JOURNAL OF CATALYSIS **134**, 469–478 (1992)

# Hydrothermal Aging of Cracking Catalysts

## V. Vanadium Passivation by Rare-Earth Compounds Soluble in the Feedstock

BÉATRICE FÉRON,*,[1] PIERRE GALLEZOT,*,[2] AND MICHEL BOURGOGNE†

**Institut de Recherches sur la Catalyse (CNRS), 2 avenue Albert Einstein, 69626 Villeurbanne Cedex, France; and †TOTAL Research Center, B.P. 27, 76700 Harfleur, France*

Received April 30, 1991; revised October 7, 1991

This study was designed to passivate vanadium on an ultrastable Y zeolite-based FCC catalyst. The passivating agents are rare-earth compounds soluble in hydrocarbons (dysprosium and samarium naphthenate, lanthanum octoate) which are introduced on the catalyst at the same time as vanadium naphthenate. Adsorption measurements show that more than 90% of the zeolite structure is preserved after high-temperature hydrothermal treatments when La/V = 1. High-resolution analytical microscopy shows that vanadates ($SmVO_4$, $LaVO_4$), in the form of small particles, are formed on the surface of the catalyst grains on the matrix and both on the external surface and in the mesopores of the zeolite. The gasoline yield measured with a microactivity cracking test is maintained at a high level, but coke and hydrogen yields remain higher than those on an unpoisoned catalyst.

## INTRODUCTION

There have been many attempts to passivate metal poisons such as nickel or vanadium to prevent them from poisoning the activities and selectivities of fluid catalytic cracking (FCC) catalysts. Most of the passivation processes claimed in the patent literature involve a modification of the catalyst formulation usually by incorporating passivating agents which combine with the metal poisons to form stable associations under the conditions encountered during passage of the catalyst either in the reactor or in the regenerator. Successful passivation processes for nickel were found early on (*1*), but vanadium passivation is a more difficult problem. Indeed, under the high temperatures and high steam partial pressures existing in the regenerator, vanadium, even in small amounts, transforms the faujasite structure into thermodynamically more stable aluminosilicates. In previous work (*2*) we have shown that vanadium combines with the extra-framework alumina of ultrastable Y (USY) zeolites to form an aluminum vanadate which is unstable above 650–700°C. Vanadium freed by the vanadate decomposition then catalyzes the transformation of faujasite into mullite at temperatures as low as 700°C. In acid-extracted USY the transformation of the silica-rich faujasite into cristobalite occurs at temperatures lower than 700°C (*2*).

The vanadium passivation processes described in the literature involve addition onto the FCC catalyst of many different types of solid phases including "sacrificial zeolites" (*3*), sepiolite (*4*), various oxides (*5, 6*), especially basic ones (*7,8*), tin (*9*), phosphorus (*10*), and germanium (*11*). The passivation of vanadium by rare earths (RE) introduced by impregnation or ion exchange is described in a few patents (*12*). Except in a few cases (*4, 5, 7*) there are no clear guidelines nor scientific bases supporting the choice of the passivating agent. Further-

---

[1] Present address: Laboratoire des Matériaux Minéraux, URA 428, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France.

[2] To whom correspondence should be addressed.

0021-9517/92 $3.00

more, most of the processes imply a change in the catalyst composition so that the amounts of passivating agent cannot be easily adapted to match variable amounts of vanadium in different feedstocks.

In a previous work (*13*) we showed that vanadium combines with the $La^{3+}$ ions of a LaY zeolite at temperatures as low as 600°C. The $LaVO_4$ compound thus formed was stable under the most severe hydrothermal treatment conditions. Since they react readily with vanadium to form stable $REVO_4$ vanadates, lanthanum or other rare-earth compounds are potentially good passivating agents. Therefore the aim of the present work was to use lanthanum and two other rare earths, dysprosium and samarium, to act as vanadium scavengers on a USY zeolite-based commercial FCC catalyst. More specifically, rare-earth compounds soluble in hydrocarbons were used so that the catalyst would not have to be modified; rather the passivating agent could be added to the feedstock in amounts proportional to the concentration of vanadium in the feedstock.

## EXPERIMENTAL

### *Materials and Treatments*

The starting material was a rare-earth-free industrial FCC catalyst based on a USY zeolite. The catalyst was subjected to a so-called equilibration treatment which consisted of heating the catalyst (100-g batch) at 770°C for 15 h under 100% steam. The equilibrated catalyst, designated Cat, was impregnated with toluene solutions of vanadium naphthenate (Pfaltz and Bauer, 3 wt% vanadium) with or without soluble rare-earth compounds. Dysprosium and samarium naphthenates were purchased from Strem Chemicals. Lanthanum octoate dissolved in a mineral spirit (12 wt% metal) was kindly supplied by Rhône-Poulenc. The impregnation was carried out at 60°C in a rotating evaporator. After evaporation of the solvent, the catalysts were calcined in air by heating at 2°C/min to 600°C. The catalysts (15-g batch) were aged under hydrothermal conditions in a quartz cell; standard conditions involved heating at 700°C for 5 h in flowing air with 20% steam produced by vaporization of water injected with a syringe pump.

