with the increasing Si/Al ratio.

As shown in Table 3, the numbers of Al atoms, structural hydroxyls PyH^+ and unchanged Na^+ ions in the cavities together with the number of skeletal Al atoms rather satisfactorily comply with the neutrality. Dealumination with citric acid consists of the extraction of skeletal Al atom by citric aluminum complexes and subsequent washing out of the non-skeletal Al complexes. Thermal stability of PyH^+ ions on the original USY and extracted USY samples increases with the increasing Si/Al ratio. Since the acid strength of the skeletal aluminum was proved to increase with the Si/Al ratio, the thermal stability of PyH^+ can be understood and used as a measure of the acid strength of zeolite.

Table 3
Acidity of USY zeolites modified with citric acid [14]

Samples	Si/Al ratio	Total acid sites (mmol g^{-1})	PyH^+ (mmol g^{-1})
Cit-1	10.4	3.12	0.77
Cit-2	11.0	3.07	0.73
Cit-3	11.3	2.73	0.78
Cit-4	13.0	2.25	0.77
Cit-5	13.7	2.55	0.756
Cit-6	14.0	2.25	0.87
Cit-7	14.7	1.73	0.63
Cit-8	16.6	2.38	0.42
Untreated	8.3	2.41	0.59

Furthermore, citric acid modification yields highly heterogeneous zeolites. A great difference in the in situ IR spectra of hydroxyl (Fig. 6) provides clear evidence of the essential influence of the modification procedure on the properties of these groups. Here the hydroxyls might be classified into two groups according to their acidity and origin. The first group consists of acidic or non-acidic hydroxyls on structural defects, OH groups on non-skeletal Al species with frequency 3680–3700 cm^{-1}. It is rather weak because the most non-skeletal Al species exists as acid aluminum complex [12]. The second hydroxyls are located on the

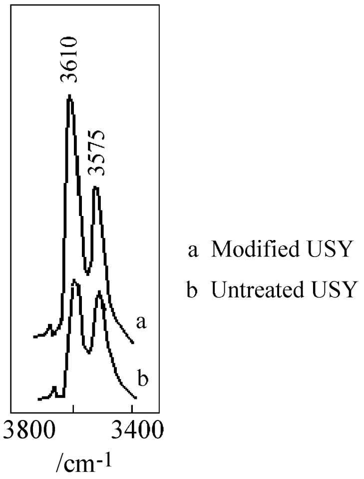

Fig. 6. In situ IR spectra of OH groups of USY zeolite.

skeleton and exhibit strongly acidic properties, being able to convert pyridine to pyridinium ion PyH^+. The bands assigned to their stretching vibrations appear in the wave number range between 3610 and $3575\,cm^{-1}$. The higher frequency bands are attributed hydroxyls in mesopore or large cages, while low frequency bands are attributed to the hydroxyls in the micropore or small cages. In such case, two factors should be taken into account. At first, the formation of PyH^+ ions depends on the acidity of OH groups, and the second, stabilization of OH groups by interaction with several skeletal oxygens in the mesopores or large cavities. The second factor might limit the number of PyH^+ ions formed, depending on the number of skeletal hydroxyls. As a consequence, the portion of structural hydroxyls are evidenced by the intensity of relevant bands as in Fig. 4. Further experiments indicated that the thermal stability of PyH^+ ions is affected by many factors as the active sites in zeolite framework, distribution of acid sites and the effect of adsorbed molecules. Of interest is that the $3610\,cm^{-1}$ bands obviously decrease with the increasing of the desorption temperature, while $3575\,cm^{-1}$ bands almost are constant with the increasing of the desorption temperature. It means that the hydroxyls in the micropore or small cages bears the stronger acidity and much more sites than those in mesopore or larger cavities. This special acid distribution is rather preferable to produce more LPG and diesel oil in FCC process. The stronger acidity and much more sites in micropores of citric acid modified samples might accelerate the deep cracking to produce much more LPG part in FCC process, while the weaker acidity and less sites in mesopores would favor the selective cracking to form diesel and gasoline distillates.

