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Applied Catalysis A: General 260 (2004) 125–132
APPLIED CATALYSIS A: GENERAL
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Temperature-programmed reduction of metal-contaminated fluid catalytic cracking (FCC) catalysts

Oguz Bayraktar [a,*], Edwin L. Kugler [b]

[a] *Department of Chemical Engineering, Izmir Institute of Technology, Gülbahçe, Köyü 35437 Urla-Izmir, Turkey*
[b] *Department of Chemical Engineering, CEMR, P.O. Box 6102, West Virginia University, Morgantown, WV 26506-6102, USA*

Received 30 June 2003; received in revised form 8 October 2003; accepted 9 October 2003

Abstract

A temperature-programmed reduction study of equilibrium fluid catalytic cracking (FCC) catalysts has shown three hydrogen-consumption peaks associated with contaminanted metals. A low-temperature peak, located near 510 °C, is produced by the reduction of several components in the catalyst. Highly-dispersed vanadium contributes to this peak. A high-temperature peak, located near 800 °C, is produced by reduction of nickel aluminate or nickel silicate compounds. A linear relationship exists between the area of the high-temperature peak and nickel concentration on equilibrium catalysts. An intermediate-temperature peak, located near 690 °C, appears to be related to some form of vanadium compound. The intermediate-temperature peak does not occur on low-vanadium-concentration equilibrium catalysts, but is observed at higher vanadium-contamination levels.

The presence of the 690 °C peak was found by deconvoluting hydrogen-consumption data. The existence of this intermediate-temperature peak was proven by external reduction of highly-contaminated equilibrium catalyst at 500 and 700 °C. External reduction at 500 °C removes the low-temperature peak from the temperature-programmed reduction (TPR) spectrum. External reduction at 700 °C removes both the low-temperature and intermediate-temperature peaks from the TPR spectrum. The difference in spectrum between calcined and 700 °C reduced samples shows a clear spectrum with only the low and intermediate-temperature peaks present.
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Keywords: Fluidized catalytic cracking catalysts; Nickel; Vanadium; Temperature-programmed reduction (TPR)

1. Introduction

Catalytic cracking of heavy feedstock increases the level of contaminated metals on fluidized catalytic cracking catalysts (FCC). These metals, such as vanadium and nickel, increase coke and hydrogen yields at the expense of gasoline and other valuable products [1,2]. Additionally, vanadium destroys the zeolite in the catalyst causing a decrease in catalytic activity. Therefore, it is important to understand the behavior of vanadium and nickel on FCC catalysts.

Temperature-programmed reduction (TPR) has been widely used to characterize supported metal catalysts. Hurst et al. [3] have written a detailed review about the method. TPR reveals information about the temperature range where reduction occurs, oxidation state of the metals, the presence of various surface phases, possible interactions between species, interaction with supportm, and the factors that affect dispersion. Several groups [4–8] using TPR to characterize FCC catalysts have found two prominent peaks. A low-temperature peak near 525 °C has been attributed to the reduction of dispersed vanadium pentoxide and a high-temperature peak near 820 °C has been assigned to nickel silicate and nickel aluminate [6,8]. These peak assignments seem reasonable. However, analysis of TPR spectra of equilibrium catalysts used in commercial refining shows a new peak near 690 °C. This peak appears to be related to vanadium deposited on FCC catalysts.

2. Experimental

2.1. Materials

Nickel oxide was prepared in the laboratory by decomposing nickel(ous) nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$,

* Corresponding author. Tel.: +90-232-498-6287; fax: +90-232-498-6355.
E-mail address: oguzbayraktar@iyte.edu.tr (O. Bayraktar).

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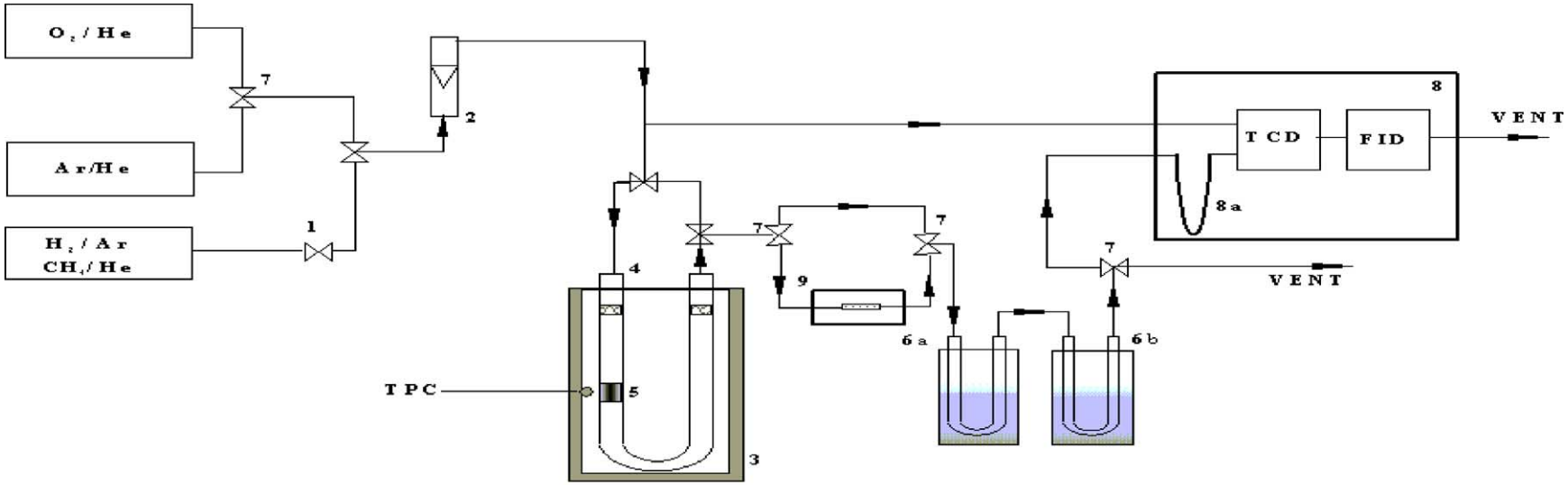
doi:10.1016/j.apcata.2003.10.013