Adsorption–desorption isotherms of nitrogen were measured by volumetry after outgassing the samples at 300°C. The micropore volume, $V_m$, was obtained by extrapolation of the pseudo-plateau of the isotherm on the ordinate axis. The crystal fraction of the zeolite was defined as $C_{ADS} = 100\ V_m(\text{catalyst})/V_m(\text{reference})$.

High-resolution transmission electron microscopy (TEM) was performed with a Jeol 100 CX microscope equipped with high-resolution pole pieces (resolution on lattice: 0.144 nm). The catalysts were embedded in an epoxy resin and cut with an ultramicrotome equipped with a diamond knife. Analytical electron microscopy was carried out with an energy-dispersive, X-ray emission spectrometer (EDX) attached to a field-emission gun scanning transmission electron microscope (STEM) VG HB 501. Because the electron probe is smaller than 1 nm, the spatial resolution of analysis is about $(1.5 \times 1.5)\ nm^2$.

The activities and selectivities of the catalysts were evaluated with a standard microactivity cracking test (MAT). The feedstock, an atmospheric resid, was injected for 20 s on 5 g of catalyst previously activated in flowing air and in nitrogen at 530°C. The product distribution was established by a complete analysis of the gas and liquids formed and of the residual solids on the catalyst. The conversion is defined as the sum of the gasoline, gas, and coke yields.

## RESULTS

Table 1 gives the composition of the different catalysts studied and the crystal fraction of the zeolite (i.e., the undestroyed portion), the equilibrated catalyst (Cat) being taken as reference. The reaction data are given in Table 2.

### *1. Passivation by Dysprosium*

After a standard hydrothermal treatment, the crystal fraction of the catalyst impreg-

TABLE 1

Crystal Fraction of the Zeolite in the Catalysts

| Catalysts | V (wt%) | RE (wt%) | RE/V (molar) | $C_{ADS}$[a] (%) |
|---|---|---|---|---|
| Cat | 0 | 0 | | 100 |
| cat 0.8V | 0.8 | 0 | 0 | 33 |
| cat 0.8V, 6.6Dy | 0.8 | 6.6 | 2.6 | 94 |
| cat 0.8V, 2.0Dy | 0.8 | 2.0 | 0.8 | 92 |
| cat 0.8V, 1.2Dy | 0.8 | 1.2 | 0.5 | 81 |
| cat 0.8V, 5.9Sm | 0.8 | 5.9 | 2.5 | 92 |
| cat 0.8V, 2.1Sm | 0.8 | 2.1 | 0.9 | 70 |
| cat 0.8V, 5.4La | 0.8 | 5.4 | 2.5 | 99 |
| cat 0.8V, 3.8La | 0.8 | 3.8 | 1.7 | 97 |
| cat 0.8V, 3.3La | 0.8 | 3.3 | 1.5 | 95 |
| cat 0.8V, 2.2La | 0.8 | 2.2 | 1.0 | 91 |
| cat 0.8V, 1.1La | 0.8 | 1.1 | 0.5 | 86 |
| cat 1.1V, 6.2La | 1.1 | 6.2 | 2.0 | 100 |
| cat 1.0V, 4.2La | 1.0 | 4.2 | 1.5 | 94 |
| cat 1.1V, 3.0La | 1.1 | 3.0 | 1.0 | 90 |
| cat 0.8V, 1.8La | 0.8 | 1.8 | 0.8 | 87 |

[a] $C_{ADS}$, crystal fraction of the zeolite deduced from the micropore volume ($V_m$) with respect to $V_m$(Cat). $C_{ADS} = 100\ V_m/V_m(\text{Cat})$.

nated with 0.8 wt% vanadium is as low as 33%. In contrast the catalysts coimpregnated with dysprosium naphthenate keep a high crystal fraction (Table 1). There is no need to add a large excess of dysprosium; thus for a ratio Dy/V = 2.6, $C_{ADS}$ (94%) is only slightly higher than for Dy/V = 0.8 (92%). Figure 1 gives a TEM view through an ultramicrotome cut of cat 0.8V, 6.6Dy. The zeolite grain is easily recognizable thanks to the images of the (111) lattice planes. There are many 3- to 6-nm-large contrasted spots inside the zeolite crystal and a 4-nm-thick crust on the edge of the zeolite

