

# Role of nickel and vanadium over USY and RE-USY coke formation

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## Abstract

The present paper approaches the role of nickel and vanadium oxidation states in the coke formation from cyclohexane model cracking reaction over USY and RE-USY zeolites. The coke yield increased for both zeolites, USY and RE-USY, due to the presence of nickel and/or vanadium contaminant metals. USY loaded with Ni and V presented about the same reducibility of USY loaded distinctly with Ni or V, when steam deactivation is not applied previously. However, coke formation decreased by a factor of 2 for RE-USY or USY loaded with Ni and V when compared to Ni or V loaded distinctly. This factor was affected neither by oxidation/reduction treatments, nor by rare-earths presence. After oxidation treatment vanadium is the principal responsible for coke formation. For V-USY catalyst the coke yield increase by a factor of 2.7 after reduction, while for Ni-USY catalyst coke yield increase by a factor of 13. For the RE-USY catalyst, the coke formation is strongly inhibited on vanadium sites and promoted on nickel sites. These results suggest that the coke formation on the zeolite acidic sites is influenced by multi-component interaction between Ni-V, Ni-RE and V-RE elements.

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## 1. Introduction

The amount of heavy feedstock used in downstream refining operations has been increasing worldwide. Generally, those heavy feedstocks present a high content of metals, therefore, resulting in a high concentration of contaminant metals in the industrial catalysts. Those metals are responsible for catalyst deactivation.

In the particular case of fluid catalytic cracking (FCC) process the most common contaminant metals are V [1], Ni [2] and Fe [3]. The FCC process consists of three distinct steps: reaction, separation and regeneration. The reaction occurs in the riser reactor during a few seconds under a reducing atmosphere due to the presence of hydrocarbons and hydrogen. After this step, catalyst and reaction products are separated by means of cyclones and a stripper. Finally, the spent catalyst with coke content in the range of 0.6–2.0 wt% is directed to the regenerator vessel at high

temperature (~700 °C) and oxidized in the presence of O<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O, SO<sub>x</sub>, NO<sub>x</sub> and other gases. The presence of steam and oxygen keeps part of the metals in a high oxidation state.

Nickel reduction has been largely explored in the literature. At low amounts (1–5 wt%), over silica support nickel reduction was controlled by water removal and it was suggested that the nucleation controls the nickel reduction [4]. In the FCC catalyst the presence of extra framework aluminum (EFAL) species decrease nickel mobility [5] and its reducibility [6]. The alumina type and atmosphere treatment also affects the amount of nickel at tetrahedron and octahedron symmetry which appear to control the above process. The reduction of nickel spinelium phases occur only above 700 °C [7].

For V impregnated on silica, a reduction at low temperature is sufficient to forming superficial V<sup>3+</sup> species [8]. In the FCC catalyst, even at high temperature a distribution of +3, +4 and +5 vanadium oxidation states is observed. The ability of rare-earth elements to form vanadate species is probably responsible for keeping part of vanadium at +5 oxidation state [8]. Also, it is important to note that vanadyl species on USY are stable even at 700 °C [9].

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Both nickel and vanadium are active in dehydrogenation reactions. While nickel is active at metallic state for dehydrogenation, hydrogenolysis and hydrogenation [10], vanadium +5 has been used for oxidative dehydrogenation (ODH) reactions [11–13]. Blasco and López Nieto [11] proposed that vanadium–oxygen double bond is the active site for that reactions; the hydrocarbons reacts with V, forming an intermediate which transfer hydrogen atoms to V=O bond forming vanadium hydroxyl species. Wachs and Weckhuysen [12] have shown that the turnover frequency (TOF) could vary more than one order of magnitude depending on the support chosen for vanadium. Based on that, they proposed that vanadium–oxygen-supported atoms were the active sites. On the other hand, Khodakov et al. [13] showed a relation between vanadium amount and propylene selectivity for different supports. These results clearly show that the chemical environment is the principal responsible for ODH reactions.

Coke formation over USY zeolites [14–17] and FCC catalysts [18] is a topic largely explored in the literature. The continuous change from reducing to oxidizing atmospheres in the FCC process can change the metals oxidation state, favouring metal interactions. Therefore, the metals effect over coke formation is a multi-variable problem and deserves a systematic study. Extrapolation of laboratorial results to industrial practical should be made with extreme caution. For instance, Woolery et al. [19] showed that when an equilibrium FCC catalyst was simulated by laboratory deactivation, nickel oxide predominates over nickel aluminate. Using Mitchell impregnation Chester [20] showed that nickel is four times more active for coke formation than vanadium, but observed no synergism between these two metals. Jen et al. [21] reported that for high vanadium contents (7500–10 000 ppm) nickel could minimize the damage to Y zeolite caused by vanadium. At lower vanadium levels (<5000 ppm) and for RE-USY (and RE containing FCC catalyst) the presence of nickel enhanced the deleterious effect of vanadium presented a coke decreased in the *n*-hexane cracking comparing Ni-V/RE-USY and Ni/RE-USY catalysts [14].

