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Irreversible deactivation of hollow TS-1 zeolite caused by the formation of acidic amorphous $TiO_2–SiO_2$ nanoparticles in a commercial cyclohexanone ammoximation process

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ABSTRACT

Commercial deactivated HTS zeolite has been investigated by multiple characterization methods and catalytic evaluations. These indicate that structural and textural properties are not mainly ascribed to the irreversible deactivation, but some framework Ti species are transformed into Ti-rich nanoparticles. Both Brønsted and Lewis acid sites are observed in deactivated HTS zeolite, which agrees well with the spectroscopic characterization results and Tanabe's acidity theory on mixed binary oxides. Hence the acidic Ti-rich aggregates are attributed to the amorphous $TiO_2–SiO_2$ nanoparticles located on the external surface of the zeolite. Furthermore, it is demonstrated that the catalytic performance of deactivated HTS zeolite in phenol hydroxylation is seriously dependent on its acidity properties, which can accelerate the decomposition of H_2O_2. As a consequence, we conclude that the irreversible deactivation of HTS zeolite in the ammoximation process is caused by the formation of acidic amorphous $TiO_2–SiO_2$ nanoparticles catalyzing the fast H_2O_2 decomposition reaction.

1. Introduction

The cyclohexanone ammoximation reaction is of great importance in the organic chemical industry, especially for the commercial manufacture of ε-caprolactam and nylon-6 via a Beckmann rearrangement process [1–6]. Traditional cyclohexanone oxime production lines in the hydroxylamine phosphate (HPO) or hydroxylamine sulfate (HSO) routes, which usually need several steps to produce hydroxylamine, use hazardous reagents and solvents and generate large amount of side-products and pollutants [7–12]. In 1987, a new one-step liquid phase ammoximation process was developed by EniChem, which was directly catalyzed by TS-1 zeolite, with ammonia and hydrogen peroxide solutions as reactants. The TS-1 zeolite is of MFI topological structure, with tetrahedral Ti species incorporated into the framework of Silicalite-1. It is well noted that only tetrahedral framework Ti species act as active sites for selective organic oxidation reactions. Since TS-1 zeolite was first synthesized by Taramasso and his co-workers in 1983, it has been widely employed in various catalytic oxidation reactions, such as phenol hydroxylation, cyclohexanone ammoximation, cyclohexane oxidation, propylene epoxidation, and ammonia oxidation to hydroxylamine [13–17]. The high catalytic performance of TS-1 zeolite is attributed to the adsorption and activation of H_2O_2 molecules via the acceptor–donor relationship of lone electron pairs between the H_2O_2 molecules and framework Ti species. Based on successful laboratory research, the first 12 kilo tons/year cyclohexanone ammoximation installation was established in 1994 at Porto Margherita, Italy [18–21]. Compared with the traditional routes, the one-step process has evident advantages: no use of dangerous reagents and no formation of ammonium sulfate and/or other by-products. Therefore, this process has attracted keen attention from both academic and industrial sectors.

Unfortunately, it was difficult to repeat the high catalytic activity of TS-1 zeolite in different batches, due to the mismatch of dehydration condensation and nucleation rates between Ti and Si precursors under hydrothermal conditions. To update the catalytic performance and stability of TS-1, the hollow titanium silicalite (HTS) zeolite was synthesized by M. Lin at SINOPEC via a "dissolution–recrystallization" treatment in the presence of organic templates under hydrothermal conditions [22–25]. Significantly, HTS zeolite has abundant mesopore volume and high framework Ti species content, which favor increasing the mass transfer of both

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reactant and product molecules inside zeolite crystal. Thus HTS zeolite shows much higher catalytic activity and stability than TS-1 zeolite in many oxidation reactions. Since 2000, it has been commercialized on the industrial scale and employed as a catalyst in the 140 kt/a industrial cyclohexanone ammoximation unit in SINOPEC's Baling branch, China. This approach has successfully replaced the traditional DSM's HPO route for cyclohexanone oxime production, with relatively low capital and operational costs and few by-products [26,27]. Nevertheless, there are still two main obstacles to this one-step ammoximation process: One is the high cost and energy consumption for HTS zeolite manufacture, involving expensive raw materials and a long production period; the other relates to the deactivation of HTS zeolite. Except for the ammonia reagent, these alkaline N-containing intermediates (such as imine, hydroxylamine, and their derivatives) can catalyze the cleavage of T–O–T bonds (T stands for Si or Ti) in a zeolite framework, reducing the catalytic activity of HTS in the ammoximation process [28–30]. Petrini et al. judged that the deactivation of TS-1 zeolite in the ammoximation process was attributable to three main aspects: (i) gradual dissolution of the framework Si atoms into the reaction medium; (ii) migration of framework Ti atoms to extra-framework positions; and (iii) organic by-products filling the micropores of TS-1 zeolite [31–33]. Differently from the first two aspects, organic substrates filling pores can be eliminated by calcination in air at 550 °C for several hours. However, the deactivation caused by the transformation of framework atoms cannot be resolved by calcination regeneration it is referred to here as irreversible deactivation. In a real industrial process, to keep a high cyclohexanone transformation rate, part of the irreversibly deactivated HTS zeolite needs to be replaced with fresh HTS zeolite. But when the deactivated HTS is regenerated by calcination more than times, its catalytic activity is too poor to meet the requirements of the ammoximation process. Hence, improvement of the utilization efficiency of HTS zeolite is an ideal path to benefit the green production of oxime in industry. Up to now, the detailed irreversible deactivated HTS zeolite from the commercial ammoximation process has not been well realized, and efficient regeneration methods are rarely proposed.

