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Luminescence as a Probe of Metal Poisoning Effects on a High-Activity Fluid Cracking Catalyst (FCC)

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The effects of nickel and vanadium on the catalytic properties of a high-activity commercial fluid cracking catalyst (FCC) have been studied using surface area, X-ray analysis, fluorescence spectra, lifetime experiments, and microactivity testing. Results show that loadings of up to 3% Ni have little effect on the catalyst surface properties and cracking activity for gas oil conversion. Nickel, however, affects product selectivities by cracking gasoline and generating high carbon, hydrogen, and light-gas yields. In contrast, the surface area, pore volume, crystallinity, and cracking activity of the vanadium-loaded catalyst monotonically decrease with V levels after aging at hydrothermal conditions; 2% V renders the catalyst totally inactive. X-ray analysis of these catalysts shows a decrease of crystallinity with increasing vanadium loadings and hydrothermal treatment; vanadium destroys the catalyst lattice and with it cracking activity. Luminescence spectra indicate movement of nickel on the fluid cracking catalyst surface. Vanadium loadings on the other hand give rise to a new luminescent specie, which is attributed to surface V_2O_5 species sensitive to catalyst treatment. Luminescence emission and lifetime experiments are useful in determining the identity of metal contaminants, quenching effects on rare earth zeolite Y emission and as indicators of degradation of initial cracking activity.

INTRODUCTION

While in the 70's, crude oil price and availability were the incentives for the refiner to process cheaper but metal-contaminated gas oil, in the 80's, the incentive for processing these crudes is a stagnant fuels market (*1*). In cracking cheaper oils, metals are continuously deposited on the fluid cracking catalyst (FCC) surface causing losses in activity as well as the promotion of nonselective cracking to undesirable products like hydrogen, light gases, and coke (*2*).

The deleterious effects of V, Ni, Fe, and Cu on cracking catalysts' activity and product selectivities have long been recognized. Nickel, like Cu and Fe, increases H_2 and coke at the expense of gasoline yields while V affects catalyst activity (*3–7*). In comparison, little has been reported on the nature of the interaction of these metals with the catalyst surface. Connor *et al.* (*8*) reported that metals tolerance can be enhanced by a catalyst matrix which prevents their dispersion. Meisenheimer (*9*) was able to correlate metals contaminant passivation to metals availability to hydrogen and oxygen chemisorption; passivation was attributed to inert silicates and aluminosilicates formation. Järas (*10*) used secondary ion mass spectroscopy (SIMS) to show that in steam-aged cracking catalysts, V is segregated in regions occupied by the rare-earth exchanged zeolite Y while Ni was found uniformly distributed on the catalyst surface. Hydrothermal treatment of the nickel catalyst resulted in nickel sintering and/or migration off the zeolite surface. The deleterious effects of nickel on cracked product selectivities can be reduced by using a catalyst with a SiO_2-rich matrix containing a partially dealuminated kaolin mineral (*11*).

Luminescence methods have been used

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to probe the surface structure of several materials (including adsorbed species) on surfaces (*12*), catalysts (*13*), electrodes (*14*), and gels (*15*). Information regarding the number of catalytic sites, the kinetic behavior of luminescent species, and the changes that occur during and after sample treatment has also been obtained using luminescence excitation, emission, and lifetime techniques (*13*). Recently, solid surface room-temperature luminescence has also been used to determine components of a mixture without the isolation of these components (*16*).

In this study, surface area, X-ray analysis, and microactivity testing were used in conjunction with luminescence techniques to show that luminescence is a valuable tool in the study of compound formation on catalyst surfaces. In addition, it is postulated that luminescence methods can be specifically used in the study of vanadium species and to predict catalyst deactivation by surface deposited metals.

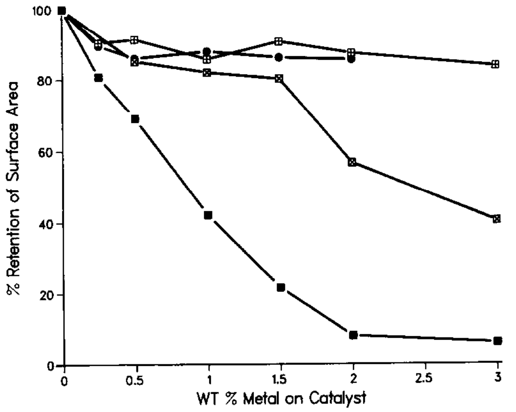

FIG. 2. The effects of Ni and V on surface area. (■) V, 95% steam, 10 h at 730°C; (⊠) V, dry air, 10 h at 730°C; (⊞) V, dry air, 10 h at 540°C; (●) Ni, 95% steam, 10 h at 730°C.

