Characterization of the Acid−Base Properties of Oxide Surfaces by ^{13}C CP/MAS NMR Using Adsorption of Nitromethane

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Adsorption of nitromethane on oxide surfaces was monitored using ^{13}C CP/MAS NMR. Stabilization of the aci-anion formed by reaction of nitromethane on acid−base pairs was apparent. A linear relationship between the ^{13}C NMR isotropic chemical shift of the methylene group of the adsorbed aci-anion of nitromethane and the heat of adsorption of CO_2 measured by microcalorimetry was established. The results suggest that nitromethane constitutes an accurate and effective NMR probe for monitoring the basicity of oxide surfaces.

Introduction

Chemical reactions catalyzed by solid acids and bases often require that molecules interact with several surface sites.[1] Therefore, understanding the mode of interaction of probe molecules with the surface of the catalyst is of prime importance. A number of infrared (FT-IR) and nuclear magnetic resonance (NMR) spectroscopic methods have been developed recently for the characterization of acid and basic sites. Such spectroscopic studies can be carried out either on neat surfaces or on samples loaded with suitable probe molecules. In that respect, adsorption of basic molecules such as pyridine, ammonia, or carbon monoxide gives rise to very specific infrared vibrations upon interaction with Lewis or Bronsted acid sites of oxides, clays, and zeolites.[2,3]

The NMR technique allows study of interaction between acid sites and adsorbed probe molecules like N_2O, amines,[4] phosphines,[5] methanol,[6] or water.[7] For instance, the adsorption of N_2O was followed by ^{15}N NMR for the study of the nature of Lewis acid sites.[8]

It is still a challenge to find a suitable probe of basicity to a measure of basic strength.[2] For example, CO_2 was used to follow the variation of the basicity of various mixed oxides TiO_2−ZrO_2[9] or TiO_2−Al_2O_3.[10] It appears that the mixed oxides (TiO_2−Al_2O_3) are much less basic than pure TiO_2 or pure Al_2O_3. CO_2 adsorption on basic sites leads to the formation of broad, intense IR bands of the carbonate species, and it is difficult from FT-IR results alone to draw any conclusion about the relative basicity of different oxides.[9−11] Pyrrole has also been widely used as a surface probe for FT-IR spectroscopy. There is a clear distinction between protonated and coordinated species,[12,13] and a measure of the basic strength is the frequency of the N−H stretching band.[14,15] However, pyrrole readily polymerizes or decomposes upon heating, which represents a major drawback. Acetonitrile is also used in FT-IR spectroscopy. Because of its amphoteric character, it is able to characterize both basic and acid sites of the surface. But it gives little information about basic strength, and acetamide dianions are observed, whose mechanism of formation is still unclear.[16]

We recently reported[17] that nitromethane adsorbed on basic solids decomposed upon heating at 473−673 K to give isocyanic acid species whose peak position in the FT-IR spectra is a measure of the basic strength of the sites. More interestingly, as reported by Kheir and Haw,[18] the adsorption of nitromethane followed by NMR spectroscopy is able to characterize the basicity, without the disadvantage of thermal decomposition required for FT-IR spectroscopy. Nitromethane deprotonated on the surface of the strongly basic oxides MgO and CaO leads to the aci-anion readily identified by ^{13}C CP/MAS NMR. On the other hand, calculations on cluster models show a stabilization of the aci-anion relative to nitromethane adsorbed on these basic solids.[19]

In this work the adsorption of nitromethane has been performed on a variety of solids known to exhibit basic sites of different nature and strength: γ-Al_2O_3, MgO, and Mg(Al)O, which are mixed oxides obtained by thermal decomposition of layered double hydroxides (LDH). The latter, whose general formula is $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A_{x/n}^{n-1}]\cdot mH_2O$, are composed of positively superposed charged metallic hydroxide sheets where M^{2+} is a divalent cation such as Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}, ... and M^{3+} is a trivalent cation such as Al^{3+}, Fe^{3+}, Cr^{3+}, Ga^{3+}, ... with an appropiate M^{2+}/M^{3+} molar ratio, ranging from 1.5 to 4. The positive charge is compensated by anions (CO_3^{2-}, NO^-, Cl^-, OH^-, ...) located in the interlayer space.[20] The basicity of the mixed oxides obtained from Mg/Al LDH has been extensively studied[21,22] and depends both on the Mg/Al ratio and on the calcination temperature of the precursor.[23] The aim of this work is to use ^{13}C CP/MAS NMR spectroscopy of adsorbed nitromethane to establish a method of basic strength measurement based on the chemical shift of a resonance, associated with the aci-anion.