Here, the irreversibly deactivated HTS zeolite from the commercial ammoximation unit has been investigated by combining characterization methods and catalytic tests, i.e., phenol hydroxylation and H_2O_2 decomposition. First, both the structural parameters and the chemical status of Ti species in deactivated and fresh HTS zeolites have been characterized by multiple methods, such as XRD, BET, TEM, and UV–vis. Then, the catalytic results in phenol hydroxylation and H_2O_2 decomposition reactions are associated with their characteristics. Finally, we propose one possible irreversible deactivation mechanism in the ammoximation process, according to the correlation between catalytic performance and number of acid sites. Above all, this study provides a good viewpoint on improving the utilization efficiency and exploiting the regeneration of deactivated HTS zeolite in commercial ammoximation process.

2. Experimental

2.1. The origination of fresh and deactivated HTS zeolites

Fresh HTS zeolite was hydrothermally synthesized following the published method [18], using tetrapropylammonium hydroxide solution (TPAOH) as template, tetraethyl orthosilicate as silicon source, and tetrabutyl orthotitanate (TBOT) as titanium source. The molar composition of the starting mixture was TEOS:TPAOH:TBOT:H_2O = 1:0.36:0.04:45. This mixture was heated at 70 °C with stirring for 6 h to let the alcohol vapor escape from the liquid phase. After that, the homogeneous mixture was heated at 160 °C for 3 days in a static autoclave to obtain the conventional TS-1 zeolite. The crystalline TS-1 zeolite was filtered, dried at 110 °C, and calcined at 550 °C for 3 h. In the second step, the calcined TS-1 zeolite was mixed with aqueous TPAOH solution with a molar ratio of TS-1 (accounted as pure SiO_2):TPAOH:H_2O = 1:0.18:45. Then this mixture was sealed in a Teflon autoclave and heated at 160 °C for 3 days under autogenous pressure under static conditions. After the postsynthesis and calcination treatment, fresh HTS zeolite was obtained.

The deactivated HTS zeolite was sampled from Baling Petrochemical Branch, SINOPEC, China. This material had been cyclically used five times in the cyclohexanone ammoximation and calcination regeneration processes. To remove the organic subtracts inside the zeolite channel, the deactivated HTS zeolite was calcined at 550 °C for 3 h in air.

2.2. Characterization methods

PXRD was performed on a PANalytical powder diffractometer equipped with CuKα radiation, $\lambda = 1.54178$ Å, under the following conditions: beam voltage 40 kV, dwell time 500 s, and 2θ range 5–80°. The unit cell parameters of both fresh and deactivated HTS zeolites were calculated by the whole-pattern refinement Rietveld method. The N_2 physisorption isotherms were measured on a Micromeritics AS-6B apparatus, using conventional BET and BJH methods to quantify the amounts of surface areas and the pore volumes of zeolite samples. Prior to analyses, the zeolites were calcined to a constant weight under vacuum (10^{-1} Pa) at 300 °C for 6 h. Transmission electron microscope (TEM) images were taken on a JEM-2100 microscope. STEM images and energy-dispersive X-ray (EDX) spectroscopies of the Ti-containing zeolites were detected by a high-angle annular darkfield (HAADF) detector and an EDAX spectrometer on a Tecnai F20 G2 S-Twin microscope. X-ray photoelectron spectroscopy was used to distinguish the surface Ti species with a PHI model 590 spectrometer, with an AlKα radiation source. The UV–vis spectra were collected by a Cary 300 Agilent, with wavelength from 200 to 800 nm.

X-ray fluorescence (XRF) spectroscopy was employed to confirm the composition of zeolites, using ZSX Primus 3271 equipment. The pyridine-adsorbed IR characterization was carried out in the BIO-RAD FTS 3000 infrared spectrum, in the wavenumber region from 1400 to 1700 cm^{-1}. Ammonia temperature-programmed desorption (NH_3 TPD) was performed on AutoChem II 2920 equipment.

2.3. Catalytic tests

Liquid-phase phenol hydroxylation was selected as a probe reaction to detect the catalytic performance of fresh and deactivated HTS zeolites. The reaction was carried out in 100 mL three-neck flask reactors, with stirring and heating at the same time. Some catalyst, 0.133 mol phenol, and 10 mL acetone were mixed homogeneously in a flask reactor. Then this mixture was heated and continuously stirred through a magnetic stirrer. When the temperature was up to 80 °C, 0.44 mol 30 wt.% H_2O_2 aqueous solutions were added into the flask reactors. After reaction for 2 h, the liquid-phase products were detected by Agilent 6890A gas-chromatography (GC) equipment, with an HP-5 column (30 m × 0.25 mm × 0.25 μm) and an FID detector.

The H_2O_2 decomposition reaction was also carried out in the 100 mL round-bottom glass flask; 10 mL aqueous 30 wt.% H_2O_2 aqueous solution was injected into the flask and heated to 90 °C, with stirring at 400 rpm. A quantity of 0.5 g catalyst was added into the H_2O_2 aqueous solution, and the concentration of H_2O_2 solution was analyzed every 5 min by FT-IR spectroscopy, due to