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Article

Kinetics study and analysis of zeolite Y destruction

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ABSTRACT

A series of zeolites, including USY zeolites without sodium, Na-USY at different Na contents, La-USY with different rare earth (RE) contents and La-Na-USY with RE and Na were prepared by an ion exchange method. They were investigated to understand the activation barriers for the destruction of Y zeolite structure under hydrothermal treatment and the effect of V using the solid-state kinetic model. The results showed that the pathways for Y zeolite destruction were dealumination, desilicization and the disappearance of La–O bonds. Zeolites were destroyed by steam through acid hydrolysis, which was accelerated by V. In addition, Na and V exerted a synergistic effect on the framework destruction, and the formation of NaOH was the rate-determining step. The presence of RE elements decreased hydrolysis and stabilized the structure of the zeolites. The interaction between V and RE destroyed zeolite structure by eliminating the stabilizing La–O [RE–OH–RE]⁵⁺ bridges in the sodalite cages.

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1. Introduction

During the reaction and regeneration offluid catalytic cracking (FCC) catalysts, they are exposed to extremely high temperatures in the presence of steam. The standard Y zeolite, which is the main active ingredient in FCC catalysts, undergoes rapid dealumination that introduces modifications that lead to the deactivation of the catalysts. Such deactivation results from the dehydroxylation of the Brønsted acid sites where the catalytic cracking reaction occurs, and this reduces the catalyst activity and selectivity by destroying the zeolite's crystallinity [1,2].

The effects of contamination by transition metals, such as V and Ni, on FCC catalysts have been extensively studied [3–7]. V is deposited on the catalyst surface, probably in the form of [VO]²⁺ along with large organic molecules and coke deposited during the catalytic cracking reaction [8]. The coke is burned off during regeneration and the V is oxidized to V₂O₅. Being

amphoteric in nature, V⁵⁺ migrates to the acid sites and is trapped as the cationic species [VO]₂⁺ poisoning the zeolite [9]:

This dynamic equilibrium moves to the left during hydrogen combustion, and the resultant water reacts with V₂O₅ to produce vanadic acid:

Since vanadic acid is a strong acid, it destroys the zeolite by hydrolyzing the SiO₂/Al₂O₃ framework.

Sodium changes the resistance of the zeolite to steam by reacting with the water to form an active center, surface NaOH, which also causes destruction of the zeolite [10,11]. Xu et al. [12,13] reported that this process was dependent on the facile formation and availability of NaOH. OH[−] attacks the framework Si–O bonds. Pine [3] found that Na and V exerted synergistic effects in the destruction of the zeolite structure. Xu et al. [13] proposed a mechanism for the destruction of zeolite Y, showing the cooperation between Na and V.

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For zeolite Y that contain rare earth (RE) elements, the cations are located in the sodalite cages and coordinated to framework oxygen. Dehydroxylation of REY occurs between the hydroxyl groups on the RE species and the neighboring Al–OH, reducing framework damage [14]. In addition, RE elements are commonly used to stabilize zeolite by decreasing the vanadium mobility and thus reducing damage to the zeolite caused by steam. The properties of these RE-containing zeolites are strongly dependent on the methodology that introduces the RE elements [15–17]. RE cations are preferentially located in the sodalite cage in RE-exchanged zeolite Y, which boosts the zeolite stability due to the coordination between the cations and the framework oxygen atoms [18–20].

Currently, many mechanisms have been proposed for the destruction of zeolite Y, but the kinetic processes, as one of the major subdivisions of physical chemistry, has not been thoroughly studied. Although kinetic studies cannot be used to prove a reaction mechanism, any mechanism proposed must at least be consistent with the kinetic data. Kinetic measurements regarding the destruction of several zeolites, with and without vanadium, were performed by Pine [3] more than 20 years ago, and remain the only kinetic data of Y zeolites destruction to date. Although that study provided many valuable theories and mechanisms, the experiments were conducted on USY samples with low unit cell sizes (UCS, 24.24–24.28 Å). Such zeolites had high framework Si/Al ratios, and as framework aluminum is less prone to vanadium acid-catalyzed hydrolysis, vanadium acid-catalyzed hydrolysis of framework aluminum is less likely to occur. In addition, Pine [3] found that the apparent activation energy of Y destruction with vanadium was 330.5 kJ/mol and with sodium it was 320.5 kJ/mol. For zeolite deactivated solid-state phase transformation, the activation energy is related to the physical and chemical performance of the zeolite, and is dependent on the passivation conditions and mechanism. Such a high value suggests that the zeolites exhibit extremely high hydrothermal stability, and therefore vanadium itself may have little effect on the crystallinity of zeolite.

