Heats of adsorption of linear CO species adsorbed on reduced Fe/Al$_2$O$_3$ catalysts using the AEIR method in diffuse reflectance mode

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ABSTRACT

IR spectra in diffuse reflectance mode are quantitatively exploited to determine the heats of adsorption of two linearly adsorbed CO species formed on Fe^{2+} and Fe$^{\circ}$ sites (denoted L$_{Fe^{2+}}$ and L$_{Fe^{\circ}}$ CO species) of reduced x% Fe/Al$_2$O$_3$ (wt%, x = 1 and 5) catalysts according to the AEIR procedure developed previously using the IR transmission mode. The IR transmission properties of iron containing catalysts are limited particularly for high iron loadings favoring the use of the diffuse reflectance mode. The heats of adsorption of the L$_{Fe^{2+}}$ CO species linearly vary with the coverage of the sites from $E_{L_{Fe^{2+}(1)}} = 45$ kJ/mol to $E_{L_{Fe^{2+}(0)}} = 66$ kJ/mol at coverage 1 and 0, respectively. These values are modified by the presence of neither Fe$^{\circ}$ sites nor carbonaceous adsorbed species. The heats of adsorption of the L$_{Fe^{\circ}}$ CO species on a C-free iron surface (for adsorption temperature $T_a < 456$ K), linearly vary with its coverage from $E_{L_{Fe^{\circ}(1)}} = 79$ kJ/mol to $E_{L_{Fe^{\circ}(0)}} = 105$ kJ/mol at high and low coverages. For $T_a > 456$ K, the CO dissociation overlaps the CO adsorption equilibrium leading to a C-containing iron surface. The presence of carbonaceous species has no significant impact on the heat of adsorption of the L$_{Fe^{\circ}}$ species at high coverages whereas it increases significantly that at low coverages: $E_{L_{Fe^{\circ}(0)}} = 120$ kJ/mol. Considering reduced iron supported catalysts, the AEIR method is particularly useful because it allows the determination of the individual heats of adsorption of two adsorbed CO species that can be simultaneously present on the surface for high iron loadings. The study confirms that quantitative exploitations of DRIFT spectra are available for well designed experimental conditions offering an alternative for solid catalysts with low IR transmission properties.

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1. Introduction

The main purpose of heterogeneous catalysis is the modification of the kinetic of a chemical reaction by offering a more favorable route. The impacts of the catalyst on the kinetic of the chemical processes can be studied by different approaches. One of them is the microkinetic approach that is based on a series of concepts and principles that have been summarized by Dumesic et al. [1]. Mainly, the catalytic activity of a solid (i.e. measured in Turnover Frequency: TOF in s^{-1}) is determined as a function of the kinetic parameters of the surface elementary steps controlling the global rate of the reaction. These kinetic parameters can be obtained either experimentally or/and by theoretical calculations (i.e. DFT and classical theories). In previous studies, we have shown for different catalytic reactions on conventional solid catalysts (i.e. involving CO as reactant such as CO/O$_2$ [2–6] and CO/NO [7] on Pt/Al$_2$O$_3$, and reconstruction of gold particles on alumina [8]) that

the kinetic parameters of interest can be predominantly obtained by using experimental procedures. This experimental microkinetic approach of the catalytic processes offers different advantages as compared with procedures using either model surfaces (i.e. mono crystals or model particles) or theoretical calculations: it can be a tool for the microkinetic assisted improvement and/or development of catalysts as suggested by Boudart (see foreword of Refs. [1] and [9]).

The experimental microkinetic imposes developing analytical tools and procedures to obtain, from experimental data, the values of the kinetic parameters of the surface elementary steps such as the adsorption coefficients (pre-exponential factor and heat of adsorption), the rate constants (frequency factor and activation energy) and the coverages of the different adsorbed species. The present study is in line with this aim: it shows how IR spectra in diffuse reflectance mode can be used for the determination of the individual heats of adsorption of adsorbed CO species on reduced Fe/Al$_2$O$_3$ solids according to the AEIR (adsorption equilibrium infrared spectroscopy) method developed using the IR transmission mode [10–15] and that has been utilized by others groups using either IR transmission [16] or PMIRRAS [17,18] mode.

