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Effects of vanadium oxidation number on desulfurization performance of FCC catalyst

Jun Long, Yuxia Zhu, Yujian Liu*, Zhijian Da, Han Zhou

Research Institute of Petroleum Processing, SINOPEC, P.O. Box 914-14, Beijing 100083, China

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Abstract

Effects of vanadium on the desulfurization performance of FCC catalysts were investigated with vanadium having different oxidation numbers (abbr. *Oxnum*). Molecular modeling studies showed that vanadium with low *Oxnum* could affect the chemical conversion of sulfur compounds. However, the vanadium deposited on equilibrium catalyst was in high *Oxnum* because of the oxidation in regenerator, so an activation method to reduce vanadium *Oxnum* named *selective activation* was introduced. It was proved with electron paramagnetic resonance (EPR) and temperature-programmed reduction (TPR) that vanadium *Oxnum* decreased when the catalyst was activated. The molecular modeling studies are well consistent with the lab evaluation results. The desulfurization performances of activated equilibrium catalysts were better than that of the unactivated catalysts. Similar results were observed with the lab vanadium-contaminated catalyst. The desulfurization performance of the catalyst was optimized when vanadium *Oxnum* was close to 2 (VO).

Keywords: FCC catalyst; Desulfurization; Gasoline sulfur; Metal deposit; Oxidation number; Vanadium; Selective activation

1. Introduction

In the 21st century, more stringent environmental legislation has stiffened requirements on reducing automotive exhaust emissions, which have challenged petroleum refineries in the clean fuel production [1]. Recently gasoline sulfur has become under further scrutiny because of the upgrading of cleaner fuel regulations [2]. In China, sulfur in the FCC (fluid catalytic cracking) gasoline is the prime contributor to the gasoline sulfur, the key in reducing gasoline sulfur is to reduce sulfur content in FCC gasoline.

Among the existing desulfurization solutions, FCC desulfurization has greater significance in economical applications, desulfurization catalyst and additive are the core of FCC desulfurization [3–5]. However, during the application of desulfurization additive, it was found that the gasoline sulfur content decreased to a certain level when the base catalyst was deposited with a little vanadium, so the additive cannot exhibit any further effect on desulfurization, and the gasoline sulfur decreased as the vanadium content increased [6]. But until now, the results of study on this subject is far from clarity.

Thus, our research is interested in the effect of vanadium on FCC desulfurization. Since all of the catalysts mentioned above had been regenerated, vanadium in catalyst was usually regarded as V_2O_5. Thus it seems that V_2O_5 should be the cause of gasoline sulfur reduction. However, Liu et al. investigated the interaction between sulfur compounds and metal oxides with quantum molecular modelling [7]. The study showed that the chemisorption between V_2O_5 and sulfur compounds was very weak. The sequence of such metal oxide is as follows as the chemisorption intensity to thiophene.

$$\mathrm{VO} \gg \mathrm{ZnO} \approx \mathrm{Zn\_Al\_Spinel} > \mathrm{NiO} > \mathrm{V_2O_5}$$

This sequence showed that vanadium with lower oxidation number (such as VO) has stronger chemisorption ability to thiophene than V_2O_5. This interaction makes thiophene molecule (especially substituted thiophene) distorted in an activated state. Further molecule modeling studies indicated that VO is able to reduce the activation energy of thiophene

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* Corresponding author. Tel.: +86 106 232 755 13420; fax: +86 106 231 1290..

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conversion, but vanadium with higher oxidation number (abbr. *Oxnum*) such as V_2O_5 lacks such function. Based on these results, we began to focus on the relationship of vanadium *Oxnum* and sulfur and predicted that vanadium with lower *Oxnum* in catalyst could have some effect on the conversion of feed sulfur.

The first step to verifying is to prepare catalysts with vanadium of various *Oxnum*. A method named *selective activation* is introduced in this paper to lower vanadium *Oxnum*. A series of activated samples of equilibrium catalyst (E-cat) and V-contaminated aged catalysts were prepared. Vanadium *Oxnum* was then characterized with electron paramagnetic resonance (EPR) and temperature-programmed reduction (TPR). The desulfurization performance of the catalysts and their activated samples were evaluated with MAT units and ACE (advanced cracking evaluation) unit.

2. Experimental

2.1. Materials

Vanadium and nickel naphthenates, commercial FCC catalysts and E-cat were obtained from Qilu Petrochemical Company, Sinopec. Physical and chemical properties of E-cat are listed in Table 1, properties of aged catalyst C_B and its metal-contaminated sample are listed in Table 2. Copper oxide was obtained from Thermo Quest Ltd., Italy.

2.2. Selective activation, a method to lower vanadium Oxnum

Several E-cat and V-contaminated catalysts were selected for testing. These catalysts were modified by a patented method [8], which can effectively reduce vanadium *Oxnum* of the V-deposited catalyst. The method is named selective activation in this paper.

2.3. Characterization of vanadium Oxnum in FCC catalyst

EPR characterization was carried out using the Brucker ESR 300E spectrometer in X-band operating with a microwave frequency of 9.75 GHz (sweep width 6000 G). The modulation frequency is 100 kHz, the centre field is 3500 G. The metal with different *Oxnum* can be characterized with the variation paramagnetism.

TPR spectra were recorded with TPD/R/O 1100 of Carlo Erba Instrument. A mixture of 5% H_2 in N_2 was used as analysis gas with a flow rate of 20 ml/min. H_2 concentration was monitored by TCD at the course of TPR. During the TPR experiment, the reactor temperature was ramped linearly from 313 to 1273 K at a rate of 10 K/min and then held for 30 min at 1273 K. The quantitative change of metal *Oxnum* can be measured with the characteristic TPR peak area of each metal component.

2.4. FCC catalyst evaluation

The evaluations of catalysts were in MAT-II of Xytel and ACE-Model unit R^+ of KTI. The operating conditions of them are given in Table 3. The feedstock was a sulfur-contained VGO with the properties given in Table 4.

2.5. Product analysis

The compounds of gas products and the liquid products were analyzed with GC HP5880A and GC HP6890A. The coke amount in catalyst was measured with BF QGS-10. The sulfur content in gasoline was analyzed with GC-AED and GC-PFPD.

Table 1
Physical and chemical properties of E-cat EQ-1 and EQ-2

	V ($\mu g\ g^{-1}$)	Ni ($\mu g\ g^{-1}$)	RE_2O_3 ($\mu g\ g^{-1}$)	Unit cell size (nm)	Surface area ($m^2\ g^{-1}$)	Pore volume ($ml\ g^{-1}$)	MA (%)
EQ-1	8300	2200	2.9	2.433	109	0.289	61
EQ-2	1800	11000	2.8	2.431	117	0.287	62

Table 2
Physical and chemical properties of catalyst C_B and its metal-contaminated sample

	V ($\mu g\ g^{-1}$)	Ni ($\mu g\ g^{-1}$)	RE_2O_3 ($\mu g\ g^{-1}$)	Unit cell size (nm)	Surface area ($m^2\ g^{-1}$)	Pore volume ($ml\ g^{-1}$)	MA (%)
C_B	–	–	1.6	2.426	104	0.275	60
C_B-1	6200	3000	1.6	2.433	102	0.278	61

Table 3
Operating conditions of evaluation units

	Test unit				
	Catalyst amount (g)	Reactor temperature (K)	Injection time (s)	WHSV (h^{-1})	N_2 ($ml\ min^{-1}$)
ACE-R^+	9	797	32	16	120
MAT-II	4	777	32–75	16	110