In Situ Diffuse Reflectance Spectroscopy of Supported Chromium Oxide Catalysts: Kinetics of the Reduction Process with Carbon Monoxide

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In situ diffuse reflectance spectra of supported chromium oxide catalysts are investigated for the first time at elevated temperatures under controlled reaction conditions using a specially designed diffuse reflection attachment. The obtained results are compared and discussed with those obtained by the classical diffuse reflectance spectroscopy technique. A novel method for studying the reduction kinetics of supported transition metal oxides is proposed. In the case of Cr(VI), the reduction is faster on silica than on alumina. A kinetic model is developed to explain the kinetics. It consists of the activation of CO by adsorption followed by the reduction of Cr^{6+} with formation of surface carboxylates.

Introduction

An important class of heterogeneous catalysis involves the interaction between a substrate and a redox active site, i.e. a transition metal ion (TMI). In order to study real catalytic conditions as closely as possible, *in situ* measurements are recommended. Up to now, measurements of the catalytic action under *in situ* conditions were possible with Fourier transform infrared,[1−4] diffuse reflectance infrared Fourier transform,[5−7] Raman,[8−11] X-ray powder diffractometry,[12] and extended X-ray absorption fine structure spectroscopies.[13] Although diffuse reflectance spectroscopy (DRS) is ideally suited for probing the oxidation state and coordination environment of TMI and for their quantitative speciation,[14] its application on supported metal oxide catalysts was not yet possible at high temperature in the presence of substrates.

Here, we present the first data of such an *in situ* DRS approach on supported chromium oxide catalysts. Because this type of catalyst was intensively studied in the past in our laboratory,[15−19] we are able to compare the *in situ* DRS technique with its room temperature counterpart, and consequently, the main advantages and disadvantages of the *in situ* DRS measurements will be discussed. In addition, we propose *in situ* diffuse reflectance spectroscopy as a promising technique for the evaluation of the reduction kinetics of supported chromium oxides. To our knowledge, this method has not yet been reported.

In the literature, there are only a few papers[20−22] which deal with the reduction of supported transition metal oxide catalysts in a solid−gas phase reaction using gas chromatography or mass spectrometry to measure the concentration of the consumed or the produced gas. Using temperature-programmed reduction (TPR), Finch[22] studied the reduction of supported chromium oxide by CO and H_2. While the factors such as Cr loading, calcination temperature, and nature of the reducing agent and the carrier influencing the determination of the kinetic parameters have been discussed by this author, the mechanism of the reduction process, the exact law describing the kinetic behavior, and the determination of the reaction order with respect to the oxide have not.

In the present work, CO reduction of CrO_3 supported on Al_2O_3 and on SiO_2 was investigated in the 400−500 °C temperature range. This is done by quantifying the concentration of Cr^{6+} on alumina and silica in the presence of CO at a fixed temperature as a function of time. A kinetic model is proposed, and the reaction order and the rate constants are estimated.

TABLE 1: Characteristics and Sample Notations of the Supported Chromium Catalysts

sample notation	support	support characteristics[a]	Cr loading (wt %)
Cr−Al-1	Al_2O_3	$S_0 = 365$ m^2/g; $V_p = 2.0$ mL/g	0.1
Cr−Al-2	Al_2O_3	$S_0 = 365$ m^2/g; $V_p = 2.0$ mL/g	0.4
Cr−Al-3	Al_2O_3	$S_0 = 365$ m^2/g; $V_p = 2.0$ mL/g	0.5
Cr−Al-4	Al_2O_3	$S_0 = 365$ m^2/g; $V_p = 2.0$ mL/g	1.2
Cr−Si-1	SiO_2	$S_0 = 735$ m^2/g; $V_p = 0.8$ mL/g	0.5

[a] S_0, BET surface area; V_p, pore volume.

Experimental Section

1. Sample Preparation and Characterization. The supported Cr catalysts were prepared by the incipient-wetness method with aqueous solutions of chromium(VI) trioxide (CrO_3) on alumina and silica supports. These supports were prepared according to procedures described elsewhere.[12] Cr contents were determined by ion-coupled plasma analysis. Characteristics of the catalysts and sample notations are summarized in Table 1. The impregnated samples were dried at 50 °C for 8 h and granulated.