EXPERIMENTAL

Catalyst Preparation and Evaluation

A commercially available, high-activity, fluid cracking catalyst was heat shocked at 590°C for 1 h prior to metal loading. The incipient wetness method was used to impregnate the catalysts to the desired metal level with benzene solutions of nickel and vanadium naphthenates (*17*). The naphthenates were obtained from Pfaltz and Bauer Inc. and contained 6.0% Ni and 2.9% V, respectively. After a 10-h calcination step at 540°C in air, the metal-loaded catalysts were aged (steam deactivated) for 10 h at 730°C in a bed fluidized by passing a 95% steam–5% nitrogen mixture at 1 atm.

The catalyst's cracking activity was evaluated with a flow system similar to the one described by Ciapetta and Henderson (*1*). Feedstock was a gas oil (260–426°C boiling range) containing 23.0 wt% furnace oil and 74.3 wt% slurry oil. The charge consisted of

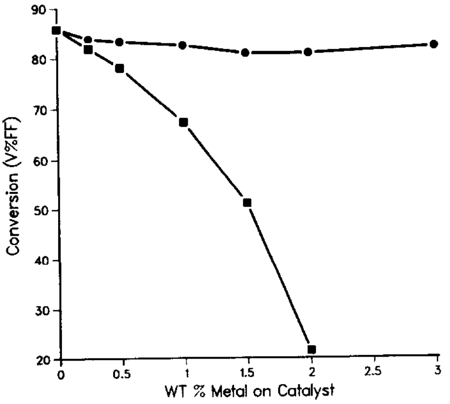

FIG. 1. The effects of Ni and V on cracking activity. (■) Vanadium, (●) Nickel.

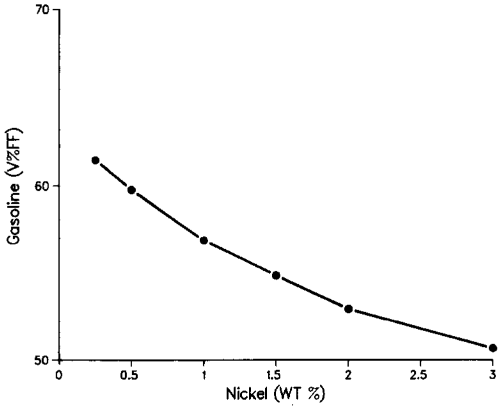

FIG. 3. The effects of nickel on gasoline generation.

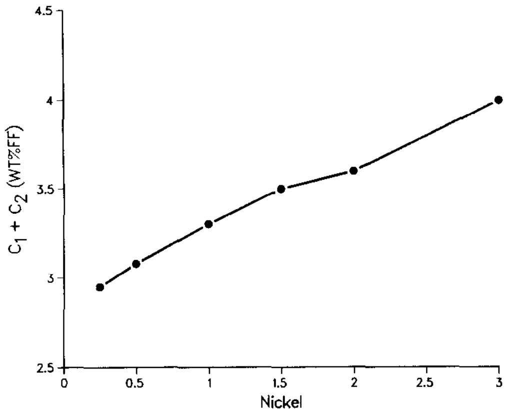

FIG. 4. The effects of nickel on light gases ($C_1 + C_2$) generation.

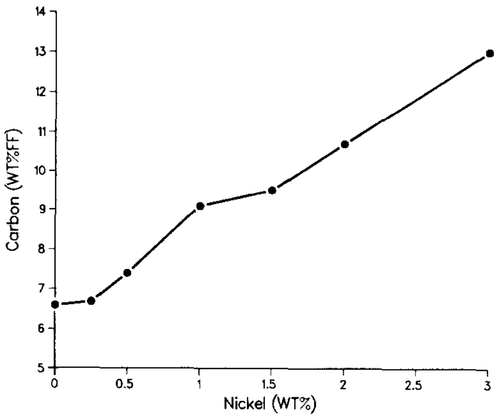

FIG. 6. The effects of nickel on carbon generation.