Experimental Section

Materials. All LDH precursors were prepared by coprecipitation at a constant pH of ca. 9.0 ± 0.2 of appropriate amounts of $Mg(NO_3)_2\cdot6H_2O$ and $Al(NO_3)_3\cdot6H_2O$ dissolved in deionized

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TABLE 1: Physicochemical Characteristics, NMR, and Microcalorimetry Data of the Samples Studied.

sample	specific surf. area (m^2 g^{-1}) ± 5	Mg/Al (mol/mol) ± 0.1	δ ^{13}C (ppm) ± 0.5	$-\Delta H$ (J mol^{-1} m^{-2}) ± 3
aci-anion nitromethane			99	
MgO	160		102	249
Mg(Al)O(3.0)	240	3.0	105.5	190
Mg(Al)O(2.5)	216	2.5	106	169
KW2200	180	2.3	108.3	131
KW2000	240	2.3	108.2	140
Mg(Al)O(2.0)	140	2.0	110.2	94
γ-Al$_2$O$_3$	172		112	48

water with a second aqueous solution of 1.0 ± 0.1 M NaOH plus $(2.0 \pm 0.1) \times 10^{-2}$ M Na$_2$CO$_3$. The rate of addition of alkaline solution and pH was controlled by a pH-Stat apparatus (718 Stat Titrino, Metrohm). The resulting gel was then subjected to hydrothermal treatment at 353 ± 3 K for 15 h. The solid was separated by centrifugation, washed thoroughly with deionized water, and dried overnight at 353 ± 3 K. The variable parameter in the synthesis was the ratio Mg/Al (2.0–3.0). As-prepared samples are designated as HT$_{Mg/Al}$(x) where x is the Mg/Al ratio. Calcination of prepared LDH was carried out in an air flow at 673 ± 3 K (ramp 2 K min^{-1}) and led to mixed oxides that are referred to as Mg(Al)O(x), where $x =$ Mg/Al.

The other materials used were a γ-Al$_2$O$_3$ (prepared by calcination of boehmite at 823 K), magnesium oxide (MgO, prepared by calcination of magnesium carbonate at 823 K), and two mixed magnesium–aluminum oxides (from Kyowa, KW2000 and KW2200 with Mg/Al = 2.3). Nitromethane-^{13}C (99% ^{13}C) was obtained from Aldrich and purified via several freeze–pump–thaw cycles before introduction to the basic catalysts.

Characterization. Powder X-ray diffraction (XRD) patterns were recorded on a CGR theta 60 instrument (40 kV, 20 mA) using Cu Kα_1 monochromated radiation ($\lambda = 0.154$ nm) from 2θ of 4–70°. Specific surface areas were determined by N$_2$ adsorption at 77 K with a Micromeritics ASAP 2000 volumetric instrument, using the BET equation. The samples were calcined at 673 ± 3 K and then outgassed at 523 ± 3 K overnight before N$_2$ adsorption. Chemical analyses were obtained from the Service Central d'Analyse, CNRS (Solaize, France). The main characteristics of the samples are given in Table 1. The heats of adsorption of carbon dioxide were measured with a modified microcalorimeter (TG-DSC-111 from SETARAM) using a silica flow reactor placed in the microcalorimetric cell. After outgassing the samples at 673 ± 3 K, the surface was saturated with CO$_2$ under He flow at 373 ± 3 K. The thermal events were recorded and integrated. Finally, the results were normalized (J mol^{-1} m^{-2}) on the basis of specific surface area (Table 1).