1. On-Off valve
2. Rotometer
3. Furnace
4. Quartz tube reactor
5. Sample
6. Cold trap (a-mixture of dry ice & acetone, b- liquid N_2)
7. 3-way switching valve
8. GC
9. Heated Pt/Al_2O_3 catalyst

TCD: Thermal Conductivity Detector
TPC: Temperature Program Controller
FID: Flame Ionization Detector

Fig. 1. Combined TPR and TPO apparatus.

Aldrich Chemical Company) at 500 °C for 4 h in the static air [9]. Vanadium pentoxide (V_2O_5, 98% purity) is also obtained from Aldrich Chemical Company and was used as received. Nickel aluminate ($NiAl_2O_4$, blue in color) was prepared as described in the literature [10] by co-precipitating a stoichiometric mixture of nitrates of nickel and aluminum using 1 N ammonium hydroxide solution to a final pH of 8.2. The precipitated hydroxide precursor was calcined at 800 °C in the static air for 24 h with intermittent grinding. Gas mixtures of 8% hydrogen-in-argon and 3% oxygen-in-helium were obtained from Matheson and used as received.

2.2. Catalysts and catalyst preparation

In this study, three equilibrium FCC catalysts (used catalysts from commercial operation) were supplied by Ashland Inc. They are named as ECat-LOW, ECat-INT, and ECat-HIGH based on their contaminanted-metals concentration. Characterization data on these equilibrium catalysts are provided in Table 1.

Nickel and vanadium were added to several catalysts to obtain reference materials for TPR studies. The FCC catalysts used were Davison Octacat and ECat-LOW (low-metals equilibrium catalyst described in Table 1). Octacat was chosen because it contains only ammonium-exchanged USY zeolite, kaolin, and a silica–sol binder, without other additives. It was calcined in air at 500 °C prior to metals addition. Aqueous solutions of nickel(ous) nitrate hexahydrate and vanadium pentoxide were used for incipient-wetness impregnation of nickel and vanadium, respectively. After impregnation, catalysts were dried in air at 100 °C overnight, then calcined in air at 500 °C for 4 h.

2.3. Temperature-programmed methods

The diagram for the apparatus used for temperature-programmed reduction or temperature-programmed oxidation (TPO) is given in Fig. 1. An earlier version of the TPR apparatus has been described previously [11]. The current equipment consists of a Hewlett–Packard 5890 gas chromatograph with thermal conductivity detector (TCD) and flame ionization detector (FID) and an external furnace connected to a temperature-program controller (Automated Test Systems, Butler, PA). The sample to be analyzed is placed in a quartz U-tube reactor and surrounded with quartz chips. For temperature-programmed reduction, a mixture of 8% hydrogen-in-argon flowed through the reactor with a flow rate of 35 ml/min. The exit stream from the reactor passed only through a cold trap filled with a mixture of dry-ice and acetone (to remove water from the exit stream), then to the TCD and FID detectors, connected in series. The TCD monitored hydrogen concentration while the FID monitored methane and carbon monoxide formation during the TPR experiments. Approximately, 250 mg of calcined catalyst was used in each TPR experiment. In all TPR experiments, the temperature was ramped linearly from room temperature to 865 °C at a rate of 10 °C/min. Then the furnace was held at 865 °C for 30 min. The TPR profiles of the samples were analyzed by deconvoluting them using PeakFit software from Jandel Scientific.

One sample received a number of TPR scans alternated with TPO scans that were used to reoxidize the catalyst before running the next TPR experiment. In all TPO scans, the temperature was ramped linearly from room temperature to 865 °C at a rate of 10 °C/min. Then the furnace was held at 865 °C for 15 min. A mixture of 3% oxygen-in-helium with a flow rate of 40 ml/min was used in the TPO experiments.

In commercial FCC units, the catalyst is cycled continuously from the reactor section to the regenerator section and then back to the reactor again. The reactor is run at high-temperatures under reducing conditions while the regenerator has sufficient air to remove most of the hydrocarbon deposits (coke) as CO, CO_2, and H_2O. Regenerators typically operate isothermally in the temperature range of 700 to 800 °C. The equilibrium catalyst samples used in this study were removed from the regenerator section of commercial FCC units. Small amounts of coke that remained on the equilibrium catalysts were removed by calcining in air at 500 °C prior to TPR characterization.