2.5 g of 100 × 325 mesh microspheres. Typical test conditions were 515°C reactor temperature, 80-s contact time, and 15 WHSV. Percentage conversion is defined as $(V_f - V_p)\ 100/V_f$ where V_f is the volume of fresh feed (FF) cracked and V_p is the volume of product boiling above 204°C.

Catalyst Characterization

Surface properties. A DIGISORB 2600 from Micromeritics Instrument Corporation measured N_2 sorption, BET surface area, and pore size distributions. Micrographs were taken with a Phillips EM-300 transmission electron microscope at 500,000× magnification.

Luminescence excitation and emission. Samples were loaded into Type 52-H 2-mm path length quartz cells purchased from Precision Cells, Inc., Hicksville, New York. Enough sample was added to totally obstruct the path of the excitation source. Spectra were recorded using a double Czerny-Turner monochromator Model 1902 Spex fluorometer. A Rhodamine B solution was used to correct for variations in the excitation source radiation. The spectrometer front face mode was used.

Lifetime studies. Luminescence lifetime measurements were made with a PRA Model 3000 system. A PRA Model LN100 nitrogen lasar pulsing at 20 Hz with a pulse width of 300 ps was used as the excitation source. A UV–Vis grating monochromator

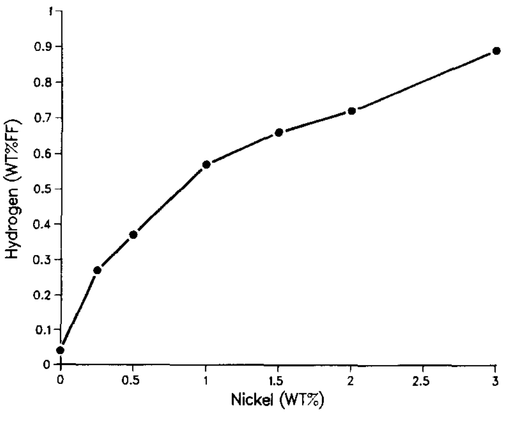

FIG. 5. The effects of nickel on hydrogen generation.

TABLE 1

Excitation Wavelengths and Luminescence Emission of Metal-Loaded Catalysts

Sample	Excitation (nm)	Emission (nm)
LaY	300	360
Fresh catalyst	300	370
V naphthenate	280	350
2% V on inert support	360	440
2% V on fresh catalyst	280	350; 550
2% V on aged catalyst	280	550
Ni naphthenate	300	350
2% Ni on fresh catalyst	290	370 (weak)
2% Ni on aged catalyst	300	370

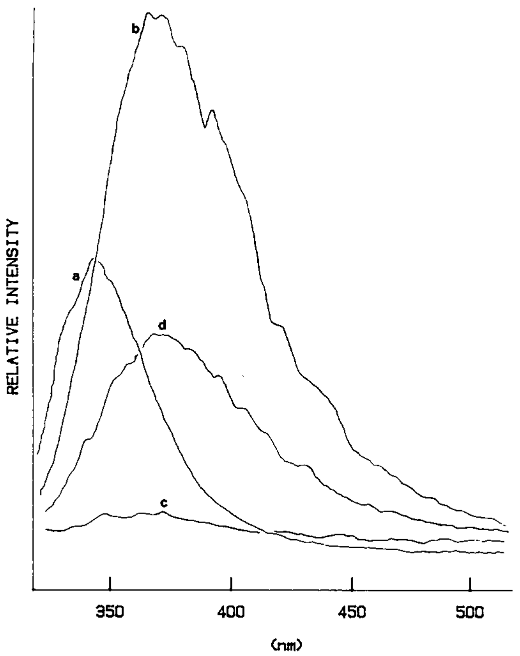

FIG. 7. Effects of deposition and treatment of nickel naphthenate on the luminescence of the catalyst surface. (a) Nickel naphthenate; (b) fresh catalyst; (c) 2% Ni on fresh catalyst; and (d) 2% Ni on aged catalyst. Excitation wavelength = 300 nm.

(PRA Model B102-2) was used between the sample compartment and the emission photomultiplier tube to select the monitoring wavelength. Data were collected on a Tracor Northern multichannel analyzer and were transferred to a Digital Corporation PDP-1103 computer for storage and manipulation. Deconvolution and statistical anallysis was done using software package Decay V3.0 purchased from PRA Corporation, London, Ontario, Canada.