TABLE 2

Microactivity Cracking Test Data

| Catalysts | RE/V | Yield (wt%) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | Gas | | Gasoline | Coke | Conversion[a] | Gasoline[b] selectivity (%) | LCO[c] | Slurry[d] |
| | | $C_1$–$C_4$ | $H_2$ | | | | | | |
| Cat | 0 | 16.1 | 0.04 | 40.4 | 2.0 | 58.5 | 69.0 | 15.2 | 26.3 |
| cat 0.3V | 0 | 12.6 | 0.6 | 35.5 | 5.1 | 53.2 | 66.8 | 16.8 | 30.0 |
| cat 0.8V | 0 | 6.2 | 0.6 | 17.5 | 5.9 | 29.6 | 59.6 | 14.7 | 55.7 |
| cat 0.8V, 2.1Sm | 0.9 | 8.8 | 0.6 | 27.4 | 5.8 | 42.0 | 65.2 | 16.3 | 41.7 |
| cat 0.8V, 5.9Sm | 2.5 | 13.7 | 0.3 | 37.0 | 4.1 | 54.8 | 67.5 | 15.7 | 29.5 |
| cat 0.8V, 1.8La | 0.8 | 11.7 | 0.6 | 35.5 | 5.4 | 52.6 | 67.5 | 16.8 | 30.6 |
| cat 1.0V, 4.2La | 1.5 | 14.2 | 0.2 | 41.2 | 3.4 | 58.8 | 70.0 | 16.0 | 25.2 |
| cat 1.1V, 6.2La | 2.0 | 13.9 | 0.3 | 38.7 | 3.6 | 56.2 | 69.0 | 15.6 | 28.2 |
| cat 0.3V, 0.4La | 0.5 | 15.1 | 0.4 | 39.5 | 4.5 | 59.1 | 66.8 | 15.6 | 25.4 |
| cat 2.0La | | 15.5 | 0.04 | 43.1 | 2.2 | 60.8 | 71.0 | 15.5 | 23.7 |

[a] Conversion is the total of gas, gasoline, and coke yields.

[b] $C_5$–$C_{12}$ fraction.

[c] Light cycle oil, boiling point between 220 and 350°C.

[d] Slurry: boiling point >350°C.

