Quantitative determination of Ni and V in FCC catalysts monitored by ESR spectroscopy

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Calibration mixtures containing Ni^0 and V^{4+} in the range from 500 to 4000 ppm have been prepared using various supports (silica, alumina, titania and ultrastable Y zeolite (USY)) with different particle sizes. ESR measurements revealed a linear relation between the impregnated metal amounts and the registered ESR signal integrals and/or intensities, suitable for the determination of the NiO (reduced to Ni^0) and V^{4+} contents in FCC catalysts, respectively. The amount of NiO in a FCC equilibrium catalyst was determined to about 1300 ppm of a total of 2500 ppm Ni compound present in this sample, whereas the amount of V^{4+} was estimated to about 1800 ppm of a total of 2800 ppm vanadium species. Hence, this catalyst contains about 1000 ppm V^{5+}.

Keywords: FCC catalyst, nickel, vanadium, calibration, ESR spectroscopy

1. Introduction

In fluid catalytic cracking (FCC), nickel and vanadium in the feed are mainly deposited on the surface of the catalyst particles. The effects of these elements are dependent on their oxidation states. V^{4+} is regarded as harmless, whereas V^{5+} has a destructive influence on the zeolite framework structure [1]: V^{5+} forms vanadic acid (H_3VO_4, strong acid) in the presence of steam during regeneration of the FCC catalyst. This acid is liquid under those conditions, and its mobility causes a distribution of vanadic acid throughout the entire catalyst particle, resulting in a destruction of the zeolite framework structure by hydrolysis of the SiO_2/Al_2O_3 lattice. Ni^0 is an active dehydrogenation catalyst, responsible for increased formation of hydrogen and coke. However, the Ni species under investigation will exist as NiO (which can be reduced easily) and other Ni compounds (which are not easily reducible, such as Ni aluminate) due to the FCC equilibrium conditions. In general, the higher oxidation states are expected to exist preferentially in a FCC equilibrium catalyst. Therefore, it is of interest for the refineries operating FCC units to determine the amount of Ni in FCC catalysts consisting of NiO and, additionally, how much of the vanadium refers to harmless V^{4+} and harmful V^{5+}, respectively. In order to evaluate this question, similar deactivation conditions should be applied for lab-deactivated systems as for catalysts deactivated in a commercial FCC unit with respect to the different metal species ratio [2].

While there is a general agreement about the oxidation state of vanadium under different operating conditions, the situation concerning nickel is somewhat more conflicting. The main problem has been to find a suitable analytical technique that is sensitive enough to detect nickel at the 1000 ppm level and at the same time can analyse for different chemical species of Ni present in the same catalyst. Petti et al. [2] have demonstrated the usefulness of photoelectron spectroscopy (XPS) in this context, however, they also clearly pointed out the problems associated with this technique: (1) the detection limit of XPS lies just in the expected concentration range of Ni (1000–3000 ppm), which means that it was not always possible to detect the metal at all, and (2) even if Ni could be detected the overlap of Ni and La (which is one of the minor ingredients in the FCC catalyst) would make an accurate estimation of the amounts of NiO and Ni aluminate difficult.

Bare et al. [3] and Woolery et al. [4] have both shown that EXAFS can be used to detect the two different Ni species on FCC catalysts. Bare et al. [3] using catalysts containing 12000 ppm metal found the Ni to be present as predominantly aluminate. Woolery et al. [4] studied catalysts containing Ni in the range of 1000–5000 ppm and found the ratio of aluminate to oxide to be about 70 : 30. They also showed that lab-deactivated catalysts seemed to contain more oxide than aluminate. They speculated that several factors, such as the processing time, the Ni content and the catalyst composition, had an influence on the amount of either oxide or aluminate formed.

