Infrared spectroscopic characterization of basic properties: Nitromethane as probe molecule

Ruth L. Martins [a,*], Claudia de O. Veloso [a,b], Claudio A. Mota [c], Martin Schmal [a,*]

[a] Universidade Federal do Rio de Janeiro – NUCAT-PEQ-COPPE, Bl G-128 Centro de Tecnologia, Cidade Universitária, CEP: 21945-970, Rio de Janeiro, RJ, Brazil
[b] Universidade do Estado do Rio de Janeiro – Instituto de Química, Rua São Francisco Xavier, 524, CEP: 20559-900, Rio de Janeiro, RJ, Brazil
[c] Universidade Federal do Rio de Janeiro – Instituto de Química, Centro de Tecnologia, Cidade Universitária, CEP: 21945-970, Rio de Janeiro, RJ, Brazil

ARTICLE INFO

ABSTRACT

Nitromethane, as probe molecule, and infrared spectroscopy, as analytical tool, were used to characterize the basic properties of alkali-exchanged X zeolites and metal oxides. It was observed that this probe molecule could adsorb molecularly, dissociatively and dissociative-associatively, according to the basic strength of the sites present on the studied solids. Alkali-exchanged X zeolites presented weak basic sites and a scale of basicity could be established, CsX > KX > NaX > LiX, based on the shift of the CH_3 rock angular bending frequency. On Al_2O_3, ZrO_2, TiO_2 weak and intermediate basic sites were identified, while on MgO, La_2O_3 and alkali-promoted MgO just strong basic sites were found. For the alkali-promoted MgO samples no basicity scale could be observed. For the universe of the studied materials nitromethane behaves as a proper probe molecule to characterize basic sites with different strengths.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Acidity and basicity are concepts largely used to explain the catalytic properties of different materials. Extensive studies have been devoted to the characterization of solid acid catalysts, as they play an important role in chemical and petroleum industries but, in contrast, less attention has been dedicated to basic sites, more specifically, O^{2-} ions and basic OH, and to the characterization of solid basic catalysts. Different from acidic solids, there are no probe molecules, such as ammonium, pyridine or luthidine, universally accepted for basic catalysts. To evaluate the proton accepting properties of basic surfaces, titration with acidic reagents, such as benzoic acid, and spectroscopic techniques using probe molecules such as pyrrole, chloroform, CO, CO_2, SO_2 are often used and they were described and discussed in a review by Lavalley [1]. The titration method allows one to infer only the total content of surface basic centers without differentiation of their properties. The spectroscopic method provides a variety of possibilities concerning to surface properties, as the use of probe molecules leads to specific interaction with surface sites.

According to Davydov [2], a probe molecule must fulfill the following requirements:

- specifically interaction only with the surface site to be tested;
- be spectral sensitive to changes on the electronic state of the adsorption site;
- no surface modification due to side reactions should occur.

The probe molecules usually indicated in the literature for basic property measurements, such as pyrrole, $CHCl_3$ and CO_2 will be analyzed based on the premises above mentioned.

Pyrrole with its acid NH is able to form an H-bond with basic surface centers and the shift in the wavenumbers of this stretching vibration is used as an evaluation of the basic strength of sites interacting with the H atom. Barthomeuf [3] applied this probe molecule in studying the basic strength of several zeolites. Scokart and Rouxhet [4] studied the pyrrole adsorption on metal oxides. The shifts in NH vibration observed were $3260\,cm^{-1}$ for Al_2O_3, $3360\,cm^{-1}$ for MgO and $3340\,cm^{-1}$ for ThO_2. These results suggested that alumina is a stronger base than MgO and ThO_2, which was unexpected. Besides, some difficulties arise by the use of this probe due to its high proton affinity and its strong interaction with OH groups and also its dissociative adsorption leading to hydroxyl species and adsorbed pyrrolate anions bringing, in that way, several surface modifications [5].

Chloroform as such or as deuterated molecule can form H (D)-complexes with basic centers. Paukshits et al. [6] used the correlation between $\Delta v_{C-H(D)}$ and proton affinity to calibrate the strength of surface basic centers on the pK_a scale. The strongest (+14) centers were observed on CaO, whereas for MgO and BeO, the strength of the sites was 9–10, and Al_2O_3, it was no more than

* Corresponding author. Tel.: +55 21 25628352; fax: +55 21 25907631.
E-mail addresses: ruth@peq.coppe.ufrj.br (R.L. Martins),
schmal@peq.coppe.ufrj.br (M. Schmal).

