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Characterization of basic catalysts by the use of nitromethane as NMR probe molecule and reactant

Enrique Lima, Monique Laspéras, Louis-Charles de Ménorval, Didier Tichit,* and François Fajula

Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, UMR 5618 CNRS ENSCM, 8, rue de l'École Normale, 34296 Montpellier cedex 5, France

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Abstract

Characterization of the basicity of mixed oxides obtained from hydrotalcite-like precursors by ^{13}C CP/MAS NMR spectroscopy using nitromethane-reactive adsorption is described. On Lewis bases, featuring acid–base pairs, the nature of adsorbed species namely nitromethane, aci-anion nitromethane, and methazonate salt analogue depends on the relative strength of the basic and acid sites on the pairs. None of these species is obtained using Brønsted bases such as layered double hydroxide (LDH) of the meixnerite type. In that case a formate analogue is proposed to be formed. Heterogeneous base catalysis of the Michael addition of nitromethane to cyclohex-2-en-1-one is studied. A relationship is established between the activity of the catalyst and the ^{13}C CP/MAS NMR chemical shift of the aci-anion nitromethane which is a measure of the basic strength. Discussion of NMR and catalytic results takes into account the respective roles of basicity and of conjugate Lewis acidity. Basicity is needed to form a reactive anion comparable to aci-anion nitromethane, but the higher the stabilization of aci-anion nitromethane by Lewis acidity, the lower the activity. Increasing the basic strength by decreasing the Lewis acidity of the acid–base pairs leads to an increase of activity concomitant with the formation of methazonate as shown by ^{13}C MAS NMR. The efficiency of meixnerite which is the most active and selective catalyst is related not only to its Brønsted basicity but also to its weak Lewis acidity.

Keywords: Base catalysis; Nitromethane; NMR; Michael addition

1. Introduction

The surface of inorganic oxides, mixed oxides, or zeolites features acid–base pairs whose strength can be measured using probe molecules [1–3]. Among the various probes nitromethane has been little studied. We showed that heating nitromethane adsorbed on various basic surfaces led to adsorbed isocyanate species. Their formation was followed by FT-IR spectroscopy and their frequencies were correlated to the heats of carbon dioxide adsorption which is a measure of the basic strength [4]. Reactive chemisorption of nitromethane as aci-anion nitromethane was investigated by Kheir and Haw [5] to probe MgO and CaO basicity, using cross-polarization magic-angle spinning (CP/MAS) solid-state ^{13}C NMR spectroscopy. Physisorbed nitromethane and aci-anion nitromethane were only observed and the role of acid–base pairs of the surface was not really established.

On the other hand, Iglesia et al. [6] claimed that bifunctional pathways are mainly involved for heterogeneous acid or base catalysis. In the domain of carbon–carbon bond formation, Michael addition of nitromethane to α,β-unsaturated carbonyl compounds is known to be catalyzed by liquid bases such as NaOH, KOH, or EtONa [7]. Results are also described in heterogeneous catalysis using KF/basic alumina [8], KF/oxides [9], basic alumina [10,11], Amberlyst A-21 [12], and Amberlyst A-27 [13]. KF/alumina or KOH/alumina exhibited high activities whatever the unsaturated compound [14]. However, these catalysts lose activity upon recycling [8]. More recently, Choudary et al. reported good yields for Michael addition catalyzed by rehydrated Mg–Al mixed oxides [15].

The adsorption of a molecule either as a probe to analyze the surface by spectroscopy or as a reactant in a catalytic

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* Corresponding author.
E-mail address: tichit@cit.enscm.fr (D. Tichit).

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Table 1
Chemical compositions of the LDH precursors

Sample	Mg/ M^{III}	Chemical formula
Mg(Al)O	3.0	$[Mg_{0.75}Al_{0.25}(OH)_2](CO_3{}^{2-})_{0.102}(NO_3^-)_{0.045} \cdot 0.41H_2O$
Mg(Al)O	2.5	$[Mg_{0.71}Al_{0.29}(OH)_2](CO_3{}^{2-})_{0.123}(NO_3^-)_{0.058} \cdot 0.63H_2O$
Mg(Al)O	2.0	$[Mg_{0.66}Al_{0.34}(OH)_2](CO_3{}^{2-})_{0.164}(NO_3^-)_{0.032} \cdot 0.49H_2O$
KW 2200	2.3	$[Mg_{0.69}Al_{0.31}(OH)_2](CO_3{}^{2-})_{0.14}(NO_3^-)_{0.04} \cdot 0.4H_2O$
Mg(Ga)O	5.0	$[Mg_{0.79}Ga_{0.21}(OH)_2](CO_3{}^{2-})_{0.098}(NO_3^-)_{0.053} \cdot 0.52H_2O$
Mg(Ga)O	3.0	$[Mg_{0.73}Ga_{0.27}(OH)_2](CO_3{}^{2-})_{0.108}(NO_3^-)_{0.055} \cdot 0.59H_2O$
Mg(Ga)O	2.0	$[Mg_{0.68}Ga_{0.32}(OH)_2](CO_3{}^{2-})_{0.151}(NO_3^-)_{0.035} \cdot 0.47H_2O$

reaction provides a valuable tool for a better understanding of the surface and its reactivity. In a previous work [16] we showed that in the Michael addition of nitromethane on cyclohex-2-en-1-one, low reaction rates were observed for catalysts which only physisorbed nitromethane (γ-Al_2O_3, NaX, CsX). Intermediate reaction rates were observed for catalysts such as Mg(Al)O mixed oxides which led to aci-anion nitromethane. The most efficient catalysts were MgO and CsX 9Cs zeolite which showed the formation of methazonate salt analogue.

