Available online at www.sciencedirect.com
SCIENCE DIRECT®
Catalysis Today 102–103 (2005) 266–272
CATALYSIS TODAY
www.elsevier.com/locate/cattod

H/D exchange using D_2O on carbon materials: A flexible tool for surface Brønsted acidity direct measurement

Nicolas Keller *, Guillaume Koehl, Barbara Pietruszka, Valérie Keller

Laboratoire des Matériaux, Surface et Procédés pour la Catalyse, UMR 7515 CNRS and ELCASS (European Laboratory for Catalysis and Surface Sciences), ECPM, Louis Pasteur University, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France

Abstract

A tool for direct determination of surface Brønsted acidities of solids, in terms of concentration and strength, was proposed and applied to carbon materials, based on the quantitative H/D exchange kinetics between D_2O and the acid solid, i.e. the –O–H acid surface groups in the case of carbons. Calibration was performed using well-characterized zeolites with known acidities, and allowed the concentration of surface Brønsted acidity sites in μmol/g to be derived from the integrated surfaces of the H/D exchange curve. This was done y the direct measurement of the OHD signal via mass spectrometry. The strength of the acidity was directly linked to the rate constant of the H/D exchange kinetic. This easy of use direct method is highly flexible and covers the whole acidity scale from weakly acidic to strongly acidic materials.

Keywords: Surface Brønsted acidity; D_2O; H/D exchange; Zeolite; Carbon nanotubes; Carbon

1. Introduction

Chemisorbed oxygen on carbon atoms, i.e. oxygenated surface groups, strongly influences many properties of carbonaceous materials, such as wetting, adsorption behavior and dispersion of supported active phases [1–4]. For example, the presence of oxygenated surface groups on carbon materials has been reported to be of high importance for anchoring metals and grafting organometallic complexes onto carbon support, as well as for direct use as a heterogeneous catalyst [5,6]. The surface of sp^2-bound carbon materials is heterogeneous, consisting of the faces and edges of graphene sheets. The carbon atoms in the interior of the graphene sheets are less reactive than the atoms located at edge sites. Oxygenated surface groups are, thus, predominantly located on the edges. According to the definition of Brønsted acidity the solid is able to donate, or at least partially transfer, a proton which becomes associated with surface anions. Amongst the different kinds of oxygenated surface groups on the carbon surface, it is the presence of –O–H groups which is responsible for the surface acidity of carbon materials.

Up to now, the most commonly used methods are based on the chemical adsorption of basic compounds, which includes titration techniques, such as the Hammett Indicator method [7] and adsorption of basic probe molecules, such as pyridine, amines or NH_3. These adsorptions are generally coupled with temperature programmed desorption, calorimetric measurements, nuclear magnetic resonnance or vibrational (IR) and Raman spectroscopies [8–10]. However, several extensive articles and reviews underline that the reliability and applicability of such methods remain strongly questionable [11–15]. Many methods have been developed yet no single technique can yield both a quantitative and qualitative determination of the surface Brønsted acidity. Although IR spectroscopy of adsorbed basic probes has emerged as a valuable and powerful tool for investigation of surface acidity [12], the determination of the extinction coefficients of the different types of hydroxyls contributing to the IR bands is required. Consequently, this difficult determination limits the use of IR analyses and, therefore, leads only to semi-quantitative measurements and sometimes to misinterpretation of the

---

* Corresponding author. Tel.: +33 3 90 24 28 11; fax: +33 3 90 24 27 61.
E-mail address: nkeller@chimie.u-strasbg.fr (N. Keller).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.02.029

results [12,15–17]. In addition, most of the methods were mainly developed for moderate and high acidity solids involved in acid catalysis, and not for low acidity carbons.

The acid properties of oxygenated surface groups on carbon materials can be conveniently determined by neutralization methods, known as Boehm titrations, using for example solutions of $NaHCO_3$, Na_2CO_3 and NaOH [3]. Nevertheless, such titration determinations are very time-consuming as equilibration in direct titration is very slow (slow diffusion in narrow pores and slow hydrolytic ring opening of carboxylic anhydrides and lactones). Moreover, with the Boehm measurements being performed in aqueous media, the hydrolysis of non-acidic surface groups, such as carboxylic anhydrides and lactones in aqueous solution generally contributes to the Brønsted acidity. When carbon is used for gas phase applications, this additional acidity should not be taken into account.