7. But $CHCl_3$ is far from being considered a perfect probe molecule because of its dissociation leading to formates and surface modifications with chlorine ions, as observed by Gordymova and Davydov [7].

Because CO_2 is acidic, it adsorbs specifically on basic sites of metal oxides, leading to the formation of several species. On basic hydroxyl groups, for instance, H-carbonate species, $HO–CO_2^-$ are formed. On basic oxygen ions, different kinds of carbonate species can be formed depending or not on the participation of neighboring metal ions to the adsorption site. So, unidentate, bidentate, bridged and others ill-defined species in which three oxygen atoms interact with metal ions such as polydentate species can be formed. The localization of these species either on the surface, unidentate, bidentate or bridged species, or in the bulk, polydentate species, is essential for the interpretation of the results by other than spectroscopic methods, like temperature programmed desorption or microcalorimetry as CO_2 interaction can result not only from adsorption on basic sites but also from its reaction with the bulk. Bernal et al. [8,9], for instance, have shown that atmospheric CO_2 not only convert lanthanum oxide into surface carbonate but also into bulk carbonates. Also, CO_2 cannot be considered an inert gas, as it can reoxidize a surface previously reduced, such is the case of CeO_2. In spite of these disadvantages (diversity of carbonate species formed, possibility of reoxidation, and formation of bulk carbonates) CO_2 has been extensively used as probe for the determination of the relative basicity of different metal oxides.

Lima et al. [10] have reported a study on characterization of basic properties based on the ^{13}C CP/MAS NMR chemical shifts observed for nitromethane chemisorbed on basic oxides. They used the compounds formed by the reaction of nitromethane with a methanolic solution of NaOH to characterize the species formed when this probe molecule chemisorbs on basic oxides. They classified the basic strength of the solid sites as weak, intermediate and strong, when spectra similar to that of physisorbed nitromethane, sodium salt of aci-anion nitromethane and sodium salt of methazonic acid were respectively obtained.

In the present work, infrared spectroscopy was used as an analytical tool to determine the basic properties of cation-exchanged X zeolites, alkali-promoted MgO, and different metal oxides (MgO, La_2O_3, Al_2O_3, ZrO_2, TiO_2) using nitromethane as a probe molecule.

2. Experimental

2.1. Material preparation

A commercial MgO (Merck) was hydrolyzed in order to prepare $Mg(OH)_2$ according to the following procedure. A mixture of commercial MgO and water was prepared using a solid ratio of 10 wt%, and was kept under continuous stirring by 24 h at room temperature. The suspension was then evaporated and dried at 100 °C for 16 h. A MgO sample was obtained by calcination of the prepared $Mg(OH)_2$ at 500 °C under vacuum using a heat ratio of 3 °C min^{-1}.

Alkali-promoted MgO samples were prepared by wet impregnation of the synthesized $Mg(OH)_2$ with the corresponding aqueous solutions of alkali nitrate (Li, Na, K) and acetate (Cs). The nominal load of alkali cation was based on a cation/Mg molar ratio of 0.05. The doped-oxides were calcined in situ at 500 °C in the presence of synthetic air.

The zeolite samples used in this work were prepared from a sodium faujasite X (silica alumina molar ratio = 2.3) using the following ion exchange procedure. The parent zeolite was exchanged twice with an alkali chloride (K, Cs) or nitrate (Li) solution at 80 °C for 1 h, using a molar ratio of alkali ion in solution to total cations in the zeolite equal to 0.76 in each step. After each exchange step, the materials were filtered, washed with hot water and dried at 120 °C.

La_2O_3 (JMC303 Specpure) and Al_2O_3 (Harshaw A13996) were used without any treatment. ZrO_2 was obtained through the calcination of zirconium hydroxide (MEL Chemicals) at 500 °C. TiO_2 was prepared by the hydrolysis of titanium isopropoxide (Aldrich) under inert environment followed by drying and calcination at 550 °C.

2.2. Infrared measurements

Infrared experiments were conducted using a Fourier Transform spectrometer, Perkin Elmer 2000, self supported wafers (9.8 mg cm^{-2} "thickness"), and a Pyrex cell with CaF_2 windows. During the sample pretreatment and gas adsorption the cell was attached to a vacuum glass system. The spectral domain was between 4000 and 1000 cm^{-1} with a 4 cm^{-1} resolution. The zeolite and oxide samples were pretreated at 400 °C for 4 h and 500 °C for 1 h, respectively, in vacuum up to 10^{-5} Torr. After cooling down to room temperature the infrared spectrum was recorded and used as background for the nitromethane adsorption experiments. Adsorption studies were conducted by exposing the pretreated wafers to 10 Torr of nitromethane at 100 °C during 30 min, followed by evacuation up to 10^{-5} Torr, at the same temperature. The diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) spectra of the sodium salt of methazonic acid and of the sodium salt of aci-anion nitromethane were obtained for comparative purpose.