Table 1
Nominal properties of commercial equilibrium catalysts from Ashland Inc.

	ECat-LOW	ECat-INT	ECat-HIGH
BET surface area (m^2/g)	178	160	115
Matrix surface area (m^2/g)	63	63	45
Zeolite surface area (m^2/g)	115	97	70
Metals ($mg\,kg^{-1}$)			
Nickel	300	900	2600
Vanadium	700	1700	6700
Microactivity	71	69	62

3. Results and discussion

3.1. Reduction of unsupported metal oxides (NiO, $NiAl_2O_4$, and V_2O_5)

The TPR spectra for bulk NiO, $NiAl_2O_4$, and V_2O_5 are compared in Fig. 2. The TPR profile for unsupported NiO (Fig. 2a) shows a strong peak at around 380 °C whereas for $NiAl_2O_4$ (Fig. 2b) a broad peak is observed near 780 °C. These reduction temperatures are in good agreement with published results [5,12]. TPR spectra show that $NiAl_2O_4$ type compounds are more difficult to reduce than NiO.

In the case of unsupported V_2O_5 reduction, given in Fig. 2c, the TPR spectrum shows three peaks at around 625, 660, and 780 °C. Prior investigators [13,14] have reported similar reduction profiles for bulk V_2O_5. Jouguet et al. [14] have observed that reduction with pure hydrogen at atmospheric pressures results in direct formation of V_2O_3. At lower hydrogen partial pressures the reduction was found to proceed in steps. The first peak occurs on reduction of V_2O_5

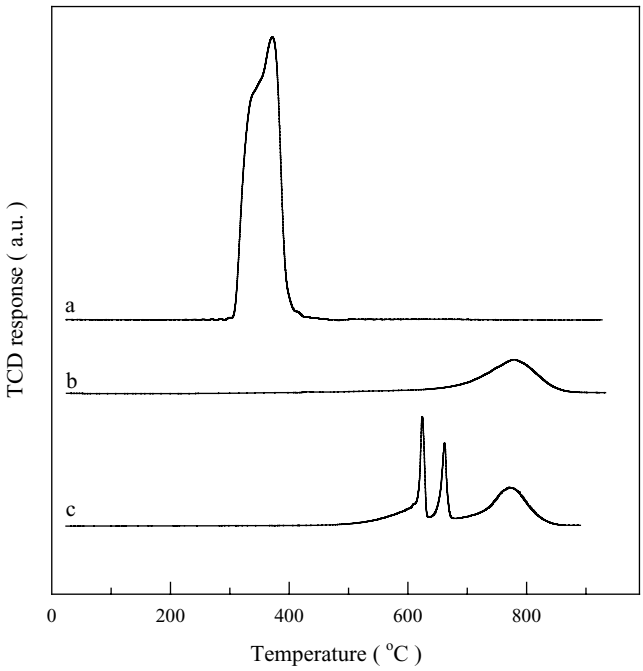


Fig. 2. TPR spectra for unsupported metal oxides using 8% hydrogen in argon: (a) NiO; (b) $NiAl_2O_4$; (c) V_2O_5.

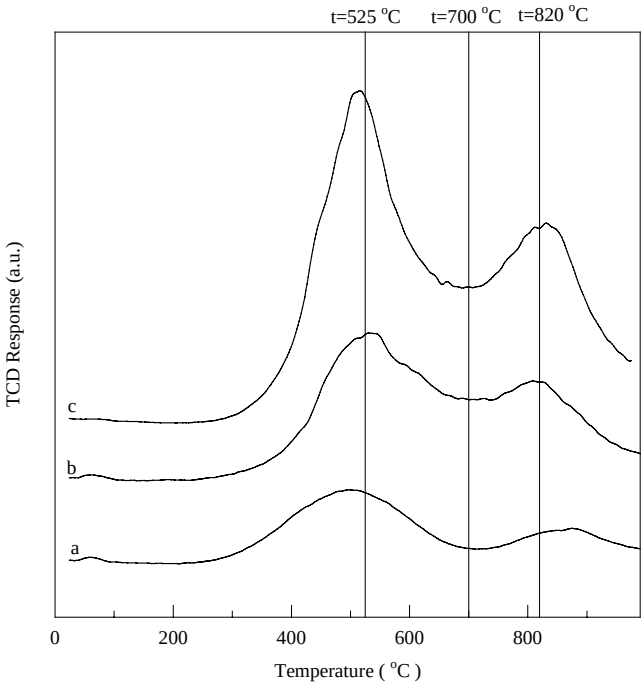


Fig. 3. TPR spectra for commercial equilibrium FCC catalysts: (a) ECat-LOW; (b) ECat-INT; (c) ECat-HIGH.

to V_6O_{13}, while the second peak results from reduction to VO_2. Complete reduction to V_2O_3 produces the final peak at a temperature of approximately 780 °C. Jouguet et al. [14] have confirmed their results by using X-ray diffraction to determine the structure of the remaining solids after each step of their TPR analysis.