The aim of this work was to use nitromethane as probe and reactant to correlate the acido–basicity and the catalytic properties of Mg(Al)O and Mg(Ga)O mixed oxides obtained by calcinations of LDH precursors, hydrated LDH (meixnerite), and MgO samples obtained from magnesium carbonate or magnesium hydroxide precursors.

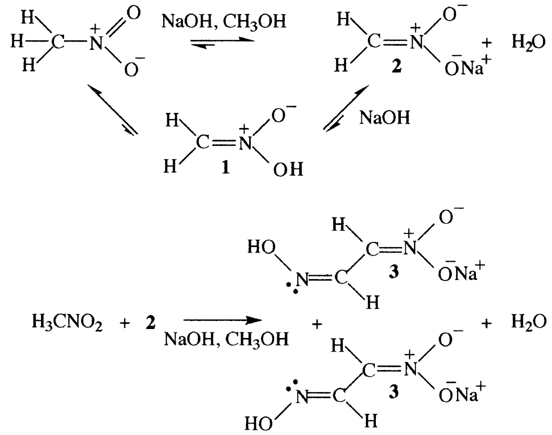
2. Experimental

2.1. Material preparation

The synthesis of LDH precursors of mixed oxides (Table 1) was performed by coprecipitation of a gel at constant pH. An aqueous solution of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 6H_2O$ or $Ga(NO_3)_3 \cdot 9H_2O$ with the desired Mg/M^{III} ratio was delivered into a polypropylene reactor by a chromatography-type pump at a constant flow of $1\ cm^3\ min^{-1}$. A second aqueous solution of 1 M NaOH + 2×10^{-2} M Na_2CO_3 was simultaneously fed by a pH stat apparatus (718 Stat Titrino Metrohm). The flow was controlled in order to maintain the pH in the reactor at a constant value of 9 ± 0.2. After completion of the precipitation the gels were refluxed at 353 ± 5 K for 15 h. The solids were separated by centrifugation, washed thoroughly with deionized water until nitrate elimination, and dried overnight in an oven at 353 K.

The Mg(Al)O and Mg(Ga)O mixed oxides were obtained by calcination of Mg/Al and Mg/Ga LDH at 723 K in a dry synthetic air flow ($25\ cm^3\ min^{-1}$, ramp: $1\ K\ min^{-1}$, 6 h plateau at 723 K).

Mg(Al)O mixed oxide KW 2200 (Mg/Al = 2.3) was purchased from Kyowa.



Scheme 1. Nitromethane reaction with sodium hydroxide in homogeneous medium.

The rehydration of the Mg(Al)O mixed oxide (Mg/Al = 3.0) calcined at 623 K to yield the meixnerite-like type compound was carried out in liquid water at 298 K for 3 days under a N_2 atmosphere.

CsX and the strongly basic overexchanged CsX 9Cs zeolites were obtained from commercially available NaX sample (Aldrich) as described elsewhere [17].

MgO_c was obtained by calcination of $MgCO_3$ (Aldrich) at 873 K under dry synthetic air. Activation in situ before catalytic reaction of $Mg(OH)_2$ (Stremm) at 623 K for 6 h led to MgO_h.

γ-Al_2O_3 was prepared by calcination of boehmite at 873 K.

2.2. Synthesis of the salts of reaction products

The addition at 273 K of a solution of NaOH (0.1 mol) in 50 mL of methanol to a solution of nitromethane in equilibrium with the aci-anion nitromethane (hereafter **1**, Scheme 1) led to the sodium salt of aci-anion nitromethane (hereafter **2**, Scheme 1). CH_3OH was then removed by distillation under vacuum, and the solid dried in an oven at 353 K.

^1H NMR ($CDCl_3$, ref TMS): $\delta = 5.7$ ppm (s), H_2C; ^{13}C NMR (CD_3OD), $\delta = 101$ ppm, ^{13}C CP/MAS NMR, $\delta = 99$ ppm, H_2C.

Synthesis of sodium salt of methazonic acid (hereafter **3**, Scheme 1) was performed by using 0.1 mol of nitromethane added to 0.2 mol of NaOH in 50 mL of CH_3OH at 323 K for 2 h. CH_3OH was then removed by distillation under vacuum, and the solid dried in an oven at 353 K.

^1H NMR ($CDCl_3$, ref TMS), $\delta = 6.82$ ppm (d, $J = 9.0$ Hz) and 7.23 ppm (d, $J = 8.8$ Hz), HC=NOH; 7.66 ppm (d, $J = 8.8$ Hz) and 8.20 ppm (d, $J = 9.0$ Hz), HC=NO_2^- Na^+. As shown by irradiation, signals at 6.82 and 8.20 ppm belong to the same isomer.