2. Diffuse Reflectance Spectroscopy. *In situ* DR spectra were taken on a Varian Cary 5 UV−vis-NIR spectrophotometer equipped with a specially designed Praying Mantis diffuse reflection attachment (DRA) of Harrick. Its construction with two ellipsoidal mirrors provides that mainly the diffuse component of the reflected light is captured. In conjunction with the Praying Mantis DRA, a stainless steel vacuum/low-pressure reaction chamber is used with quartz windows and with three gas ports for evacuating the chamber and/or for introducing gas. The chamber can be used under static or dynamic conditions. In the last case, the gas passes through the sample. The cell temperature is controlled with an automatic temperature controller (e.g. Harrick Model ATC-30D). The sample is in the middle of a stainless steel block which contains the heating rods and the thermocouple. The measuring head of the thermocouple is situated exactly under the sample. The body of the reaction

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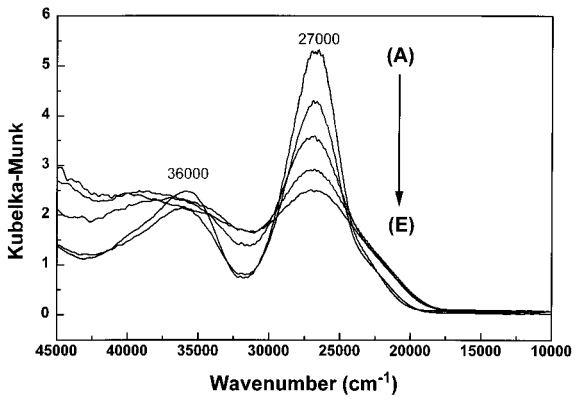

Figure 1. *In situ* diffuse reflectance spectra of the Cr−Al-3 catalyst taken as a function of the calcination temperature: 25 °C (A), 100 °C (B), 200 °C (C), 300 °C (D), and 400 °C (E). Spectra were taken at the indicated temperatures.

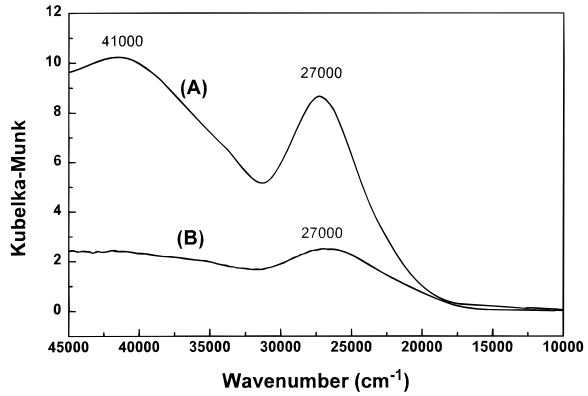

Figure 2. Comparison for the Cr−Al-3 catalyst of (A) the classical diffuse reflectance spectrum at room temperature after pretreament at 400 °C and (B) the *in situ* diffuse reflectance spectrum at 400 °C.

chamber is cooled by circulating water. White reflectance standard $BaSO_4$ (Kodak) was used to take a base line at 25 °C in the Praying Mantis equipment. The thickness of the sample layer is 3 mm, and the amount of catalyst used was around 40−65 mg. Some samples were calcined as a function of temperature in an O_2 flow (1.8 L/h) in the range 25−400 °C in order to study the influence of the heating on the *in situ* DRS spectra. The samples for the kinetic measurements were calcined in an O_2 flow (1.8 L/h) at 500 °C (during 1 h) and then evacuated under He flow (1.8 L/h) at the applied reduction temperature (during 0.5 h). The samples were then reduced in a gas stream of a mixture of CO and He, containing 12.5% CO (1.8 L/h). The computer processing of the DRS spectra with a commercial software package Grams/386 (Galacties Industries Corp.) consisted of (1) conversion to wavenumbers and (2) calculation of the Kubelka−Munk (KM) function.