Sommer and co-workers have recently developed a highly interesting and innovative four-step method based on H_2O/D_2O exchange in the gas phase for characterizing the surface Brønsted acidity of zeolite. This consists of its deuteration, followed by the back-titration of the –O–D exchanged sites with distilled water. The resulting partially-exchanged H_xOD_y species were then chemically trapped by trifluoroacetic anhydride before the liquid NMR analysis of the acidic solution allowed the determination of the total number of Brønsted acid sites [15,17].

The aim of the present article is to report on a flexible one-step alternative to the method developed by Sommer, based on quantitative H/D exchange between the acid solid and gaseous D_2O. This allows the determination of the acid strength and the number of Brønsted acid sites by dynamically analyzing the recovered HDO in the gas phase with mass spectrometry. This method was applied to carbon materials.

2. Experimental

2.1. The H/D exchange micropilot and experimental procedure

The H/D exchange reaction was carried out in a tubular quartz reactor of 8 mm inner diameter and 185 mm length. Helium (40 ml/min) was fed by a mass-flow controller (Tylan FC-260) while gaseous D_2O in the helium stream was provided by a saturator kept at room temperature, corresponding to 3 vol.% of gaseous D_2O. Since the number of –O–H sites on solids is dependent on the pre-treatment (activation) temperature, and in order to remove adsorbed water molecules, the materials were pretreated under helium and subsequently submitted to the D_2O (3 vol.%)/He flow at 150 °C, leading to exchange of the hydron present on the solid surface with gaseous D_2O. Different pretreatment temperatures have been tested up to 500 °C, without observation of significant changes in the HDO signal. The pretreatment temperature has, consequently, been standardized at 300 °C for 1 h. The direct titration of the –O–H acid sites, via the H/D exchange on Brønsted acid groups according to the reaction mechanism presented in Fig. 1, was continuously followed by Mass Spectrometry. This was done using the $m/z = 19$ signal corresponding to HDO gas molecules in the outlet stream, with a sampling of one measurement point recorded per second. The residual H/D exchange on the stainless steel micropilot and the quartz reactor was removed from the HDO evolution curve by performing a control experiment without any acidic material and then subtracting the $m/z = 19$ signal of the blank experiment from that obtained on the acid solid. Before the exchange experiment, the mass spectrometer was calibrated using 20 Torr of Ar ($m/z = 40$). Depending on the Brønsted acidity of the materials, the exchange was performed using between 50 and 200 mg of catalyst, necessitating normalization of the exchange curve for a gram of material. Both argon and helium lines were equipped with a water filter, to avoid the detrimental presence of residual water in the feed.

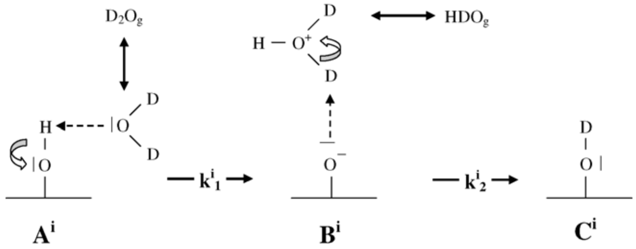

Fig. 1. Mechanism of the H/D exchange on the surface Brønsted acid sites of type i considering a series of two consecutive first-order reactions. k^i_1, k^i_2 are the reaction rate constants corresponding to the consecutive reactions involved for the type i of surface Brønsted acid sites, and used for kinetic modeling.

It is worth noting that increasing the flow rate higher than 100 ml/min led to decreasing values for the integrated normalized HDO signal (i.e. the number of total Brønsted acid sites), probably indicating that the H–D exchange was not complete. On the other hand, decreasing the flow rate lower than 15 ml/min resulted in diffusion limited kinetic. The optimal experimental conditions have, thus, been determined at a 40 ml/min flow rate and a catalyst weight between 50 and 200 mg.

2.2. Kinetic modelling

A kinetic model of the reaction has been proposed assuming a series of two consecutive first-order reactions described by Eq. (1) for a type i of surface Brønsted acidity [18]:

$$A^i \xrightarrow{k^i_1} B^i \text{ and } B^i \xrightarrow{k^i_2} C^i \text{ with } A^i = A^i_0 e^{-k^i_1 t} \quad (1)$$

where A^i_0 is the number in μmol/g of surface Brønsted acidity sites of type i; k^i_1, k^i_2, the reaction rate constants

