

EFFECT OF VANADIUM POISONING AND VANADIUM PASSIVATION ON THE STRUCTURE AND PROPERTIES OF REHY ZEOLITE AND FCC CATALYST

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INTRODUCTION

The effects of vanadium and nickel contaminants on the performance of cracking catalysts are well known [1,2]. These metals are deposited continuously on the catalyst during the cracking reaction and promote dehydrogenation reactions, which result in an increased formation of coke and light gases. Vanadium has an additional effect of reducing catalyst activity and selectivity by destroying zeolite crystallinity. Antimony passivation is widely practiced to control the effect of nickel poisoning [3], while vanadium poisoning is more difficult problem. Although much work has been done in the field, the exact mechanisms of the interaction of vanadium and zeolite and of the passivator for vanadium tolerance are still a matter of controversy [2,4-5]. However, application of a vanadium passivator in commercial FCC units also verified that a vanadium passivator can reduce the effect of the activity and the dehydrogenation by 30-50% and 65%, respectively [6].

Until recently, the vanadium passivation processes discussed extensively in the literature [7-9] involved addition onto the FCC catalyst of many different passivators, including rare earth metal oxides and alkali-earth metal oxides. These vanadium passivators can react with vanadium acid or V_2O_5 , forming stable high melting compounds in the FCCU regenerator, so that vanadium poisoning is reduced and the crystal structure of zeolite is well protected.

In this paper, the mechanism of vanadium poisoning and vanadium passivation is proposed. The crystal structure of zeolite and its activity were well correlated with cracking activity.

EXPERIMENTAL

Catalyst Preparation and Evaluation

The RHZ-300 type cracking catalyst used in this work is a commercial heavy oil FCC catalyst composed of more than 30% REHY zeolite imbedded in 65-70% SiO_2 - Al_2O_3 -Kaolin matrix. The RHZ-300 catalyst and REHY (rare earth HY) zeolite were supplied by the Catalyst Factory of Qilu Petrochemical Company, Zibo, Shandong, China.

The vanadium poisoning of cracking catalyst procedure is used to impregnate RHZ-300 catalysts to the desired vanadium level with ammonium metavanadate solutions of different concentrations. The RHZ-300 catalysts contained 6000 ppm vanadium were then impregnated respectively with an acetate (such as lanthanum, magnesium, calcium, and so on) at various mole ratios of the passivator metal element to vanadium. After drying for 24 h at 120°C and calcination at 550°C for 4 h in air, the metal-loaded catalysts were aged at 760°C for 6h in 100% steam. The catalysts without vanadium passivators experienced the same procedure.

The catalyst's cracking activity was evaluated by a MAT test similar to one described by the RIPP-92-90 procedure [10] of The Research Institute of Petroleum Processing, China. The conditions of the MAT testing were 460°C for 70 s, catalyst-to-oil ratio = 3.2, WHSV (h-1) = 16,

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5.0 g catalyst, and the feedstock was a 1.56 g Dagang straight-run light diesel oil boiling range 230-350°C. The compositions of the products were analyzed using SQ-206 gas chromatography.

Catalyst Characterization

The relative crystallinity of the zeolite in the catalyst was obtained from the peak intensities of (533) plane of Y zeolite by XRD method with a Rigaku D/max IIIA X-ray diffractometer using Cu K α radiation. The surface acid sites were characterized by NH₃-TPD-TG technique with a CAHN-200 thermal balance in the presence of a nitrogen atmosphere. The heating rate was 8°C/min. Analysis of the BET surface area and pore volume was measured by liquid nitrogen adsorption static state capacity method with an ASAP 2010 Multifunction Physisorption Instrument. Coke deposition on the catalyst was carried out in a micro fixed-bed reactor.

RESULTS AND DISCUSSION

The Effect of Vanadium Poisoning on the Cracking Activity and the Coke Formation of the RHZ-300.

The different effects of vanadium on the RHZ-300 cracking activity and coke formation are illustrated in Table 1. As shown in Table 1, microactivity monotonically decreased and the coke formation increased gradually with vanadium levels deposited on the catalyst. Little effect of MAT was observed up to 4000 ppm as vanadium, but above that amount, the activity decreased markedly with vanadium. Particularly, the coke formation on the catalyst was high when the deposition of vanadium reached 6000 ppm, a result consistent with the findings in the literature⁽¹¹⁾. It is well known that the deposited vanadium reduces catalyst activity and selectivity and has catalytic activity towards dehydrogenation after aging at hydrothermal conditions, so that the dehydrogenation increases with vanadium levels, leading to an increase in the coke formation and a decrease in selectivity.