The synthesis of the sodium salt of methazonic acid was performed by using 0.1 mol of nitromethane added to 0.2 mol of NaOH in 50 cm^3 of CH_3OH at 50 °C for 2 h. The sodium salt of aci-anion nitromethane was prepared by adding a solution of NaOH (0.1 mol) in 50 cm^3 of methanol to 0.1 mol of nitromethane at 0 °C. In both synthesis methanol was then removed by distillation under vacuum and the solid dried at 80 °C.

3. Results and discussion

This study is based on the interaction between acid hydrogen atoms of nitromethane and oxygen atoms of basic solids generally used as catalysts. According to Lima et al. [10], nitromethane, as shown in Fig. 1, presents two resonances forms one of them is called aci-anion (**1**). These forms could react with a NaOH methanolic solution producing either the sodium salt of aci-anion nitromethane (**2**) or the sodium salt of methazonic acid (**3**). The authors classified the sites of the solids in relation to basicity as weak, intermediate and strong, depending on the product formed after the exposure of the solid to nitromethane. Weak basic sites produce aci-anion nitromethane while the sodium salt of aci-anion nitromethane and the sodium salt of methazonic acid were formed in the presence of intermediate and strong basic sites, respectively. Products (**2**) and (**3**) were synthesized and their IR spectra were measured in order to interpret the spectra obtained after nitromethane adsorption on zeolites and metal oxides.

Fig. 2 shows the spectrum of pure nitromethane. The nitro group of nitromethane presents two resonances forms that vibrate asymmetrically causing a strong absorption at 1560 cm^{-1} and symmetrically causing a weaker absorption at 1378 cm^{-1} [11,12].

The CH_3 symmetric and asymmetric bending usually appear at 1375 and 1465 cm^{-1}, however due to the electronegativity of the neighbor nitro group they appear at 1404 and 1427 cm^{-1}, respectively. This electronegative group also influences the CH_3 rock vibration of nitromethane, absorbing at 1101 cm^{-1}, this frequency is quite shifted compared to those of aliphatic chains.

Fig. 3 shows the infrared spectra of nitromethane chemisorbed on alkali-exchanged X zeolites. The asymmetric stretching vibration of the nitro group (1560 cm^{-1}) is the most intense band and its intensity varies with the nature of the compensating cation.
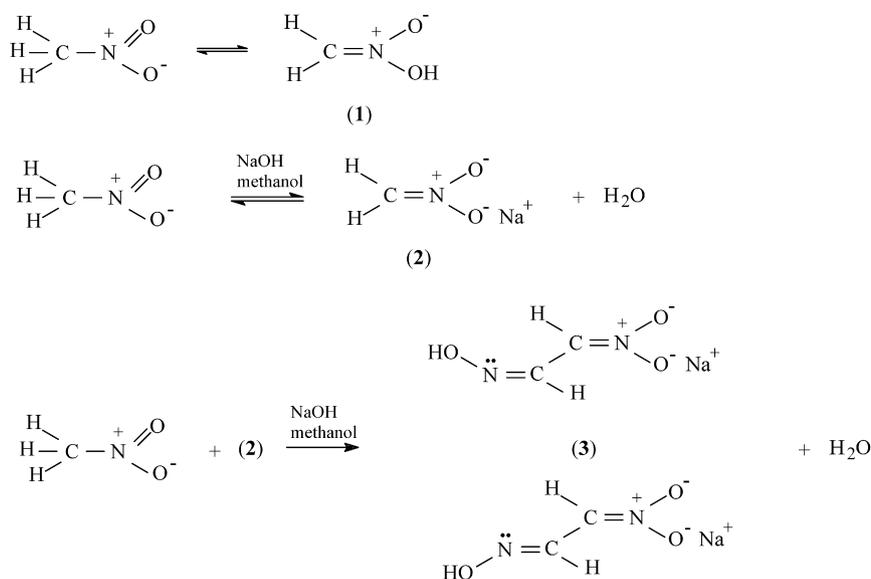
Fig. 1. Reaction of nitromethane and NaOH in a homogeneous medium according to [10].