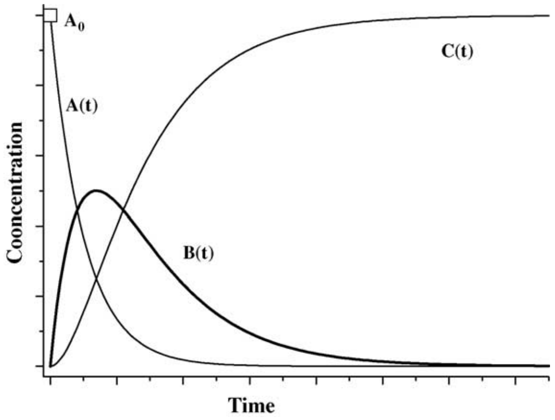

Fig. 2. Theoretical concentration–time curves for species *A*, *B* and *C* obtained for a series of consecutive first-order reactions.

corresponding to the consecutive reactions involving surface Brønsted acidity sites of type *i*.

When several kinds of Brønsted acidity were present at the solid surface (generally the case), this kinetic model was applied to each contribution (indexed with *i*) which represents a type of surface Brønsted acidity. The surface of each is representative of the number of –O–H surface groups and the k_1^i value, defined as the rate constant of the first reaction of hydron abstraction for site *i*, is directly linked to the acid strength of site *i*.

Fig. 2 shows the theoretical plot of the concentrations *A*, *B* and *C* as a function of time. The integration of the differential equations leads to an expression for the B^i concentration of sites *i* as a function of time during the exchange (Eq. (2)):

$$B^i(\mathrm{t}) = \frac{A_0^i k_1^i}{k_2^i - k_1^i}(\mathrm{e}^{-k_1^i t} - \mathrm{e}^{-k_2^i t}) \qquad (2)$$

It should be noted that only a small fraction of the HDO-containing outlet stream was analyzed by mass spectrometry. The B^i(t) evolution was, thus, related to a fraction of the HDO molecules present in the outlet stream and the A_0^i values (calculated following the kinetic model) corresponded to fraction of the total number of surface acid sites. Thus, the obtained A_0^i could not be taken directly. Building up a calibration curve was, therefore, necessary allowing correlation of the gas phase measurement with the solid characteristics, i.e. linking the mass spectrometry signal corresponding to HDO molecules to the number of surface Brønsted acid sites exchanged (see Section 3.1 below).

2.3. Characterization techniques

For comparison, determination of the acid surface concentration of carbon materials was performed by the well-known and classical Boehm titration method [3,19–21], using 50 ml of 0.05 M solutions of $NaHCO_3$, Na_2CO_3 and NaOH to neutralize the acidic groups. After an equilibration period of several days and a subsequent filtration, the remaining Na^+ ions were titrated by adding excess HCl to an aliquot, boiling off the CO_2 and subsequently performing back-titration with standard NaOH.

XPS characterization was carried out in a ThermoVG Scientific apparatus equipped with a hemispherical analyzer and a Mg Kα source (1253.6 eV) at a pass energy of 20 eV.

Deconvolution of the spectra has been performed using a Doniach–Sunjic shape [22] and a Shirley background subtraction.

2.4. The carbon materials

Purified, open, multi-walled carbon nanotubes (MWNTs) were supplied by Applied Sciences Inc. (OH, USA). They had mean inner and outer diameters of 50 and 90 nm, respectively, with lengths up to 200 μm. Surface oxidation of MWNTs was performed by treating fresh MWNTs with concentrated HNO_3 or a mixture of HNO_3/H_2SO_4 under reflux for 0.5 h, following the procedure described by Toebes et al. [4]. Activated charcoal (AC) powder was purchased from Fluka. Nanodiamonds or ultra-dispersed-diamonds (UDD) were obtained by firing of high explosive TNT/RDX (2,4,6-trinitrotoluene/hexahydro-1,3,5-trinitro-1,3,5-triazine) mixtures in water confinement [23,24]. Large non-carbonaceous impurities contained in the detonation products were removed by filtration. The solid residue after water evaporation was further treated with boiling concentrated sulfuric acid to eliminate smaller impurities, before being washed thoroughly and dried. Removal of materials still unconverted to UDD was performed by selective oxidation of the material with a H_2O_2/HNO_3 mixture.