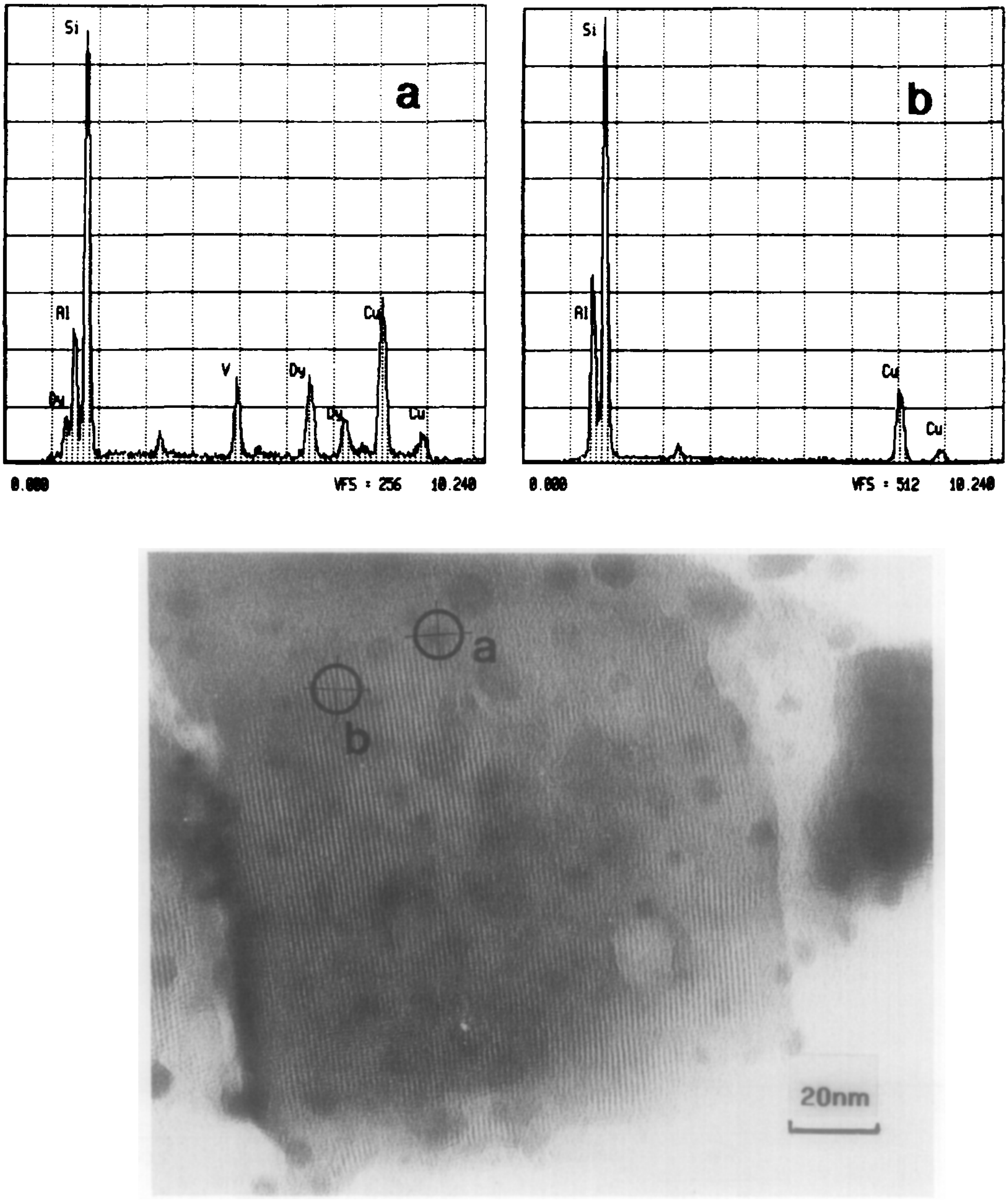

FIG. 1. TEM view through an ultramicrotome cut of cat 0.8V, 6.6Dy. (a) EDX spectrum taken on a particle, (b) EDX spectrum in the vicinity of a particle.

microcrystal. These spots and crust were not present in the equilibrated catalyst nor in the catalyst aged in presence of vanadium (*2*). They correspond to a new phase which has been analyzed by STEM–EDX. Spectrum (1), in Fig. 1, taken on the area circling a dark spot shows that, in addition to the silicon and aluminum of the zeolite framework, there is a high concentration of dysprosium and vanadium in a ratio Dy/V = 1. Spectrum (b) taken on a circled area apart from a dark spot shows that there is no dysprosium and vanadium present. The dark spots and crust probably correspond to $DyVO_4$ particles located in the mesopores and on the external surface of the zeolite, respectively. This is confirmed by the presence on the X-ray pattern of cat 0.8V, 6.6Dy of the Bragg reflections corresponding to $DyVO_4$.

### 2. *Passivation by Samarium*

Catalysts coimpregnated with vanadium and samarium naphthenates were aged under standard conditions. Table 1 shows that the crystal fractions are 92 and 70% for the molar ratios Sm/V = 2.5 and 0.9, respectively.

TEM views taken through an ultramicrotome cut of cat 0.8V, 5.9Sm are given in Figs. 2a and 2b. On the former, a 50-nm-thick deposit of particles is clearly observed on the external surface of the catalyst grain. Particles are also detected on the zeolite and on the matrix inside the catalyst grain. Figure 2b shows particles encapsulated in the mesopores and deposited on the external surface of a zeolite crystal. STEM–EDX analysis of the particles inside the zeolite indicates that the Sm/V ratios are close to 1. Some of them form facetted crystals; they correspond to well-crystallized $SmVO_4$. On the other hand, the Sm/V ratios measured on the deposit on the external surface of the grain are in the range of 2 to 4. Because samarium was introduced in great excess with respect to vanadium, the deposit is probably a mixture of $SmVO_4$ and $Sm_2O_3$ particles.

The reaction data from the MAT cracking test are given in Table 2 for samples cat 0.8V, 2.1Sm and cat 0.8V, 5.9Sm. Figure 3 shows that there is a linear relationship between the conversion and the crystal fraction of the zeolite in the different catalysts aged with, or without, samarium naphthenate.

### 3. *Passivation by Lanthanum*

Table 1 and Fig. 4 show that the crystal fraction of the zeolite in the catalyst can be kept higher than 90% by passivation with lanthanum octoate. The TEM study on cat 1.0V, 4.2La shows that there is a deposit of particles on the surface of the catalyst grain (Fig. 5a), on the matrix (Fig. 5b), and in the mesopores of the zeolite (Fig. 5c). In the zeolite, the particles are either isolated or agglomerated on the external surface and in the mesopores, which then appear as dark veins. STEM–EDX analysis of cat 1.0V, 4.2La shows that there is no vanadium nor lanthanum outside the particles. The zeolite and the matrix are thus entirely preserved from vanadium. The isolated particles have a ratio La/V close to 1; they probably correspond to pure $LaVO_4$ also detected on the X-ray pattern. The La/V ratios measured on the deposits either on the surface of the catalyst grain or on the surface of the zeolite and matrix components are between 1 and 3. The deposit could be a mixture of $LaVO_4$ and $La_2O_3$ or, more probably, a mixture of $LaVO_4$ and $4La_2O_5$–$V_2O_5$ since the X-ray pattern exhibits a new line which could correspond to the main line of this solid phase described by Brusset *et al.* (*14*). However, the low concentration of this compound and its high state of division prevents an unambiguous characterization.

Table 2 and Fig. 6 give the reaction data obtained on the catalyst coimpregnated with vanadium naphthenate and lanthanum octoate. Sample cat 2.0La, impregnated with lanthanum octoate but vanadium-free, was studied to check the effect of lanthanum on the cracking pattern.

