



The combined effect of sodium and vanadium contamination upon the catalytic performance of USY zeolite in the cracking of *n*-butane: Evidence of path-dependent behavior in Constable–Cremer plots

Luis-Ernesto Sandoval-Díaz^a, José-Manuel Martínez-Gil^a, Carlos Alexander Trujillo^{b,*}

^aGrupo de Investigación Catálisis Heterogénea y Termodinámica, Programa de Química, Facultad de Ciencias Básicas, Universidad del Atlántico Ciudadela km 7 Vía Puerto Colombia, Barranquilla, Colombia

^bLaboratorio de Catálisis Heterogénea, Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Carrera 45 No. 26-85, Bogotá, Colombia

ARTICLE INFO

Article history:

Received 14 May 2012

Revised 9 July 2012

Accepted 10 July 2012

Available online 9 August 2012

Keywords:

USY zeolite

Sodium contamination

Vanadium contamination

n-butane cracking

n-butane dehydrogenation

Apparent activation energy

Isopropylamine decomposition

Fluid catalytic cracking

Constable–Cremer plot

Isokinetic relation

ABSTRACT

NaCl and $[\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2]$ were impregnated on a commercial ultra-stabilized Y zeolite (USY). Samples were calcined in dry air at 700 °C and examined by X-ray diffraction (XRD), N_2 adsorption, isopropylamine decomposition and the *n*-butane cracking reaction. Sodium concentration was kept constant but in excess related to a variable vanadium concentration. Dry thermal treatment in the presence of metal contamination was found to induce framework destruction by sodium but not by vanadium. Vanadium was found to neutralize preferentially the Brønsted acid sites (BASs) responsible for alkane cracking. Selectivity to dehydrogenation increases with vanadium loading due to its intrinsic redox activity. No evidence of a vanadium–sodium compound was found; sodium reacts preferentially with the framework than with vanadium. Arrhenius plots rendered quite linear relations, and isokinetic behavior was established for cracking and dehydrogenation reactions. The findings clearly show that the slopes in Constable–Cremer plots are sensitive to the reaction mechanism.

© 2012 Elsevier Inc. All rights reserved.

1. Introduction

The issues of compensation plots might be a consequence of the mechanistic characteristics of catalyzed reactions [1]. Although there is an ongoing debate about this claim, the idea continues to be attractive because compensation, beyond controversy, seems to be inherent to catalytic systems. The motivation for the present research was to highlight the action of metal contamination in crude oil over fluid catalytic cracking (FCC) catalysts. Toward this objective, some evidences of the mechanistic interpretation of the slope of Constable–Cremer plots were found.

The effects of contamination by transition metals such as vanadium and nickel over the performance of FCC catalysts are well known and have been extensively described in the literature [2–8].

Vanadium reaches the catalyst surface in the riser as part of coordination compounds containing VO^{2+} [6]. Coke is burnt off during the regeneration step, but vanadium is not removed from

the solid. It is oxidized to V(V) in a mobile specie known to migrate from the equilibrium catalyst to the freshly added particles [2,3,7]. Gaseous H_3VO_4 [9] and liquid V_2O_5 [6,10,11] are thought to be the stable forms of vanadium during this stage.

Vanadium is deposited preferentially onto amorphous alumina from the matrix [12], but a significant amount also accumulates over zeolitic components, which have aluminum in both framework (FAI) and non-framework or extra-framework (EFAI) forms. Vanadium–aluminum compounds are sensitive to temperature [13].

The mechanism by which vanadium attacks the FCC catalyst has been proposed to take place either by the neutralization of acid sites [13] or by the destruction of zeolitic components [14–18]. Both effects could be responsible for the negative action of this contaminant upon the performance of the catalysts.

Sodium is another important contaminant. It may come from different sources, including naturally contaminated oil feedstocks, as a remnant from oil extraction due to a faulty desalter, or as a residual material from catalyst preparation. Sodium is known to induce framework destruction [14], and it has been proposed to participate in ionic exchange, reducing the actual amount of Brønsted acid sites [6,15].

* Corresponding author.

E-mail address: catrujillo@unal.edu.co (C.A. Trujillo).

It is well established that vanadium neutralizes the Brønsted acid sites (BASs) which are responsible for cracking and isomerization activity of zeolites [2,3,6,13,16–18]. The negative effects of vanadium are thought to be more pronounced in the presence of sodium [3,16,17]. Hagiwara et al. [17] and Xu et al. [16] proposed that beyond ionic exchange, these contaminants could interact synergistically with steam to yield NaOH, which readily dissolves crystalline components and exerts a marked negative action in both the activity and selectivity of the process.

The objective of this study is to contribute to the elucidation of the combined effects, if any, of these metals upon the performance of Y zeolite. USY was selected because it is the most important constituent of current FCC catalysts. Steam was excluded to simplify the analysis of experimental data. It is perhaps an unrealistic situation compared to actual FCC conditions, but conclusions might, to some extent, be applied to the industrial process.

Activation parameters for the reactions of *n*-butane scission were determined and used to describe the process of catalyst deactivation. The use of compensation phenomena for the overall interpretation of zeolite deactivation by metals has not been previously reported.