PyAl complexes found on modified zeolites can be considered as being formed from skeletal three-coordination aluminum atoms (Fig. 7) [13]. The thermal stability of PyAl complexes, and their number in citric modified USY zeolite, is always considerably increased with the increasing of evacuation temperature. It means that the acid strength of Al Lewis acid sites is rather strong. It means that such Lewis Al acid sites are also important to catalytic cracking.

Table 3 and Fig. 7 indicate that the number of total acid sites decreases with the increase of the Si/Al ratio of modified samples, it is in agreement with Corma et al. [2]. He proposed the aluminum gradient distribution model. Here, the dealumination process might be occurred gradually from the upmost surface to inner surface, then to bulk sites of the USY framework because of the larger volume of citric acid molecules. It will result in the gradient distribution of acid sites in the modified USY zeolites. Simultaneously, the acid strength of acid sites should also have a gradient. It means that the acid sites in mesopores or supercages are obviously decreased in the process of citric acid modification, while the acid sites in micropore or small cages changed just a little due to the size of active acid molecule. This gradient distribution is preferable to process heavy oil and to improve the LPG and diesel selectivities. It means that LPG is preferably produced in micropores or small cavity, while the diesel distillate is mainly formed in mesopores or supercages.

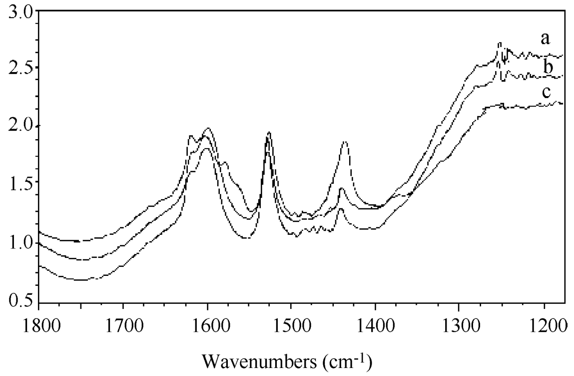

Fig. 7. In situ IR spectra of PyH^+ ions and PyAl complexes in citric modified USY zeolites: (a) 423 K; (b) 523 K; (c) 623 K.

3.3. MAT evaluation

Compared to the parent sample, Table 2 indicates that the external surfaces of modified samples were obviously decreased, however, the micropore and mesopore volumes were greatly increased at the appropriate conditions. Fig. 4 illustrated that a relative narrow pore size distribution of modified samples is appeared, which would be benefit to the improvement of the catalyst selectivity.

Coke is an unavoidable product of catalytic cracking. The accumulation of coke on the catalyst leads to catalyst deactivation. It is largely undesirable in catalytic cracking and it is therefore of some considerable interest to examine the rates and source of coke formation. Coke deposition in FCC process is correlated with nanopore size distribution, feed molecule diffusion rate, acid site concentration and acid strength distribution [15]. Experimentally, the initial coke deactivation of untreated samples is rather rapid and then decreases more slowly with increasing time-on-stream. Generally, the loss in activity is greater than the loss in the number of acid sites. Correlating the activity with the amount of coke deposited on catalyst shows the activity to decrease rapidly the first deposition of coke and then more slowly as the content of coke increases. It means that this initial, rapid deactivation is due to inhomogeneity of the active sites. According to the above gradient distribution of acid sites and nanopores, LPG should be preferably produced on stronger acid sites in micropores or small cavity, while the diesel distillate is mainly formed on the medium of stronger acid sites in mesopores or supercages. This gradient distribution of acid sites in mesopores or large cavity might effectively inhibits the occurrence of the hydrogen transfer reaction and deep cracking and coke formation, whereas gradient distribution of acid sites in micropore or small cavity might positively accelerate the deep cracking to form LPG products.

Table 4 shows the catalytic performance of each citric modified catalyst. It indicated that the LPG and diesel yields of citric modified samples were effectively improved. Simultaneously, the coke formation of modified samples was obviously inhibited. This positive tendency should be resulted in the gradient distribution of acid sites in nanopores or cavities and rather developed nanopores. It is in good agreement with above deduces in gradient distribution of nanopores and acid sites in different nanopores or cavities. Optimization of nanopores and acid sites of ultrastabilized faujasite zeolite modified with citric acid in unbuffered system might result in an industrial process to design novel FCC catalysts.