^{13}C NMR (CD_3OD), $\delta = 108$ and 114 ppm, C=$NO_2{}^-$–Na^+; 142 and 145 ppm, C=NOH; ^{13}C CP/MAS NMR: $\delta = 106, 111, 140$, and 143 ppm.

Moreover ^{13}C CP NMR spectra of the previous solid show a peak at $\delta = 167.2$ ppm corresponding to the same shift as the sodium formate ($\delta = 167.4$ ppm) or formic acid ($\delta = 166.7$ ppm). ^{1}H NMR corroborates this assignment: HC δ (CD_3OD) = 8.6 ppm (s).

The same products are identified when reaction is performed in water. No reaction is observed without addition of base.

2.3. Characterizations

Chemical analyses were performed at the Service Central d'Analyse du CNRS (Solaize, France) by ICP-MS.

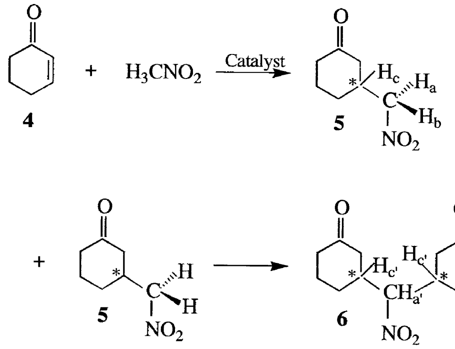
XRD powder patterns were collected on a CGR Theta 60 instrument using monochromatized Cu-K_{α_1} radiation ($\lambda = 0.15401$ nm, 40 kV, and 50 mA).

BET specific surface areas were determined by N_2 adsorption at 77 K with a Micromeritics ASAP 2000 apparatus on samples outgassed at 523 K and 10^{-4} Pa.

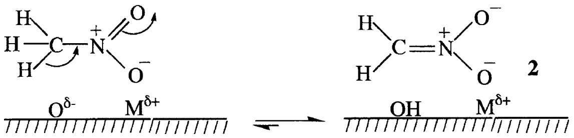
For ^{13}C CP/MAS NMR studies, 99% ^{13}C-enriched nitromethane (Aldrich) was distilled under vacuum before admission onto the solids. Solids were activated in situ under vacuum at 673 K for 8 h before nitromethane adsorption. Equilibration was performed under 30 Torr of $^{13}CH_3NO_2$ at room temperature for 30 min, and then the samples were evacuated at 323 K for 20 min. Spectra were recorded at 50.32 MHz with a contact time of 5 ms, a 4 KHz spinning rate, and 90° pulses of 5 us [16,18] using a ASX-200 Bruker spectrometer with a home-built NMR probehead [19]. Chemical shifts were referenced to solid CH_2 adamantane shift at 38.2 ppm relative to TMS.

2.4. Catalytic tests

Before reaction, catalysts were activated in situ in a glass reactor at 623 K for 6 h under a dry synthetic air flow (ramp: 2 $K\,min^{-1}$). Meixnerite was activated at 323 K under vacuum. After adjusting the temperature to reaction temperature under N_2 flow, stoichiometric amounts of reactants (0.01 mol) in 20 mL of DMSO were introduced on the activated catalyst (0.4 g) in the batch reactor with a syringe, under magnetic stirring. The progress of the reaction was monitored by periodically withdrawing samples which were analyzed by gas chromatography on a HP-5890 with capillary column HP-1. Calibration of **3** was performed using decane (Aldrich) as a reference. Retention times of nitromethane, cyclohex-2-ene-1-one (hereafter **4**, Scheme 2), decane, mono-adduct (hereafter **5**, Scheme 2), bis-adduct (hereafter **6**, Scheme 3) were 0.9, 5.5, 7.1, 10.9, and 14.8 min, respectively.



Scheme 2. Model Michael addition of nitromethane to cyclohex-2-en-1-one.



Scheme 3. Formation of the aci-anion sodium salt analogue on acid–base pairs.

The concentration of reaction products was determined from ^{1}H NMR spectra performed with a Bruker Avance DRX—400 MHz spectrometer, after solvent evaporation and dissolution of the residual fraction in CD_3Cl. The following parameters were determined to evaluate the catalytic properties:

cyclohex-2-ene-1-one **4** conversion (mol%),

$$C = 100 \times \left([\mathbf{4}]_0 - [\mathbf{4}]_t\right)/[\mathbf{4}]_0;$$

selectivity of mono-adduct (mol%),

$$S = 100 \times \left[\tfrac{1}{2}(I_{Ha} + I_{Hb})/\tfrac{1}{2}(I_{Ha} + I_{Hb}) + I_{Ha'}\right],$$

where I_{Ha} and I_{Hb} are the integrated intensities of the signals corresponding to 2 protons of the mono-adduct **5**, and $I_{Ha'}$ to that of a proton of the bis-adduct **6**.

Nitromethane (98% purity, Lancaster) and cyclohex-2-en-1-one **4** (Fluka) were used without purification. DMSO purchased from SDS was kept on molecular sieve A under N_2 atmosphere.