Adsorption of Nitromethane on Mixed Oxides and ^{13}C CP/MAS NMR. Batches of ca. 75 mg of the samples were packed in NMR tubes (5 mm) equipped with a resealable valve suited for attachment to a vacuum line and then evacuated for 15 h at 670 ± 3 K under 10^{-6} Torr. The samples were equilibrated with 30.0 ± 0.5 Torr of ^{13}CH$_3$NO$_2$ at room temperature for 30 min and then desorbed at 323 ± 3 K for 20 min. The NMR tubes were sealed at a height of 4 cm. The ^{13}C CP/MAS NMR spectra were obtained at room temperature using a Bruker ASX-200 spectrometer with a home-built NMR probehead[24] able to spin the sealed NMR tubes up to 4.5 kHz. Spectra were recorded at 50.32 MHz, with a contact time of 5 ms, a spinning rate 4 kHz, and 90° pulses of 5 μs. Typically, 4000–16 000 signal acquisitions were accumulated for each spectrum with a recycle
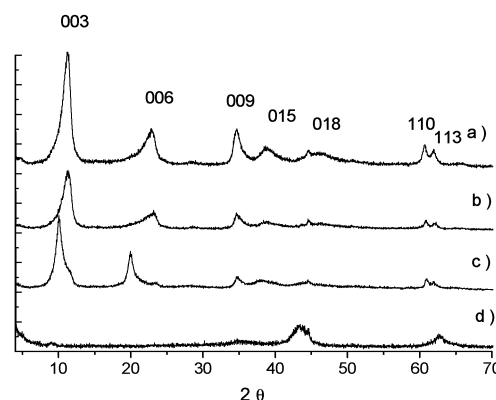
Figure 1. XRD spectra of (a) HT$_{Mg/Al}$(3.0), (b) HT$_{Mg/Al}$(2.5), (c) HT$_{Mg/Al}$(2.0), and (d) Mg(Al)O(3.0) samples after activation under vacuum at 673 K.
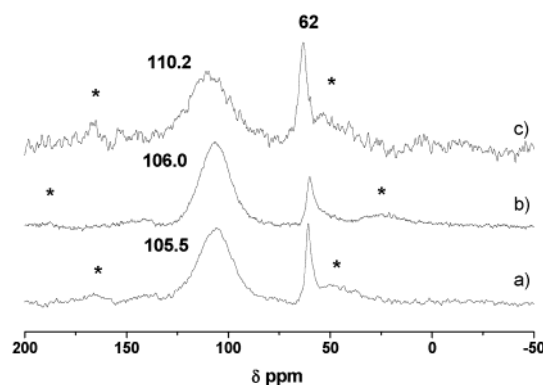
Figure 2. ^{13}C CP/MAS NMR spectra of adsorbed nitromethane at room temperature and then desorption at 323 K on mixed oxides: (a) Mg-(Al)O(3.0), (b) Mg(Al)O(2.5), (c) Mg(Al)O(2.0). The number of scans and the spinning speed were as follows: (a) 16 000 and 3000, (b) 4000 and 3000, (c) 4000 and 3000. (*) denotes spinning sidebands.

delay of 5 s. Chemical shifts were referenced to the CH$_2$ groups of solid adamantine at 38.2 ppm relative to TMS.

Results and Discussion

X-ray Diffraction. XRD of the as-synthesized samples shows in all cases the characteristic patterns of layered double hydroxide structures (Figure 1). The crystallinity of the samples decreases with increasing aluminum content. For HT$_{Mg/Al}$(2.0) a shoulder appears toward high 2θ values on the 003 line which could indicate the presence of a LDH phase with a different Mg/Al ratio.

The calcination (673 ± 3 K) of LDHs leads to poorly crystallized Mg(Al)O mixed oxides having a structure similar to MgO, of periclase type (Figure 1d).

^{13}C CP/MAS NMR. The ^{13}C CP/MAS NMR spectra of nitromethane adsorbed on Mg(Al)O samples at room temperature followed by desorption of physisorbed species at 323 ± 3 K are shown in Figure 2. Two isotropic lines are observed. A narrow one near 62 ppm with a full width at half-maximum (ΔH_{fwhm}) of ca. 4 ppm and a broad one at 105–110 ppm with a ΔH_{fwhm} of ca. 20 ppm. The former line is attributed to CH$_3$-NO$_2$ adsorbed on the oxide surface and the latter to the methylene group of chemisorbed aci-anion nitromethane. These assignments are in line with those previously reported for nitromethane adsorbed on MgO.[18] They are consistent with shifts of a solid aci-anion nitromethane sample prepared under homogeneous conditions (obtained by adding at 273 ± 1 K equivalent amounts of nitromethane and NaOH in methanol

SCHEME 1

nitromethane **2**   aci-nitrométhane **1**
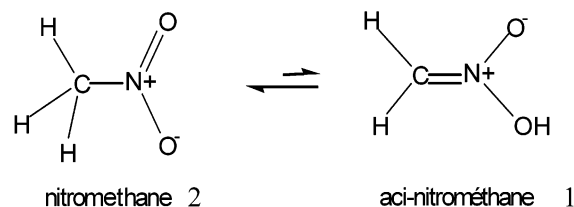
SCHEME 2
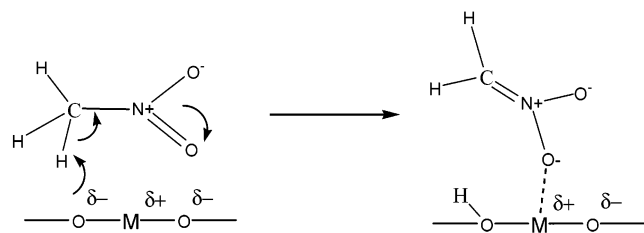
solution (0.20 ± 0.01 mol^{-1})). Adsorption of nitromethane on MgO, γ-Al$_2$O$_3$, and two commercial mixed oxides (KW2000 and KW2200) led to similar spectra (Table 1).