RESULTS AND DISCUSSION

The different effects of Ni and V on catalyst activity and product selectivity are illustrated in Figs. 1–6. Activity decreases monotonically with V levels. With 1.5% V, the catalyst has lost most of its useful activity; with 2.0% V, it becomes inactive (Fig. 1). This irreversible deactivation correlates well with surface area losses with V loadings (Fig. 2). Deactivation depends on aging temperatures, and it is accelerated when aging is performed at hydrothermal conditions. In contrast, with as much as 3% Ni, the aged catalyst was found to retain 95% of its original surface area as well as most of its cracking activity (Fig. 2). Nickel, however, is an effective dehydrogenation catalyst; it cracks gasoline (Fig. 3) generating high yields of dry gases, hydrogen, and coke deposits (Figs. 4–6).

The luminescence data of Table 1 and Fig. 7 indicate that a change occurs when nickel napththenate is deposited on the catalyst surface. The emission band observed at 350 nm, when nickel naphthenate was excited at 300 nm, is no longer evident in the spectra of 2% nickel-loaded catalyst. Instead, a weak, broad band centered at ~370 nm is observed (Fig. 7c); it increases in intensity after hydrothermal aging (Fig. 7d). The similarity and location of this band to that observed for LaY (Fig. 8) suggests that the luminescence observed in the nickel-loaded catalyst is largely due to the presence of this zeolite. Luminescence intensity differences appear to be a function of nickel coverage of the zeolite surface. Without nickel, the 370-nm band is very intense. Deposition of 2% nickel on the cata-

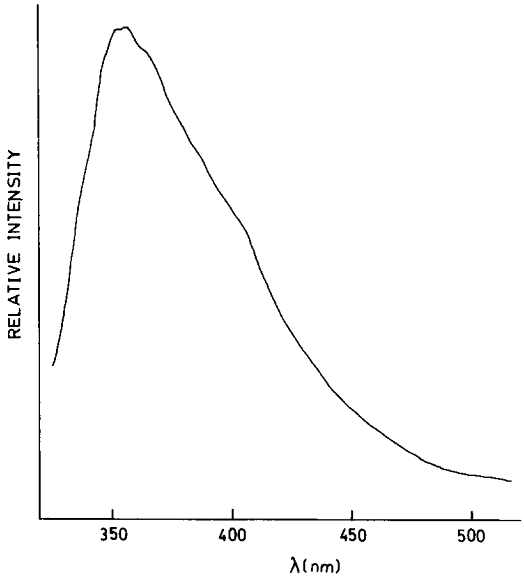

FIG. 8. Luminescence emission of LaY. Excitation wavelength = 300 nm.