After more than 20 years of study, the detailed mechanisms for zeolite dealumination by steam have been widely postulated. However, kinetic evidence is still lacking. In this study, a kinetic study on the zeolite Y destruction with and without vanadium has been conducted to improve information on the mechanism of zeolite destruction. Zeolite samples with Na, RE and both sodium and rare earths were prepared to evaluate the properties of the FCC catalysts.

2. Materials and methods

2.1. Preparation of catalysts

The zeolite Y used herein was exchanged four times with NH_4Cl aqueous solution at 80 °C for 1 h to lower the Na content. The zeolite was then washed, filtered, dried overnight, and calcined at 550 °C for 2 h.

Samples with different Na_2O contents were prepared by wetness impregnation with a sodium oxalate solution at pH 7. Lanthanum was incorporated into the zeolite by ion exchange

at 80 °C using aqueous solutions of LaCl_3 . All samples were dried at 100 °C overnight and calcined at 550 °C for 2 h. Vanadium was introduced by wetness impregnation from a water solution of vanadyl oxalate following the procedure described by Mitchell [21], and the samples were dried and then calcined at 550 °C for 4 h.

The samples (Na_2O , La_2O_3 and V) were analyzed by X-ray fluorescence spectroscopy. Table 1 lists the properties of all the starting materials. A Rigaku D/max-3C diffractometer using $\text{Cu K}\alpha$ radiation was employed to measure the relative crystallinity of the zeolite samples. The UCS was determined from the positions of the reflection in the diffraction pattern.

The sample was hydrothermally deactivated in a laboratory furnace at 740, 760, 780 or 800 °C for the desired time in a 100% steam environment.

2.2. Theoretical: Solid-state kinetic models and activation energies

The kinetics of many solid-state reactions have been described by nucleation models. Nucleation is the formation of a new phase at reactive sites (nucleation sites) in the lattice of the reactant [22]. The relative rates of nucleation and growth can be derived from solid-state kinetic data. When this ratio approaches either infinity or zero, only the nucleation rate or the growth rate can be obtained. When the process is nucleation-controlled, the kinetic data can be displayed as a simple first-order plot, i.e. single-step nucleation. For N_0 potential nucleation sites, once the nuclei (N) form, they grow and nucleate at a rate that follows a simple first-order process:

$$\frac{dN}{dt} = k_N(N_0 - N)$$

According to Pine's study [3], the steam destruction of zeolite Y was a process of nucleation-limited solid-state phase transformation. Therefore, the deactivation rate of zeolites in this study can be expressed by the simple kinetic equation:

$$\frac{dc}{dt} = k_c(c_0 - c)$$

where c is the relative crystallinity and k_c is the deactivation rate constant.

The rate constant of a reaction depends on the temperature, which was described by Arrhenius:

$$\ln k/dT = E_a/RT^2$$

where E_a is the activation energy. The activation energy is the height of the potential barrier separating two potential energy minima. For a chemical reaction to proceed, different reaction mechanisms generally have different activation energies.

3. Results and discussion

Selected properties of the prepared samples are listed in Table 1. The UCS of a zeolite is directly related to its framework Al (FAI) content, where FAI/u.c. increases with the UCS because Al–O (1.74 Å) bonds are longer than Si–O (1.61 Å) bonds. As the Na content increases, the UCS changes only slightly, suggesting that the Al–O bonds remain intact when the Na is loaded and calcined in dry air. Notably, the UCS increased as the Na content increased when it had been exchanged out of starting NaY

Table 1

Physical and chemical properties of the Y zeolite samples.