Results

1. *In Situ* Diffuse Reflectance Spectroscopy. As an example, the *in situ* DR spectra of the Cr−Al-3 catalyst taken at different calcination temperatures are shown in Figure 1. The spectra are characterized by two intense bands at around 27 000 and 36 000−41 000 cm^{-1}, which are the O → Cr^{6+} (d^0) charge transfer (CT) transitions. In addition, a shoulder at 47 000 cm^{-1} (not shown) is present which is due to the alumina support. Upon the calcination temperature being increased, the first CT band broadens and decreases in intensity. Its weak low-frequency shoulder around 22 500 cm^{-1}, on the other hand, becomes more intense. The high-frequency band flattens out, especially toward higher wavenumbers. The increase in the intensity of the 22 500 cm^{-1} shoulder and the flattening of the high-frequency CT band occur at 573 K. This indicates that at that temperature Cr^{6+} is anchored to the support *via* M−O−Cr bonds (M = Si, Al) as was previously concluded from conventional DR spectroscopy.[15,16] Note that the observed changes in the DR spectra are not reversible with temperature because upon heating H_2O is removed and Cr^{6+} is anchored to the surface oxygens.[15,16]

Figure 2 compares the *in situ* DRS spectra of the calcined Cr−Al-3 catalyst with its room temperature counterpart. The following observations are made: (1) all bands become broader upon heating with a significant intensity loss, (2) the 41 000 cm^{-1} band is completely submerged in the background, and (3) there are no significant frequency shifts for the anchored species Cr^{6+} up to 500 °C. Essentially the same results are obtained for the other catalysts. Since the intensity of the CT band (27 000 cm^{-1}) against the Cr loading (wt %) is linear even

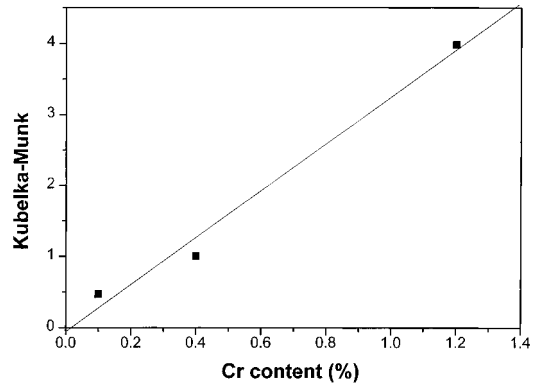

Figure 3. *In situ* DRS of the CrO_3/Al_2O_3 system: influence of the Cr loading on the intensity of the 27 000 cm^{-1} band at 500 °C under O_2 flow.

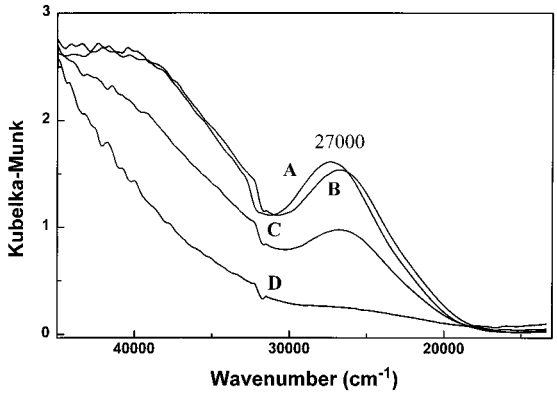

Figure 4. *In situ* diffuse reflectance spectra of the CO-treated Cr−Al-2 catalyst taken as a function of the reduction temperature (reduction time = 0.5 h): 200 °C (A), 300 °C (B), 400 °C (C) and 500 °C (D).

at high temperature (see Figure 3), *in situ* DR spectroscopy can be used to evaluate the reduction process with CO as a function of temperature. This is shown in Figure 4 for the Cr−Al-2 catalyst. Both CT bands of Cr^{6+} gradually decrease upon increasing the reduction temperature and are totally absent after reduction at 500 °C. A weak residual band around 25 000 cm^{-1} and the intensity increase around 15 000 cm^{-1} are indicative for Cr^{3+}.