The goal of this work is to discuss the role of impregnated nickel and vanadium in the coke formation of USY zeolite. Both the effects of metals oxidation state and rare-earth elements were investigated.

## 2. Experimental

The ultra-stable Y zeolite used in this work was exchanged twice with a  $\text{NH}_4\text{NO}_3$  aqueous solution at 70 °C for 1 h, in order to lower the sodium content. After this, the zeolite was filtered under vacuum and washed with hot water, followed by calcination at 600 °C for 3 h. RE-USY was prepared by ion exchange of rare-earth elements into the USY zeolite. Nickel and vanadium were added to the USY or RE-USY zeolite by impregnation with a toluene solution of  $\text{Ni}^{2+}$  (nickel octanoate) and vanadyl octanoate using a volume 20% higher than the corresponding to the wet point of sample. After homogenization for 30 min, the solvent was removed by means of a rotating evaporator. The zeolite was then calcined at 600 °C for 3 h. The

Table 1  
Prepared catalyst samples

Catalyst	Ni (ppm)	V (ppm)
USY	–	–
Ni/USY	2424	–
V/USY	–	3048
Ni-V/USY	956	2738
RE-USY	–	–
Ni/RE-USY	1720	–
V/RE-USY	–	5930
Ni-V/RE-USY	1010	5720

samples containing both Ni and V were prepared by co-impregnation.

The amounts of Ni, V, Si and Al of the samples were determined by X-ray fluorescence, using Rigaku RIX3100 equipment (Table 1). Samples of approximately 300 mg were used. The final silica to alumina ratio (SAR) of the USY zeolite was 19.0 determinate by infrared spectroscopy. Zeolite surface areas were determined by nitrogen adsorption at –196 °C in Gemini 2360 Micromeritics equipment.

USY and V/USY samples underwent hydrothermal treatment in a fixed-bed reactor at 788 °C (heating rate of 10 °C  $\text{min}^{-1}$ ) for 3 h, using a saturator with water at partial pressure of 0.66 atm. Compressed air was used as carrier gas and a total flow of 60  $\text{ml min}^{-1}$  (air and water) was used.

All the catalysts underwent pre-reduction in a fixed-bed at 500 °C (heating rate of 10 °C  $\text{min}^{-1}$ ) for 12 h using 20  $\text{ml min}^{-1}$  of pure hydrogen (99.999%). Oxidation was carried out in an oven at 500 °C for 12 h (heating rate of 10 °C  $\text{min}^{-1}$ ) using air.

The cyclohexane model reaction [22,23] was performed at 300 °C for 2 h. The reactant was maintained at 20 °C in a saturator and was directed to the reactor using pure nitrogen as carrier gas, resulting in a flow of 20  $\text{ml min}^{-1}$ . Although the temperature in this study is lower compared to commercial FCC operation (500–520 °C), under these conditions the amount of carbon deposited on the catalysts determined by complete burning with air in a LECO CS244 equipment was close to the commercial values. Under these experimental conditions, the cyclohexane conversion was lower than 20% in all cases.

The USY catalysts were submitted to an oxidation treatment after pre-reduction at 500 °C for 12 h (heating rate of 10 °C  $\text{min}^{-1}$ ) with a mixture of 1.51%  $\text{H}_2/\text{Ar}$  at a flow rate of 30  $\text{ml min}^{-1}$ . The pre-reduced catalysts were heated in helium flux until 800 °C, when the oxidation started switching to a mixture of 0.5%  $\text{O}_2$  in He, at flow of 100  $\text{ml min}^{-1}$ . The consumption of oxygen was followed by mass spectrometry (MS), which was previously calibrated with a 500  $\mu\text{l}$  pulse of the same oxidant mixture.

## 3. Results and discussion

### 3.1. Effect of Ni and V over USY coke formation

The area of USY catalyst was measured by BET analysis and presented a surface area of 605  $\text{m}^2 \text{g}^{-1}$ . In the absence of metals and after treatment with water partial pressure of 0.33 atm,

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