3. Results

Nitromethane and its tautomeric form, aci-nitromethane **1** lead in the presence of sodium hydroxide to the sodium salt **2** [20]. A typical reaction of nitromethane also concerns the formation of the sodium salt of methazonic acid **3** [21] by condensation with an equivalent of the aci-anion salt (Scheme 1).

Sodium aci-anion salt **2** and sodium methazonate **3** were obtained by reaction of nitromethane with NaOH in methanol and characterized by ^{13}C NMR (Fig. 1). The singlet observed in ^{13}C CP/MAS NMR at 99 ppm (Fig. 1a) for the methylene group of **2** gives a multiplet in CD_3OD centered at 101 ppm (Fig. 1c) explained by H/D exchange [22]. Two isomers of sodium methazonate are clearly observed in $CDCl_3$ (Fig. 1c) (108, 114, 142, 145 ppm) which correspond to Z and E isomers around the C=N–OH double bond (Scheme 1) [23]. Their ^{1}H NMR spectra agree with the formula **3**. Another signal (167 ppm) is observed when

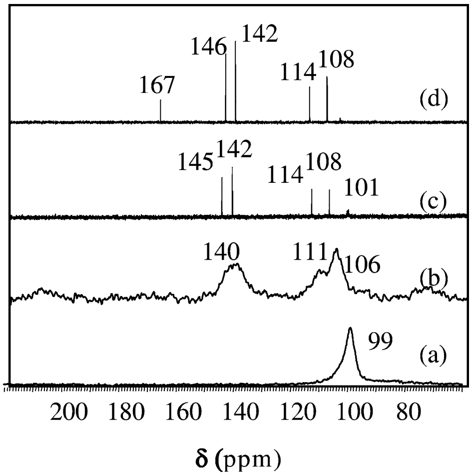


Fig. 1. ^{13}C CP NMR spectra of solid sodium aci-anion salt (a), solid sodium methazonate (b), sodium methazonate in CD_3OD (c), and products in D_2O (d).

reaction is performed in water (Fig. 1d) which is assigned to formic acid [23] or sodium formate by comparison with an authentic sample.

3.1. *Reactive adsorption of nitromethane on oxides and mixed oxides followed by ^{13}C CP/MAS NMR*

Species formed by reactive adsorption of nitromethane on the surface of various solids were identified by comparison of the resulting ^{13}C CP/MAS NMR spectra with those of the compounds obtained in homogeneous conditions.

Their nature depends on the acid–basic properties of the surface. Only physisorbed nitromethane (62 ppm) is observed for zeolites NaX and CsX [16]. Reactive adsorption of nitromethane on Al_2O_3 (Fig. 2e) led to physisorbed nitromethane ($\delta = 62$ ppm) and aci-anion analogue **2** ($\delta = 112$ ppm). The same species are observed by adsorption of nitromethane on Mg(Al)O mixed oxides (Fig. 2b–d). On MgO_c (Fig. 2a) physisorbed nitromethane and aci-anion **2** are also obtained. However, the presence of a peak at 143 ppm and of a signal at 107 ppm, which could be decomposed into 2 peaks at 110 and 102 ppm, show that methazonate **3** analogue ($\delta = 110$, 143 ppm) and aci-anion **2** ($\delta = 102$ ppm) are also formed on this surface after decomposition.

Therefore, incorporation of Al in the MgO structure leads to the disappearance of the signals of the methazonate anion analogue **3**. The decrease of the Mg/Al ratio from 3.0 to 2.0 by increasing the Al content (from Figs. 2b to d) has no effect on the species formed (physisorbed nitromethane and aci-anion **2**). However, on the one hand, the CH_2 signal of **2** shifts upfield and, on the other hand, as shown by the signal to noise ratio obtained under the same conditions, the amount of **2** decreases with increase of the Al content.

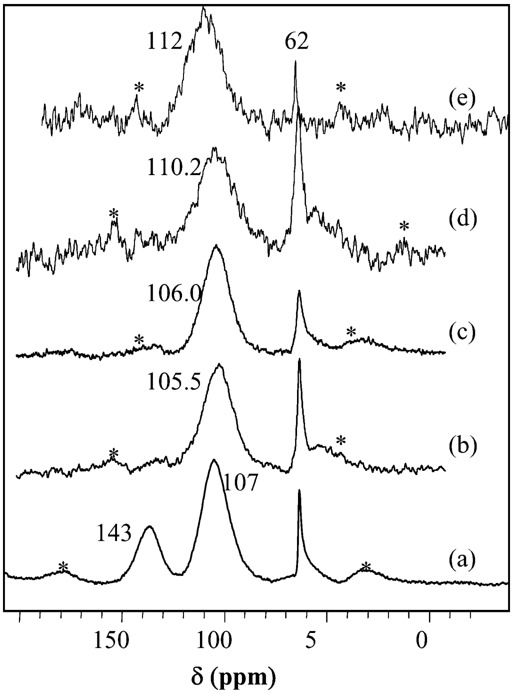


Fig. 2. ^{13}C CP/MAS NMR spectra of species formed from nitromethane adsorption on MgO_c (a), Mg(Al)O mixed oxides with Mg/Al = 3.0 (b), 2.5 (c), 2.0 (d), and Al_2O_3 (e).