TABLE 1. Microactivity and coke formation vs vanadium deposition on the catalyst.

V/ $\times 10^3$ ppm	0	2	4	6	8	10
MAT/wt%	80.40	76.12	72.01	54.32	51.47	31.53
Coke yield/wt%	0.54	0.61	0.72	0.96	1.35	1.72

Vanadium Passivator Study

The effectiveness of one and two active constituent passivators prepared by loading on RHZ-300 individuality and mixture of rare earth oxides and alkali-earth oxides is shown in Table 2. As shown in Table 2, all active constituents are effective for vanadium passivation. However, vanadium passivation of performance of any one and two active constituent passivators was inferior to that of the pure lanthanum type. The vanadium passivator with a rare earth as the active constituent has an advantage over others in microactivity of RHZ-300, but the vanadium passivator with alkali-earth oxides as the active constituent greatly decreased the coke yields of RHZ-300. The phenomenon is primarily that the rare earth is weaker than alkali-earth oxide in neutralizing strong acidic sites of the catalyst, but greatly improves vanadium tolerance, whereas alkali-earth oxides easily neutralize excessively acidic sites, including weak acid sites and middle strong acid sites, owing to having strong basicity, leading to difference in activity and selectivity of RHZ-300.

TABLE 2 Vanadium passivation performance of the active constituents of passivators

Samples	Blank	La	Mg	Ca	La-Mg	La-Ca	La-Ce	La-Sr
MAT/wt%	54.32	72.88	67.34	64.46	69.87	67.56	71.74	67.76
Coke yield/wt%	0.96	0.75	0.53	0.56	0.65	0.67	0.73	0.69

The Effect of Vanadium Poisoning and Introduction of Passivator on the Structure and Microactivity of RHZ-300

It is shown in Table 3 that after poisoning of the RHZ-300 catalyst by vanadium, the crystallinity of the REHY zeolite in the catalyst decreased from 10.5 % to 4.7%, a 55.2% reduction. Similarly, the BET surface area and pore volume of catalyst decreased respectively 55.3% and 7.8 %. This could indicate that the crystal structure of REHY zeolite in RHZ-300 was severely destroyed. Zeolite is often the cracking activity center of an FCC catalyst, and the activity drop could certainly be due to the destruction of zeolite structure. The reaction data from the MAT cracking testing (Table 3) verified that the microactivity of catalysts decreased from 80.4% to 54.32 %, while the coke formation increased from 0.80% to 0.96 %, as compared before and after poisoning with vanadium. These results agree with the conclusion made by Occeili et al.^[2]. The addition of passivator could prevent vanadium from poisoning the activity and selectivity of a FCC catalyst, so that the physicochemical and catalytic properties of RHZ-300 improved markedly, and the crystal structure of zeolite was recovered partially.

TABLE 3. Crystal Structure and Activity of Three Samples as Measured by Surface Area (BET), Pore Volume, XRD, Coke Formation, and Microactivity after Calcination at 550°C and Hydrothermal Treatment at 760°C

Sample	RHZ-300	RHZ-300+V	RHZ-300+V+Passivator
MAT/wt%	80.4	54.32	75.60
Coke yield/wt%	0.80	0.96	0.65
BET S.A /m ² .g ⁻¹	135.7	60.6	130.9
Pore volume/cm ³ .g ⁻¹	0.192	0.177	0.182
Crystallinity/%	9.7	4.7	7.2

Effect of Vanadium Poisoning and Introduction of Passivator on the Acidity of and Catalyst

Amounts of desorbed NH₃ were determined with the NH₃-TPD-TD method. The data of Table 4 show that total acidity of catalyst decreased from 2.21 to 1.08 after vanadium poisoning, indicating that over 50% of acid sites were destroyed. The distribution of acid intensity also indicated that acid sites destroyed were primarily weak acid sites and middle strong acid sites, over 65% of acid sites were destroyed whereas the middle strong acid sites have middle intensity adsorption, offer primary acid sites of catalytic activity. Cracking catalytic activity decreased greatly with the amounts of middle strong acid sites. In contrast, the amounts of strong acid sites increased from 0.37 to 0.45, so that the selectivity to coke formation could have an adverse effect (Table 4), since the coke is formed on the strong acid sites by polymerization of the unsaturated hydrocarbon molecules. The introduction of passivator (La₂O₃) can protect some of the acid sites leading to an increase in the number of acid sites of catalyst.