3. Results and discussion

3.1. Calibration of the Brønsted acidity

Calibration of the acidity in μmol/g was performed using different well-characterized zeolites with known Brønsted acidity, such as ZSM-5 and H-EMT. These showed a concentration of surface Brønsted acid sites of 1210 and 2260 μmol/g, respectively, as determined by the method developed by Sommer and co-workers. Fig. 3 shows the calibration curve, representing the normalized integrated surface of the $m/z = 19$ signal (integrated surface for 1 g of catalyst) as a function of the number of Brønsted acid sites in μmol/g. The reproducibility and the reliability of the method have been verified by performing the exchange experiments three times on each zeolite used for calibration. It should be mentioned that with the number of acid sites being usually reported in μmol/g, it could also be considered as an acid site concentration or density in the literature.

Fig. 4 reports the example of a mordenite zeolite, for which three kinds of Brønsted acidity, i.e. Al–O–H (64%),

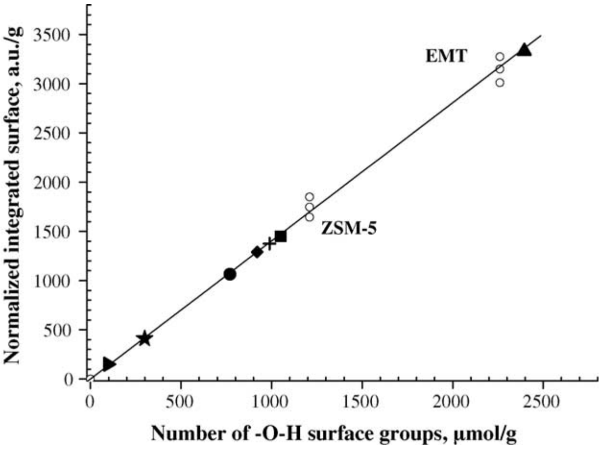

Fig. 3. Calibration curve (normalized integrated surface vs. number of –O–H surface groups in µmol/g) obtained from well-characterized ZSM-5 and EMT zeolites with known acidities: (○) calibration points. Quantification of surface –O–H groups has been performed using the calibration curve for: (★) AC, (◀) MWNTs, (●) HNO_3-acidified MWNTs, (◆) HNO_3/H_2SO_4-acidified MWNTs, (+) UDD, (▲) mordenite, (■) γ-alumina.

Al–O–H extra-framework (10%) and Si–O–H silanols (26%), have been previously determined by ^{27}Al NMR studies and IR Spectroscopy of adsorbed pyridine at 150 °C for *Al*- and Si-linked acid sites, respectively [25]. It was worth noting that the experimental exchange curve was similar to the theoretical curve derived from the kinetic model hypothesis and shown in Fig. 2. This close agreement allowed the extension of the simple kinetic model proposed, usually applied to well-mixed batch-type reactors, to a flow tubular reactor [26]. It could be decomposed into three contributions, each of them displaying an integrated surface linked to the relative content of each acidity via the calibration curve (and with the adequate relative molar ratio of each acidic contribution reported above) and following the theoretical kinetic model described in Eqs. (1) and (2).

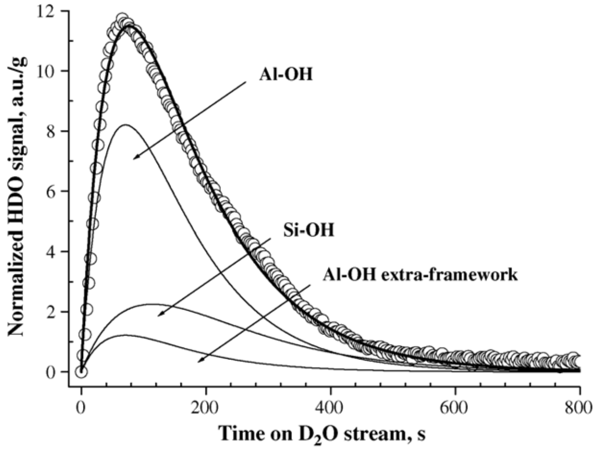

Fig. 4. Deconvoluted normalized $m/z = 19$ signal, i.e. proportional to the concentration of HDO molecules in the gas phase, as a function of time on D_2O stream for a mordenite zeolite. For clarity, only one in every four measuring points was reported in the graph.

Table 1
Total surface Brønsted acidity derived from the calibration curve

Material	Concentration of–O–H acidic surface groups (µmol/g)
Activated charcoal	300
MWNTs	98
HNO_3-acidified MWNTs	770
HNO_3/H_2SO_4-acidified MWNTs	920
Nanodiamonds (UDD)	989
γ-Al_2O_3	1050
Mordenite	2396

The deconvolutions have been performed using an appropriate algorithm recently developed for extracting site-specific rate constants for H/D exchange in gas phase protonated peptides [27].