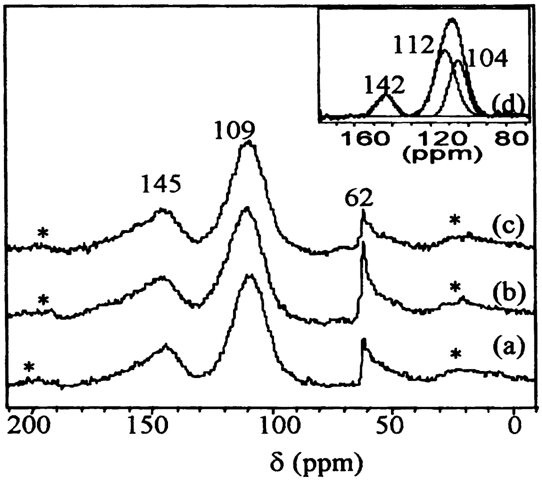


Fig. 3. ^{13}C CP/MAS NMR spectra of species formed from nitromethane adsorption on Mg(Ga)O mixed oxides with Mg/Ga = 5.0 (a), 3.0 (b), and 2.0 (c). Decomposition of the peak at 109 ppm in (a) leads to two peaks in (d) at 104 and 112 ppm.

Adsorption of nitromethane onto Mg(Ga)O mixed oxides leads to three species (Fig. 3) as for MgO_c. Whatever the Mg/Ga ratio between 2.0 and 5.0 methazonate **3**, aci-anion **2**, and physisorbed nitromethane are obtained.

Species formed upon nitromethane adsorption allow consideration of 3 distinct families of solids, i.e., zeolites NaX and CsX leading to physisorbed nitromethane; Al_2O_3 and Mg(Al)O mixed oxides leading to physisorbed nitromethane and aci-anion nitromethane **2**; and Mg(Ga)O mixed oxides, MgO_c, and modified CsX 9Cs zeolite leading to physisorbed nitromethane, aci-anion nitromethane **2**, and methazonate anion analogue **3**.

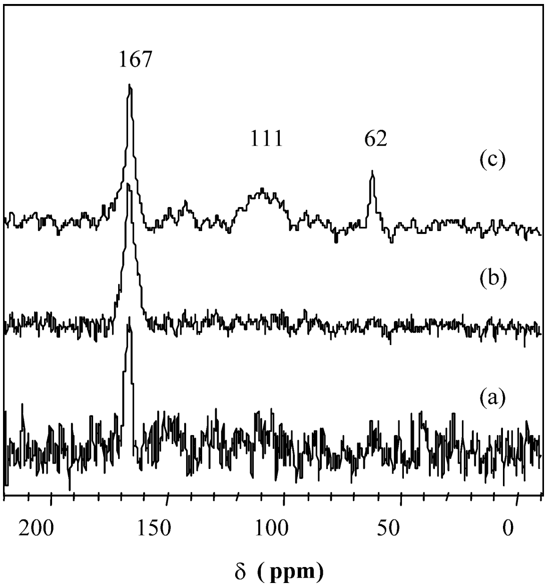


Fig. 4. ^{13}C CP/MAS NMR spectra of species formed from nitromethane adsorption on the meixnerite activated at 323 K (a), 353 K (b), and 473 K (c).

3.2. *Example of reactive adsorption of nitromethane on LDH followed by ^{13}C CP/MAS NMR*

By adsorption of nitromethane under the same conditions on meixnerite activated at 323 K a single signal assigned to a formate analogue species is observed at 167 ppm (Fig. 4). None of the previous species are identified for activation temperatures of 323 or 353 K. Physisorbed nitromethane (62 ppm) and aci-anion nitromethane (111 ppm) appear after activation of meixnerite at 473 K (Fig. 4c).

3.3. *Michael addition of nitromethane on cyclohex-2-en-1-one* **4**

The model reaction (Scheme 2) was performed using stoichiometric amounts of nitromethane and **4** (0.5 mol L^{-1}) in DMSO.

This reaction was usually performed in protic solvents, but dimethyl sulfoxide (DMSO) rather than ethanol was likely used taking into account our previous results showing that it was a better solvent in the Knoevenagel reaction catalyzed by basic zeolites [24]. Initial rates were calculated from cyclohexenone consumption with time. Two products were identified: (i) the mono-adduct **5** resulting from mono addition of nitromethane on cyclohex-2-en-1-one **4**, (ii) the bis-adduct **6** formed by the consecutive reaction of **5** with **4** (Scheme 2). **5** and **6** were well characterized by ^{1}H NMR (Fig. 5). Two quartets are observed for H_a and H_b of **5** and two doublets for $H_{a'}$ of **6**.

The two diastereotopic protons H_a and H_b of the prochiral methylene group of the CH_2NO_2 moiety in **5** present an AB spectra ($J\ H_aH_b = 12$ Hz), each proton being coupled with the vicinal H_C ($J\ H_aH_C = 6$ Hz). The formation of the bis-adduct **6** with two asymmetric centers leads to the obtention of two diastereoisomers (*RR*, *SS*) and (*RS*, *SR*) which give two doublets ($J\ H_{a'}H_{c'} = 7.1$ Hz). Selectivities were determined from ^{1}H NMR spectra of the crude media (Fig. 5).