3.2. Reduction of nickel and vanadium on FCC catalysts

The TPR spectra of three equilibrium FCC catalysts are shown in Fig. 3. In general, two broad peaks are observed in these TPR profiles, a low-temperature peak near 525 °C and a high-temperature peak near 820 °C. The profiles show sharper peaks with increasing metal concentrations. The TPR spectra of equilibrium FCC catalysts do not match the profiles of unsupported NiO or V_2O_5 shown in Fig. 2. However, the high-temperature peak does match the temperature observed for nickel aluminate reduction.

Prior investigators [6,8] have observed two strong peaks in TPR spectra of metal-contaminated FCC catalysts. The low-temperature peak near 525 °C has been assigned to the reduction of supported V_2O_5 while the high-temperature peak has been assigned to nickel silicate and nickel aluminate. The basis for these assignments is demonstrated in the next two figures.

Fig. 4 shows TPR spectra for a laboratory prepared sample with 9100 mg kg^{-1} nickel on Davison Octacat. The calcined catalyst (Fig. 4a) has a strong peak near 450 °C, a higher temperature than 380 °C observed for bulk nickel oxide. The higher temperature for supported nickel oxide shows that interaction with the FCC catalyst makes nickel more difficult to reduce. After Fig. 4a was recorded, the catalyst was then oxidized and reduced seven times in the TPR and TPO apparatus. After each TPR experiment, the system was cooled to room temperature. Then 3% oxygen-in-helium was passed through the catalyst sample while the temperature was ramped to 865 °C at a rate of 10 °C/min. After seven

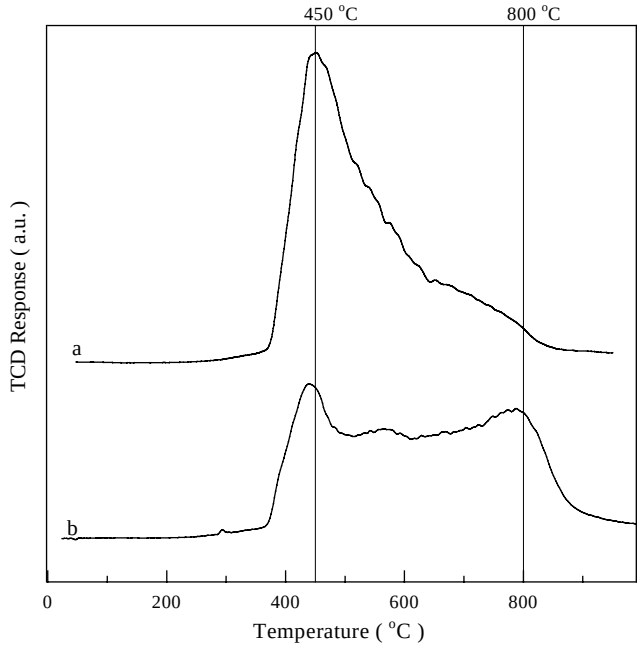


Fig. 4. TPR spectra for NiO impregnated on FCC catalyst: (a) TPR of supported NiO after impregnation; (b) TPR of supported NiO after seven reduction–oxidation cycles.

repetitive reduction–oxidation steps, the low-temperature peak at 450 °C associated with NiO reduction became smaller while a distinct high-temperature peak appeared around 800 °C (see Fig. 4b). This high-temperature peak has been attributed to the formation of nickel aluminate and/or nickel silicate compounds [5,6,15].

The results shown in Fig. 4 were obtained from a catalyst prepared by incipient-wetness impregnation using nickel nitrate. It was dried and calcined in air at 500 °C prior to TPR measurement. This protocol was chosen because calcining in air at 500 °C converts nickel nitrate to nickel oxide, providing a comparison for the TPR spectra of bulk and supported nickel oxide. Subsequent high-temperature treatments cycling between TPR and TPO measurements converts some of the nickel oxide to nickel silicate or nickel aluminate. Haas et al. found a single peak near 800 °C when nickel is added to FCC catalysts [8]. However, Haas used smaller amounts of nickel (1000–2000 mg kg^{-1}) and his catalysts were aged at 825 °C with 100% steam or with air–steam mixtures. Cycling between TPR and TPO measurements are dry treatments which are much less severe than steam treatments. Some water will be produced (and removed from the sample) during the TPR cycle, but the high-temperature oxidation in the TPO apparatus should be entirely without water.

Fig. 5 shows that when 3700 mg kg^{-1} of vanadium is added to ECat-LOW, a significant peak is observed near 500 °C that tails off toward higher temperatures. The reduction temperature of 510 °C for supported vanadium is lower than that of bulk V_2O_5 (see Fig. 2). The TPR profile of supported vanadium does not change significantly with steam treatments or oxidation–reduction cycles.