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A key point of the AEIR method is that the intensity of an IR band characteristic of an adsorbed species must be proportional to its amount on the surface. This facilitates the exploitation of the experimental data. For the IR transmission mode, this has been verified experimentally for the adsorbed CO species formed on the Pt°- [19], Cu°- [20] and Ir°- [21] sites of reduced metal particles supported on Al_2O_3, by following the change of their adsorption equilibrium coverages using either the absorbance unit or volumetric measurements. In a previous study [22], it has been shown that quantitative exploitation of IR spectra in diffuse reflectance mode can be performed to measure the heats of adsorbed CO species on metal oxides (TiO_2 and CuO/Al_2O_3) using the AEIR procedure, provided that the design of the experiments respects some criteria in line with the works of Matyshak and Krylov [23] and Meunier et al. [24,25]. However, in Ref. [22] we have indicated in the conclusions that we failed applying the AEIR method using the IR cell in diffuse reflectance mode on reduced metal supported catalysts due to a contamination of the gas mixtures by oxygen traces entering by effusion processes through tiny leaks. This was a significant drawback of a DRIFT Cell. In the present study after identifying the location of these leaks, it is shown how to solve this problem, using the measurement of the heats of adsorption of a linear CO species on the Cu° sites of a reduced Cu/Al_2O_3 solid as a proof by comparison with a previous work using IR transmission mode [26]. Then the DRIFT cell is used to measure the heats of adsorption of two linearly adsorbed CO species on Fe^{2+} and Fe° sites of $x\%$ Fe/Al_2O_3 solids ($x = 1$ and 5) having poor IR transmission properties at high loading. The interests of these measurements are linked to the well known catalytic properties of iron containing catalysts for the CO/H_2 reactions [27,28] and they constitute the first step of an experimental microkinetic approach of these reactions.

2. Experimental

2.1. Catalysts and pretreatments

A chlorine free 4.7% Cu/Al_2O_3 (in wt%) catalyst has been prepared using copper nitrate and Al_2O_3 from Rhodia (531P, BET area of 115 m^2/g) according to the incipient wetness method described in more details previously [26]. Briefly, the alumina was impregnated with an appropriated aqueous solution of $Cu(NO_3)_2$, 3 H_2O and then the solvent was evaporated slowly at 353 K. After crushing, the powder was dried at 383 K in air and then treated at 673 K in O_2 to decompose the nitrate. After a purge in N_2, the solid was reduced in H_2 at 773 K during 6 h, cooled to 300 K in H_2, purged in N_2 and stored in air before use. The iron catalysts x wt%Fe/Al_2O_3 ($x = 1$ and 5) were prepared according the same procedure using the appropriate amount of $FeNO_3 \cdot 9H_2O$ and alumina from Degussa (110 m^2/g). After the treatment in air at 713 K, the solids were stored and then reduced in situ on the different analytical systems.

2.2. IR cells

2.2.1. Transmission mode

Few experiments have been performed using a small internal volume stainless steel IR cell in transmission mode described in more detail previously [10]. Briefly, it allowed in situ treatments of a compressed disk of solid ($\Phi = 1.8$ cm, $m \approx 40$–240 mg), in the temperature range of 293–800 K with a controlled gas flow rate in the range of 150–2000 cm^3/min at atmospheric pressure selected using different valves and purified by different traps (in particular a liquid nitrogen trap was positioned before the inlet of the IR cell). This IR cell has been used to develop the AEIR

procedure for the measurements of the individual heats of adsorption of adsorbed CO species on reduced metal particles on alumina such as Pt° [29], Cu° [26] and Ni° [30]. This IR Cell is not adapted for solids with low IR transmission properties such as Fe/Al_2O_3 at high iron loadings, justifying the interest for a DRIFT cell. The FTIR spectrometer used with the transmission IR cell was a Nicolet Protégé.