The total amount of nickel and vanadium can be determined through chemical analysis. However, the knowledge of how much of these metals are in the specific oxidation states of V^{4+}/V^{5+} and $Ni^0/Ni^+/Ni^{2+}$ require additional application of a very specific and sensitive method like XPS, EXAFS, as mentioned earlier, or electron spin resonance spectroscopy (ESR). Since ESR is a bulk method (and very sensitive at even low concentrations (few thousand ppm)) compared to the surface specific XPS technique we choose

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the first one for our investigations. Furthermore, ESR is usually easily accessible compared to EXAFS, which requires access to a synchrotron facility. V^{4+} and Ni^0 as well as Ni^+ species are ESR active, while V^{5+} and Ni^{2+} species are not ESR sensitive. Temperature-programmed reduction (TPR) has been used besides ESR in order to transfer the Ni species in the desired oxidation states, since the aim of this study was to determine the amount of Ni as NiO and the ratio of V^{4+}/V^{5+}. This requires the application of proper reduction conditions for NiO to Ni^0 without simultaneous reduction of other Ni compounds, like, for example, Ni aluminate.

The scope of the study was to use calibration mixtures of known amounts of Ni^0 and V^{4+} impregnated on a carrier and to check whether a linear relation exist between the amount of impregnated metals (Ni^0 and V^{4+}) and their ESR signal integral and/or intensity. Furthermore, various carriers such as silica, alumina, titania and ultrastable Y zeolite (USY) were used in order to investigate the influence of different carriers on the ESR line shape and quantitative determination. In addition, the influence of the particle size was studied as well. Finally, in case of linear relations between the amount of impregnated metals (Ni^0 and V^{4+}) and their ESR signal integrals and/or intensities, these calibration curves could be applied to determine the amounts of NiO and V^{4+} (and following V^{5+}) in FCC equilibrium catalysts. In the case of nickel, the impregnated samples must be reduced selectively to Ni^0 and kept at this oxidation state before a quantitative ESR determination can take place.

2. Experimental

2.1. Sample preparation

The calibration mixtures containing Ni^0 in the range of 500–2000 ppm (in the case of a silica carrier) and V^{4+} in the range of 1000–4000 ppm (alumina as carrier, dried at 200 °C) were prepared applying the well known incipient wetness impregnation method using $Ni(NO_3)_2{\cdot}6H_2O$ and $VOSO_4{\cdot}5H_2O$, respectively.

A master recipe is given for the sample 2000 ppm Ni/silica (particle size distribution 60–90 μm) as follows: The silica carrier (SiO_2-40 from Merck) was first dried at 100 °C overnight. 66.4 mg $Ni(NO_3)_2{\cdot}6H_2O$ (Merck) was dissolved in 10 ml distilled water, the mixture was then added to 6.69 g silica (SiO_2-40, Merck) and treated according to the incipient wetness impregnation procedure (three times stirring and knocking) before the mixture was placed in a dry box at 100 °C for 2 h (from time to time stirring and knocking). Finally, the product was dried at 100 °C overnight. The other samples were prepared according to the same procedure.

Similar impregnations using titania (calcined at 900 °C) and USY (CBV 780 from PQ Corporation, calcined at 540 °C) as support were performed. However, the amounts of impregnated ESR sensitive species always corresponded with the same number of metal atoms per volume unit in order to be able to compare quantitatively the ESR signal integrals/intensities of samples with various carriers possessing different densities. The effect of particle sizes on the ESR signal integral/intensity was investigated using different ranges of particle size distributions: 60–90, 60–210 and 210–500 μm, respectively.

2.2. Temperature-programmed reduction (TPR)

The Ni-containing samples were reduced applying TPR procedures (10% hydrogen in argon) according to the following profiles, which represent optimised conditions with respect to a complete reduction and minimum sintering of the catalysts:

Ni on silica: Drying at 120 °C in air for 24 h, TPR up to 825 °C (rate 15 °C/min), kept at 825 °C for 10 min, cooling in 10% hydrogen in argon to RT.

Ni on titania: Drying at 120 °C in air for 24 h, TPR up to 600 °C (rate 15 °C/min), kept at 600 °C for 10 min, cooling in 10% hydrogen in argon to RT.

Ni on USY: Drying at 120 °C in air for 24 h, TPR up to 1000 °C (rate 15 °C/min), kept at 1000 °C for 30 min, cooling in 10% hydrogen in argon to RT.

An AutoChem 2910 instrument from Micromeritics was used, and the nickel samples were treated inertly and finally sealed in ESR quartz tubes in order to preserve the Ni^0 oxidation state.