Comparing the intensities of all bands present in the spectra of Fig. 3, it can be noted that the nature of the compensating cation mostly influenced the asymmetric stretching vibration of the nitro group than the intensity of the bands associated to the symmetric stretching of the same nitro group (1377–1381 cm^{-1}) and to the symmetric (1407–1414 cm^{-1}), asymmetric (1427 cm^{-1}) and rock (1231–1281 cm^{-1}) bending of methyl group.

The CH$_3$ angular bending vibrations showed an interesting behavior after the chemisorption of nitromethane on the studied zeolite surfaces, as shown below.

The asymmetric bending appears at 1427 cm^{-1} on Cs-exchanged zeolite that is the same wavenumber value observed for pure nitromethane. As the electronegativity of the cation increases, K < Na < Li, this band becomes less intense. At the same time, the intensity of the CH$_3$ symmetric bending band (1408–1414 cm^{-1}) increases compared to the nitro group symmetric stretching (1377–1381 cm^{-1}). A possible explanation is the interaction between the nitro group with the alkali compensating cation of zeolite. It is expect that this interaction will be the highest for LiX, and decreases according to the following order NaX > KX > CsX, due to cation radius. This interaction could cause the shift toward lower wavenumbers of the CH$_3$ asymmet-

ric bending band as the cation electronegativity increases, which could be overlapped by the symmetric bending band increasing its intensity. The symmetric bending appears at 1404 cm^{-1} on pure nitromethane and on exchanged zeolites the wavenumber increases with cation electronegativity, 1408, 1411, 1413 and 1414 cm^{-1} for Cs, K, Na and Li, respectively.

The rock angular bending is the most sensitive vibration to cation electronegativity. It appears at 1101 cm^{-1} in nitromethane IR spectrum and at 1232, 1253, 1268 and 1281 cm^{-1} in the exchanged zeolites, Cs, K, Na and Li, respectively. The shift of this band reflects the influence of electronegativity: LiX > NaX > KX > CsX, the higher the cation electronegativity, the lower the interaction of the oxygen associated to the cation with the hydrogen of the CH$_3$ group, so the strength of the bond of this hydrogen and carbon is higher causing a shift of the absorption frequency of the C–H bond in CH$_3$ to a higher wavenumber. Considering the oxygen atoms associated to the cations as basic sites and the increase of basic strength related to the increase of the negative charge of this oxygen atom, it is expected that basic strength increases as cation ionic radius increases: CsX > KX > NaX > LiX. Corma et al. [13] studied the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate and ethyl malonate using X and Y zeolites exchanged with alkali
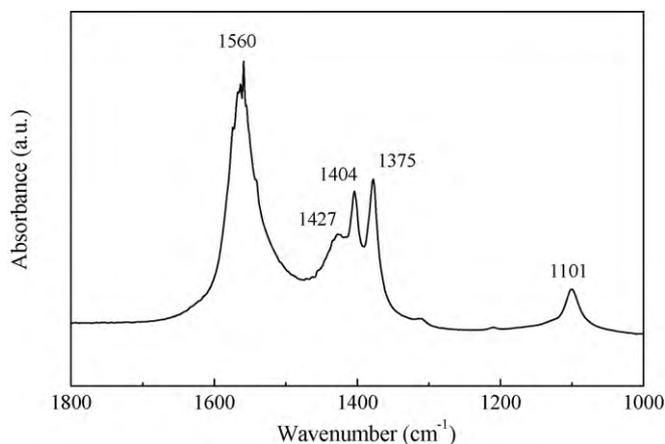

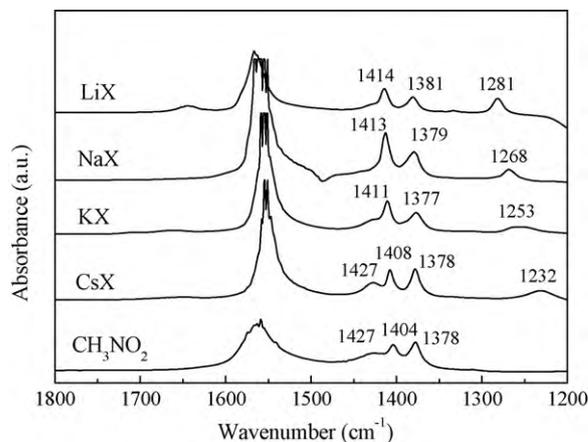**Fig. 2.** Infrared spectrum of liquid nitromethane.