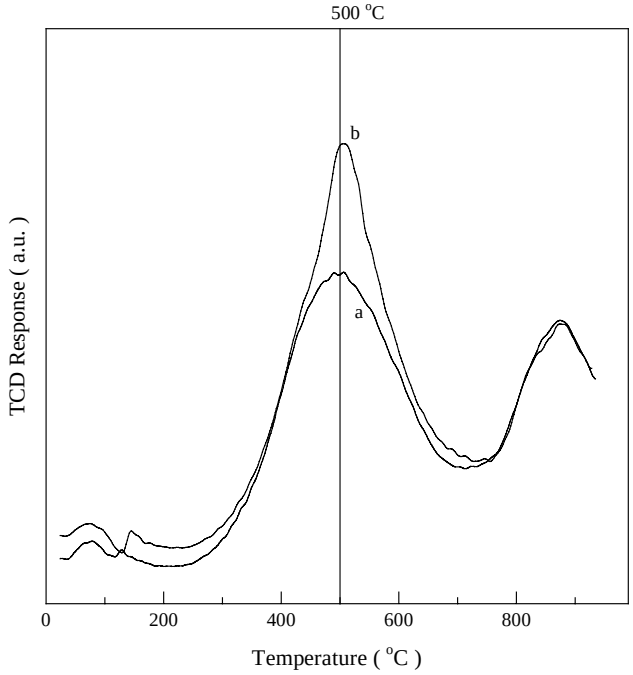


Fig. 5. TPR spectra for V_2O_5 impregnated on FCC catalyst (ECat-LOW): (a) before vanadium impregnation; (b) after vanadium impregnation.

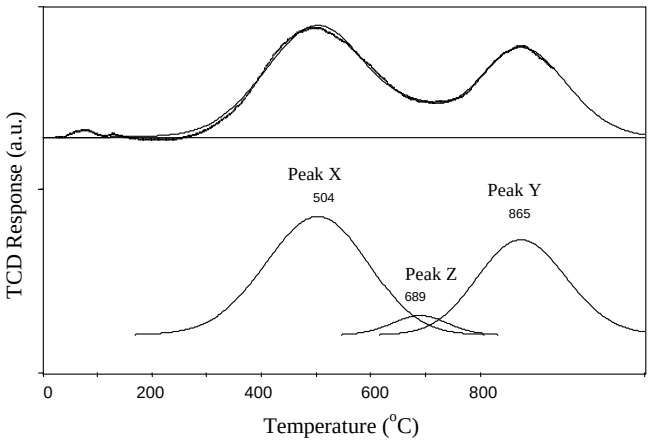


Fig. 6. Analysis of TPR spectrum for FCC catalyst (ECat-LOW) before vanadium impregnation.

Kijenski et al. [16] have reported that a low concentration of V_2O_5 on many different supports resulted in only one significant TPR peak located at a temperature between 440 and 590 °C. This lower reduction temperature for supported V_2O_5 compared to bulk V_2O_5 has been attributed to the formation of a highly-dispersed, surface-monolayer phase on the support, and the weakening of vanadium–oxygen bonds due to formation of a polymeric-vanadium-oxide species [6,17,18].

The TPR spectra for the three equilibrium catalyst samples shown in Fig. 3 are deconvoluted in Figs. 6–8. The spectra are fitted with Gaussian-type functions using three peaks to fit the TPR data. Three is the minimum number of peaks needed to get an adequate fit for ECat-INT and ECat-HIGH. For consistency, three peaks are used for ECat-LOW, although it can be fitted adequately with only two. The peaks are labeled X, Y, and Z in the order of their intensity. Peak X occurs near 510 °C, peak Y near 830 °C, and peak Z near 690 °C. Peaks X and Y have been described previously. Peak Z is a new peak assignment for FCC catalysts.

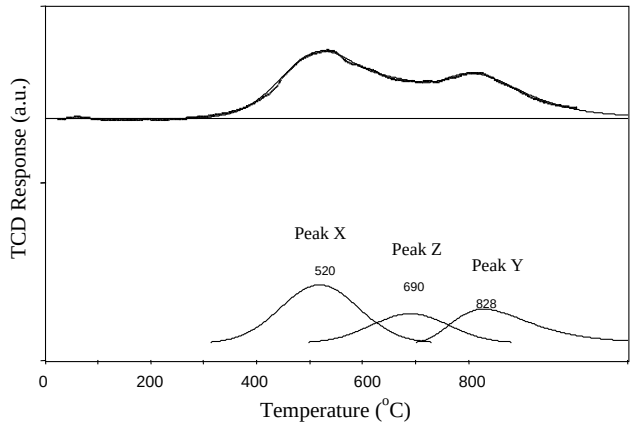


Fig. 7. Analysis of TPR spectrum for commercial equilibrium FCC catalyst (ECat-INT).

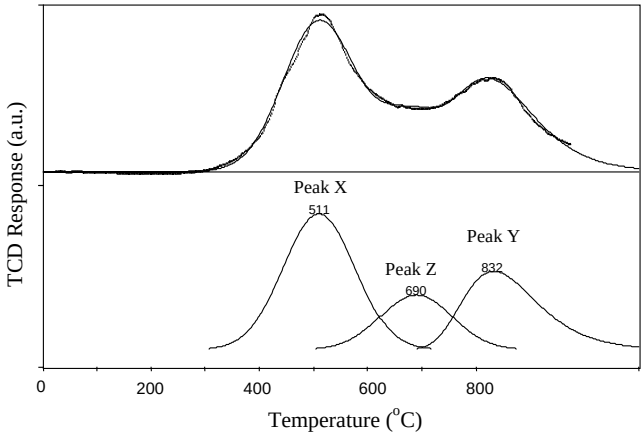


Fig. 8. Analysis of TPR spectrum for commercial equilibrium FCC catalyst (ECat-HIGH).