On the other hand, it is worth noting (Table 1) that the chemical shift of the methylene group of the chemisorbed aci-anion nitromethane depends on the composition of the surface.

Adsorption of the probe on MgO leads to an upfield shift (102 ± 0.5 ppm). Conversely, adsorption on Al$_2$O$_3$ leads to a downfield shift (112 ± 0.5 ppm) (Table 1).

For mixed oxides, the lower the aluminum content, the lower the chemical shift and the higher the shielding of the methylene groups of aci-anion nitromethane.

To understand the origin of the observed ^{13}C isotropic chemical shift of chemisorbed aci-anion nitromethane, we have to consider the reactivity of adsorbed nitromethane on acid–base surfaces. Taking into account the pK_a of nitromethane and of aci-nitromethane (aci-nitromethane **1** is a tautomeric form of nitromethane **2**, Scheme 1) in water at 298 K, 10.2 and 3.2, respectively, the reaction that requires basicity is considered to be the abstraction of a proton from the methyl group of nitromethane (Scheme 2). The anion so obtained may either react with the surface hydroxyl group to give aci-nitromethane or be directly stabilized by interaction with the conjugate Lewis acid sites of the surface. Moreover, deprotonation of aci-nitromethane by a basic site leads to the anion.

Interactions of the aci-anion nitromethane with the conjugate Lewis acid site infers an electron shift from the double bond. The isotropic downfield shift of the ^{13}CH$_2$ for the adsorbed aci-anion nitromethane can be attributed to a strong interaction between the conjugate Lewis acid site and the adsorbed molecule. Therefore, the NMR shift reflects the strength of the Lewis sites or of the conjugate base sites since increasing Lewis acidity strength corresponds to lowering the basic strength.

Microcalorimetry. The heat of CO$_2$ adsorption is generally considered to be a measure of the strength of the surface basicity of oxides.[25] CO$_2$ adsorption on mixed oxide samples leads to various carbonate species,[3] many of them being stabilized by the conjugate acid of the base as is the case for aci-anion nitromethane.

The NMR shifts of aci-anion nitromethane (Table 1) are linearly correlated with the corresponding heats of adsorption of carbon dioxide (Figure 3). The higher strength of MgO basic sites shown by the lower stabilization of aci-anion nitromethane and the lower chemical shift ($\delta = 102 \pm 0.5$ ppm) correlates with the higher heat of CO$_2$ adsorption ($\Delta H = -249 \pm 3$ J
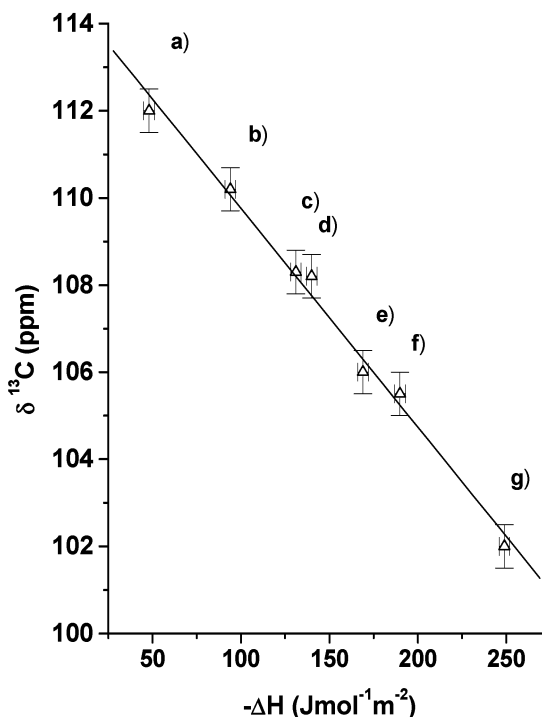

Figure 3. ^{13}C isotropic chemical shift of the adsorbed aci-anion nitromethane, CH$_2$NO$_2^-$, as a function of the heats of adsorption of CO$_2$ measured by microcalorimetry on (a) γ-Al$_2$O$_3$, (b) Mg(Al)O(2.0), (c) KW2000, (d) KW2200, (e) Mg(Al)O(2.5), (f) Mg(Al)O(3.0), and (g) MgO.

mol^{-1} m^{-2}). The opposite is true for γ-Al$_2$O$_3$ ($\delta = 112 \pm 0.5$ ppm, $\Delta H = -48 \pm 3$ J mol^{-1} m^{-2}). Mg(Al)O mixed oxides obtained by incorporation of aluminum in MgO are situated between these two extreme sets of values. The correlation between the NMR and microcalorimetry is explained because both techniques monitor properties of the same surface sites in the adsorption and stabilization of the two probes. Though the driving force is logically the basic site strength for the adsorption of the two probes, the present results show that the Lewis acid strength of the conjugate basic sites plays a major role in the stabilization of the species.