2.3. Chemical analysis

The total amounts of nickel and vanadium were determined using X-ray fluorescence analysis. A Siemens SRS 303 AS sequential X-ray spectrometer was used based on sample excitation with a rhodium window tube (Ni Kα1.2, LiF crystal, $2\theta = 71.25°$; V Kα1.2, LiF crystal, $2\theta = 123.23°$).

2.4. ESR investigations

ESR measurements were carried out using the Bruker ESP 300 E spectrometer in X-band operating with a microwave frequency of 9.5 GHz (sweep width 6000 G (Gauss)). The modulation frequency was 100 kHz, the modulation amplitude 6.323 G, the sweep time 671 s and the centre field 3500 G, respectively. 500 mg samples in 4 mm quartz tubes were investigated at a temperature of -196 °C.

3. Results and discussion

ESR investigations of Ni- and V-containing supports are reported in the literature, both for micro- and mesoporous materials based carriers as well as for supported oxides

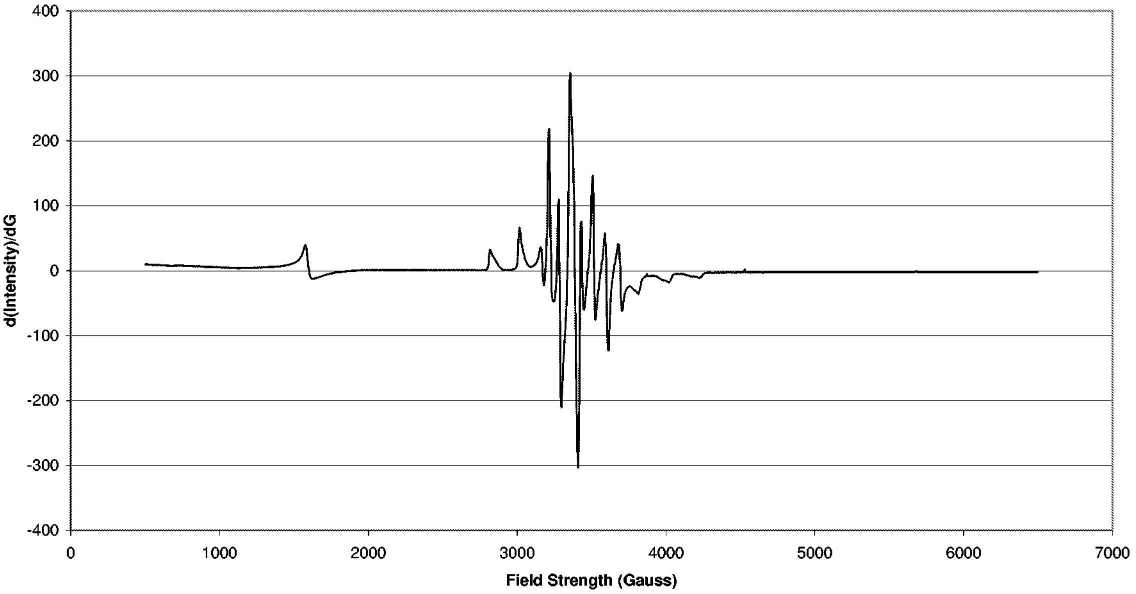

Figure 1. ESR spectrum of 4000 ppm V^{4+}/alumina (dried, particle size distribution 60–90 μm).

catalysts [5–12]. A typical Ni^0 ESR signal consists of an intense but broad peak centred at a magnetic field of about 2950 G in the case of Ni/NaX zeolite (g-value of 2.19). Usually, ESR spectra are recorded as the first derivative of the adsorption signal. However, a very small peak due to Ni^+ can be observed with its centre at about 3130 G in the case of incomplete reduction (g-value of 2.06) of Ni in Ni/NaX zeolite [6]. The ESR spectra of vanadium-impregnated solid catalysts (see figure 1) consist of a hyperfine structured signal centred at about 3355 G, with a g-value of 2.04 in the case of V^{4+}/Y zeolite, characteristic of isolated (not interacting) vanadyl ions [1]. The small signal centred at about 1580 G is due to an iron impurity of the carrier. ESR spectroscopy is a very sensitive technique, detecting and quantifying very small amounts of, for example, V^{4+} below 1×10^{-6} g [1], as also demonstrated in figure 1 for the case of 4000 ppm V^{4+} impregnated on alumina.