Sample	$\omega_{\text{Na}_2\text{O}_3}$ (%)	$\omega_{\text{La}_2\text{O}_3}$ (%)	UCS (nm)	c/c_0 (%)
USY	0.1	0	2.450	69
Na-USY(1)	0.7	0	2.448	64
Na-USY(2)	1.7	0	2.448	65
Na-USY(3)	2.7	0	2.449	65
La-USY(1)	0.1	2.0	2.448	58
La-USY(2)	0.1	4.0	2.449	56
La-USY(3)	0.1	6.0	2.451	50
Na-La-USY	1.7	2.0	2.449	57

zeolite. In other words, Na inhibited dealumination. The UCS was also slightly increased as the RE content increased. The increase of UCS can be ascribed to the enhanced attraction between La cations located at the SI' site of the sodalite cage and framework oxygen atoms. Meanwhile, elongation of the T–O bond distance may also play a part in enlarging the unit cell parameters. The relative crystallinity of the catalysts containing La appears lower than the original USY because of X-ray absorption by lanthanum.

The crystallinity of each sample was calculated based on the ASTM 3906-03 methodology [23]. The XRD patterns of the sample and the reference were obtained under the same conditions. The relative crystallinity was determined from the area of the peaks where $2\theta = 22.0^\circ$ – 24.5° , and a standard zeolite was used as the reference sample. The peak-area ratio was expressed as a percentage crystallinity:

$$\text{Relative crystallinity } (c/c_0, \%) = \frac{(\text{Y zeolite peak-area in the sample})}{(\text{Y zeolite peak-area in the standard zeolite})} \times 100$$

Figure 1 shows the crystallinity of the samples impregnated with vanadium or sodium. The crystallinity was not affected appreciably by heat treatment in dry air at 800 °C even in the

Fig. 1. Relative crystallinity of zeolite impregnated with vanadium or sodium. **Fig. 2.** Dependence of the rates of USY destruction on the hydrothermal treatment time.

presence of V or Na. Under hydrothermal treatment at 800 °C, the crystallinity plummeted. It is well known that vanadium affects the zeolite crystallinity only in cooperation with steam.

Our study showed that Na did not have any structural effects in dry conditions, as Hagiwara et al. [6] observed. Sandoval-Díaz et al. [24] proposed that dry thermal treatment in the presence of high Na loading (0–25 wt%) induced framework destruction. Although there was no water in the reaction atmosphere, the zeolites trapped a considerable amount of water and the reaction may have proceeded while the material dehydrated or with water molecules produced from the thermal dehydration of the silanol groups. In the presence of steam, the effect was more severe due to the constant supply of water, which was accompanied by the decrease in crystallinity seen in this study.

Figure 2 shows the relative crystallinity of the USY zeolites after heat treatment in 100% steam, where the data have been plotted as the logarithm of relative crystallinity versus time. Fig. 3 is an Arrhenius plot of the data from Fig. 2. From the slope of the lines, the average activation energy was calculated to be 93 kJ/mol, and this activation energy was independent of the vanadium level, indicating that vanadium was not involved in the kinetically significant step of Y destruction. In other words, vanadium accelerated the destruction of zeolite but did not change its pathway.

The mechanism for zeolite destruction by steam in the presence of vanadium can be described as [25]:

As a strong acid, vanadic acid accelerates dealumination by catalyzing framework hydrolysis. V^{5+} is prone to polymerization, and liquid V_2O_5 functions as a solvent for zeolite components at V^{5+} concentrations higher than those found in FCC catalysts. Kerr [26,27] postulated that the zeolite was dealuminated by electrophilic attack by hydronium ions on the negatively charged oxygens at the acid site:

In this scheme, the hydronium ion, as an electrophile,

Fig. 3. Temperature dependence of the first-order rate constant for the destruction of USY.

attacks the Si–O–Al bond by extracting aluminum from the lattice, causing the collapse of the structure. Vanadium catalyzes zeolite framework hydrolysis because it is not consumed during the destruction. At high temperatures, vanadium forms H_3VO_4 in the presence of water, thus increasing the hydrogen ion concentration and accelerates the electrophilic reaction.

