On the simultaneous removal of FAL and EFAL from commercial USY

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Abstract:

Zeolite-Y is the prominent member of zeolite family for the application of transforming low value hydrocarbons to high value products especially in resid fluid catalytic cracking. The simultaneous removal of non-framework Al (EFAL) as well as framework Al (FAL) is carried out systematically in commercial USY (Ultrastable Y) zeolite by sodium silicate solution with varying concentration. The presence of silanol nest, Al–OH, four-coordinated framework Al, six-coordinated framework Al, six-coordinated non-framework Al and five-coordinated non-framework Al) was detected by MAS NMR and their changes were followed during the extraction of aluminum. This analysis gives evidence that the breakdown of the parent USY zeolite and extracted USY sample exerts a great effect on the acidity. The model reaction with n-dodecane cracking showed the different distribution of Al species in parent and extracted samples.

Keywords: Simultaneous removal, aluminum, catalytic cracking.

1. Introduction

Zeolite Y has been widely used as a fluidized catalytic cracking (FCC/RFCC) catalyst [1] having good thermal and hydrothermal stability. Industrial practices and related studies reveal that high silica zeolite Y exhibits outstanding catalytic activity and hydrothermal stability [2]. Highly siliceous zeolite Y was obtained by the post-synthesis method which results a non-framework Al species is formed [3]. Among various methods, hydrothermal treatment is the most frequently used one, and the resulting material, USY (ultrastable Y) zeolites, being modified in the framework Si/Al ratio, structure and acidity, usually exhibit improved reactivity, selectivity and coking behavior for a catalytic reaction, which is of great interest to the petroleum industry [4]. These changes have been attributed to the structural dealumination and the presence of non-framework aluminum [5]. It has been suggested that the amount of non-framework Al species, formed during the ultrastabilization, is one of the key factors that influences significantly the cracking activity towards hydrocarbons [6]. Meanwhile, the presence of a large amount of non-framework Al has a detrimental effect on the catalytic and transport properties, so that a subsequent alkali treating to extract them is necessary.

In this work, USY zeolites were modified through alkali solution procedures by removing different fractions of framework and/or framework Al atoms. The conditions of removal, the type of alkali, the concentration and the temperature, were varied systematically in order to obtain a regular change of structural and acidic properties of the USY zeolite as well as the Al coordination during the dealumination process. The resulting samples were characterized by XRD and solid state NMR spectroscopy, with XRD measurements for structure breakdown, and NMR measurements for analysis of structure, Al coordination, and acid sites (types, strength, and number of hydroxyl groups in zeolites). The different distribution of Al species in these samples accounted for the different catalytic performance of n-dodecane cracking.

2. Experimental (or Theoretical)

A commercial USY zeolites (CBV 300, CBV 600) were obtained from Zeolyst, treated with sodium silicate solution (SSS, Sigma-Aldrich, 27%SiO2 and 14% NaOH) using a proportion of 1 g zeolite per 20 ml solution. The alkali treatment was carried out at room temperature or under reflux conditions for 30-60 mins (4-24h). The concentration of SSS was varied systematically from 0.01 to 0.5N. The suspension was then filtered, washed with deionized water and dried in an oven at 110^{O}C overnight. Powder XRD patterns were collected on a D-2 PHASER type X-ray diffractometer (BRUKER) using Cu $K\infty$ radiation. The scan speed was 5◦/min and the scan range was 5–70◦ 2θ. The crystallinity was determined by using HY zeolite as the reference material and the total intensity of the strongest reflections in the region $15 < 2\theta < 36$◦. The NMR spectra were obtained at 9.4 T on a Bruker DRX-400 spectrometer using 4mm ZrO_2 rotors at room temperature. ^{29}Si MAS NMR spectra with high power proton decoupling were obtained at 79.49MHz using a pulse of 1μs, a repetition time of 4s, and 2048 scans. The ^{27}Al MAS NMR spectra were recorded at 104.3MHz (9.4 T) using a 0.75μs $\pi/12$ pulse with a 3 s recycles delay and 400 scans. The N2 adsorption-desorption isotherm was recorded using Micromeritics ASAP 2020.