2. Spectroscopic Method for Measuring Reduction Kinetics. *2.1. Theory.* The overall reduction reaction can be represented as

$$Cr_a + nCO \leftrightarrow Cr_r + nCO_2 \quad (1)$$

where Cr_a stands for anchored Cr^{6+} and Cr_r for reduced Cr. Cr_a

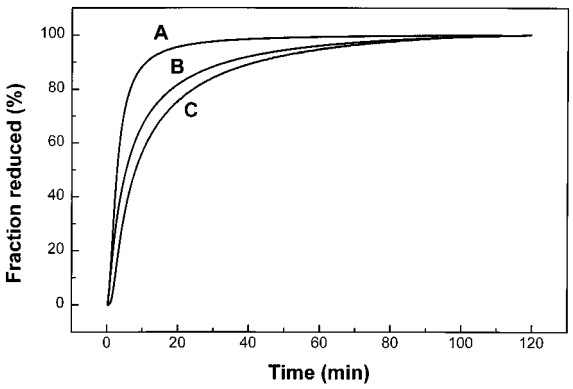

Figure 5. The fraction reduced as revealed by DRS in function of Cr loading: (A) Cr−Al-4, (B) Cr−Al-2, and (C) Cr−Al-1.

can be chromate-like or dichromate-like. The former is predominant on alumina, the latter on silica at the loading of the present investigation.[15,16,18] Cr_r is Cr^{3+} on alumina and a Cr^{3+}, Cr^{2+} mixture on silica.

The corresponding rate equation is

$$\frac{d[Cr_a]}{dt} = k[Cr_a]^{\alpha}[CO]^{\beta} \quad (2)$$

which at constant partial pressure of CO becomes

$$\frac{d[Cr_a]}{dt} = k'[Cr_a]^{\alpha} \quad (3)$$

Equation 3 can be used to determine the kinetic parameters of the reduction if $[Cr_a]$ can be followed as a function of time at constant temperature. The CT band around 27 000 cm^{-1} can be used for that purpose, as its intensity varies linearly with the amount of Cr in the range of loading envisaged (Figure 3). This means that the Kubelka−Munk function is proportional to the loading of Cr^{6+}:

$$F(R_\infty) = (1 - R_\infty)^2/2R_\infty = (K/S) \propto [Cr_a] \quad (4)$$

In other words, the conditions of the validity of the KM function are fulfilled, and the apparent scattering coefficient S is constant. Other conditions are (1) CO gas must flow through the sample and (2) the diffusion limitations must be avoided. First, we carried out a preliminary study to find the optimal working conditions.

2.2. Experimental Conditions. The Praying Mantis reaction chamber can be considered as a fixed bed integral microreactor. The partial pressure of CO in the catalyst bed must be constant. Thus flow rates should not influence the kinetics, and this was verified in the present study for flow rates in the range 10−60 mL/min.

The Cr content affects the rate of reduction but not the shape of the kinetic curves. This result was deduced from experiments carried out on CrO_3/Al_2O_3 samples with 0.1, 0.4, and 1.2 wt % Cr (Figure 5).

The thickness of the catalyst bed does influence the Cr_a intensity profile as a function of reduction time, in that complete reflectance of the nonabsorbed light must be assured. We found that for thicknesses of 2 and 3 mm the reduction curves are the same but that for a 1 mm thickness deviations occur.

In conclusion, the following working conditions were optimal: thickness of the catalyst bed, 3 mm; grain size, 0.4−0.5 mm; flow rate, 30 mL/min.

2.3. Results. Figure 6 shows examples of Cr_a intensities *versus* time profiles of the Cr−Al-2 and Cr−Si-1 catalysts at 450 °C. Similar plots are obtained at other reduction temperatures and Cr loadings. Figure 6 shows that (1) the Cr_a intensity decreases exponentially with reduction time, indicating first-order kinetics, and (2) the reduction is faster on silica than on alumina. The intensity−time profiles can be simulated by a sum of two exponentials, i.e. $y(t) = A_1e^{-t/x_1} + A_2e^{-t/x_2}$ (Figure 6).