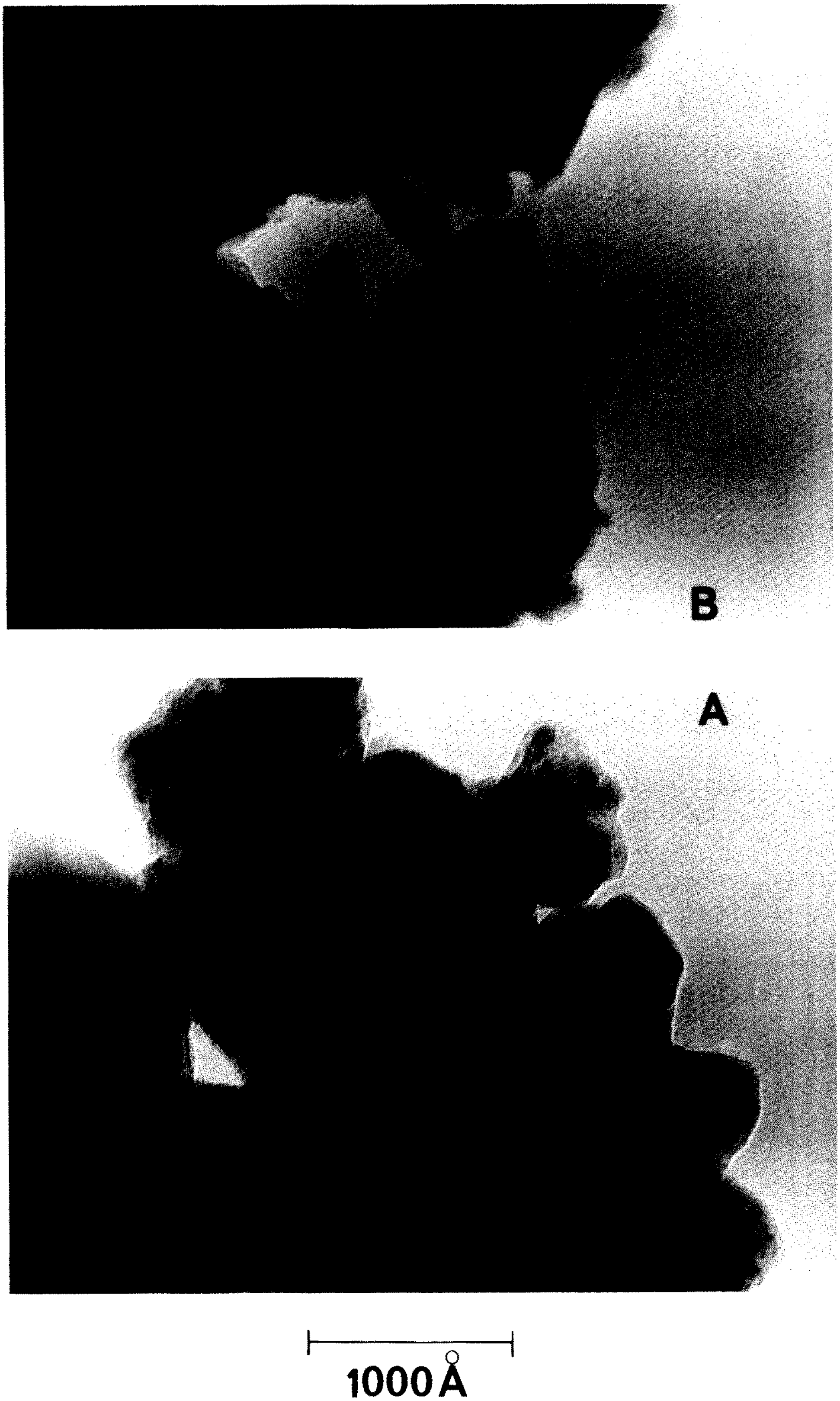

FIG. 9. Electron micrographs of catalyst with 2% Ni. (A) Before aging and (B) after aging.

lyst surface results in a drastic and almost complete quenching of the LaY band (Fig. 7c). Hydrothermal treatment of the catalyst returns some of the lost intensity (Fig. 7d).

The above data suggest that nickel initially covers the zeolite surface rather uniformly. Aging at hydrothermal conditions results in nickel migration from the zeolite. However, the zeolite retains some nickel and the original luminescence intensity is not regained (see Fig. 7). The electron micrographs in Fig. 9 show that nickel, upon steaming, redistributes itself on the aged catalyst surface yielding metal crystallite sizes about half the size of those observed on the calcined (in dry air) catalyst.

Luminescence quenching is also apparent in the 2 wt% vanadium-loaded catalysts; in addition a new band appears (Fig. 10). Vanadium naphthenate and the untreated vanadium-loaded catalysts have similar luminescent behavior in the 350-nm region. At the 550-nm spectral region, however, the vanadium-loaded catalyst exhibits a broad emission band which is not evident in the vanadium naphthenate emission spectrum. After aging the vanadium-loaded catalyst, this 550-nm band dominates the emission and the intensity of the 350-nm band is almost nonexistent. The irreversible LaY luminescence quenching in the steamed catalysts (Figs. 11 and 12) suggests that upon deposition on the surface, vanadium interacts with the zeolite destroying the catalyst activity. X-Ray diffractograms of the vanadium-containing catalysts shows