The effect of the amount of Na on the steam stability of zeolite was also evaluated. Fig. 4 shows the apparent activation energy for the destruction of Na-USY is 168 kJ/mol and is independent of the Na concentration. The higher value suggests that the Na-USY destruction pathway is different from that of USY without Na or where the Na content is very low.

In this case, Na is responsible for the zeolite hydrothermal instability. Na reacts with steam to form an active center, a surface NaOH, which aids the zeolite destruction. However, NaOH is not well solvated and the ionic species Na^+ and OH^- form in high-temperature steam. According to Xu et al. [13], NaOH partially ionizes, allowing it to react with Si–O, which also destroys the framework. The detailed mechanism can be described as the nucleophilic attack of hydroxide ion on the framework Si–O bonds.

Fig. 4. Temperature dependence of the first-order rate constant for the destruction of Na-USY.

dealumination [11], which suggests the framework destruction mediated by Na does not involve Al atoms.

Pine [3] reported that vanadium and sodium ions catalyze the framework destruction synergistically, which was seen in the kinetic data in this study. Fig. 5 shows that rate constants are directly proportional to the sodium level at several levels of vanadium. Without synergism, the lines are bound to be parallel because the slopes are similar. In order to explain this synergy, Xu et al. [13] suggested that some vanadium ions could promote the formation of NaOH:

The deposited vanadium, as vanadic acid, catalyzes the above reactions which convert framework sodium ions into NaOH. This increase in the NaOH content then further promotes the dissolution of zeolite crystal.

Temperature response data for several levels of sodium on vanadium zeolite are plotted in Fig. 6, which give the activation energy of 127 kJ/mol. There are two pathways for Na-USY destruction in the presence of steam and they may or may not be independent. If there is no interaction between sodium and vanadium, vanadium increases the dealumination rate instead of affecting the activation energy. However, the decrease of activation energy suggests that the vanadium and sodium catalyzes the destruction of zeolite by steam with significant synergistic effects.

Without vanadium, sodium is removed through the hydrolysis of Na^+Y :

This uncatalyzed formation of NaOH is the rate-determining step. Therefore due to the catalytic action of vanadium, the concentration of available NaOH is always greater when vanadium is present. This is the first kinetic proof of synergy between sodium and vanadium.

RE-containing Y-type zeolites play an important role in the FCC process. It is well-established that the RE cations on Y zeolites are able to improve the acidity, cracking activity, and thermal stability. The most widely accepted theory states that the increased stability results from the formation of coordination bonds between the RE cations and framework

Fig. 5. Effect of sodium on the rates of USY destruction at constant vanadium. Steaming conditions: 800 °C, 100% steam.

Fig. 6. Temperature dependence of the first-order rate constant for the destruction of Na-USY at constant vanadium.

oxygen atoms. H^+ ions from the HO–Al bond are replaced by RE cations, thus preventing the dehydroxylation of neighboring Al hydroxyls [28–30].

In order to isolate the effects of the RE on the zeolite stability, La-USY samples with La_2O_3 levels from 2.0 to 6.0 wt% were prepared by exchanging lanthanum into the starting USY sample containing 0.1 wt% Na_2O . Temperature response data for several levels of lanthanum are plotted in Fig. 7. The activation energy of La-USY zeolite destruction is about the same as that for the USY zeolite without the rare earth, indicating the destruction reaction proceeds along the same pathway. In the presence of vanadium, the interaction between lanthanum and vanadium affected the zeolite destruction, as evidenced by the change in the activation energy (124 kJ/mol, Fig. 8).

Figure 9 shows relative crystallinity of the USY and La-USY zeolites after hydrothermal treatment in the presence of 6000 ppm vanadium. For V-containing La-USY samples, the decrease

Fig. 7. Temperature dependence of the first-order rate constant for La-USY destruction.