Usually, quantitative ESR signal amplitudes are registered as the measured signal integrals. However, as long as the ESR transitions consist of only one line (including the hyperfine structure), both the measured integral as well as the intensity (measured signal height) can be used for quantitative purposes. Due to base line correction differences we used the signal integral for analysis of the nickel lines and the intensity of the hyperfine structured lines nos. 3 and 4 for investigation of the vanadium signals, since both transitions consist of only one line.

3.1. Nickel

Figure 2 shows the ESR spectrum of the sample 2000 ppm Ni^0/silica with a particle size distribution of 60–90 μm. Again, an intense but broad peak centred at a magnetic field of about 3060 G was recorded due to the Ni^0 species. In addition, a small signal at about 1580 G is always observed, which corresponds to an iron impurity of the carrier.

The Ni^0 ESR signal integral vs. the amount of impregnated Ni for the calibration series Ni/silica (60–90 μm particle size distribution, all Ni reduced to Ni^0) is shown in figure 3. A linear relation between the impregnated Ni amount (0–2000 ppm) and the registered ESR signal integral is observed (regression coefficient of 0.9826). A control experiment showed that a non-reduced sample did not reveal any ESR response.

Various particle size distributions were applied for the silica carrier. It turned out that Ni/silica samples prepared with a particle size distribution in the range of 210–500 μm exhibited a very inhomogeneous metal distribution. Ni/silica samples with a particle size distribution of 60–210 μm revealed a clearly larger ESR Ni signal integral size compared to the corresponding Ni/silica samples with a particle size distribution of 210–500 μm. However, there was only a very small difference (within the experimental error) in the ESR Ni signal integral size between the Ni/silica samples prepared with particle size distributions of 60–210 and 60–90 μm, respectively. In conclusion, samples for the ESR investigations were prepared using particle size distributions close to those of commercial FCC catalysts (60–90 μm).

Various carriers besides silica were used (titania from Aldrich and ultrastable Y zeolite (USY) from PQ Corporation (CBV 780)) in order to investigate a possible effect of those carriers on the ESR Ni signal integral. The amounts of impregnated Ni always corresponded with the same number of metal atoms per volume unit of the samples in order to be able to compare quantitatively the ESR signal integrals of samples with various carriers possessing different densities. However, within the experimental error, the measured ESR signal integrals are independent of the nature of the support, as demonstrated in figure 4, where the