## DISCUSSION

In a previous paper (*2*) the industrial FCC catalyst used in this investigation was fully characterized before and after poisoning with vanadium. The initial amount of zeolite in the fresh catalyst is 38 and 43% as determined by X-ray diffraction and by adsorption measurements. After the catalyst has been equilibrated by a hydrothermal treatment at 770°C for 15 h under 100% steam, the unit cell shrinks from 24.58 to 24.26 Å because of the dealumination process. We

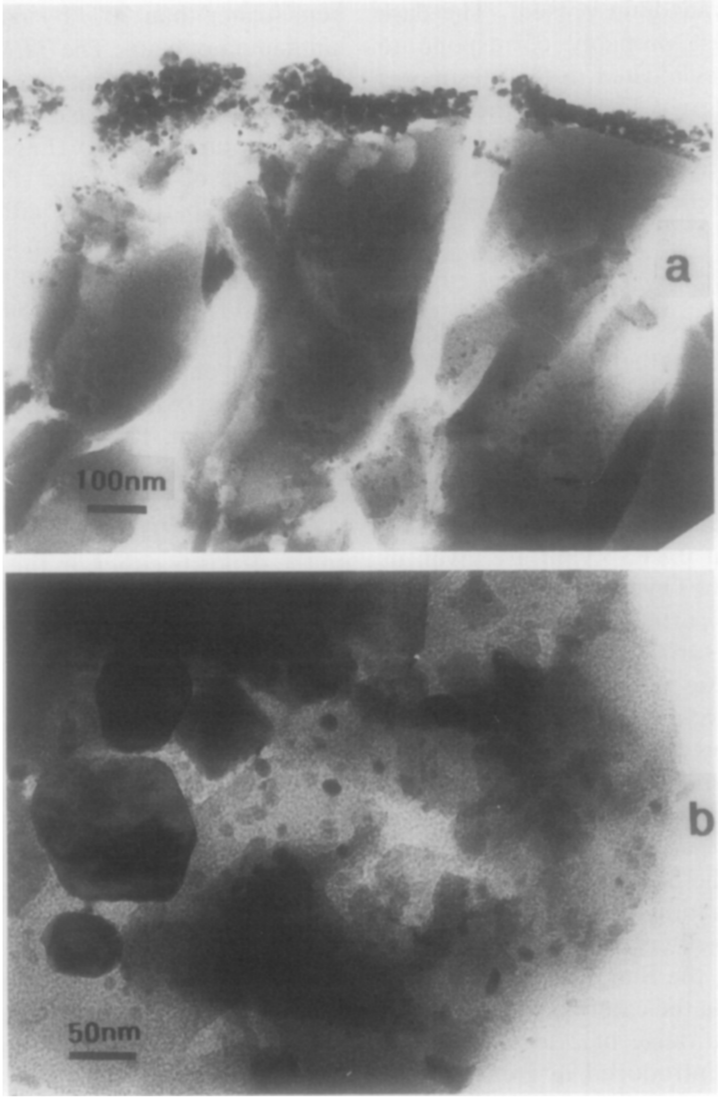

FIG. 2. TEM view through an ultramicrotome cut of a grain of cat 0.8V, 5.9Sm. (a) External surface of the catalyst grain, (b) zeolite with encapsulated $SmVO_4$ particles.

have checked that the standard aging treatment (700°C, 5 h, 20% steam) does not produce further change of the unit-cell constant, crystal fraction, or cracking properties. The equilibrated catalyst, Cat, is taken as a reference sample. After standard aging treatment in presence of 0.8 wt% vanadium, the crystal fraction is 33% with respect to Cat (Table 1). A detailed study (2) of the local composition of the catalyst by TEM and STEM–EDX analysis with a 1-nm spatial resolution showed that vanadium is mostly concentrated on the zeolite which is transformed into mullite and cristobalite after hydrothermal treatments.

### *1. Preservation of the Crystal Fraction*

It is conspicuous from the data given in Table 1 that by adding a rare-earth compound to the toluene solution of vanadium

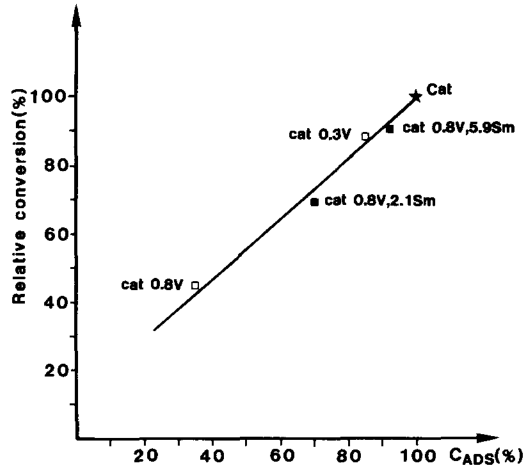

FIG. 3. Conversion vs crystal fraction, $C_{\mathrm{ADS}}$ (both expressed relative to the equilibrated catalyst Cat).

naphthenate that is used to impregnate the catalyst, the crystal fraction of the zeolite can be preserved to a large extent. The best results are obtained with lanthanum octoate and dysprosium naphthenate. Thus the crystal fraction is 99% instead of 33% after adding lanthanum with a ratio La/V = 2.5. However, there is no need to add a large excess of the passivating agent since for the ratios Sm/V = 0.8 and La/V = 1 the crystal fractions are as high as 92 and 91%, respectively.

