



Role of nickel on vanadium poisoned FCC catalyst: A study of physiochemical properties

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ABSTRACT

Active sites of Fluid catalytic cracking (FCC) catalyst are poisoned during operation in the FCC reactor due to causes including feedstock contaminant metals deposition. This leads to activity, selectivity and increasing coking problems, thereby raising concern to the refiner. This work investigated effect of nickel coexisting with vanadium in the FCC feedstock on the standard FCC catalyst during cracking process, in which destruction of active sites occurs as a result of the metals deposition. Laboratory simulated equilibrium catalysts (E-cats) were studied by XRD, FTIR spectroscopy, N₂ adsorption, solid state MAS-NMR, SEM and H₂-TPR. Results revealed that vanadium, above a certain concentration in the catalyst, under hydrothermal conditions, is highly detrimental to the catalyst's structure and activity. Conversely, nickel hardly affects the catalyst structure, but its co-presence in the catalyst reduces destructive effects of vanadium. The mechanism of nickel inhibition of vanadium poisoning of the catalyst is discussed.

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1. Introduction

During industrial fluid catalytic cracking (FCC) operation feedstock of various kinds such as vacuum gas oil and atmospheric residue, containing unwanted contaminant metals including vanadium (V), nickel (Ni), iron (Fe), calcium (Ca) and sodium (Na) are employed [1]. As opposed to hydrocarbon molecules which are cracked to useful products on contact with the FCC catalyst, metals tend to deposit on the catalyst gradually poisoning its surface, decreasing its activity and promoting coke formation. Amongst the metals, V and Ni are more dangerous than any others because when they deposit on the catalyst, they interact with the catalyst, change the main reaction pathway and establish parallel reactions such as dehydrogenation, thereby shifting catalyst selectivity. The actions of these metals therefore become a problem to the petroleum refiner relying on the FCC process and hence, implicating refining cost. Vanadium and nickel have been shown to exhibit dissimilar behaviors on contact with the FCC catalyst [2]. For instance, vanadium, in the presence of steam, at high temperature, causes dealumination of framework aluminum, destruction of zeolite crystallinity and collapse of zeolite structure [3–8]. On the contrary, dealumination and/or catalyst framework destruction caused

by Ni is insignificant compared with V, but Ni acts as a catalyst for dehydrogenation reaction, thereby promoting coking and shifting the selectivity away from the desired cracked product(s) [9]. The effects of other metals such as iron and calcium on the FCC catalysts are not too severe like those of vanadium and nickel, but they cause textural dysfunction and contribute to high coking [10].

Despite the number of reports on catalyst deactivation by metals available in the literature [10–19], only very few [20–22] have studied the interaction between V and Ni and all of these studies were focused on pure zeolite as FCC catalyst. The standard FCC catalyst, used in the commercial FCC unit, comprises Y-zeolite, usually REY or USY, dispersed in active matrix (alumina or silica alumina) and clay particles and spray dried to the form of a microsphere (Fig. 1) [23], which can withstand high attrition, with strong resistance against sintering during high temperature catalyst circulation in the FCC regenerator. These support particles may subject the commercial FCC catalyst to different interactions with the contaminant metals. To the best of our knowledge, no report that objectively studies V–Ni interaction on composite catalyst is available in the literature, leaving much to be comprehended. Therefore, detailed studied of V and Ni co-deposited on a standard FCC catalyst are required to deepen understanding of the interaction between these contaminant elements deposited on the catalyst in the commercial FCC unit. In this article, the roles of nickel on vanadium poisoned FCC catalyst are highlighted and the mechanism of interaction is discussed.

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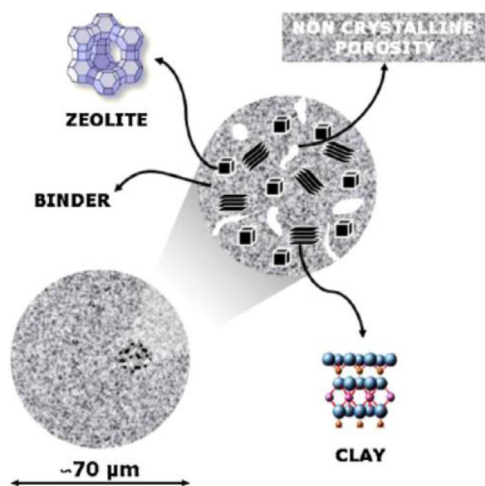


Fig. 1. A typical FCC catalyst particle microspherule [23].

Table 1. Properties of commercial catalyst and feedstock used for this study.