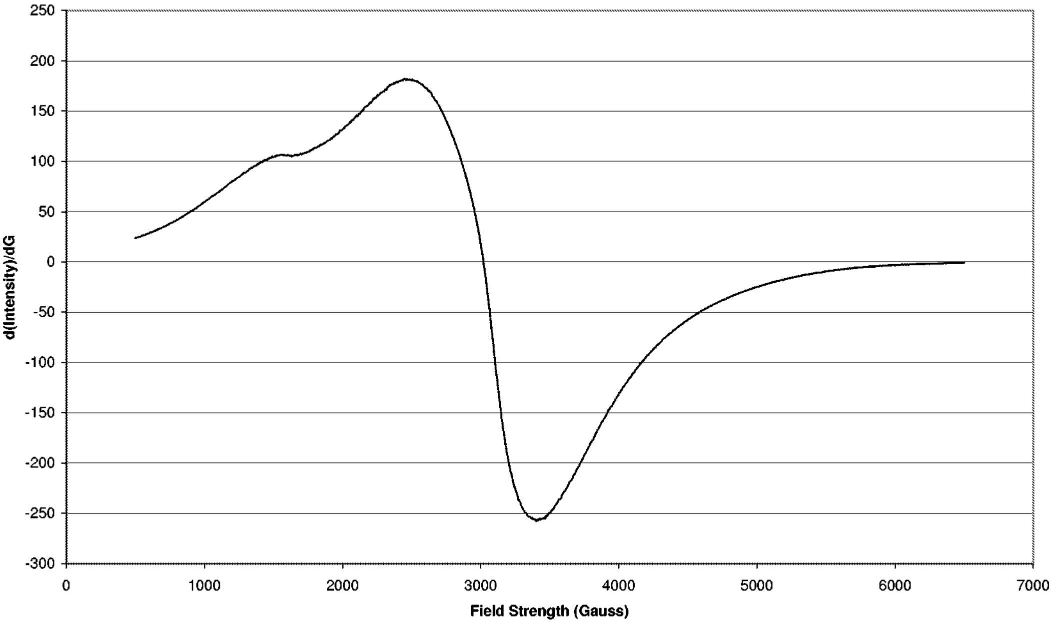

Figure 2. ESR spectrum of 2000 ppm Ni^0/silica (TPR treated at 825 °C, particle size distribution 60–90 μm).

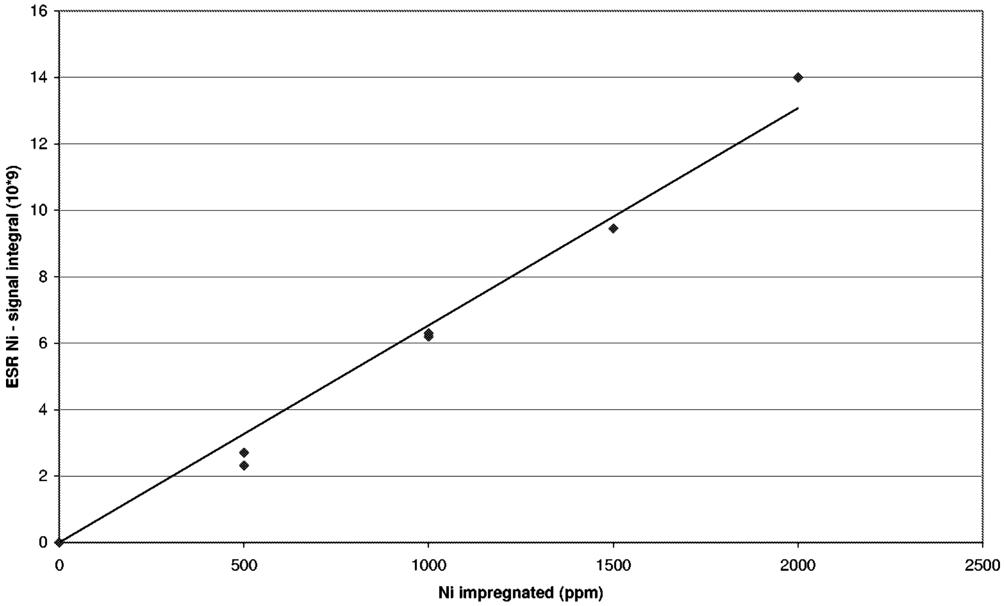

Figure 3. Ni^0 calibration curve for the Ni^0/silica samples (TPR treated at 825 °C, particle size distribution 60–90 μm).

Ni integrals of the samples 1500 ppm Ni^0/silica (9.4×10^9) and 773 ppm Ni^0/titania (9.2×10^9) are compared. On the other hand, the shape of the recorded Ni signals can vary to some extent from one carrier to another.

3.2. Vanadium

Figure 1 shows the ESR spectrum of 4000 ppm V^{4+} impregnated on alumina (dried, particle size distribution 60–90 μm). The spectrum consists of a hyperfine structured signal centred at about 3355 G, characteristic of isolated (not interacting) vanadyl ions [1]. The small signal centred at about 1580 G is due to an iron impurity of the carrier.

The V^{4+} ESR signal intensities for the hyperfine signals nos. 3 and 4 vs. the amount of impregnated V for the calibration series V^{4+}/alumina (60–90 μm particle size distribution) are shown in figure 5. Again, linear relations between the impregnated V amount (0–4000 ppm) and the registered ESR signal intensities are observed (regression coefficients of 0.966 and 0.956, respectively).