2. Experimental part: materials and methods

2.1. Catalyst impregnation with sodium and vanadium

A commercial USY (CBV712 from Zeolyst International) was used for this study. According to the X-ray diffraction (XRD) results shown in Table 1, this sample has 16.6 FAIs per unit cell. We assumed that this zeolite is 100% crystalline and that it has 192 T atoms per unit cell following the expected formula of Y zeolite [19]. These data were used to calculate the amount of sodium (as NaCl) and of vanadium (as $[\text{VO}(\text{C}_5\text{H}_7\text{O}_2)_2]$) to reach the desired contaminant contents per unit cell. As zeolite mass is strongly dependent on atmospheric humidity, samples were kept and weighted in a room with controlled relative humidity of 45%. Mass data were corrected by weight loss determined at 550 °C from TG-DSC analysis, and are provided in Table 1.

A solution of NaCl, in deionized water (0.480 mol L⁻¹), was prepared from pure reagent. 5.00 mL of solution and 20.00 mL of deionized water were added over 5.000 g of parental USY. The suspension was vigorously stirred during 1 h in a rotary evaporator, and the solvent extracted under reduced pressure. The remaining solid was impregnated with the corresponding amount of vanadyl-bisacetylacetonato (of analytical grade from Merck) dissolved in 5 mL of analytical grade methanol. The solution containing the vanadyl complex was transferred quantitatively, washing twice with pure methanol. The sample was stirred a second time for

0.5 h, and the solvent extracted under reduced pressure. The remaining solid was calcined at 700 °C for 5 h in a vertical quartz tube provided with a frit, while a stream of dry air (60 mL_N min⁻¹) was passed through. The heating ramp was 10 K min⁻¹. The calcined sample was allowed to cool down at ambient temperature and was then stored in a vessel covered with cloth located in a room with controlled humidity of 45%. Six samples were prepared with different vanadium loads and constant sodium content (9.6Na atoms per unit cell, or 960Na atoms per 100 unit cells), namely 960Na–XV, where X reads for the number of vanadium atoms nominally loaded per 100 unit cells. Table 1 shows that, in atomic terms, sodium is found in excess as compared to vanadium.

2.2. X-ray characterization

Unit cell sizes (UCSs) were determined for parental and prepared samples by powder XRD collected on a Philips X' Pert Plus using a Cu K α source. Metallic Si was used as an internal reference. Patterns from 5° to 50° 2 θ and 2 s per step were recorded; zeolite powder was pretreated as outlined in ASTM-3942-97. CELREF version 3 was used to calculate UCSs. Crystallinities were determined using the same equipment, as outlined in ASTM D-3906-03. We used parental CBV712 as standard with an arbitrary crystallinity of 100. Framework aluminum atoms (FAI) per unit cell (u.c.) were calculated according to Breck and Flanigen's equation [20].

2.3. Nitrogen adsorption

N₂ adsorption isotherms were measured in an Autosorb 1-C from Quantachrome. Micropore volume was calculated according to the *t*-method using the data where the plot was linear. Average pore sizes were estimated by means of the Saito-Foley algorithm using the equipment's software.

2.4. *n*-Butane catalytic cracking

n-Butane reaction conditions were set according to Ref. [2]. The reaction was run at four different temperatures (typically 550 °C, 530 °C, 505 °C and 485 °C). *n*-Butane research grade (99.9%) from Matheson Gas Products Inc., with no detectable olefin impurities, was used. Nitrogen 5.0 was used as the diluent. 150 mg of catalyst were used per run. A U-shaped quartz tube (4 mm i.d. expanded to 8 mm i.d. at the catalyst bed) was used as a fixed bed reactor. It was provided with a K-type thermocouple (1.6 mm o.d.) placed directly inside the catalytic bed. Catalysts were kept in place by particles of silicon carbide approximately 0.5 mm in diameter (acid washed and precalcined at 1000 °C for 10 h) below and over the zeolite bed. The sample was set initially at 550 °C during 0.5 h at a heating

Table 1
Properties of fresh parental and prepared samples.

Sample ^a	UCS ^b (Å)	Water loss at 550 °C ^c (%w)	Nominal Na content referred to parental zeolite at 550 °C (Na ₂ O%w)	Actual Na content referred to parental zeolite at 550 °C (Na ₂ O%w)	Nominal V content referred to parental zeolite at 550 °C (V ₂ O ₅ %w)	Micropore volume ^d (cm ³ /g)	Average pore size ^d (Å)
Parental CBV712	24.335 = 16.60 FAI/u.c.	14.7	0.000	0.032	0.000	0.228	15.3
960Na–0V	24.324 = 15.40 FAI/u.c.	11.9	1.338	1.340	0.000	0.227	15.9
960Na–33V	24.329	11.7	1.338	1.335	0.265	0.224	15.1
960Na–83V	24.319	11.9	1.338	1.329	0.659	0.226	15.0
960Na–166V	24.322	10.6	1.338	1.336	1.309	0.219	15.1
960Na–249V	24.319	11.1	1.338	1.341	1.947	0.225	15.2
960Na–332V	24.327	11.4	1.338	1.337	2.585	0.222	15.8

^a Nominal content referred to 100 u.c. of parental zeolite.

^b Determined from XRD by use of the Breck and Flanigen equation [20].

^c Measured by TG–DSC after equilibration in a room with 45% of relative humidity.

^d Determined through nitrogen adsorption.

Download English Version:

<https://daneshyari.com/en/article/61384>

Download Persian Version:

<https://daneshyari.com/article/61384>

[Daneshyari.com](https://daneshyari.com)