Fig. 3. Infrared spectra of nitromethane chemisorbed on cation-exchanged X zeolites and the spectrum of liquid nitromethane.
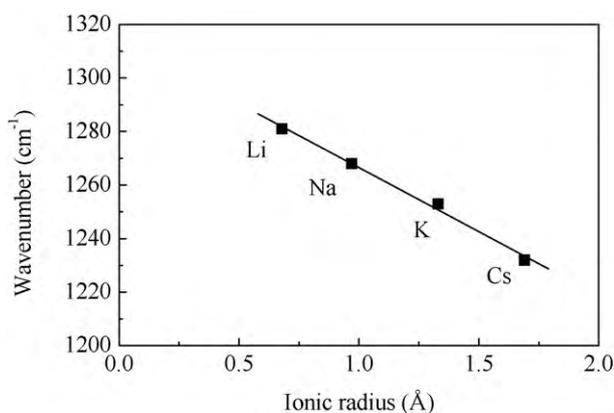
Fig. 4. Variation of the frequency of the CH_3 rock angular bending band with cation ionic radius after chemisorption of nitromethane on cation-exchanged X zeolites.

cations. The authors observed the following sequence of activity: Li < Na < K < Cs and Y < X. The activity increases as the negative charge over the oxygen atom, calculated by the Sanderson's electronegativity equalization principle, increases.

Fig. 4 shows the variation of the frequency of the CH_3 rock angular bending band with the cation ionic radius. A perfect linear correlation is observed indicating that the probe molecule and especially this band are sensitive to zeolite basicity. The equation $y = -47.538x + 1313.8$ correlates the wavenumber of the CH_3 rock angular bending band (y, cm^{-1}) with cation ionic radius (x, Å). The rock angular bending band was sensitive to the electrostatic field produced by the alkali cation.

Similar phenomenon was observed with CO_2 adsorption on alkaline zeolites. A band at ca. $2360\,cm^{-1}$, assigned to the asymmetric stretching vibration υ_3, is sensitive to cation-dipole interactions. The higher the polarization strength of the cation ($Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$) the more pronounced was the shift of its wavenumber towards higher frequency. This kind of interaction induces a loosing of CO_2 molecular symmetry, leading to activation of the stretching υ_1 mode, explaining the appearance of a weak band near $1380\,cm^{-1}$ [14].

As the spectra of nitromethane chemisorbed on alkali-exchanged X zeolites are very similar to the spectrum of pure

nitromethane, the basic sites of these materials could be classified as weak since the probe molecule was sensitive to basic sites with weak strength.

Fig. 5 shows the spectra of nitromethane adsorbed on Al_2O_3, TiO_2 and ZrO_2 (Fig. 5A), pure liquid nitromethane and sodium salt of aci-anion nitromethane (Fig. 5B), the last two spectra were used for comparison. The characteristic feature of the spectra of sodium salts is lack of both symmetric and asymmetric NO_2 frequencies. Two bands corresponding to $\upsilon_{C=N}$ carbonitronate asymmetric and symmetric vibrations of aci-anion structure appear at 1628 and $1539\,cm^{-1}$, while bands at 1282 and $1180\,cm^{-1}$ are presumably due to $N \rightarrow O$ nitronate asymmetric and symmetric vibrations. In the CH stretching region, three peaks were observed at 2860, 3026 and $3129\,cm^{-1}$ and were assigned to aci-anion of nitromethane reported by Jonathan [15]. The two later correspond to sp^2 hybridized carbon atom. In Fig. 5A, two types of sites were identified: the first type is considered a weak basic site and it was associated to the bands 1560, 1405, 1379 and $1100\,cm^{-1}$ related to nitromethane adsorbed in its molecular form; the second type of basic sites was classified as intermediate basic sites and identified by the bands 1623–1604 (C=N), 1285–1160 ($N \rightarrow O$) and $1030–1011\,cm^{-1}$ ascribable to the sodium salt of aci-anion nitromethane. After comparing the spectra it could be suggested that alumina presents a higher amount of intermediate basic sites than zirconia and titania that mainly possess weak sites. Yamaguchi [16] also observed two types of sites on alumina when nitromethane was adsorbed.

The spectra of sodium salt of metazonic acid and nitromethane chemisorbed on magnesium oxide and lanthanum oxide are compared in Fig. 6A. Some differences are observed on the relative intensities of the bands and on wavenumber of the vibrations related to the sodium salt. In order to explain these differences two points should be considered: the asymmetry caused by nitromethane adsorption and the comparison between spectra obtained in homogeneous and heterogeneous media (chemisorbed nitromethane).