The role of the passivating agent is easily interpreted in view of the result of the TEM and STEM–EDX studies on the hydrothermally aged catalysts. Indeed, for the three rare-earth compounds used, the vanadium has been found completely trapped in the form of particles of rare-earth vanadate, either the monoclinic $LaVO_4$ or the orthorhombic $DyVO_4$ and $SmVO_4$, while no vanadium can be detected on particle-free zeolite areas. The particles are distributed on the surface of each component of the catalyst, namely the silica-rich envelope, the matrix, and the zeolite. In addition, particles are scattered throughout the secondary pore system of the ultrastabilized zeolite, i.e., in the mesopores created by the dealumination process. They are in the form of well-crystallized individual $REVO_4$ particles (Fig. 2b) or they fill the mesopores, which then appear as dark veins (Fig. 5c). Rare earths introduced in excess with respect to vanadium are mainly concentrated on the external surface of the catalyst grain. Indeed, STEM–EDX analysis of the deposit shows that the RE/V ratios are much larger than 1. TEM photographs (Figs. 2a and 5a) show that this deposit is formed by the agglomeration of small particles that are too close together to be analyzed individually by STEM–EDX. In the case of lanthanum, the deposit is probably a mixture of $LaVO_4$ and of $4La_2O_3$–$V_2O_5$ since the main Bragg reflection of this compound was detected on the X-ray pattern.

To sum up, a high crystal fraction can be maintained because the rare earth and the vanadium organic salt added to the catalyst in the same hydrocarbon solution can easily decompose and react together to give a stable rare-earth vanadate. The concentration of residual vanadium not combined with the rare earth was too low to be detected or to product a large destruction of the zeolite structure.

### 2. *Preservation of the Conversion and Selectivity*

The cracking reaction data obtained on the different catalysts are given in Table 2. As noted previously, the presence of vanadium on the catalyst produces a dramatic loss of the total conversion and of the gasoline yield, while the unwanted production of

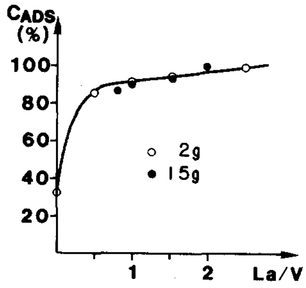

FIG. 4. Crystal fraction vs molar ratio La/V.