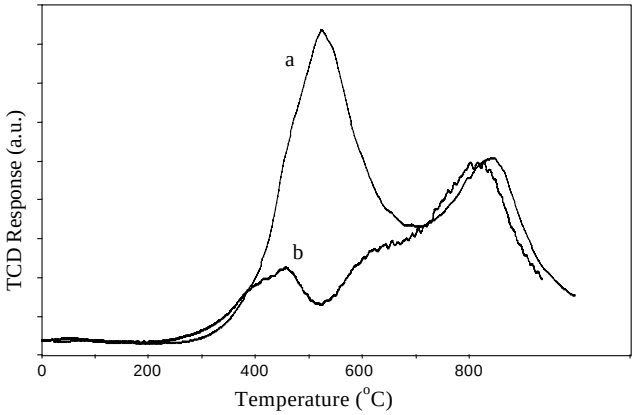


Fig. 10. Comparison of TPR spectra of ECat-HIGH: (a) calcined; (b) reduced with hydrogen at 500 °C.

The intensity of Peak Z has been plotted in Fig. 9 as a function of vanadium concentration. Peak Z has nearly zero peak area for ECat-LOW, but significant peak areas for ECat-INT and ECat-HIGH. It appears that after a threshold concentration has been achieved on equilibrium FCC catalyst, vanadium accumulates in some more-difficult-to-reduce form. The 690 °C peak is similar to the peaks observed at 625 and 660 °C when bulk V_2O_5 was reduced stepwise to V_2O_4. Koranne et al. [13] reported a peak at 630 °C for 8% V_2O_5 on silica and at 640 °C for 25% V_2O_5 on alumina, but reported no peaks above 550 °C for lower concentrations of V_2O_5. The peaks observed near 630 °C were produced by the reduction of crystalline V_2O_5. However, no hydrogen-consumption peaks near 690 °C were reported.

The individual contributions of Peak X and Peak Z can be observed by external reduction of ECat-HIGH. The TPR spectrum of calcined ECat-HIGH is shown in Fig. 10a. Fig. 10b shows the TPR spectrum of ECat-HIGH externally

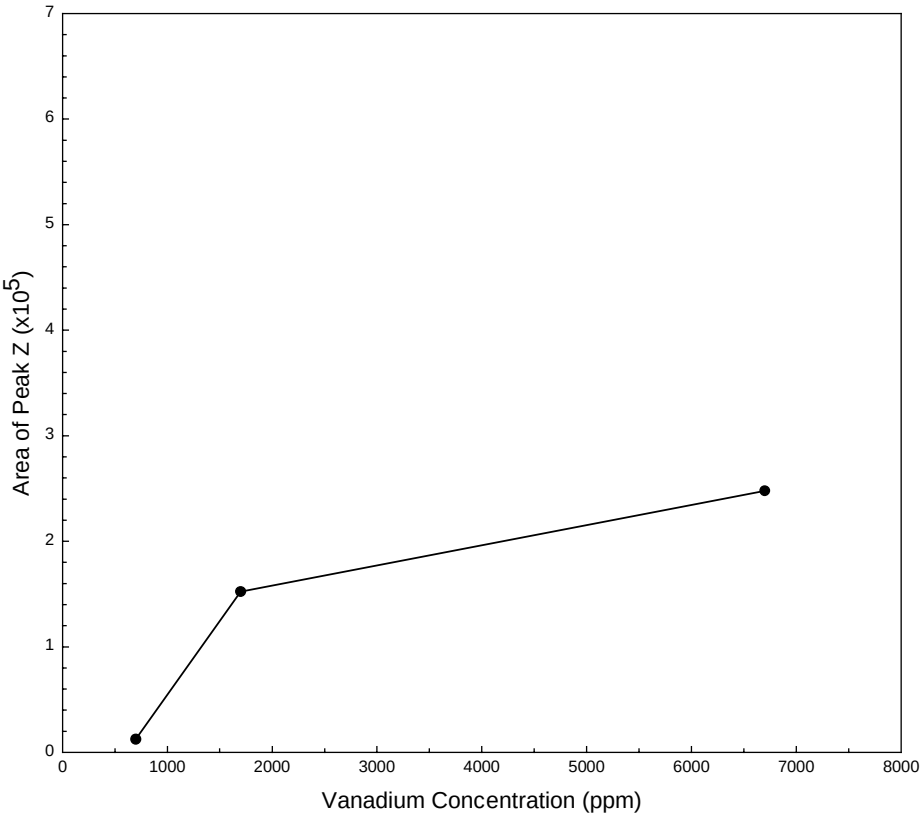


Fig. 9. Area of Peak Z as a function of vanadium concentration on equilibrium catalysts.