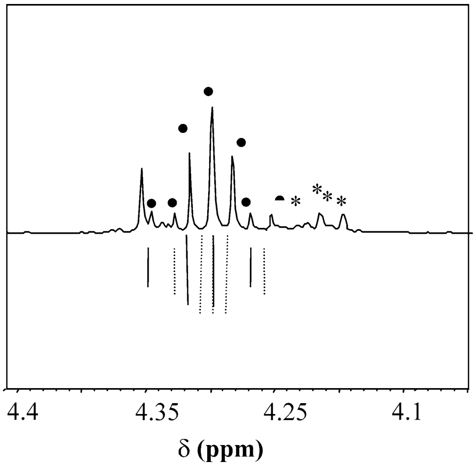


Fig. 5. ^{1}H NMR spectra of the mono-adduct **5** (●) and bis-adduct **6** (∗) implied in the calculation of the mono-adduct selectivity.

Table 2
Effect of the order of addition of reactants using stoichiometric concentrations and MgO_h as catalyst (m catalyst = 0.4 g)

Method	r_0 (mol min^{-1})	Conversion (t = 4 h) (%)	**5** Selectivity (%)
a[a]	0.18	56	54
b[a]	1.10	97	35
c[b]	0.36	73	70

[a] Nitromethane or enone **4** was added as the first reactant, and the second reactant was added after 5 min at 353 K.

[b] The two reactants were added together.

3.4. *Effect of the order of addition of reactants*

Table 2 shows results obtained with MgO_h using stoichiometric amounts of reactants (0.5 mol L^{-1}).

The order of addition of the reactants on the catalyst presents a major effect either on the initial rate or on the mono-adduct selectivity. The initial rate is six times higher when enone **4** (method b) instead of nitromethane is first added (method a). Comparison of methods a and b shows that selectivity decreases when conversion decreases as expected for consecutive reactions. Therefore the bis-adduct **6** is the major product by method b. Higher conversion and selectivity are reached by method c, when reactants are simultaneously added, than by method a. Method c will be used throughout the rest of the study.

3.5. *Effect of the weight of catalyst on the reaction rate and selectivity*

The reaction does not proceed without catalyst. The reaction rate increases with the weight of catalyst (Table 3) and does not vary with the stirring rate (not shown). Thus

Table 3
Effect of the weight of MgO_h catalyst using stoichiometric concentrations of **4** and nitromethane

m (g)	r_0 (mol min^{-1})	Conversion ($t = 4$ h) (%)	**5** Selectivity (%)
0.0	0.0		
0.28	0.24	62	76
0.40	0.36	73	70
0.50	0.46	85	52

the reaction rate is not controlled by external diffusional constraints. The mono-adduct selectivity, as previously described, decreases with conversion.

3.6. Catalytic results in the model reaction

For a given catalyst the selectivity in mono-adduct decreases when the conversion goes on, as expected when consecutive reactions are taking place (Table 3). The reaction rates vary within broad limits depending on the nature of the catalyst (Table 4).

A first series (Table 4, entries 1–5) of catalysts includes γ-Al_2O_3, Mg(Al)O, and MgO_c. The initial reaction rate increases when going from γ-Al_2O_3 to MgO_c. The same trend is observed when the surface area of the catalyst is taken into account. This is consistent with the concurrent increase in the amount of aci-anion nitromethane already reported (Fig. 2).

The mono-adduct selectivity is lower for Mg(Al)O (entry 4) than for MgO_c (entry 5) at the same conversion. This selectivity slightly increases when the conversion decreases for the various Mg(Al)O mixed oxides.

Mg(Ga)O mixed oxides (Table 4, entries 6, 7) lead to initial reaction rates and selectivities markedly higher than with the previous catalysts. Higher conversions and mono-adduct selectivities (Table 4) are achieved. Moreover formation of methazonate **3** and aci-anion nitromethane **2** is also observed (Fig. 3).

The activity of exchanged NaX and CsX (Table 4, entries 8, 9) is low but increases markedly with the basicity for CsX 9Cs (entry 10), the selectivity remaining similar. Activity of CsX 9Cs zeolite is higher than that of MgO_c with similar selectivity. Accordingly physisorbed nitromethane is identified for NaX, CsX, and γ-Al_2O_3, whereas methazonate **3** is also obtained for CsX 9Cs zeolite.

Finally, the better activities and selectivities in mono-adduct are obtained with MgO_h and meixnerite (Table 4, entries 11, 12). The increase of the initial rate when going from MgO_c to MgO_h does not accounted for an increase of the surface areas. Formation of formate upon nitromethane adsorption shows the different behavior of the meixnerite and the other catalysts.