3.2. Brønsted acidity measurements

The normalized integrated surfaces for the HDO molecule signals obtained on different kinds of carbon materials were reported in the calibration curve (Fig. 3), from which the corresponding concentrations of –O–H acidic surface groups were derived and reported in Table 1. For comparison, non-carbonaceous catalysts or supports, such as γ-Al_2O_3 and mordenite zeolite were reported too, and displayed a total number of surface Brønsted acid sites of 1050 and 2396 µmol/g, respectively. Most studies, using FT-IR of adsorbed pyridine, have reported that the γ-Al_2O_3 surface is not Brønsted acidic, but is usually considered to act as a pure Lewis acid, because no protonation occurred with the basic probe molecules used. However, the Brønsted content of the γ-Al_2O_3 global acidity remains very controversial in the literature since the strength of the acid-base interaction depends directly on the strength of the base used [28]. It has been shown by Busca than stronger bases, such as *n*-butylamine [29] and piperidine [30] are protonated by alumina, which leads, thus, to consider the γ-Al_2O_3 –O–H surface groups as weak Brønsted acidic groups. It should be mentioned that the method proposed does not take into account the Lewis acidity of the γ-Al_2O_3, and that the acidity deduced from the measurement could, thus, be considered as a Brønsted acidity.

It was found that fresh untreated MWNTs had 98 µmol/g –O–H groups, while the oxidizing acidic treatments increased the number of –O–H surface groups up to 770 and 920 µmol/g with HNO_3 and HNO_3/H_2SO_4, respectively. It is well known that the presence of oxygenated surface groups is directly related to the perfectness of the carbon material. With MWNTs consisting of concentric graphene sheets rolled to form tubes, oxygen was predominantly located at the edges of such graphene layers (broken sheets, defect areas, . . .) and not on the faces of graphene sheets. The increase in the oxygenated surface groups and the resulting surface Brønsted acidity due to the oxidizing treatments was in close agreement with the literature [4,31]. The nanodiamonds had a surface Brønsted acidity of

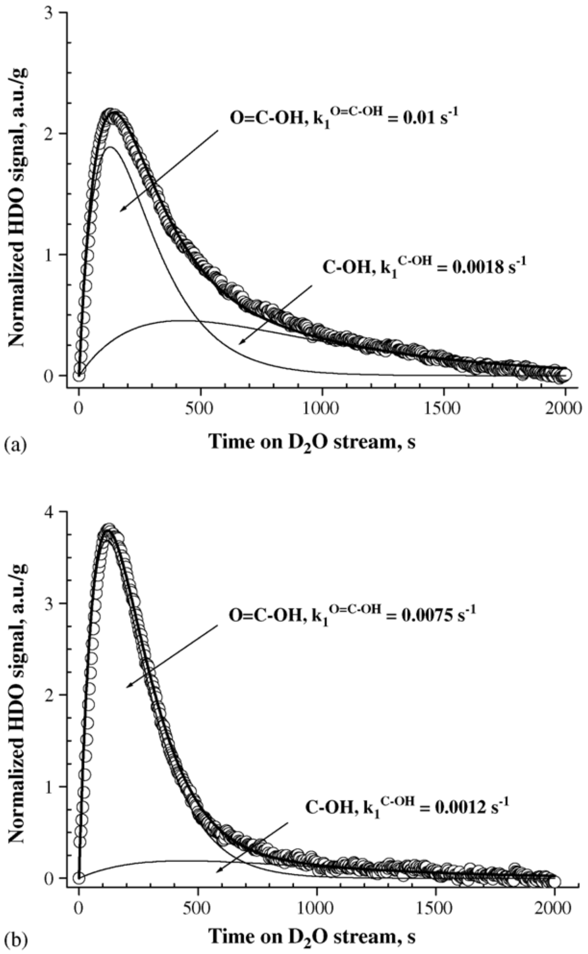

Fig. 5. Deconvoluted normalized $m/z = 19$ signal, i.e. proportional to the concentration of HDO molecules in the gas phase, as a function of time on D_2O stream for (a) HNO_3/H_2SO_4-acidified MWNTs and (b) nanodiamonds (UDD), with the corresponding k_1 rate constants. For clarity, only one in every four measuring points was reported in the graph.

989 μmol/g, which could result from the highly oxidizing post-synthesis purification treatments using both boiling concentrated sulfuric acid and a H_2O_2/HNO_3 mixture. It should be noted that the oxidizing treatments on MWNTs and nanodiamonds did not introduce hetero-elements, such as nitrogen or sulfur at the carbonaceous material's surface, which could modify the acid properties. This was proved by XPS and chemical analysis.