It was suggested that the coke was formed from olefins which are produced in the primary cracking reactions [16]. Simultaneously, if the feed contains polyaromatic components, the formation of coke is found to be a primary reaction, though it is not entirely clear whether the coke formed is a product of a catalytic reaction or merely represents the adsorbed polynuclear aromatics of the feed in some dehydrogenated form. Herein, the coke formation is being further investigated.

However, the usefulness of any laboratory testing techniques depends on how representative it is of commercial operation. The laboratory evaluation methods herein operate at a long catalyst/oil contact time (10–100 s) compared to commercial operation (approximately 1 s), and hence, this is a major drawback in their use for commercially representative catalyst evaluation. At first, the long contact time in an MAT unit increase the importance of the slow hydrogen transfer reaction [17], thus the olefinicity of both

Table 4
MAT results of citric modified USY zeolites[a]

Samples	Activity (wt.%)	H_2 (wt.%)	Dry gas (wt.%)	LPG (wt.%)	Gasoline (wt.%)	Diesel (wt.%)	Coke (wt.%)
Cit-2	73	0.29	5.89	18.78	43.76	19.95	4.42
Cit-3	70	0.24	6.66	17.70	39.30	20.92	3.01
Cit-4	71	0.25	5.76	17.17	40.74	20.49	3.95
Cit-5	68	0.27	6.47	15.06	36.72	22.64	3.33
Cit-6	72	0.21	5.60	15.59	41.34	21.70	3.17
Cit-7	69	0.33	6.80	16.13	36.07	22.42	2.94
Cit-8	68	0.35	7.26	15.56	36.49	22.20	3.45
ZCM-7[b]	64	5.79		10.10	52.98	13.29	7.03
CRP-1[c]	59	9.16		42.00	26.60	13.49	8.24
Untreated	60	0.28	8.10	14.39	35.19	18.38	5.75

[a] Feedstock: Shenghua VGO, density 0.9165 g/cm^3 (20°C), CCR 0.25%, reaction temperature 550°C, catalyst/feedstock 2.8.

[b] ZCM-7, FCC catalyst with hydrothermal treated USY zeolites produced by Zhoucun Catalyst Work, Sinopec. Feedstock: pipeline residue, density 0.9057 g/cm^3 (20°C), CCR 3.35%, reaction temperature 510°C, catalyst/feedstock 6.4.

[c] CRP-1, FCC catalyst with USY and ZSM-5 zeolites produced by Zhoucun Catatlyst Work, Sinopec. Feedstock: Mixed VGO, density 0.9085 g/cm^3 (20°C), CCR 0.71%, reaction temperature 550°C, catalyst/feedstock 9.5.

liquid and gaseous products is underestimated from MAT units. Simultaneously, the long contact time also causes a different conversion-coke selectivity behavior from that of a commercial unit. But MAT evaluation is still important to catalyst screening and might also be the important references to commercial unit.

4. Conclusions

1. The modification of USY zeolites with citric acid in unbuffered system is feasible in practice. Chemical dealumination of USY zeolite is believed to result in framework reconstruction with the USY zeolite skeleton. Aluminum is subsequently removed from the zeolite framework as a soluble citric aluminum complex.
2. The nitrogen adsorption amount of the modified samples is positively increased, but the shape of the isotherm is not change. It means that the pore volume of the modified samples is rather more developed than that of the parent zeolite and the pore distribution gradient is not obviously changed. It also indicates that micropores and mesopores might be generated by skeletal reconstruction.
3. The dealumination process might be occurred gradually from the upmost surface to inner surface, then to bulk sites of the USY framework because of the larger volume of citric acid molecules. It will result in the gradient distribution of nanopores and acid sites in modified USY zeolites.
4. The hydroxyls with IR bands of 3610 and $3575\,\mathrm{cm}^{-1}$ in the micropore or small cages bears the stronger acidity and much more sites than those in mesopore or larger cavities. This special acid distribution is rather preferable to produce more LPG and diesel oil in FCC process.
5. MAT evaluations indicated that the LPG and diesel yields of citric modified samples were effectively improved and the coke formation of modified samples was obviously inhibited.
6. Optimization of nanopores and acid sites of ultra-stabilized faujasite zeolite modified with citric acid in unbuffered system might result in an industrial process to design novel FCC catalysts.

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