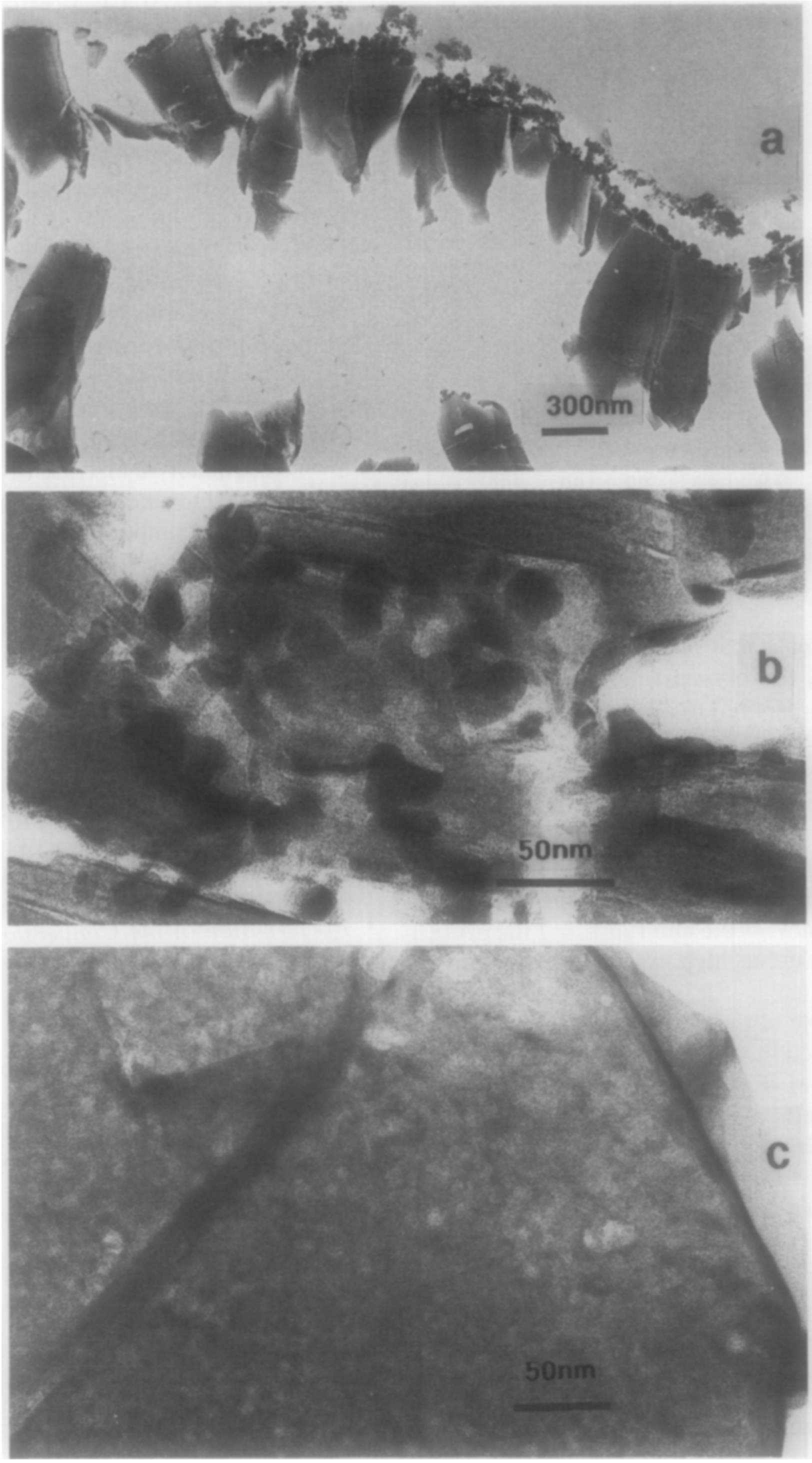

FIG. 5. TEM views through an ultramicrotome cut of cat 1.0V, 4.2La. (a) External surface of catalyst grain, (b) particles on the matrix, (c) deposit on the external surface and in the mesopores of a zeolite crystal.

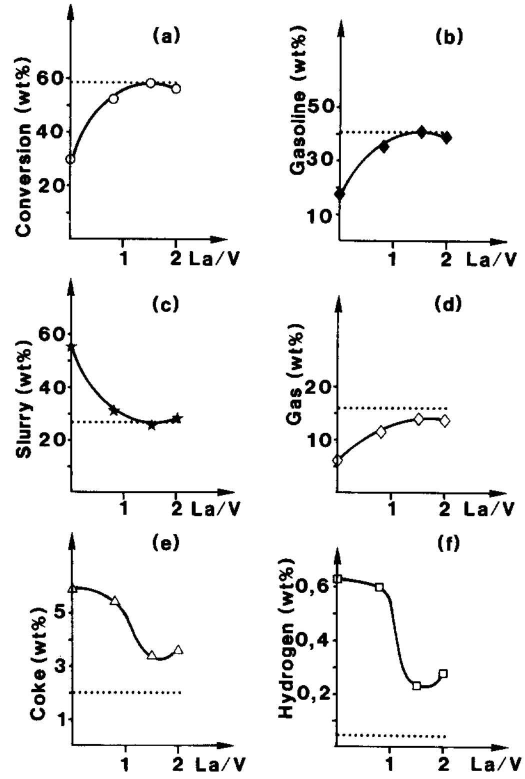

FIG. 6. MAT cracking data vs molar ratio La/V.

coke and hydrogen increases. The coimpregnation with samarium is helpful since the conversion and the gasoline yield are maintained at a reasonable level; however, the coke and hydrogen productions remain very high with respect to those of an unpoisoned catalyst. Figure 3 shows that there is a linear relation between the conversion and the crystal fraction of the zeolite in the different catalysts. This indicates that the cracking activity and especially the gasoline yield are primarily associated with the acid sites in the microporous lattice. The ordinate intercept corresponds roughly to the cracking activity measured on a pure kaolin matrix treated under similar hydrothermal conditions. Lanthanum is a more efficient passivating agent than samarium. Thus for La/V = 0.8 and Sm/V = 0.9, 90% of the conversion is maintained with lanthanum compared to only 72% with samarium. This could be related to the ability of samarium to take two oxidation states [(II) and (III)], and thus the vanadate $SmVO_4$ might not be as stable as $LaVO_4$. Dysprosium, which, like lanthanum, takes only one oxidation state (III), is also more efficient than samarium at maintaining the crystal fraction.