Various particle size distributions were applied for the alumina carrier. However, there was only a very small difference (within the experimental error) in the ESR V signal intensities between the V/alumina samples prepared with particle size distributions of 60–210 and 60–90 μm, respectively. In conclusion, samples for the ESR investiga-

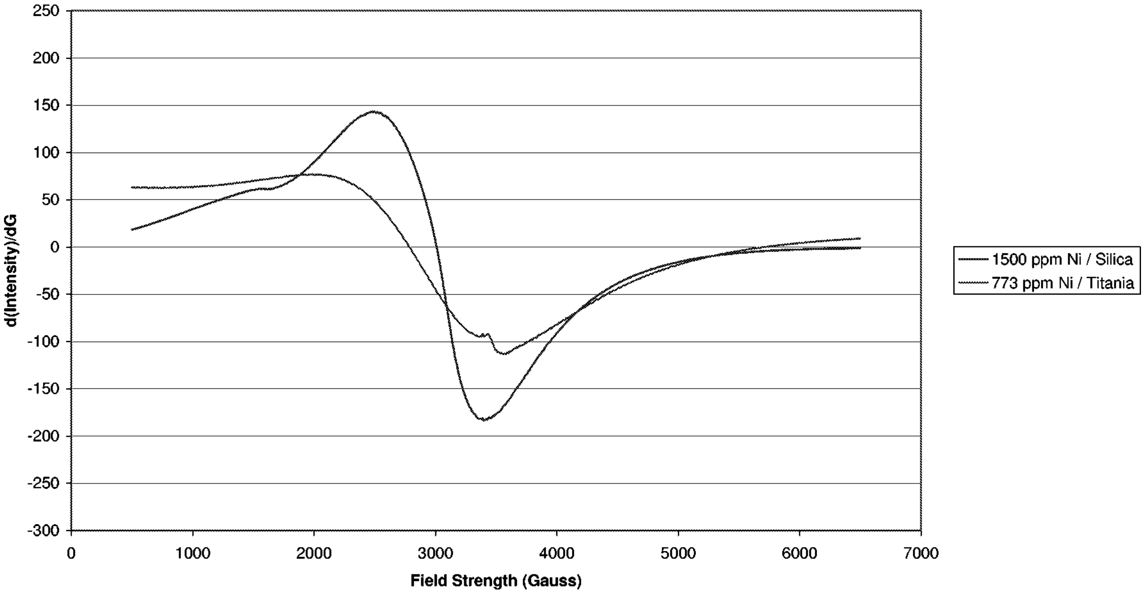

Figure 4. ESR spectra of 1500 ppm Ni^0/silica (TPR treated at 825 °C) and 773 ppm Ni^0/titania (TPR treated at 600 °C). Particle size distribution 60–90 μm.