Fig. 5 shows two examples of deconvoluted signals in the case of HNO_3/H_2SO_4-acidified MWNTs and nanodiamonds. The signals obtained on both materials could be deconvoluted into two acidic contributions, the O=C–O–H carboxylic and C–O–H alcohol functions in 47:53 and 79:21 molar ratios for treated MWNTs (corresponding to 433 μmol/g of O=C–O–H and 487 nmol/g of C–O–H) and nanodiamonds (778 nmol/g of O=C–O–H and 211 μmol/g of C–O–H), respectively. The assignment of the two acidic contributions was performed on the following basis: (i) the most acidic contribution, i.e. the carboxylic groups, corresponded to the most labile proton and could, thus, be assigned to the higher k_1 exchange rate; (ii) performing HNO_3 and HNO_3/H_2SO_4 oxidative treatments on carbon-based materials is generally acknowledged to result in a strong increase in the number of carboxylic surface groups compared to the number of alcohol groups [4,6,31–33]. The observed increase in the high k_1 exchange rate contribution with increasing oxidative treatment strength, thus, led to its assignment to the carboxylic groups (not shown). This was in good agreement with the XPS characterization (not reported) performed on fresh and acidified MWNTs, which showed an increase in the carboxylic acid surface group content subsequent to the HNO_3/H_2SO_4 treatment. The O=C–O–H/C–O–H surface ratio was bewteen 45:55 and 56:44 depending on the way of fitting (in terms of peak asymmetry, line-width, presence of a ‘‘defect’’ peak beside the sp^2 graphitic carbon [34]). Contributions with the higher rate constants were assigned to carboxylic acid groups whereas the lower rate constant was assign to alcohol –O–H groups. Treated MWNTs displayed k_1 values of 0.01 s^{-1} (O=C–O–H) and 0.0018 s^{-1} (C–O–H), whereas k_1 values of 0.0075 s^{-1} (O=C–O–H) and 0.0012 s^{-1} (C–O–H) were obtained for nanodiamonds. It was worth noting that the $k_1^{C–OH}$ and k_1^{COOH} rate constants obtained on the nanodiamonds were lower that those obtained on the HNO_3/H_2SO_4-acidified MWNTs. The alcohol and carboxylic groups showed a lower acidity on the nanodiamonds than on the treated MWNTs.

This could be explained by the stabilization of the corresponding $O{=}C{-}O^-$ and $C{-}O^-$ conjugate bases by resonance phenomena on the conjugated system of the sp^2-hybridized carbon structure of MWNTs, which does not occur on the sp^3-hybridized nanodiamonds.

Comparison was made between Boehm titrations and the H/D exchange using activated charcoal and untreated MWNTs as examples. For AC, a total number of surface Brønsted acid sites of 300 μmol/g was derived from the normalized integrated surface of the HDO molecule mass spectrometry signal using the calibration curve, whereas the Boehm titrations led to a total number of acid sites of about 500 μmol/g. The same discrepancy was observed in the case of untreated MWNTs, the Boehm titration leading to a total number of acid sites of 300 μmol/g whereas 98 μmol/g was obtained by H/D exchange. The over-estimation obtained in both cases by the liquid-phase titration was explained by the opening in aqueous media of non-acidic oxygenated groups. In addition, the increase in the estimated number of Brønsted acid sites in μmol/g as a function of the equilibrium duration evidenced that 7 days were required to titrate all the sites of both carbon catalysts.

3.3. Discussion

The method based on H/D exchange using D_2O displays advantages when compared to conventional methods. Determining adequate experimental conditions in terms of flow rates and catalyst weight is of high importance. First of all, these experimental parameters have to be set carefully to ensure the exchange of all –OH surface groups, so as not to underestimate the number of Brønsted acid sites and to ensure measurement of the global surface Brønsted acidity. Secondly, validating the extension of the kinetic model from batch-type reactors to a flow tubular reactor requires well-chosen parameters to maintain slight and acceptable deviations from perfect plug flow reactor. This method gives a direct measurement of the hydron lability and allows the determination of surface Brønsted acidity for the whole range of acidity, even for solids classified as non or weakly acidic, such as carbonaceous materials. Nevertheless, for weakly acidic solids, significant amounts of sample should be used in order to obtain a HDO MS signal with an acceptable signal/noise ratio.