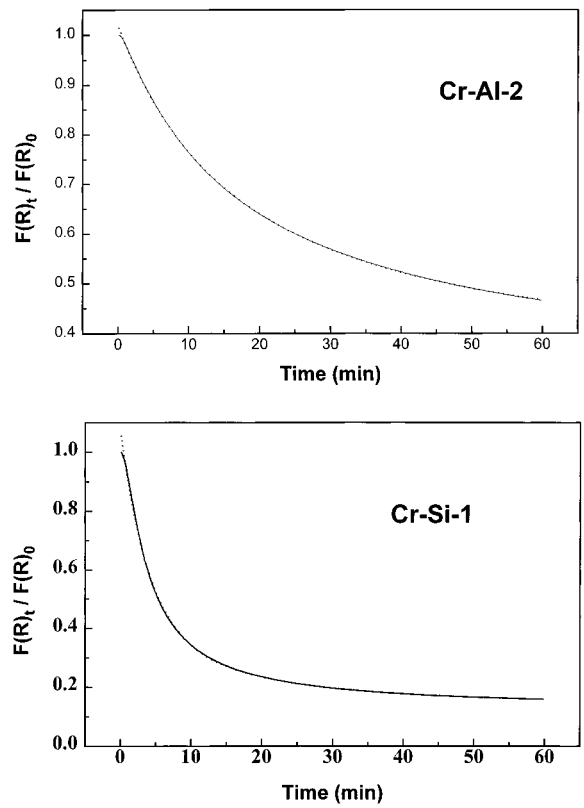

Figure 6. Kinetic curves of CO reduction of the Cr−Al-2 and Cr−Si-1 catalysts at 450 °C: solid line, experimental data and dotted line, bifunction exponential fit.

3. Kinetic Model. Supported Cr catalysts are by definition heteregeneous systems. Chromate- and dichromate-like species are anchored at the surface, and a variety of anchoring sites may be envisaged on the surface of amorphus oxides such as silica and alumina. The CT band at 27 000 cm^{-1}, used to follow the reduction kinetics, contains contributions of all the possible Cr_a species. Therefore, only an overall reduction scheme can be proposed with the oxidation state $m < 6$:

$$Cr_a + CO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr_a(CO)_{ads} \xrightarrow{k_2} Cr^{m+}(CO_2)_{ads} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Cr^{m+} + CO_2\ (m < 6) \quad \text{(I)}$$

The first step is the adsorption of CO on Cr_a; the second one is the reduction, whereby CO_2 remains adsorbed as a carboxylate species. This carboxylate complex then decomposes into CO_2 and a Cr^{m+} species on the surface. This idea of intermediate surface carboxylates was also proposed for the reduction of bulk metal oxides such as TiO_2, SnO_2, and ZnO.[23]

The experimental evidence for a two-exponential decay of Cr_a suggests that intermediate $Cr_a(CO)_{ads}$ is neither in steady state nor in equilibrium with the reactants. It is preferable then to obtain the exact solutions of the rate equations. In addition, by using exact solutions we can calculate three rate constants instead of only one when using the steady state and equilibrium approximations (leading to mono-exponential decay).

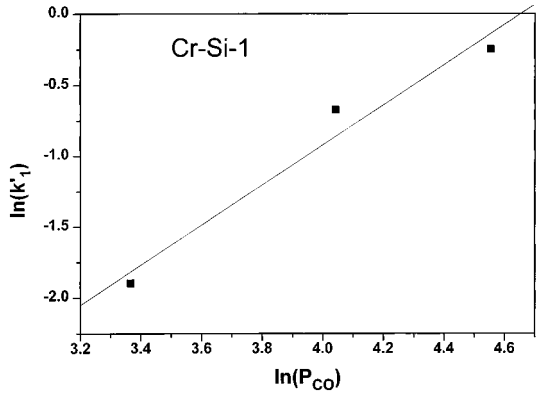

Figure 7. Double-logarithmic plot of the pseudo-first-order rate constant against CO partial pressure of the Cr−Si-1 catalyst.