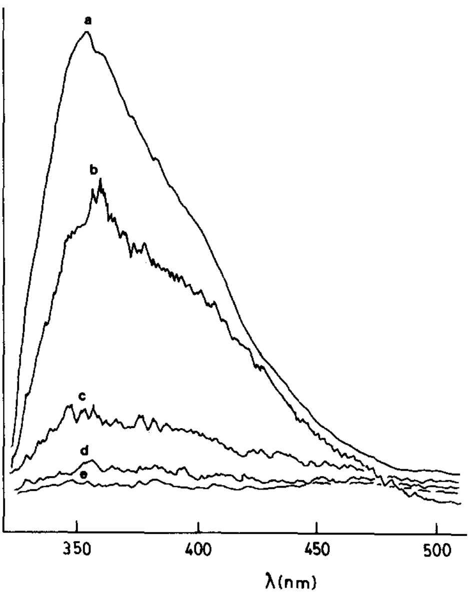

FIG. 11. Luminescence emission quenching of vanadium on LaY after aging. (a) 0.0% V; (b) 0.5% V; (c) 1.0% V; (d) 1.5% V; and (e) 2.0% V. Excitation wavelength = 300 nm; steam deactivated.

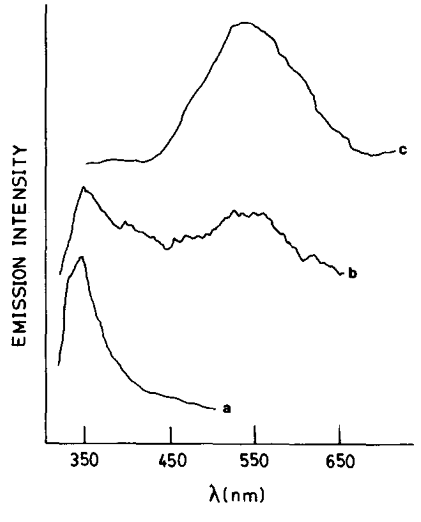

FIG. 10. Emission spectra of vanadium naphthenate. (a) Before deposition; (b) after deposition (2% V) and calcination; and (c) after aging of the catalyst with 2% V. Excitation wavelength = 300 nm.

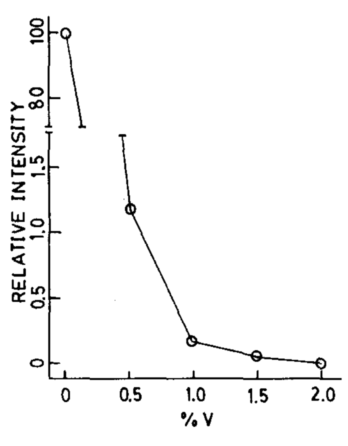

FIG. 12. Quenching of LaY emission (at 360 nm) by vanadium after catalyst aging. (a) 0.0% V; (b) 0.5% V; (c) 1.0% V; (d) 1.5% V; and (e) 2.0% V.

a decrease in crystallinity with vanadium concentration (Fig. 13). The decrease in intensity of the characteristic peak at $2\theta = 23.8°$ correlates well with the luminescence emission quenching exhibited by vanadium-loaded LaY samples (Fig. 12).

Roozenboom *et al.* (*18*) have shown that V_2O_5 forms on the surface of γ-Al_2O_3 and SiO_2 at very low metal loadings: 0.5% for γ-Al_2O_3 and 1.2% for SiO_2. Anpo *et al.* (*19*) have reported luminescence emission spectra of V_2O_5 on porous Vycor glass which closely resemble those obtained in the present study. The luminescence observed in vanadium-loaded catalysts is attributed to a surface species very similar in structure and luminescence properties to those of V_2O_5. It is believed that catalyst LaY oxygens are part of this species. Anpo *et al.* (*19*) have attributed V_2O_5 luminescence to the V=O bonds. Bond calculations for V=O of the V_2O_5 system, similar to those of Iwamoto *et al.* (*20*) obtained from the luminescence spectra, show the progressive V=O formation upon deposition of vanadium on the catalyst and its subsequent hydrothermal treatment (Table 2).