The flexibility of the method, especially in terms of temperature and in situ pretreatment conditions, allows the measurement to be performed in similar conditions to those used during the catalytic testing of the material. The solid can be easily in situ pre-treated (e.g. activation treatment) under the reactional flow or in a reductive/oxidative/inert atmosphere without being exposed to air, giving in situ information on the stabilized surface phases.

It is worth noting that there is no influence of the porosity on the acidity measurement. Indeed, other methods based on the adsorption of basic molecules are strongly time-consuming, mass transfer limited and prone to long equilibration times to reach the thermodynamic equilibrium between the basic probe and the solid Brønsted acid surface. By contrast, the high accessibility of –O–H surface groups for D_2O molecules is very advantageous in terms of experimental duration, particularly for solids, such as zeolites and microporous carbons. In this last case, the Boehm method led to only 60% of titration after 24 h. Unlike the classical base adsorption methods which underestimate the number of –O–H surface groups in the case of microporous materials [14], the high accessibility towards D_2O molecules permits the counting of all Brønsted acid sites.

More pertinently for carbonaceous materials, the exchange method provides more information on the –O–H surface groups compared to the XPS surface characterization technique, which only averages out the content of oxygenated surface groups with the rest of the material due to the XPS analysis depth (between 10–15 Å, thus, also considering the oxygen-free carbon structure behind the surface, such as graphene sheets of MWNTs), resulting in a decrease in the measurement accuracy. In addition, although XPS is nowadays a classical and well-used characterization technique for carbonaceous materials, strong discrepancies could be observed in the literature in the method of fitting in terms of asymmetry, binding energy, line-width and presence of a ‘‘defect’’ peak close to the graphitic asymmetric peak representing the population of carbon atoms out of regular planar sp configurations [34]. Moreover, the use of the O 1 s signal is usually imprecise, due to a much smaller shift sensitivity than the C 1 s and the usual presence of a film of molecular water which cannot be removed in UHV at low temperatures and which creates a large signal masking many structures in the oxygen functional group spectrum [1]. Those drawbacks of both C1s and O1s spectra generally lead to large discrepancies in terms of oxygenated surface group content. In addition, XPS remains inflexible and subject to restrictive experimental conditions.

In parallel to the determination of the global surface Brønsted acidity, for which no fitting model is necessary, estimating the different acidic contributions in terms of number and strength of acidic centers requires the careful use of an appropriate algorithm. It should be noted that, performing the exchange measurement on a series of samples, such as oxides with different pre-treatment temperatures or carbonaceous materials with different oxidative acidic treatments, allows the improvement of the method accuracy, by providing more analytical datas for each type of acid sites (e.g. alcohol and carboxylic acid groups).

4. Conclusion

A tool for direct determination and quantification of surface Brønsted acidity of solids, based on quantitative H/D exchange kinetics using D_2O, has been developed and applied to carbon materials. In this method, deconvolution of the total exchange signal can allow the determination of the number and strength of the different surface Brønsted acid sites. The aim of this article was to present the advantages and validity of this easy of use method compared to conventional techniques, such as Boehm titrations, IR, XPS or Thermo-Desorption. This method is highly flexible and could give information on the –O–H surface groups in real ‘‘working’’ conditions. It could also allow in situ pre-treatment or activation to be performed without exposing the material to air. This rather cheap method is also non-destructive, a simple back-exchange with steam allowing the initial material to be recovered.

It should be noted that this one-step, direct titration method could be applied to catalysts or supports which are generally classified as non- or weakly-acidic materials, such as β-silicon carbide or multi-walled carbon nanotubes. In parallel to the titration of Brønsted acid sites, quantitative determination of the number and types of –O–H surface groups on most of the oxide supports or catalysts, such as TiO_2, MoO_3, etc. ... remains of great interest in catalysis and is currently under investigation.

Performing the titration at different exchange temperatures is currently under investigation to calculate an ‘‘*activation energy of acidity*’’ for each kind of acidity, which could be seen as the energy required for breaking the O–H bond, i.e. for abstracting the proton. Work is ongoing in order to develop new algorithms for determining site-specific exchange reaction rate constants and further increasing the accuracy of this method.

Acknowledgments

P. Bernhardt (LMSPC) is gratefully thanked for helping in MS and XPS analyses. Prof. J. Sommer, Dr. B. Louis and A. Simon are acknowledged for having supplied some of the zeolite samples. Dr. E. Fousson is thanked for having synthesized the nanodiamond materials. D. Edwards is acknowledged for having carefully checked the manuscript.