Using scheme I, one can write

$$\frac{d[Cr_a]}{dt} = k_{-1}[Cr_a(CO)_{ads}] - k'_1[Cr_a] \quad (5)$$

and

$$\frac{d[Cr_a(CO)_{ads}]}{dt} = k'_1[Cr_a] - k_{-1}[Cr_a(CO)_{ads}] - k_2[Cr_a(CO)_{ads}] \quad (6)$$

where k_1' is the pseudo-first-order rate constant (defined as $k'_1 = k_1[CO]^{\beta}$). The following exact kinetic law describing the reduction of Cr_a can be calculated using the chemical matrix formulation[24,25]

$$[Cr_a] = [C_0/(\lambda_1 - \lambda_2)][(k_{-1} + k_2 - \lambda_2)e^{-\lambda_2 t} - (k_{-1} + k_2 - \lambda_1)e^{-\lambda_1 t}] \quad (7)$$

where λ_1 and λ_2 are defined as $\lambda_1 = {}^1/_2(p + q)$ and $\lambda_2 = {}^1/_2(p - q)$ with $p = k'_1 + k_{-1} + k_2$, $q = (p^2 - 4k'_1k_2)^{1/2}$, and $C_0 = (F(R_\infty)_{t=0} - F(R_\infty)_{t=\infty})/K$; C_0 is the initial concentration.

4. Determination of Rate Constants and Reaction Orders. Equation 7 is a sum of two exponentials. Thus, we can write

$$A_1e^{-t/x_1} + A_2e^{-t/x_2} = [(F(R_\infty)_{t=0} - F(R_\infty)_{t=\infty})/K(\lambda_1 - \lambda_2)] \times [(k_{-1} + k_2 - \lambda_2)e^{-\lambda_2 t} - (k_{-1} + k_2 - \lambda_1)e^{-\lambda_1 t}] \quad (8)$$

from which it follows that

$$k'_1 = 1/x_2 - [A_1(1/x_2 - 1/x_1)/(A_1 + A_2)] \quad (9)$$

$$k_2 = [(1/x_2)(1/x_1)]^2/k'_1 \quad (10)$$

$$k_{-1} = (1/x_2) + (1/x_1) - k_2 - k'_1 \quad (11)$$

and indirectly $k_1 = k'_1/[CO]$ if we assume that the reaction order with respect to CO, β, equals 1. We have tried to determine the order in CO by measuring the reduction kinetics for three partial pressures of CO at 500 °C. The double logarithmic plot of Figure 7 does give an order of 1.4 ± 0.60, and we consider 1 to be a reasonable number. The values of A_1, A_2, x_1, and x_2 for Cr−Al-2 and Cr−Si-1 are reported in Tables 2 and 3, respectively, and the calculated rate constants are summarized in Tables 4 and 5. One can deduce from Tables 4 and 5 that (1) CO reduction on CrO_3/SiO_2 catalysts is much faster than that on CrO_3/Al_2O_3 catalysts and (2) the rate constant k_2 is at least 100 times smaller than the other rate constants, which means that the first-order irreversible reaction is the slowest step and consequently rate determining.

TABLE 2: Calculated Fitting Parameters for the Cr−Al-2 Catalyst

T (°C)	x_1 (min^{-1})	x_2 (min^{-1})	A_1	A_2
400	14.06	74.77	119.7	194.0
425	37.94	8.668	43.67	26.38
450	33.37	8.832	42.62	24.70
475	6.09	33.16	45.23	33.28
500	4.455	25.77	39.50	23.00

TABLE 3: Calculated Fitting Parameters for the Cr−Si-1 Catalyst

T (°C)	x_1 (min^{-1})	x_2 (min^{-1})	A_1	A_2
400	5.84	24.22	544.8	411.8
425	3.85	17.55	358.6	293.6
450	4.07	19.95	311.8	97.41
475	2.43	11.57	112.0	48.07
500	1.21	7.625	1368	99.66

TABLE 4: Calculated Rate Constants of the Cr−Al-2 Catalyst

	calculated rate constants			
T (°C)	$10^{+2}\,k'_1$ (min^{-1})	$10^{+2}\,k_{-1}$ (min^{-1})	$10^{+5}\,k_2$ (min^{-1})	$10^{+2}\,k'_1$ (min^{-1} mol^{-1} g)
400	3.5 ± 0.7	4.8 ± 0.9	2.4 ± 0.4	15.1 ± 3.0
425	5.9 ± 1.0	8.1 ± 1.6	15.4 ± 3.0	24.0 ± 4.8
450	6.0 ± 1.2	8.2 ± 1.6	19.0 ± 3.8	26.4 ± 5.2
475	10.3 ± 2.6	8.7 ± 1.5	30.0 ± 6.0	50.5 ± 10.0
500	15.5 ± 3.1	10.5 ± 2.1	47.7 ± 9.5	66.8 ± 13.3