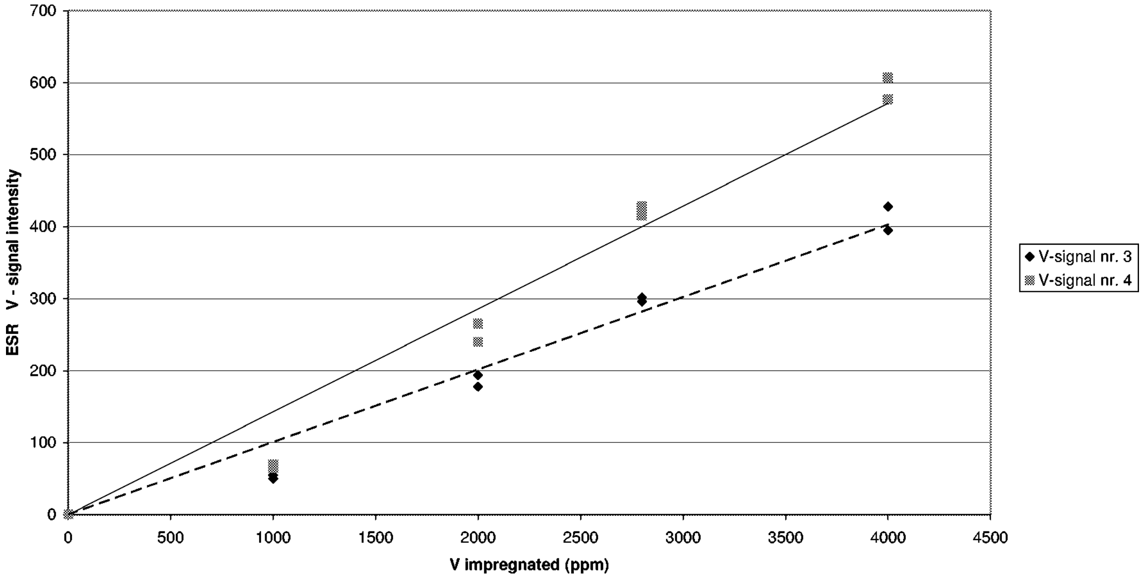

Figure 5. V^{4+} calibration curve for the V^{4+}/alumina samples (dried, particle size distribution 60–90 μm).

tions were prepared using particle size distributions close to those of commercial FCC catalysts (60–90 μm).

A different carrier besides alumina was used (namely silica) in order to investigate a possible effect of this carrier on the ESR V signal intensity. The amounts of impregnated V always corresponded with the same number of metal atoms per volume unit of the samples in order to be able to compare quantitatively the ESR signal intensities of samples with various carriers possessing different densities. Within the experimental error, the measured ESR signal intensities are independent of the nature of the support. However, the V^{4+} ESR signals of the V^{4+}/silica samples were much less resolved compared to those of the V^{4+}/alumina samples, in contradiction to the observation reported by Catana et al. [5]. A possible reason might be the use of different metal oxide sources even so the chemical compositions are equal.

3.3. FCC equilibrium catalyst

Using the Ni^0/silica calibration curve (figure 3) the amount of NiO for an FCC equilibrium catalyst (TPR treated at 825 °C, particle size distribution 60–90 μm) was estimated to about 1300 ppm of a total of 2500 ppm Ni compound present in this catalyst, taking into account the difference in sample density as well. The TPR conditions for the FCC equilibrium catalyst were chosen in order to obtain the following pattern: complete reduction of NiO to Ni^0, however, no reduction of other Ni compounds. The

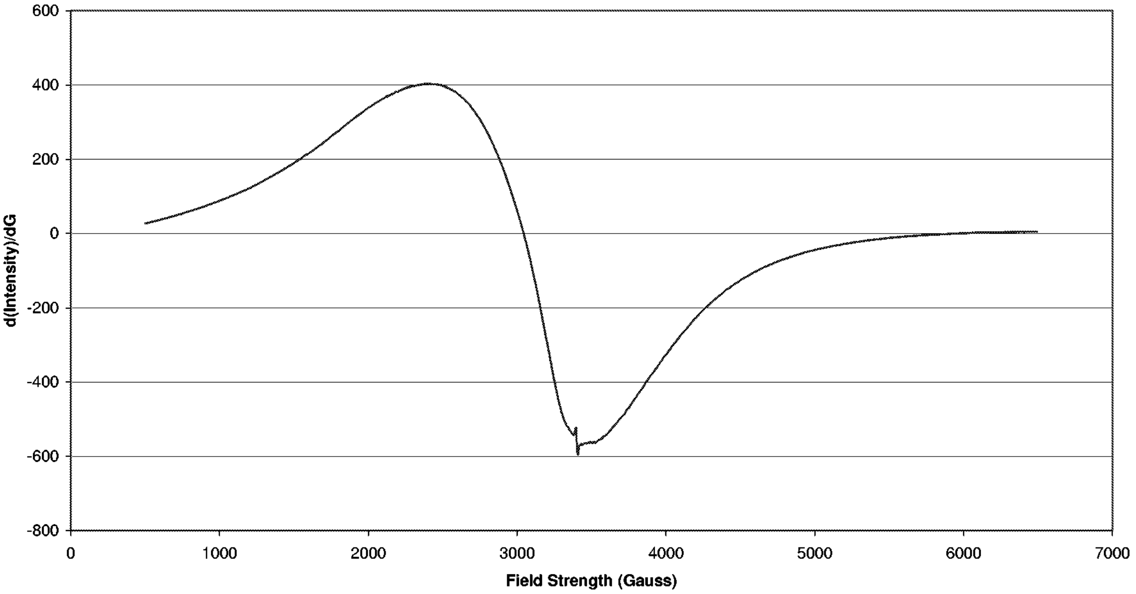

Figure 6. ESR spectrum of the FCC equilibrium catalyst (TPR treated at 825 °C, particle size distribution 60–90 μm).