In Fig. 6B, two absorption bands in the region of $=C–H$ stretching at different chemical environmental (3114 and $3072\,cm^{-1}$ related to sodium salt of metazonic acid, 3178 and $3075\,cm^{-1}$ related to magnesium oxide, and 3178 and $3058\,cm^{-1}$ related to lanthanum oxide) are associated to structure 3 in Fig. 1. Taking into account the hydroxyl groups of magnesium oxide and lanthanum oxide, it
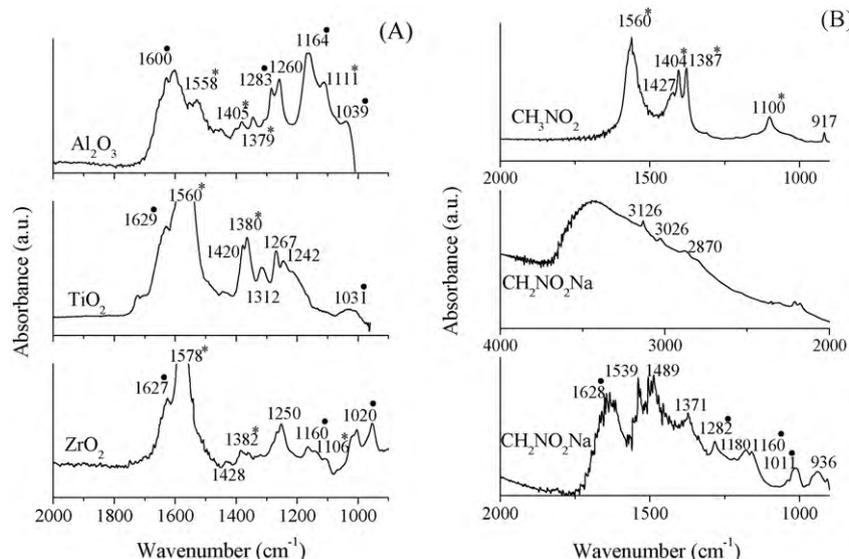

Fig. 5. (A) Infrared spectra of nitromethane chemisorbed on Al_2O_3, TiO_2 and ZrO_2; (B) infrared spectra of liquid nitromethane (CH_3NO_2) and sodium salt of aci-anion nitromethane (CH_2NO_2Na) $4000–2000\,cm^{-1}$ and $2000–900\,cm^{-1}$. Bands assigned with (●) and (*) are related to intermediate and weak basic sites, respectively.
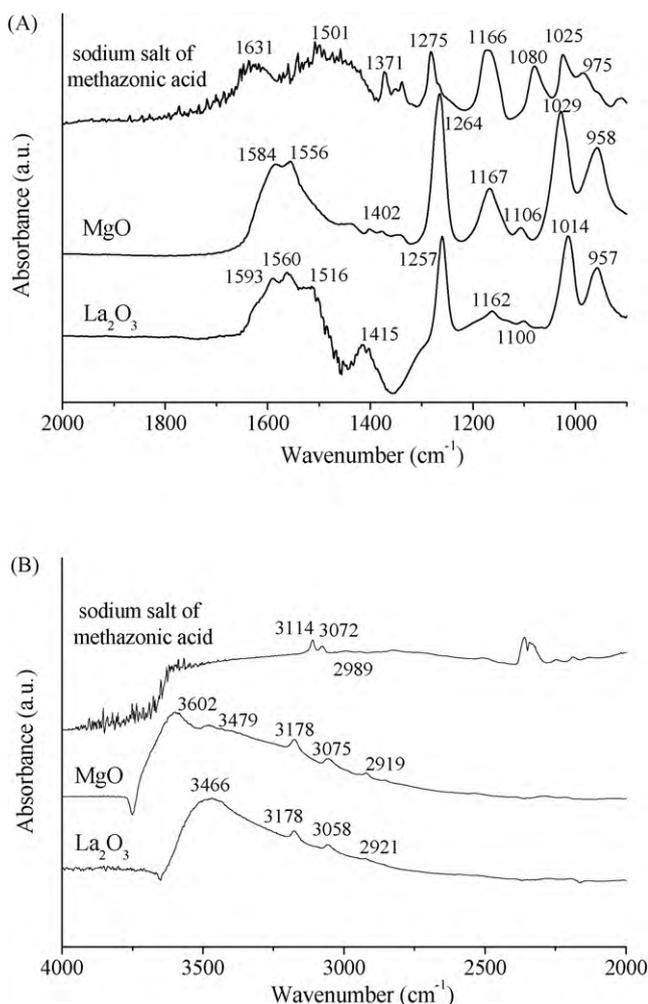
Fig. 6. Infrared spectra of sodium salt of metazonic acid and nitromethane chemisorbed on magnesium oxide and lanthanum oxide. (A) 2000–900 cm^{-1} and (B) 4000–2000 cm^{-1}.