Sample catalyst		Feedstock/MAT conditions	
TSA (m ² /g)	234	Type	Light diesel oil
Pore volume (cm ³ /g)	0.19	Boiling pt range (°C)	230–350
Zeolite UCS (Å)	24.71	Catalyst-to-oil ratio	3.2
Re ₂ O ₃ (%)	5.20	Feed injection time (s)	70
Fe (%)	0.46	WHSV (h ⁻¹)	16
Na ₂ O (%)	0.17	MAT temperature (°C)	480
Al ₂ O ₃ (%)	51.61	Mass of catalyst (g)	1.56
SiO ₂ (%)	24.23		
Ni (ppm)	117		
V (ppm)	203		

2. Experimental

2.1. Materials and samples preparation

All materials including catalyst and metals precursor were supplied by HuiCheng catalyst manufacturing company, Qingdao, China. Vanadium and nickel naphthenates containing 2% and 3% of the metals, respectively, were used as the metals sources. The catalyst produced by the company and containing a REY zeolite contained about 5 wt% rare earth in its formulation. Properties of the catalyst are given in Table 1. Catalyst samples with different contents of vanadium and/or nickel were prepared by incipient wetness impregnation method. The metal naphthenates were deposited on the catalyst by single or co-impregnation according to Mitchell [24]. All metal impregnated samples were oven dried at 110 °C for 12 h, heated in air at 550 °C for 6 h by multi-step calcinations and subsequently steamed at 760 °C for 4 h to simulate equilibrium catalysts (E-cats). Two controlled samples (not impregnated with metals) were also prepared. One sample was only calcined at 550 °C, and the other calcined and further steam-aged at 760 °C for 4 h. In order to evaluate the effect of steam-ageing on the textural properties of the catalysts, samples impregnated with the metals were calcined at 760 °C. NiO was obtained by decomposition of Ni(NO₃)₆H₂O at 500 °C for 4 h [25]. Ni₂V₂O₇ was prepared as reported in the literature [26]. Analytical grade V₂O₅ was purchased from Sinopharm Chemical Reagent Co., Ltd. Feedstock properties and detail Micro Activity Test (MAT) conditions are summarized in Table 1. MAT method described in ASTM-D3907/D3907M-13 was followed in catalyst testing. The liquid product was collected in a receiver immersed in ice bath and subsequently analyzed on a Varian 3800 chromatograph GC (model 2014C). The catalyst activity was determined according to Eq. 1.

$$M(\%) = \frac{w_f - w_u}{w_f} \times 100, \quad (1)$$

$$w_u = w_p \times \%R, \quad (2)$$

where M is the catalyst activity, w_f is the weight of the feed, w_u is the weight of unconverted product, w_p is the weight of the product in the receiver after cracking, and R is the area of chromatography peak with boiling point greater than 216 °C.

2.2. Characterization

Bulk metal (V, Ni, Fe and Na) concentrations in the samples were measured using PAN Analytical Axios X-ray fluorescence (XRF) spectrometer. Textural characterizations including surface area (calculated by BET method) and pore volume (extrapolated from t -plot) were obtained by nitrogen physisorption at 77 K following degassing of the samples for 4 h at 300 °C, using Micromeritics Tristar 3000. Surface morphology was analyzed with SEM instrument (S-4800, Japan HQ) accelerating at 0.5–30 kV at a target of 20 kV. Powder X-ray diffraction patterns were collected on PAN analytical X'pert PROX-ray diffractometer using CuK α radiation generated at 40 kV and 40 mA, at 2θ range from 5° to 50°. Solid state MAS-NMR was measured for ²⁷Al, ²⁹Si and ⁵¹V using a Bruker Advance III-400 MHz spectrometer. ²⁷Al was measured at a frequency of 104 MHz at a spinning rate of 12 kHz using a 4 mm probe head, single pulse length of 6 μ s ($\pi/20^\circ$) with AlK(SO₄)₂·H₂O as standard. ²⁹Si and ⁵¹V MAS-NMR spectra were acquired at 80.4962 MHz and 104.848 MHz, respectively, at the same spinning rate with reference to DSS-(4,4-dimethyl-4-silapentane-1-sulfonic acid) for silicon and 0.16 M NaVO₃ for vanadium. Temperature-programmed reduction (H₂-TPR) technique using a Chem-BET 3000 TPD/TPR analyzer (Quantachrome) was employed to investigate interaction of the metals with each other and with the catalyst. DRIFT-IR studies and acidity characterization were carried out on a 6700 Nicolet FTIR spectrophotometer (Thermo Fisher, USA), equipped with a MCT liquid nitrogen cooled detector and a KBr beam splitter. The spectra of the samples were recorded after 64 scans at 4 cm⁻¹ resolution. Before analysis, all samples were vacuum dried for 1 h to eliminate adsorbed water and gaseous impurities. Samples for acidity studies were adsorbed with pyridine for 24 h and the physisorbed species desorbed by vacuum drying at 150 °C for 2 h prior to analysis.

3. Results and discussion

3.1. Metal analysis

The results of the elemental analysis of the catalysis samples shown in Table 2 reveal that contents of the metals are in close agreement with the amounts impregnated. This was measured in order to check the effect of steam-ageing on the metals introduced.

Table 2. Nominal and actual metal contents in the samples.

Sample	Metal content (mg/kg)			
	V _(nominal)	Ni _(nominal)	V _(actual)	Ni _(actual)
Fresh ST	0	0	207	113
V ₃	3000	0	3649	115
V ₅	5000	0	5378	113
V _{7.5}	7500	0	8033	114
V ₁₀	10,000	0	10,524	201
Ni _{5.4}	0	5400	157	6268
V ₂ Ni _{2.5}	2000	2520	2371	3311
V ₃ Ni _{5.4}	3000	5400	3262	5763
V ₃ Ni _{1.5}	3000	1500	3341	1721
V _{5.3} Ni _{3.9}	5286	3857	5341	3607

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