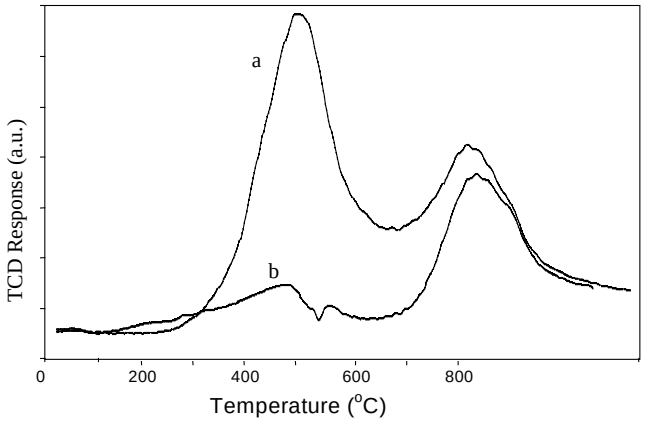


Fig. 11. Comparison of TPR spectra of ECat-HIGH: (a) calcined; (b) reduced with hydrogen at 700 °C.

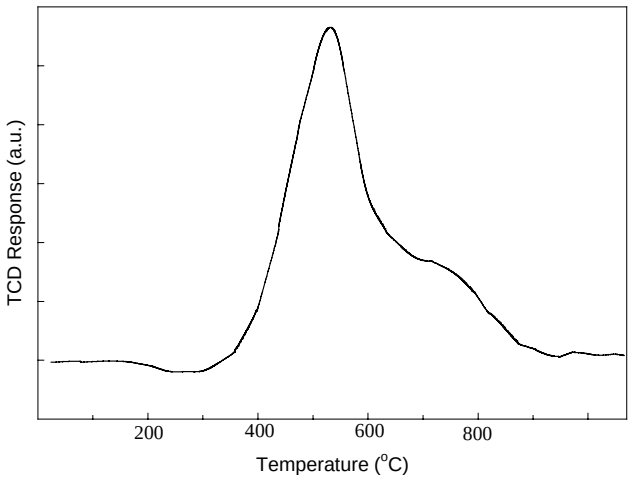


Fig. 12. Difference spectrum obtained by subtracting spectrum 11b from spectrum 11a.

reduced at 500 °C for 6 h with 8% hydrogen-in-argon. The externally reduced sample was cooled to room temperature in the 8% hydrogen-in-argon mixture before being handled to air. The TPR spectrum of ECat-HIGH externally reduced at 500 °C does not contain Peak X. The higher temperature portion of the TPR spectrum remains unchanged.

The external reduction with 8% hydrogen-in-argon was repeated on another ECat-HIGH sample at 700 °C. This sample was reduced at 700 °C for approximately 6 h and cooled to room temperature in the 8% hydrogen-in-argon mixture. The results are shown in Fig. 11. The difference spectrum is plotted as Fig. 12. The difference spectrum shows Peak X with its maximum near 510 °C and Peak Z with its maximum near 690 °C. The external reduction at 700 °C reduces the metals responsible for Peak X and Z. It has little effect on the metals that produce Peak Y.

Peak Y is produced by reduction of mixed oxides containing nickel. Fig. 4 shows that NiO is converted to some other form, usually assigned to nickel aluminate or nickel silicate [5,6,15]. The intensity of Peak Y is plotted in

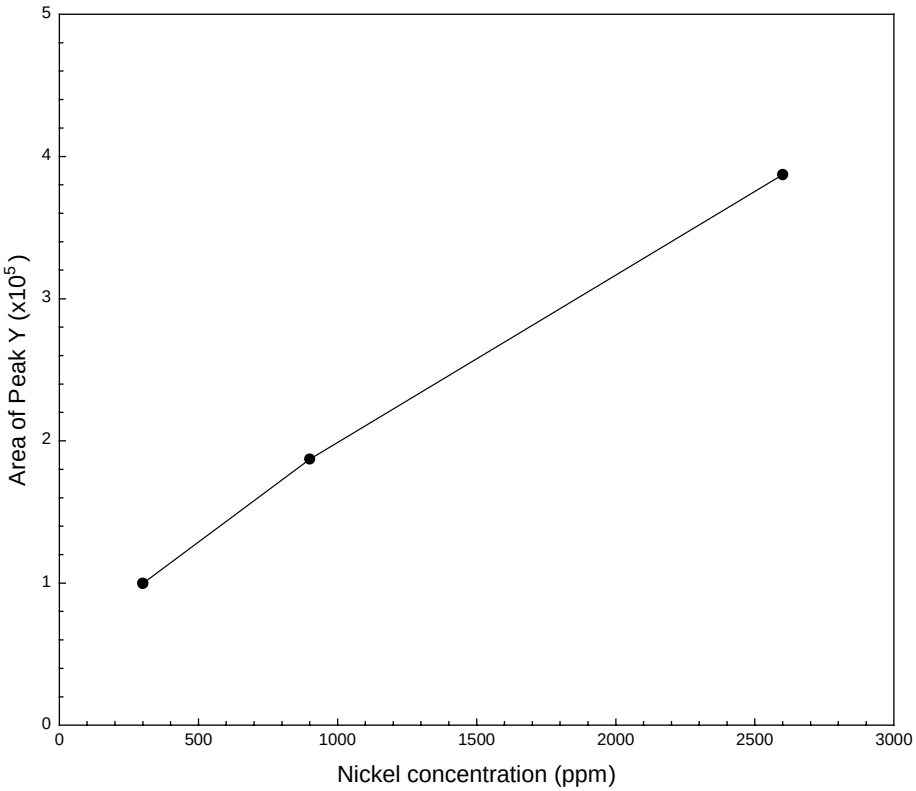


Fig. 13. Intensity of Peak Y as a function of nickel concentration for equilibrium catalysts.