References

[1] R. Schlögl, Carbons, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 1, Wiley-VCH, Weinheim, 1997.
[2] F. Rodriguez-Reinoso, Carbon 36 (3) (1998) 159.
[3] H.P. Boehm, Carbon 40 (2002) 145.
[4] M.L. Toebes, J.M.P. van Heeswijk, J.H. Bitter, A.J. van Dillen, K.P. de Jong, Carbon 42 (2) (2004) 307.
[5] N. Keller, N.I. Maksimova, V.V. Roddatis, M. Schur, G. Mestl, Yu.V. Butenko, V.L. Kuznetsov, R. Schlögl, Angew. Chem. Int. Ed. 41 (11) (2002) 1885.
[6] P. Serp, M. Corrias, Ph. Kalck, Appl. Catal. A: Gen. 253 (2003) 337.
[7] L.P. Hammet, A.J. Deyrup, J. Am. Chem. Soc. 54 (1932) 2721.
[8] W.N. Delgass, G.L. Haller, R. Kellermann, J.H. Lunsford, Spectroscopy in Heterogenous Catalysis, Academic Press, New York, 1979.
[9] G.T. Haller, Catal. Rev.-Sci. Eng. 18 (1981) 477.
[10] J.W. Ward, J. Catal. 17 (1970) 355.
[11] G.A. Olah, A. Molnar, Hydrocarbon Chemistry, Wiley International Edition, New York, 1995.
[12] A. Corma, Chem. Rev. 95 (1995) 559.
[13] J.J. Fripiat, J.A. Dumesic (Eds.), Topics in Catalysis, vol. 4(1–2), Springer Science, New York, USA, 1997.
[14] R.J. Gorte, Catal. Lett. 62 (1999) 1.
[15] R. Olindo, A. Goeppert, D. Habermacher, J. Sommer, F. Pinna, J. Catal. 197 (2001) 344.
[16] C. Morterra, E. Garrone, V. Bolis, B. Fubini, Spectrochim. Acta A 43 (1987) 1577.
[17] B. Louis, S. Walspurger, J. Sommer, Catal. Lett. 93 (1–2) (2004) 81.
[18] A.A. Frost, R.G. Pearson, Kinetics and Mechanisms, Wiley International Edition, 1953.
[19] H.P. Boehm, E. Diehl, W. Heck, R. Sappok, Angew. Chem. Int. Ed. 3 (1964) 669.
[20] H.P. Boehm, in: D.D. Eley, H. Pines, P.B. Weisz (Eds.), Advances in Catalysis, vol. 16, Academic Press, New York, London, 1966, pp. 179–274.
[21] H.P. Boehm, Carbon 32 (5) (1994) 759.
[22] S. Doniach, M. Sunjic, J. Phys. C: Solid State Phys. 3 (2) (1970) 285.
[23] J.B. Donnet, E. Fousson, T.K. Wang, M. Samirant, C. Baras, M. Pontier Johnson, Diamond Relat. Mater. 9 (2000) 887.
[24] J.B. Donnet, E. Fousson, M. Samirant, T.K. Wang, M. Pontier Johnson, A. Eckhardt, C. R. Acad. Sci. IIc 3 (2000) 359.
[25] Non published results.
[26] R.J. Farrauto, C.H. Bartholomew, Fundamentals of Industrial Catalytic Processes, Blakie Academic and Professional, London, UK, 1997.
[27] B.G. Reuben, Y. Ritov, O. Geller, M.A. McFarland, A.G. Marshall, C. Lifshitz, Chem. Phys. Lett. 380 (2003) 88.
[28] G. Busca, Phys. Chem. -Chem. Phys. 1 (1999) 723.
[29] G. Ramis, G. Busca, J. Mol. Struct. 193 (1989) 93.
[30] G. Busca, Catal. Today 41 (1998) 1991.
[31] T.G. Ros, A.J. van Dillen, J.W. Geus, D.C. Koningsberger, Chem. Eur. J. 8 (5) (2002) 1151.
[32] A. Kuznetsova, I. Popova, J.T. Yates, M.J. Bronikowski, C.D. Huffman, J. Liu, R.E. Smalley, H.H. Hwu, J.G. Chen, J. Am. Chem. Soc. 123 (2001) 10699.
[33] T. Kyotani, S. Nakazaki, W.-H. Xu, A. Tomita, Carbon 39 (2001) 771.
[34] H. Estrade-Szwarckopf, Carbon 42 (8–9) (2004) 1713.