2.2.2. Diffuse reflectance mode

The DRIFT Cell (Praying Mantis^{TM} type HVC-DR3) was from Harrick Scientific Corporation. The sample of catalyst (≈ 100 mg) was introduced in a small cup positioned on top of an heating cartridge allowing the treatment of the solid in the 300–873 K range (temperature recorded using the thermocouple inserted in the sample holder) with a gas flow rate ($\lesssim 150$ cm^3/min) at atmospheric pressure. The preparation of the catalyst sample for the quantitative exploitation of the IR spectra in diffuse reflectance mode was similar to a previous study [22]: the catalyst is slightly compressed and then crushed and sized to obtained particles of ≈ 100 μm diameter. The gas flow rate passed from the top of the bed of particles to the bottom of the cup. This commercial IR cell has been improved on two main points. Firstly, due to the aims of the AEIR procedure, a second thermocouple (K type coaxial of 0.25 mm) has been positioned on top of the catalyst bed to measure temperature gradient in the sample of catalyst. Secondly, in Ref. [22], dedicated to the measurements the heats of adsorption of adsorbed CO species on $Ti^{\delta+}$ and $Cu^{\delta+}$ sites of TiO_2 and CuO/Al_2O_3 solids using IR diffuse reflectance mode, we have mentioned that we failed to perform similar measurements on the Cu° sites of a reduced 4.7% Cu/Al_2O_3 catalyst. This was due to the contamination of the gas flows by O_2 entering by effusion processes through tiny leaks in the DRIFT Cell. The present study has been performed after the elimination of this contamination using the adsorption of CO on Cu° sites as a test. It has been found that the tiny leaks were located at the sealing of the two KBr windows (maintained whatever the experiment at $T < 330$ K) on the stainless steal body of the DRIFT cell. The diameter and thickness of the windows were $D = 1.5$ cm and $e = 0.2$ cm, respectively whereas the wide of the sealing was ≈ 2 mm. We have observed that the replacement of the sealing and KBr windows allowed the suppression of the O_2 contamination only during a short period of time (3–4 days of experiments). Our opinion was that because KBr is hygroscopic, the air tightness of the sealing was progressively lost in some places due to the presence of H_2O (a) outside (in air) and (b) in inside (in particular during the reduction treatment of the catalysts) the IR cell. The present study has been performed after using CaF_2 windows that are not hygroscopic. In these conditions, the O_2 contamination was prevented for long periods of time allowing performing several experiments on the same of sample of catalyst to verify the reproducibility of the data. The absence of O_2 contamination has been ascertained considering as reference the data of a previous study [26] dedicated to the adsorption of CO on Cu° sites of a reduced 4.7% Cu/Al_2O_3 using the IR Cell in transmission mode. The DRIFT spectra were transformed by the commercial software using the pseudo absorbance mode: $\ln(R'_\infty/R_\infty)$ where R_∞ and R'_∞ are the absolute reflectances before and after the formation of the adsorbed species, respectively. As discussed previously and in agreement with different literature data [23–25], for the quantitative exploitation of the data, the experiments are designed such as ($R_\infty - R'_\infty/R_\infty$) is not too high (the criterion considered in Ref. [23] is Cr1: ($R_\infty - R'_\infty/R_\infty$) $\ll 2(1 - R_\infty)/\sqrt{R_\infty}$). This is satisfied if the value of the relative reflectance is >0.5 at the highest coverage of the adsorbed CO species [22]. The FTIR spectrometer used with the DRIFT cell was a Nicolet 6700 from ThermoScientific with a MCT detector cooled to 77 K.