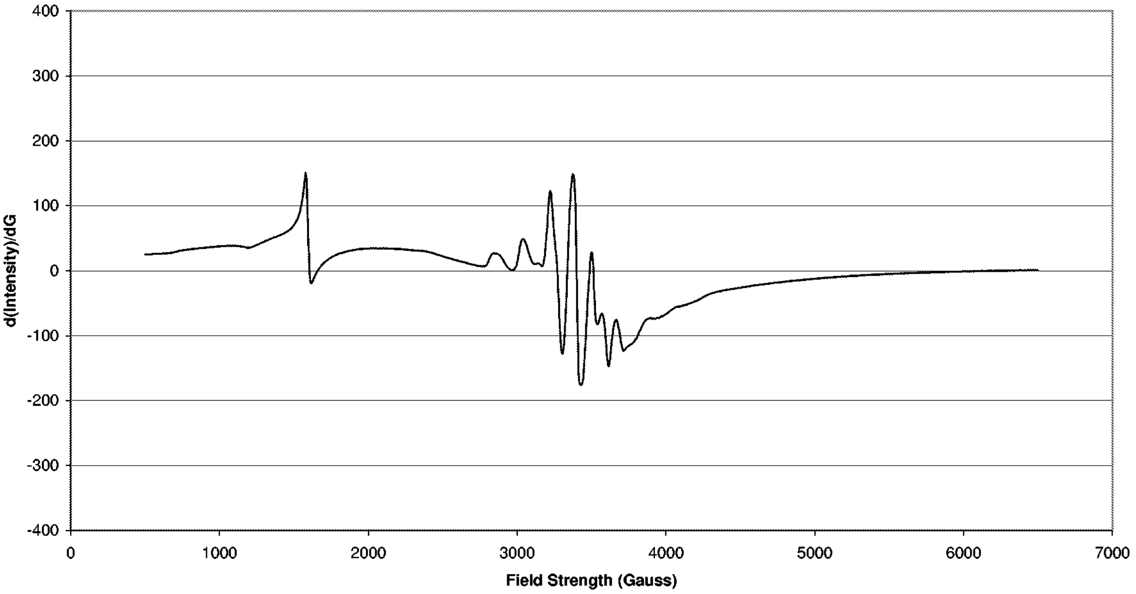

Figure 7. ESR spectrum of the FCC equilibrium catalyst (dried, particle size distribution 60–90 μm).

ESR spectrum of the FCC equilibrium catalyst is shown in figure 6. Besides the broad and intense signal centred at about 3080 G (due to Ni^0 species) a small signal at about 3380 G was observed due to Ni^+ species.

Using the V/alumina calibration curves (figure 5), the amount of V for the same FCC equilibrium catalyst (dried, particle size distribution 60–90 μm) was estimated to about 1800 ppm of a total of 2800 ppm V compound present in this catalyst, taking into account the difference in sample density as well. The ESR spectrum of the FCC equilibrium catalyst is shown in figure 7. The hyperfine structured V^{4+} signal centred at about 3380 G is superimposed by the broad Ni^0 signal. In addition, a small signal centred at about 1580 G is due to an iron impurity of the carrier.

4. Conclusions

ESR spectroscopy allows the determination of small amounts of Ni^0 and V^{4+} species present in FCC equilibrium catalysts (and following the amounts of NiO and V^{5+} as well). A quantitative evaluation of those measurements revealed linear relationships between the impregnated metal amounts (Ni and V, respectively) and the registered ESR signal integrals and/or intensities. The amount of NiO in a FCC equilibrium catalyst was determined to about 1300 ppm of a total of 2500 ppm Ni compound present in this sample, whereas the amount of V^{4+} was estimated to about 1800 ppm of a total of 2800 ppm vanadium species.

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