The highest gasoline yield among the V + RE impregnated catalysts (41.2 wt%) was obtained for a ratio La/V = 1.5; it is even better than that of the reference catalyst (40.4 wt%). These better performances are probably due to the excess of lanthanum. Indeed, we have checked that by impregnating the reference catalyst with lanthanum octoate (cat 2.0La, Table 2) the gasoline yield increases from 40.4 to 43.1 wt%. Two factors could account for this improvement: (1) the introduction of lanthanum into the zeolite creates new acid sites which increase the activity of cracking and hydrogen transfer reactions and (2) small paticles of $La_2O_3$ on the surface of catalyst grain, matrix, and zeolite could increase the precracking activity, i.e., the conversion of the slurry into light cycle oil (LCO), which is subsequently converted into gasoline in the zeolite pores.

There is no need to add a large excess of lanthanum octoate; for a ratio La/V = 2 there is no improvement with respect to La/V = 1.5 (Table 2, Figs. 6a and 6b). Practically, a La/V ratio smaller than 1 gives a satisfactory passivation as far as the gasoline yield is concerned. Thus for 0.8 wt% vanadium and La/V = 0.8 (cat 0.8V, 1.8La) the yield is similar to that of a catalyst with only 0.3 wt% vanadium (cat 0.3V). Also for 0.3 wt% vanadium, which is a more realistic concentration of vanadium on a cracking catalyst, a ratio La/V = 0.5 is sufficient to maintain the gasoline production.

As far as the hydrogen and coke yields are concerned, the passivation is not as successful since these unwanted products remain at a high level whatever the amount of the passivating agent (Table 2, Figs. 6e and 6f). The hydrogen and coke yields are closely related because coke is formed on the acid sites by the polymerization of the unsaturated hydrocarbon molecules, which are produced on dehydrogenating sites. Since the structure and texture of the catalyst components are preserved, the dehydrogenation could occur on the vanadate $LaVO_4$ or on $4La_2O_3$–$V_2O_5$. The lanthanum uncombined with vanadium is not involved since the addition of lanthanum octoate on an unpoisoned catalyst does not produce significant amounts of coke and hydrogen (cat 2.0La, Table 2).

## CONCLUSION

This study shows that rare-earth compounds soluble in an organic medium are efficient passivating agents. The main interest of the process, which has been patented (*15*), is that the composition of catalysts need not be modified since the passivating agent can be added in amounts proportional to the concentration of vanadium in the feedstock. This allows a greater flexibility of operation since different vanadium-containing charges can be cracked with the same catalyst. Rare-earth compounds are efficient because they trap vanadium in the form of vanadates which are stable even at the highest temperatures reached in the regenerator unit. The rare-earth vanadates are distributed homogeneously on the different components of the catalyst grains, which avoids clogging of pore mouths on the external surface of the grains.

## ACKNOWLEDGMENT

We thank Dr. Lemaire from Rhône Poulenc for kindly supplying samples of lanthanum octoate.

## REFERENCES

1. McKay, D. L., *Hydrocarbon Process* **97** (1987).
2. Gallezot, P., Féron, B., Bourgogne, M., and Engelhard, Ph., *in* "Zeolites: Facts, Figures, Future" (P. A. Jacobs and R. A. van Santen, Eds.), Vol. B, pp. 1281. Elsevier, Amsterdam, 1989.
3. Eur. Pat. 0063712.
4. Occelli, M. L., *in* "Fluid Catalytic Cracking: Role in Modern Refining" (M. L. Occelli, Ed.), ACS Symposium Series, No. 375, p. 162, 1988.
5. Occelli, M. L., and Stencel, J. M., *in* "Zeolites: Facts, Figures, Future" (P. A. Jacobs and R. A. van Santen, Eds.), Vol. B, p. 1311. Elsevier, Amsterdam, 1989.
6. US Pat. 3,977,963; 4,198,320; 4,283,309; 4,292,169; 4,289,608; Eur. Pat. 0069842.
7. Wormsbecher, R. F., Peter, A. W., and Maselli, S. M., *J. Catal.* **100,** 130 (1980).
8. US Pat. 4,414,098; 4,451,355; 4,465,779; Eur. Pat. 0043358.
9. US Pat. 4,101,417; 4,466,884; 4,504,381.
10. US Pat. 4,397,767; 4,430,199.
11. Eur. Pat. 0038047.
12. US Pat. 4,480,047; 4,432,890.
13. Maugé F., Courcelle, J. C., Engelhard, Ph., Gallezot, P., and Grosmangin J., *in* "New Developments in Zeolite Science and Technology" (Y. Murakami, A. Lijima, and J. W. Ward, Eds.), p. 803. Kodansha, Tokyo, 1986.
14. Brusset, H., Madoule-Aubry, F., Blank, B., Glaziou, J. P., and Lande, J. P., *Can J. Chem.* **49,** 3700 (1971).
15. Maugé, F., Courcelle, J. C., and Gallezot, P., Eur. Pat. 173596.