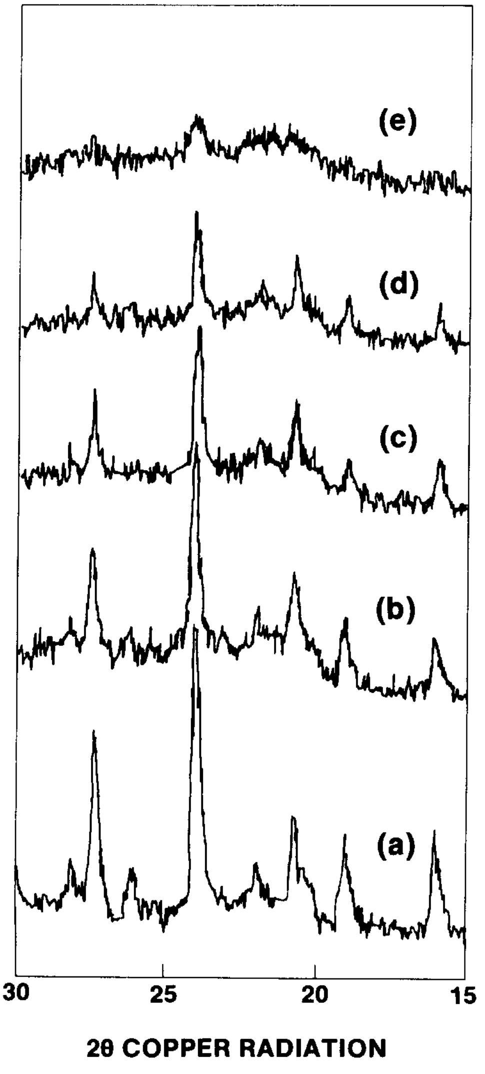

FIG. 13. X-Ray diffractograms showing vanadium effects on crystallinity. (a) 0.0% V; (b) 0.5% V; (c) 1.0% V; (d) 1.5% V; and (e) 2.0% V. Catalysts were aged for 10 h at 730°C, with 95% steam at 1 atm.

TABLE 2

Calculated V=O Bond Lengths for the Vanadium–Catalyst System

Sample	Bond length (Å)
V_2O_5	1.54 (Ref. (*20*))
2% V on fresh catalyst	2.27
2% V on aged catalyst	1.60

Luminescence lifetime behavior of vanadium-contaminated catalyst is rather complex (Table 3). In all the samples tested, T_1 is very short (exceeds instrumental limits) but is, nevertheless, present. A definitive assignment to T_1 is not possible since this short lifetime is present in all the samples. If vanadium on the inert support (clay) is assumed to be a nonquenched surface spe-

TABLE 3

Luminescence Emission Lifetimes of LaY, Vanadium Naphthenate, Fresh Catalyst, and Vanadium-Loaded Catalysts

Sample	T_1; % Int.	T_2; % Int.	T_3; % Int.
V naphthenate	<0.5; 69.49	11; 11.91	125; 18.60
LaY	<0.5; 76.49	—	130; 23.50
Fresh catalyst	<0.5; 78.77	—	131; 21.23
2% V on inert support	<0.5; 84.50	7.98; 3.89	118; 11.61
2% V on fresh catalyst	<0.5; 68.26	61.5; 4.70	136; 27.23
2% V on aged catalyst	<0.5; 60.23	38.8; 10.95	172; 28.99

cies, with respect to the T_1 component, then a decrease can be observed in the contribution (of the very short-lived species, T_1) to the percentage intensity of the decay when vanadium is deposited on the fresh catalyst surface and steam aged. This decrease could be attributed to the luminescence quenching of the LaY emission by vanadium.

The middle lifetime component, T_2, is instead in the microsecond regime and is attributed to the presence of vanadium since it appears only in vanadium-containing samples. Fresh and aged catalysts loaded with 2% V have longer T_2 and T_3 values than V naphthenate and 2% V on an inert support. Apparently, a new vanadium species is formed on the fresh catalyst which changes on aging. The third lifetime component (T_3), is also present in the microsecond regime, but luminescence from LaY in the same time frame complicates its interpretation. T_3 of the aged vanadium catalyst approaches that reported for a V_2O_5 species (218 ± 5 μs), supporting the argument for surface V_2O_5 formation (*20*).

CONCLUSION

Luminescence and luminescence lifetime experiments provide a wealth of information regarding catalyst surface–metal interactions. It was possible to correlate the loss of luminescence intensity and total metal surface coverage in nickel-loaded catalysts. Furthermore, luminescence emission spectroscopy and luminescence lifetime information can be used to identify a surface species (V_2O_5) formed upon deposition of vanadium naphthenate on the catalyst surface. A decrease in catalyst activity with the formation of such species and the identification of such species with luminescence spectroscopy suggests that these identification techniques could be used as a diagnostic tool to predict catalysts' behavior.

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