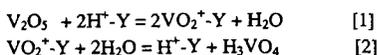
TABLE 4: Effect of Introduction of Vanadium and Passivator on Acidity of FCC Catalyst after Calcination at 550°C and Hydrothermal Treatment at 760°C

Sample	Acid sites (Desorbed NH ₃ Amounts / mmol.g ⁻¹ Cat.)			
	Weak acid sites	Middle strong acid sites	Strong acid sites	Total acid sites
RHZ-300	1.29	0.55	0.37	2.21
RHZ-300+V	0.45	0.18	0.45	1.08
RHZ-300+V+La ₂ O ₃	0.94	0.55	0.38	1.87

Mechanism of Vanadium Poisoning and Passivation

In order to investigate interaction of zeolite and vanadium, steam-aging (at 760°C) experiments of REHY zeolite (with and without vanadium) were carried out in a flowing tube reactor. Fig. 1a shows the XRD pattern of REHY zeolite without vanadium; the crystal structure of zeolite is

completely retained without loss of crystallinity. Fig. 1c shows XRD pattern of the 2% vanadium-loading REHY zeolite. As evidenced by Fig. 1c, the zeolite completely loses crystallinity after vanadium poisoning, as the zeolite structure collapses with the formation of mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), silica (tridymite) and rare earth vanadate (CeVO_4). The X-ray diffractograms for RHZ-300 catalysts with vanadium in the presence of steam at 760°C for 6 h are shown in Fig. 2a. It is very similar to the vanadium-loading REHY zeolite structure collapse with the formation of mullite. The above results and literature ^[2] suggest that the vanadium first deposits on the outside of the zeolite and catalyst particles, then migrates to pores, channels, or cages of the zeolite and catalyst and reaches acid sites during steaming at high temperature, where besides neutralized acid sites vanadium is trapped as cationic VO_2^+ species poisoning the catalyst according to the following reactions:



Vanadic acid is a strong acid, $\text{P}_K = 0.05$ ^[20]. It behaves as a catalyst in the hydrolysis of the framework Al-O and Si-O tetrahedra and contributes to the accelerated destruction of the zeolites, causing zeolite de-alumination and lattice collapse with total loss of catalytic activity. The amorphous product recrystallizes then into mullite and the excess silica forms tridymite (Figs. 1c, 2a, 2b).

In REHY crystals it is believed that Ce^{4+} ions, present as an oxycerium complex, is preferentially loaded near the supercages, where it can more readily react with the stable oxyvanadyl cations (VO_2^+ or VO^{2+}) and form CeVO_4 (Fig. 4c).

The deleterious effects of vanadium deposits on zeolite-containing FCC can be greatly reduced by addition of certain materials (vanadium passivators) capable of minimizing V-FCC interactions by selectively (and irreversibly) sorbing migrating vanadium compounds such as H_3VO_4 (Figs. 1b, 2b). Since vanadic acid is not consumed as a catalyst in the hydrolysis reaction of framework. When a basic species exists in this system, it will compete with the zeolite for vanadic acid to form stable orthovanadates. The rare earth oxides such as La_2O_3 and alkali-earth metal such as MgO have basicity and react with vanadic acid to form orthovanadates, which are stable even at the highest temperatures reached in the regenerator unit.

Fig. 3 shows DTA thermograms of La_2O_3 , V_2O_5 , and the mixture of La_2O_3 and V_2O_5 . There is a strong endothermic peak at 668°C in Fig. 3b, indicating the melting of V_2O_5 . The strong exothermic peak at 670°C in Fig. 3c is probably an indication that a new compound is formed from the reaction of La_2O_3 and V_2O_5 as the melting point of V_2O_5 was reached. The XRD pattern (Fig. 4) verified the above observation that LaVO_4 indeed formed via the reaction, exhibiting the vanadium passivation by La_2O_3 .

The DTA thermograms of MgO and V_2O_5 are shown Fig. 5, which were similar to Fig. 3. A strong exothermic reaction between MgO and V_2O_5 occurred at 670°C , and the reaction product characterized by XRD was MgV_2O_6 and $\text{Mg}_2\text{V}_2\text{O}_7$ (Fig. 6).