4. Discussion

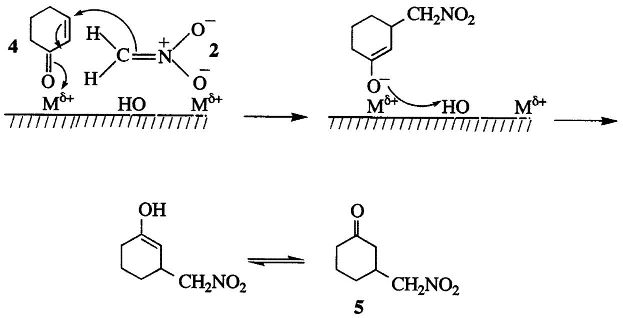
Nitro and aci tautomeric forms of nitroalkanes (Scheme 1) with hydrogen atoms on the α-carbon position exhibit acidic properties. pKa's of nitromethane and of its aci-form **1** in water at 25 °C were evaluated to 10.2 and 3.2, respectively [20]. The equilibrium proportion of the aci-form **1** under these conditions represents 0.000011%. Reaction with sodium hydroxide leads to the sodium salt of the aci-anion **2**. However, nitromethane has a peculiar behavior among nitroalkanes because the sodium salt of methazonic acid **3** can be readily obtained [21] (Scheme 1).

So, in order to generate the reactive aci-anion analogue a basic site is needed. Taking into account the pKa's of nitromethane and aci-nitromethane **1**, 10.2 and 3.2, respectively, a higher basic strength is required for the abstraction of a proton from adsorbed nitromethane leading either to **1** and then to **2** or directly to **2** (Scheme 1).

Oxides, mixed oxides, and zeolites bear acid–base pairs which can be differentiated by their overall basicity or acidity. By adsorption of nitromethane on acid–base pairs an analogue of aci-nitromethane **2** is obtained (Scheme 3) when basic strength is able to abstract a proton. The Lewis acid site allows the stabilization of the aci-anion.

Table 4
Catalytic results using a same weight of activated catalyst

Entry	Catalyst	Mg/M^{III} (mol mol^{-1})	Surface area ($m^2\ g^{-1}$)	$r_0 \times 10^2$ (mol min^{-1})	$r_0 \times 10^4$ (mol $min^{-1}\ m^{-2}$)	Conversion ($t = 8$ h) (%)	**5** Selectivity (%)
1	γ-Al_2O_3		172	0.2	0.12	15	–
2	Mg(Al)O	2.0	140	4.8	3.4	25	40
3	KW 2200	2.3	180	7.2	4.0	39	42
4	Mg(Al)O	3.0	240	8.8	3.7	45	34
5	MgO_c		160	13.2	8.2	45	59
6	Mg(Ga)O	5.0	176	40.0	22.7	65	57
7	Mg(Ga)O	2.0	140	26.0	18.6	60	60
8	NaX		666	0.2	0.03	10	–
9	CsX		471	1.0	0.21	15	60
10	CsX 9Cs		423	24.0	5.7	55	58
11	MgO_h		200	36.0	18.0	73	70
12	Meixnerite	3.0	–	92.0	–	95	80



Scheme 4. Reaction mechanism proposed for acid–base catalysis of the Michael addition.

LDH such as meixnerite are characterized by a Brønsted basicity provided by OH-compensating anions and by a very weak Lewis acidity due to their hydration [25].

The adsorption of nitromethane on this solid (Fig. 4) probably leads to the formation of formate. Such a compound has been evidenced in the presence of water under basic conditions (Fig. 1d).

In the base-catalyzed Michael addition of nitromethane on α, β-unsaturated carbonyl compounds, nitromethane acts as the donor, the nitro group being particularly effective in stabilizing a negative charge on an adjacent carbon [7], and cyclohex-2-en-1-one **4** as the acceptor (Scheme 4). So, the formation and the reactivity of **2** may be considered as the key factor for the catalytic activity or the reactive adsorption of nitromethane.

The formation of the two products **5** and **6** obtained by the Michael addition of cyclohexenone **4** and nitromethane (Scheme 2) is well explained by consecutive reactions. Abstraction of a proton from nitromethane or mono-adduct **5** leads to competitive addition of the anions on the C=C double bond of cyclohexenone **4**. Selectivity to **5** decreases with conversion as observed for a same catalyst, MgO_h (Table 3). Reaction rate is not controlled by external diffusion as checked by varying catalyst weight:reactant ratio for MgO_h (Table 3) and the order of activity of the various solids varies only slightly if the surface area of the catalysts is taken into account (Table 4).

The influence of the order of addition of the reactants on reaction rates and selectivities accounted for their competitive adsorption on the surface (Table 2). Higher enone activation occurring by adsorption on a Lewis acid site (Scheme 4), and in contrast lower stabilization of aci-anion nitromethane, leads to an enhanced initial reaction rate (method b). In this case, mono-adduct **5** reacts easily with chemisorbed enone to give the bi-adduct **6**. Chemisorption of nitromethane limits chemisorption of enone **4** (method a). Thus, a good compromise is achieved by method c involving simultaneous addition of the reactants. It is noteworthy that a higher selectivity in the mono-adduct **5** is obtained at a high conversion level, indicating the role of chemisorbed enone.