Fig. 13 as a function of nickel concentration on equilibrium catalyst. Three points provide a reasonable straight line with a small, positive intercept, suggesting that FCC catalyst without nickel would still produce a small TPR peak near 800 °C. The linear relationship between Peak Y and contaminanted-nickel concentration suggests that the area of Peak Y could be used to estimate nickel concentration on equilibrium catalyst.

4. Conclusions

This temperature-programmed reduction study of equilibrium FCC catalysts has shown three hydrogen-consumption peaks associated with contaminanted metals. A low-temperature peak, located near 510 °C, is produced by the reduction of several components in the catalyst. Highly-dispersed vanadium contributes to this peak. However, it is difficult to determine the extent of the vanadium contribution. A high-temperature peak, located near 800 °C, is produced by reduction of nickel aluminate or nickel silicate compounds. A linear relationship exists between the area of the high-temperature peak and nickel concentration on equilibrium catalyst. An intermediate-temperature peak, located near 690 °C, appears to be related to some form of vanadium compound. The intermediate-temperature peak does not occur on low-vanadium-concentration equilibrium catalysts, but is observed at higher vanadium-contamination levels.

The presence of the 690 °C peak was found by deconvoluting hydrogen-consumption data. The existence of this intermediate-temperature peak was proven by external reduction of highly-contaminated equilibrium catalyst at 500 and 700 °C. External reduction at 500 °C removes the low-temperature peak from the TPR spectrum. External reduction at 700 °C removes both the low-temperature and intermediate-temperature peaks from the TPR spectrum. The difference spectrum between calcined and 700 °C reduced samples shows a clear spectrum with only the low and intermediate-temperature peaks present. Much of this difference spectrum is produced by contaminanted vanadium on equilibrium FCC catalyst.

Acknowledgements

Support from the Turkish Ministry of National Education and the West Virginia University Department of Chemical Engineering is gratefully acknowledged. We express our thanks to Howard F. Moore, Marathon–Ashland Petroleum for both helpful discussions and for supplying the equilibrium catalysts used in this study.

References

[1] J.E. Connor, J.J. Rothrock, E.R. Birkhimer, L.V. Leum, Ind. Eng. Chem. 49 (1957) 276.
[2] H.R. Crane, J.E. Connor, G.P. Masologites, Pet. Refin. 40 (1961) 168.
[3] N.W. Hurst, S.J. Gentry, A. Jones, B.D. McNicol, Catal. Rev. 24 (1982) 233.
[4] D.F. Tatterson, R.L. Mieville, Ind. Eng. Chem. Res. 27 (1988) 1595.
[5] V. Cadet, F. Raatz, J. Lynch, Ch. Marcilly, Appl. Catal. 68 (1991) 263.
[6] W.C. Cheng, M.V. Juskels, W. Suarez, Appl. Catal. 103 (1993) 87.
[7] P.K. Doolin, J.F. Hoffman, M.M. Mitchell Jr, Appl. Catal. 71 (1991) 233.
[8] A. Haas, W. Suarez, G.W. Young, in: K.C. Chuang, G.W. Young, M. Benslay (Ed.), AIChE Symposium Series: Advanced Fluid Catalytic Cracking Technology, 88, 1992, p. 133.
[9] I. Chen, D.W. Shine, Ind. Eng. Chem. Res. 27 (1988) 429.
[10] I.A.P.S. Murthy, C.S. Swamy, J. Mater. Sci. 28 (1993) 1194.
[11] L. Feng, X. Li, D.B. Dadyburjor, E.L. Kugler, J. Catal. 190 (2000) 1.
[12] C. Li, Y.W. Chen, Thermochim. Acta 256 (1995) 457.
[13] M.M. Koranne, J.G. Goodwin Jr., G. Marcelin, J. Catal. 148 (1994) 369.
[14] B. Jouguet, A. Gervasini, A. Auroux, Chem. Eng. Technol. 18 (1995) 243.
[15] M. Afzal, C.R. Theocharis, S. Karim, Colloid Polym. Sci. 271 (1993) 1105.
[16] J. Kijenski, A. Baiker, M. Glinski, P. Dollenmeier, A. Wokaun, J. Catal. 101 (1986) 1.
[17] A.W. Stobbe-Kreemers, G.C. van Leerdam, J.P. Jacobs, H.H. Brongersmu, J.J.F. Scholten, J. Catal. 152 (1995) 130.
[18] N.P. Samchenko, Z.M. Zdornaya, G.I. Golodets, V.I. Kutepov, L.V. Frolova, R.M. Masagutov, Ukran. Khim. Zh. 54 (1988) 696.