Fig. 8. Temperature dependence of the first-order rate constant for La-USY destruction at constant vanadium.

in crystallinity was more dramatic than in a USY zeolite without RE, indicating that vanadium affects the zeolite more severely in the presence of RE. However, it is important to point out that, although the experimental results confirm the effect of vanadium on the La-USY destruction is stronger, RE elements also boost the zeolite stability due to the additional bonding between the cations and the framework oxygen atoms.

Fig. 9. Effect of vanadium on the crystallinity of USY and La-USY.

Fig. 10. Temperature dependence of the first-order rate constant for La-Na-USY destruction at constant vanadium.

The beneficial effect of RE elements on the zeolite stability is related to the formation of RE–O–RE bonds inside the zeolite cavities, which stabilizes the zeolite because of the additional bridges between tetrahedra. The ability of RE elements to form vanadate species may help retain vanadium in the structure. However, the chemical environment of the RE affects the properties of zeolites [31–33]. When the La-USY zeolite is prepared by ionic exchange, RE cations are located in the sodalite cages, which stabilize the zeolite due to the coordination between the cations and the framework oxygen atoms. In this case, vanadium can interact with the RE to form high-melting-point RE–vanadates that remove the RE ions, thus destroying the zeolite structure [34,35]. In other words, the destabilization of the zeolite can be attributed to the disappearance of La–O–La stabilizing bridges in the sodalite cages.

Commercial FCC catalysts contain zeolite-associated Na and

Table 2

The apparent activation energy for Y zeolite destruction.

Sample	Activation energy (kJ/mol)	Pathways for Y zeolite destruction		
		Dealumination	Desilication	Disappearance of RE–O
USY/USY+V	93	✓		
Na-USY	168	✓	✓	
Na-USY+V	127	✓	✓	
La-USY	96	✓		
La-USY+V	124	✓		✓
La-Na-USY	166	✓	✓	
La-Na-USY+V	103	✓	✓	✓

RE elements simultaneously. In order to understand the process of zeolite destruction, a La-Na-USY sample with 1.7 wt% Na₂O and 2.0 wt% La₂O₃ was prepared and tested. At this standard commercial catalyst sodium level, sodium catalyzed the steam destruction of USY and the activation energies for the destruction is independent of the presence of RE (Fig. 10(a)).

In the presence of vanadium, the rate constant of destruction increased and the activation energy was obviously decreased. These results, along with those for USY in Fig. 10(b), indicate that Y destruction was enhanced in the presence of vanadium. The coexistence of three pathways for La-Na-USY destruction may adversely affect the zeolite stability.

Table 2 lists the apparent activation energies for Y destruction. The activation energy is defined as the minimum energy required to start a chemical reaction and is related to the reaction mechanism. In other words, the same reaction has different activation energies for different mechanisms. In this study, the pathways for Y zeolite destruction were postulated by comparison and statistical analysis of the activation energies (Fig. 11).

Hydrothermal deactivation occurred via the hydrolysis and elimination of Al from the tetrahedral sites of Y zeolite. Dealumination (pathway A) inevitably led to zeolite collapse under steaming conditions. In addition, vanadium accelerated framework dealumination, which is slowed down by the presence of RE elements. The destructive pathway of sodium, referred to as desilication, is distinctively different from that of steam (pathway B). Sodium is responsible for zeolite collapse

Fig. 11. Pathways for Y zeolite destruction.

by reacting with steam to form NaOH. The formation of NaOH is necessary for the destruction of Y zeolite when the pathway involves the attack of OH⁻ on a Si–O bond. For RE-containing zeolites, the destabilization is mainly ascribed to the disappearance of La–O–La stabilizing bridges in sodalite cages.