The first step (Scheme 3) of the base-catalyzed mechanism (Scheme 4) implies the abstraction of a proton. Therefore weak reaction rates are observed with poorly basic NaX and CsX catalysts leading to nitromethane physisorption, or Al_2O_3 leading to a low amount of **2**. As previously suggested from theoretical calculations [26], nitromethane physisorption likely takes place between the nitro group and a Lewis acid site as shown by ^{133}Cs CP/MAS NMR for CsX zeolite [16].

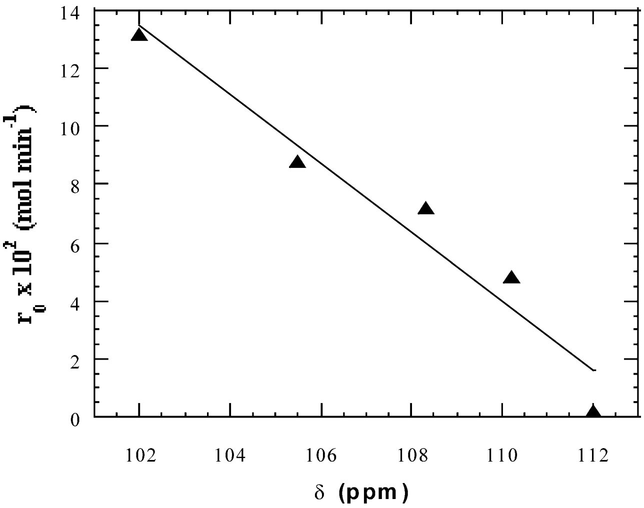


Fig. 6. Correlation between the initial reaction rate and the ^{13}C chemical shift of the methylene group of the aci-anion nitromethane **2**.

Then, the initial reaction rate (Table 4, entries 2–5) increases with the amount of **2** (Scheme 2). Moreover it is well correlated with the ^{13}C chemical shift of the methylene group of aci-anion nitromethane **2** (Fig. 6). The higher the initial rate, the lower the chemical shift.

This correlation is in line with previous results showing that ^{13}C chemical shifts of the aci-anion nitromethane **2** are correlated with the heat of carbon dioxide adsorption [18]. Taking into account the species involved in the adsorption of CO_2 on the oxide surface [27], the same acid–base pairs are concerned with the various processes.

When it is formed, aci-anion nitromethane **2** is stabilized by interaction with a Lewis acid site. Therefore, it is highly stabilized on Lewis acid sites of high strength as previously suggested by Allouche for MgO and CaO [26], and its reactivity decreases (Scheme 4). The withdrawing effect of the Lewis acid site lowers the anionic character of the methylene group of **2**. This feature accounted for both the decrease of the initial rate and the deshielding in ^{13}C CP/MAS NMR in the series MgO_c, Mg(Al)O, Al_2O_3.

Considering the acid–base pairs the strength of the basic sites decreases as that of the conjugated acid site increases. Therefore, reaction rate is well correlated with the basic strength of the catalyst.

When **2** is weakly stabilized on Lewis acid sites formation of methazonate **3** occurs. Concomitantly, for Mg(Ga)O mixed oxides (Table 4, entries 6, 7) and CsX 9Cs (entry 10) the higher basic strength leads to an enhancement of initial reaction rates when the decrease of Lewis acid strength accounted for the increase of selectivities.

One can note the different behavior of MgO_c obtained from $MgCO_3$ (Table 4, entry 5), and of MgO_h obtained from $Mg(OH)_2$ (entry 11). On the other hand, it has been previously shown that meixnerite is particularly efficient for this kind of condensation (entry 12) [15]. It is generally agreed that their mild Brønsted basicity allows high selectivities to be reached [15]. However, meixnerite-type materials are able to perform self-condensation of acetone [28,29]. Considering acetone and nitromethane pKa's, abstraction of a proton is easier from the latter compound. So, in our opinion, the remarkable behavior of the meixnerite leading to high activity and selectivity is related both to its low acidity and to mild Brønsted basicity. Poisoning of basic sites by the remaining ${CO_3}^{2-}$ in the case of MgO catalyst obtained from $MgCO_3$ precursor probably accounted for the different behavior of the two MgO catalysts. The activation of enone by Lewis acid sites, easily performed, is not the limiting factor.

Good indications about the involvement of acid–base pair catalysts may be obtained from the ^{13}C MAS NMR study of the reactive adsorption of nitromethane. Only physisorption occurs on poorly active catalysts. Aci-anion nitromethane **2** is formed on catalysts exhibiting moderate activity and selectivity. Formation of methazonate **3** with a net increase of both the activity and the selectivity is observed for highly basic catalysts. For meixnerite the weak acid strength and the presence of remaining water concur to the formation of a formate analogue.

5. Conclusions

Nitromethane adsorption on inorganic oxides gives rise to reactions which were well described through identification of the different species formed using ^{13}C CP/MAS NMR: physisorbed nitromethane, aci-anion nitromethane, methazonate, and formate analogues, depending on the acid–basicity of the surface. The use of nitromethane as a reactive probe in NMR and as a reactant in the base-catalyzed Michael addition with cyclo-2-en-1-one led to consistent results. The strength of the basic sites influences the formation of aci-anion nitromethane. The role of the conjugate Lewis acid sites of acid–base pairs is demonstrated and determines activity and selectivity.

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