TABLE 5: Calculated Rate Constants Of The Cr−Si-1 Catalyst

	calculated rate constants			
T (°C)	$10^{+2}\,k'_1$ (min^{-1})	$10^{+2}\,k_{-1}$ (min^{-1})	$10^{+5}\,k_2$ (min^{-1})	$10^{+2}\,k_1$ (min^{-1} mol^{-1} g)
400	11.5 ± 2.3	6.0 ± 1.2	43.2 ± 8.6	44.0 ± 8.8
425	16.8 ± 3.3	14.6 ± 2.9	129.7 ± 25.9	64.2 ± 12.8
450	19.9 ± 3.9	9.5 ± 1.9	76.0 ± 15.2	78.6 ± 15.7
475	31.3 ± 6.2	35.9 ± 7.1	401.8 ± 80.3	128.2 ± 25.6
500	73.1 ± 14.6	13.9 ± 2.7	1105.9 ± 221.1	309.2 ± 61.8

When an Arrhenius plot is made of the k_2 values of Tables 3 and 4 (Figure 8), the scattering of the data points prohibits the obtainment of physically meaningful activation energies. There is some indication that the high-temperature slope is different from the low-temperature slopes, both for Al_2O_3 and SiO_2, but looking for interpretation would be too speculative.

Discussion

Heterogeneous catalysts usually act above room temperature in a catalytic reaction after a suitable activation treatment. The fundamental understanding of the heterogeneous catalysis requires knowledge of the nature and amount of the active sites. This knowledge is usually obtained from spectroscopic measurements at room temperature or below, often in conditions far from real activation or catalysis conditions. It is not straightforward to extrapolate the spectroscopic results to real catalytic conditions. There is therefore a need to perform spectroscopic measurements in conditions as close as possible to activation and catalytic conditions. In the present paper this has been attempted with the DRS technique and the reduction of supported Cr catalysts, a common activation procedure of these catalysts.

1. Evaluation of *in Situ* DRS Spectroscopy. As expected, a high-temperature DRS spectrum contains bands which are considerably broadened when recorded at high temperature. If

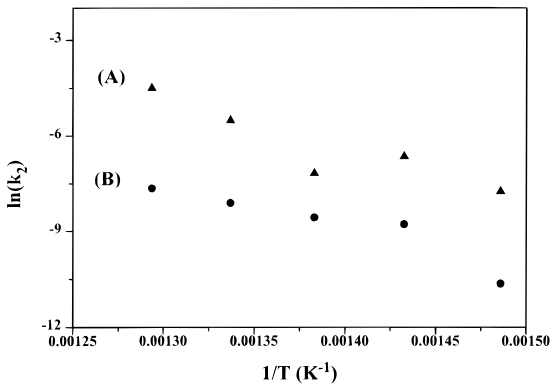

Figure 8. Arrhenius plots of Cr−Si-1 (A) and Cr−Al-2 (B) catalysts.

the bands are characterized by a high molar extinction coefficient (are intense), such as charge transfer bands in general and the O → Cr^{6+} charge transfer in particular, then even at high temperature a linear relation results between the band intensity and the Cr content, similar to what was obtained from room temperature spectra.[15] The 27 000 cm^{-1} band of chromate is such a band. The second O → Cr^{6+} charge transfer band around 40 000 cm^{-1} is (1) broader and (2) superposed on the background spectrum of the support. As a consequence, its high-temperature profile becomes almost undetectable. It cannot be used for quantitative purposes. This was also the case for the room temperature spectra.[15]

As an extention of these observations, one can propose that d−d transitions of transition metal ions will be difficult to measure at high temperature because they are inherently weak (mostly symmetry forbidden) and broad. Only in the case of allowed d−d transitions, and therefore strong bands, may one attempt to do quantitative high-temperature DRS. This is the case for pseudo-tetrahedral complexes.