Conclusions

Nitromethane was used as a NMR probe molecule to monitor the basicity of the surface of a series of oxides. Proton abstraction by basic sites leads to the formation of aci-anion nitromethane that is stabilized by the conjugate Lewis acid site. The chemical shift of the carbon of nitromethane adsorbed on various oxides has been show to be correlated with the heat of adsorption of carbon dioxide on the same materials. Since it is known that the heat of adsorption is proportional to the basicity of the sites, these results show that one may use the chemical shift of nitromethane as a measure of basicity of these oxide surfaces.

References and Notes

(1) Iglesia, E.; Barton, D. G.; Biscardi, J. A.; Gines, M. J. L.; Soled, S. L. *Catal. Today* **1997**, *38*, 339.

(2) Zecchina, A.; Lamberti, C.; Bordiga, S. *Catal. Today* **1998**, *41*, 169.

(3) Lavalley, J. C. *Catal. Today* **1996**, *27*, 377.

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(4) Maciel, G.; Haw, J. F.; Chuang, I.; Hawkins, B. L.; Early, T. H.; Mckay, D. R.; Petrakis, L. *J. Am. Chem. Soc.* **1983**, *105*, 5529.

(5) Lunsford, J. H.; Rothwell, W. P.; Shen, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 1540.

(6) Anderson, M. W.; Barrie, P. J.; Klinowski, J. *J. Phys. Chem.* **1991**, *95*, 235.

(7) Hunger, M.; Freude, D.; Pfeifer, H. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 657.

(8) Mastikhin, V. M.; Mudrakovsky, I. L.; Filiminova, S. V. *Chem. Phys. Lett.* **1988**, *149*, 175.

(9) Lahousse, C.; Aboulayt, K.; Maugé, F.; Bachelier, J.; Lavalley, J. C. *J. Mol. Catal.* **1993**, *84*, 283.

(10) Lahousse, C.; Maugé, F.; Bachelier, J.; Lavalley, J. C. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2907.

(11) Di Cosimo, J. I.; Apesteguia, C. R.; Dinés, M. J. L.; Iglesia, E. *J. Catal.* **2000**, *190*, 261.

(12) Scokat, P. O.; Rouxhet, P. B. *J. Chem. Soc., Faraday. Trans. 1* **1980**, *76*, 1476.

(13) Angell, C. L.; Howell, M. V. *J. Phys. Chem.* **1969**, *73*, 2551.

(14) Barthomeuf, D. *J. Phys. Chem.* **1984**, *88*, 42.

(15) Huang, M.; Kaliaguine, S. *J. Chem. Soc., Faraday. Trans.* **1992**, *88*, 751.

(16) Binet, C.; Jadi, A.; Lavalley, J. C. *J. Chim. Phys.* **1992**, *89*, 31.

(17) Nesterenko, N.; Lima, E.; Graffin, P.; de Ménorval, L. C.; Laspéras, M.; Tichit, D.; Fajula, F. *New J. Chem.* **1999**, *23*, 665.

(18) Kheir, A. A.; Haw, J. F. *J. Am. Chem. Soc.* **1994**, *116*, 817.

(19) Allouche, A. *J. Phys. Chem.* **1996**, *100*, 1820.

(20) Engelke, R.; Earl, W. L. *J. Chem. Phys.* **1986**, 84.

(21) Cavani, F.; Trifiro, F.; Vaccari, A. *Catal. Today* **1991**, *11*, 2.

(22) Tichit, D.; Lhouty, M. H.; Guida, A.; Chiche, B. H.; Figueras, F.; Auroux, A.; Betalini, D.; Garrone, E. *J. Catal.* **1995**, *151*, 50.

(23) Corma, A.; Fornés, V.; Martin Aranda, R. M.; Rey, V. *J. Catal.* **1992**, *134*, 58.

(24) Rachdi, F.; Reichenbach, J.; Firlej, L.; Bernier, P.; Ribet, M.; Aznan, R.; Zimmer, G.; Helmle, M.; Mehring, M. *Solid State Commun.* **1993**, *87*, 547.

(25) Rao, K. K.; Gravelle, M.; Sanchez Valente, J.; Figueras, F. *J. Catal.* **1998**, *173*, 115.