could be suggested that magnesium oxide is more basic because it absorbs in a higher wavenumber. Both samples showed a shift, $\triangle_{OH, MgO} = -148$ cm^{-1} and $\triangle_{OH, La_2O_3} = -198$ cm^{-1}, due to the formation of hydrogen bridges with nitromethane.

For the magnesium and lanthanum oxides, the interaction between the basic oxygen of the oxide and the acid hydrogen atoms of the probe molecule was very strong as observed in Fig. 6B. Due to this strong interaction that forms hydroxyl groups, large bands at 3600 and 3400 cm^{-1} for MgO and 3400 cm^{-1} for La$_2$O$_3$ were observed. Analyzing Fig. 6A, with respect to the synthesized sodium salt of metazonic acid it can be observed that the nitro group asymmetric stretching vibrations of nitromethane gave rise to two bands that absorb at 1603 and 1576 cm^{-1} which corresponds to $\upsilon_{C=N}$ carbonitronate asymmetric and symmetric vibrations of sodium salt of metazonic acid. Bands in 1275–1080 cm^{-1} are due to N → O nitronate asymmetric and symmetric vibrations and 1371–975 cm^{-1} bands were ascribable to δ_{OH} and υ_{N-O} vibration of N–OH group [17]. For MgO and La$_2$O$_3$, the δ_{OH} vibration is shifted to higher frequency when compared to synthesized sodium salt of metazonic acid, 1402 and 1415 cm^{-1}, respectively. The similarities between the spectra of sodium salt of methazonic acid and nitromethane chemisorbed indicate that MgO and La$_2$O$_3$ possess strong basic sites. This result is in agreement with those of Davydov [18] about the basicity of these materials measured by CO$_2$ adsorption.
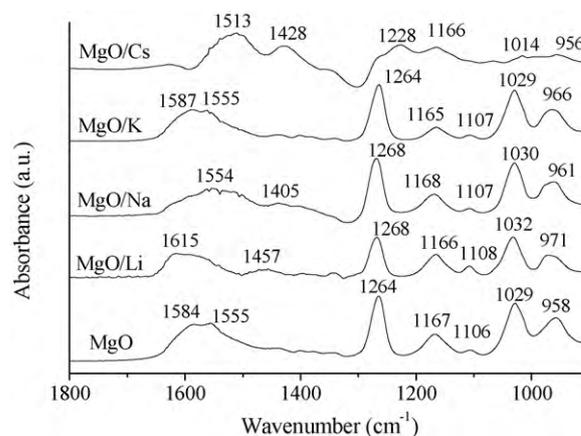

Fig. 7. Infrared spectra of nitromethane chemisorbed on MgO and alkali-metal doped MgO.

As observed with X zeolites, nitromethane was able to identify weak, intermediate and strong basic sites on oxides such as Al$_2$O$_3$, TiO$_2$, ZrO$_2$, MgO and La$_2$O$_3$, being effective as a probe molecule.

Fig. 7 shows the infrared spectra of nitromethane chemisorbed on MgO and alkali-promoted MgO that are very similar. So MgO and alkali doped MgO, despite the alkali cation used, can be classified as strong basic materials, considering the similarities of the spectra of sodium salt of methazonic acid on MgO (Fig. 6A and B). The differences on bands intensities were attributed to the nature of species in homogenous and heterogeneous media. For both spectra the stretching vibration of the two bands at =CH in different chemical environments (3109–3072 cm^{-1}) reflected the structure 3 of Fig. 1.

The basic hydroxyls of MgO were sensitive to the presence of alkali cation causing a shift of this band due to formation of a hydrogen bridge with nitromethane. This shift increased according to the following sequence: $\triangle_{OH, MgO/Li} = -122 < \triangle_{OH, MgO/Na} = -147 < \triangle_{OH, MgO/K} = -176 < \triangle_{OH, MgO/Cs} = -177$, and the shift observed for pure MgO was $\triangle_{OH, MgO} = -148$. It could be suggested that the presence of alkali cations modified the basicity of the hydroxyls and also improved the basicity of the O^{2-} sites.