4. Conclusions

Contamination with vanadium or sodium did not severely affect the crystallinity of USY zeolite in dry oxidizing conditions. Vanadium or sodium reduced the crystallinity in the zeolite by steam, which was supported by the observed reduction in destruction in a dried sample compared with that of freshly prepared sample. Steam was a necessary reactant for zeolite destruction, and vanadium and sodium affected the performance of the catalysts. The solid-state kinetics showed that zeolite Y was destroyed by framework dealumination and desilicization. These materials increased zeolite destruction synergistically. Vanadium destroyed zeolite Y by acid hydrolysis through forming H₃VO₄ at high temperatures in the presence of water, which elevated the hydrogen ion concentration and the rate of hydrolysis. During framework desilicization, sodium reacted with steam to form NaOH, which was responsible for zeolite hydrothermal instability. Basic OH⁻ attacks the framework Si–O bonds. The activation energies suggested that sodium could not destroy Y as easily as vanadium did, but the overall first-order rate constant was higher because the sodium level exceeded that of vanadium. As a result, sodium actually led to more severe Y destruction. The formation of NaOH was an energetically unflavored step. V facilitated the removal of Na⁺ from a zeolite exchange site via an acid-base reaction, and the Na–V compound was more easily hydrolyzed to NaOH. Thus, sodium and vanadium exerted a

synergistic effect on the framework destruction. Rare earth elements reduced hydrolysis and stabilized the structure of the zeolites, but combining vanadium with lanthanum may cause rare earth migration, resulting in the disappearance of La–O–La stabilizing bridges in sodalite cages, again destabilizing of the zeolite. Coexistence of the three pathways for La–Na–USY destruction may exert more serious effects on zeolite stability in the absence of steam.

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Graphical Abstract

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Zeolite Y destruction investigated by a kinetics study and analysis, which shows the pathways for Y zeolite destruction are dealumination, desilicization and the disappearance of La–O bonds.

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Y型分子筛结构破坏的动力学分析

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摘要: Y型分子筛是催化裂化(FCC)的速率控制组分。FCC过程中, 催化剂在反应器和再生器中往往面临高温水蒸气存在的苛刻环境。因此, 分子筛的热稳定性和水热稳定性是催化剂最为关注的性能之一。由于FCC原料中通常含有V、Ni、Na、Fe等不同数量的金属污染物, 会对催化剂造成污染及钝化。进料中存在的吡啶类有机复合物持续不断的沉积在催化剂表面, 由于含钒的有机金属吡啶化合物在反应中转化形成 V_2O_5 , V_2O_5 在水热条件下形成 H_3VO_4 组分, 在高温水热气氛下加速分子筛骨架结构水解, 破坏了Y型分子筛的晶体结构, 从而降低了催化剂活性, 影响产品选择性。稀土Y型分子筛在FCC中扮演重要的角色, 稀土交换分子筛可以提高催化酸性、裂化活性和热与水热稳定性。此外, Na在高温水蒸气条件下也会对分子筛结构造成破坏。一方面, 钠能够中和Y型分子筛B酸中心, 降低催化裂化活性; 另一方面, 水热条件下钠的存在会加速破坏Y型分子筛的结构。

有关Y型分子筛结构破坏的机理解释较多, 然而该过程的动力学研究鲜有报道。反应动力学不能提供一个直接的反应机理, 但是任何反应机理的提出必须符合反应动力学的数据。本文采用离子交换法分别制备了一系列不同Na含量USY, 不同稀土含量USY, 以及含钠和稀土的USY分子筛, 通过固相动力学模型考察了上述Y型分子筛水热结构破坏活化能的变化及钒对其活化能的影响。结果表明, Y型分子筛的结构破坏存在三种路径, 分别是脱铝、脱硅和La-O键的断裂。钒加速了分子筛骨架水解速率; 钒钠具有协同作用, 同时存在时对分子筛破坏作用更加显著; NaOH的形成是速率控制步骤; 稀土稳定了分子筛的结构, 降低了分子筛的水热脱铝速率; 钒与定位于分子筛小笼里稀土作用, 破坏分子筛的 $[RE-OH-RE]^{5+}$ 的RE-O键夺取分子筛的骨架氧, 导致骨架结构崩塌。由于稀土本身稳定了分子筛的结构, 同时钒稀土作用时形成稳定的 $REVO_4$ 固定了钒的流动性, 因此钒对REY结构的影响是几种因素相互叠加和抵消的结果。

关键词: Y型分子筛; 钒; 钠; 稀土; 水热稳定性; 结构破坏; 表观活化能

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