CONCLUSIONS

This study shows that when vanadium is deposited on a REHY zeolite and a RHZ-300 catalyst, the surface area, pore volume, crystallinity, acidity, and cracking activity of the vanadium-loading catalyst decrease with vanadium levels after aging at hydrothermal condition. In addition, vanadium forms a volatile vanadic acid during steaming at high temperature, which then catalyzes the hydrolysis of the framework Al-O and Si-O tetrahedra causing the collapse of the zeolite structure with the formation of mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), silica (tridymite) and rare earth vanadate (CeVO_4). The activity and acidity of catalyst is completely lost at the same time. In contrast, the deleterious effects of vanadium deposits on zeolite-containing FCC catalyst can be greatly reduced by addition of certain vanadium passivators. The rare earth oxides and alkali-earth metal oxides are efficient passivators because they trap vanadium in form of vanadates, which are stable high melting compounds. Vanadium passivation reduces the

hydrolysis of zeolite framework, preserves the crystal structure of zeolites and acidity of FCC catalysts, and enhances the activity and selectivity of FCC catalyst. The optimum La/V mole ratio among the vanadium and La impregnated catalysts (0.75) was obtained at the highest microactivity (72.88 wt%).

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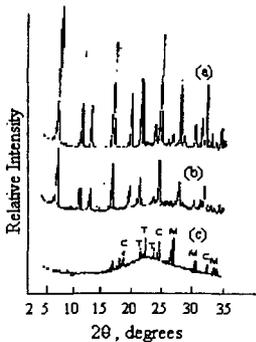


Fig. 1 X-ray diffractograms of REHY crystals steam-aged: (a) REHY, (b) REHY + 2% V + Passivator, (c) REHY + 2% V M-Mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), T-Silica (tridymite) C-Cerium vanadate (CeVO_4)

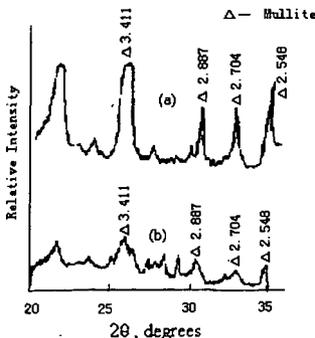


Fig. 2 X-ray diffractograms of catalysts with or without V-passivator: (a) no passivator, (b) passivator added

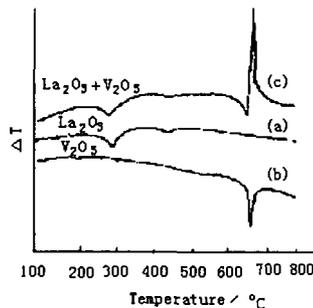


Fig. 3 DTA thermograms of La_2O_3 , V_2O_5 and mixture of $\text{La}_2\text{O}_3 + \text{V}_2\text{O}_5 = 1$ (mole ratio)

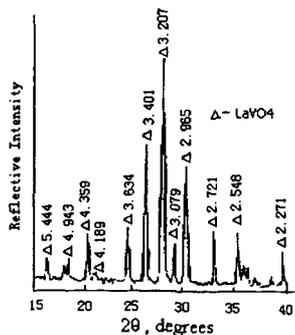


Fig. 4 X-ray diffractogram of the reaction product of La_2O_3 with V_2O_5

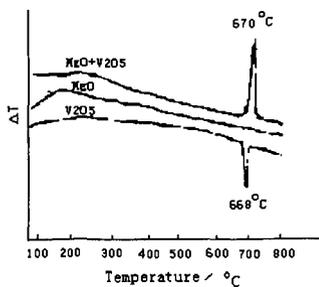


Fig. 5 DAT thermograms of MgO, V₂O₅ and mixture of MgO/V₂O₅ = 1 (mole ratio)

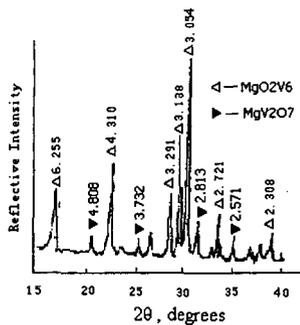


Fig. 6 X-ray diffractogram of the reaction product of MgO with V₂O₅