Concerning the basicity of the O^{2-} sites, nothing could be concluded from the spectra because no significant shift of the bands assigned to sodium salt of metazonic acid could be attributed to the presence of alkali cation. So different from X zeolites, no scale into the class of strong basic sites could be established for the alkali-promoted MgO samples.

4. Conclusions

As shown in this work, nitromethane has fulfilled the requirements proposed by Davydov [2] to be used as a probe molecule to study basic solids such as zeolites and metal oxides. This study was based on the interaction between acid hydrogen atoms of nitromethane and oxygen atoms of basic materials used as catalysts. As a probe molecule, nitromethane allowed the determination of the strength of basic sites using infrared spectroscopy. The comparison between the spectra obtained after nitromethane chemisorption over the studied materials and the standards liquid nitromethane, sodium salt of aci-anion nitromethane, and sodium salt of methazonic acid allowed to classify the sites as weak (alkali-exchanged X zeolites), intermediate (Al$_2$O$_3$, ZrO$_2$, TiO$_2$) and strong (MgO, La$_2$O$_3$ and alkali-promoted MgO).

For alkali-exchanged zeolites, a linear correlation of the frequency of the CH$_3$ rock angular bending and ionic radius of the

zeolite compensating cation was observed so that the basic strength could be established as CsX > KX > NaX > LiX. The overall basic sites of alkali-exchanged zeolites were classified as weak. Intermediate and weak basic sites were identified on Al_2O_3, ZrO_2, TiO_2 with a slight predominance of intermediate basic sites on Al_2O_3. For La_2O_3 and MgO, the interaction between hydrogen atoms of nitromethane and their oxygen atoms was so strong that hydroxyl bands appeared after nitromethane chemisorption and bands related to CH_3 group disappeared. However, no scale into the class of strong basic sites could be established for the alkali-promoted MgO samples.

Acknowledgments

References

[1] J.C. Lavalley, Catal. Today 27 (1996) 377–401.
[2] A.A. Davydov, IR Spectroscopic in the Surface Chemistry of Oxides, Nauka, Novosibirsk, 1984.
[3] D. Barthomeuf, J. Phys. Chem. 88 (1984) 42–45.
[4] P.O. Sokart, P.G. Rouxhet, J. Chem. Soc. Farad. Trans. 76 (1980) 1476–1489.
[5] C. Binet, A. Jadi, J. Lamotte, J.C. Lavalley, J. Chem. Soc. Farad. Trans. 92 (1996) 123–129.
[6] E.A. Paukshitis, N.S. Kotsarenko, L.G. Karakchiev, React. Kinet. Catal. Lett. 12 (1979) 315–319.
[7] D.A. Gordymova, A.A. Davydov, React. Kinet. Catal. Lett. 23 (1983) 233–238.
[8] S. Bernal, J.A. Diaz, R. Garcia, J.M. Rodriguez-Izquierdo, J. Mater. Sci. 20 (1985) 537–541.
[9] S. Bernal, F.J. Botana, R. Garcia, J.M. Rodriguez-Izquierdo, React. Solid 4 (1987) 23–40.
[10] H. Lima, M. Laspéras, L.-C. Ménorval, D. Tichit, F. Fajula, J. Catal. 223 (2004) 28–35.
[11] N.B. Colthup, Infrared and Raman Spectroscopy, Academic Press Inc., New York, 1975.
[12] J. Wang, H. Busse, D. Syomin, B. Koel, Surf. Sci. 494 (2001) L741–L747.
[13] A. Corma, V. Fornes, R.M. Martin-Aranda, H. Garcia, J. Primo, Appl. Catal. 59 (1990) 237–248.
[14] M. Förster, M. Schumann, J. Chem. Soc. Faraday Trans. I 85 (1989) 1149–1158.
[15] N. Jonathan, J. Mol. Spectrosc. 7 (1961) 105–115.
[16] M. Yamaguchi, J. Chem. Soc. Farad. Trans. 93 (1997) 3581–3586.
[17] M. Kimura, Y. Kuroda, O. Yamamoto, M. Kubo, Bull. Chem. Soc. Jpn. 34 (1961) 1081–1086.
[18] A. Davydov, M. Shepot' Ko, A. Budneva, Kinet. Catal. 35 (1994) 272–278.