3. Results and discussion

All the prepared samples were calcined at 550 °C for 4 h. The N2 adsorption– desorption isotherm of USY(0.01N) is a typical type-I and type-IV sorption isotherm, corresponding to the apparent microporous character of the zeolite. These characterization results indicate that the product USY(0.01N) is highly crystalline zeolite USY without any impurity(Fig. 1)..

The conversion and selectivity for cracking of n-dodecane were measured and compared. With the progress of dealumination, the catalytic activity increased at the beginning of the process, reached a maximum, and then decreased. The increase in alkenes (propylene and iso-butene) was due to the appearance of non-framework tetrahedral Al species resulting from the severe dealumination of USY. The different distribution of Al species in these samples accounted for the different catalytic performance

Figure 1. USY(0.01N) after treatment (A) XRD, (B)TEM, (C) N2 adsorption isotherm, (D) ^{27}Al-NMR spectrum

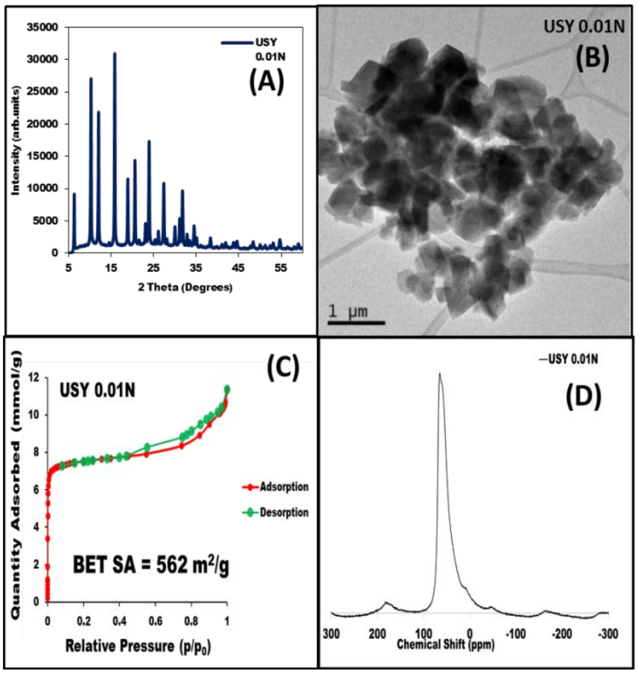

Table 1. Product composition of HY, USY and USY (0.01N)

Catalyst	**HY**	**USY**	**USY0.01N**
Methane	0.27	0.24	0.27
Ethane	0.94	0.79	0.60
Ethylene	1.27	0.91	0.89
Propane	9.64	7.66	8.15
Propylene	9.52	7.61	6.74
Iso-Butane	27.34	27.14	25.52
N-Butane	6.93	6.92	6.98
Trans-2-Butene	2.58	2.53	2.35
1-Butane	1.59	1.47	0.95
Iso-Butylene	3.16	2.21	1.40
Cis-2-Butene	1.84	1.74	1.56
Iso-Pentane	14.82	18.98	19.66
N-Pentane	1.50	1.66	1.58
C6+	13.99	15.78	19.06

Table 1 lists the products distribution and the n-dodecane conversion at 400 ^{O}C , WHSV, 9.6h^{-1}and TOS 60 min reaction shows that the product distribution is different from parent HY and USY. The differences in conversion between parent HY, USY and USY0.01N can be attributed to the different Al sites distribution (type and amount) and, consequently, different reaction mechanisms. USY having EFAL undergoes mono-molecular cracking involves secondary reactions which contribute to the formation of light alkenes. These results suggest that the kinetics of cracking is sensitive to any possible differences in Al sites distributions among these catalysts.

4. Conclusions

Modification of the aluminum distribution of the USY zeolite was carried out by the alkali treatment with varying concentration, temperature and time. It is evidenced that the removal of EFAL and FAL aluminum species can be controlled by the type and the concentration of the alkali and the temperature employed. The conversion and selectivity for cracking of *n*-dodecane were measured and compared. The different distribution of Al species in these samples accounted for the different catalytic performance

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