Finally, our results also indicate that the conditions for application of the Kubelka−Munk theory remain valid in the temperature range investigated. When a chemical reaction such as the reduction of Cr^{6+} has to be studied *in situ* spectroscopically, supplementary conditions have to be fulfilled. The light beam probes some thickness of catalyst bed. This thickness depends on the particle size and shape, the particle density, and the amount of light absorbed. During a reaction, such as the reduction of Cr^{6+} to Cr^{3+}/Cr^{2+}, in which the 27 000 cm^{-1} decreases in intensity with time, the probed sample thickness will slightly change with time. In any case, one must assure that (1) the reactant concentration (CO in our case) is constant over the probed bed thickness and (2) the reaction is homogeneously spread over the probed bed. The optimum experimental conditions have been determined in this paper for the reduction of Cr^{6+} with CO. They will have to be determined for every catalyst−reaction combination experimentally.

2. Kinetics of the Reduction of Supported Chromium Catalysts. In kinetic studies one usually follows the concentration of a reagent or a product with time. With the present *in situ* DRS method the transition metal ion is probed directly. It is therefore complementary to conventional kinetic techniques.

The surface of silica and alumina is by definition heterogeneous. Thus, after activation the anchored (di)chromate species have slightly different chemical environments. This is well-known and gives chromate bands which are broader than those in solution. This phenomenon is called inhomogeneous line broadening. When one then follows the intensity decrease of the O → Cr^{6+} CT band at 27 000 cm^{-1}, one obtains "average" kinetics of the heterogeneous samples.

The first step in reduction is the activation of the reducing agent.[26] According to our model the first step of the reduction is the adsorption of CO on the surface at some unspecified site, resulting from in its activation. The second step, the actual reduction of Cr^{6+}, is rate determining and occurs with formation of surface carboxylates, which decompose to CO_2. The oxygen comes from the chromate or di(poly)chromate species. Thus, the reduction of Cr^{6+} is accompanied by a decrease in the number of oxygens in its coordination sphere, thus leaving empty coordination sites, which can be used for specific adsorption and catalysis. This mechanism invokes a reaction between anchored "chromate" and adsorbed CO. It can therefore be classified as a stepwise mechanism with alternating reduction of the surface and oxidation of the reagent, in which the rate is proportional to the surface coverage of both chromate and CO. The former is constant, and the latter is proportional to the partial pressure of CO (as in unimolecular decomposition following Langmuir law). In that way, the first-order dependence on CO pressure is explained.

The overall reaction order is 2, but taking into account the experimental uncertainties, it is safer to state between 2 and 3. This is exactly what was found by Finch on the basis of TPR study.[22] No explanation was offered at that time. Our model is, as explained, to be considered as an averaged model, which explains the kinetics of the Cr^{6+} reduction in general terms, without taking into account the heterogeneous nature of the surfaces, the presence of different Cr^{6+} species, and the fact that the degreee of reduction may be different for silica and alumina.

In any case, the rate constants of the rate-determining step clearly indicate that reduction of Cr^{6+} on silica is faster than on alumina. Several reasons can be put forward to explain this behavior: (1) whereas there is only chromate on alumina, silica contains chromate and dichromate;[15,18] (2) the Cr^{6+}- - -O (Al) bond is stronger than the Cr^{6+}- - -O (Si) bond; (3) alumina stabilizes intermediate oxidation states such as Cr^{5+} and Cr^{3+}; and (4) these Cr^{5+}, Cr^{3+} species might migrate into the bulk of alumina, where their reduction is much more difficult.

Conclusions

The technique of *in situ* DRS has been proposed to study the reduction kinetics of supported chromium catalysts. Its advantage is that the TMI is probed directly. Therefore, the technique is complementary to more conventional methods. The experimental conditions must be chosen carefully, and we anticipate also that, due to band intensities, not all supported TMI can be studied.

The reduction of supported Cr^{6+} is faster on silica than on alumina. In both cases the overall order is stated between 2 and 3. A model to explain the kinetics is a two-step mechanism: the adsorption of CO to activate it and the reduction, which is rate-determining. On the basis of this model we anticipate (1) the presence of adsorbed CO and (2) carboxylates and possibly carbonates on the surface. *In situ* FTIR studies are in progress to verify these hypotheses and the proposed mechanism.

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