Letter

Probing the basicity of oxide surfaces by FTIR spectroscopy of isocyanic acid generated *in situ* by thermal decomposition of nitromethane

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Infrared spectroscopy of isocyanic acid generated *in situ* by the thermal decomposition of nitromethane provides an efficient and easy method to probe the basic strength of the surface of oxides. The frequencies of the adsorbed isocyanate species are directly correlated with the heats of adsorption of carbon dioxide determined by microcalorimetry.

The decomposition of nitromethane has been extensively studied on a variety of oxides and metal-exchanged zeolites in recent years in order to model the behaviour of the organic nitro compounds, which are thought to be involved as reaction intermediates during the selective catalytic reduction of nitric oxides by hydrocarbons under oxygen-rich conditions.[1–4] At room temperature nitromethane adsorbs on basic and amphoteric surfaces in the form of its *aci*-anion whereas the latter is not observed on acidic supports.[1,5,6] On all types of supports however, the adsorbed nitromethane and *aci*-anions ($CH_2NO_2^-$) undergo dehydration into isocyanic acid (HNCO) upon heating at 200–400 °C. The acid adsorbs dissociatively on the surface, leading to anionic and covalently bonded isocyanate species with characteristic intense infrared absorptions in the range 2200–2300 cm^{-1}.[1,7] The position of the infrared bands of the NCO adsorbed species was demonstrated to be highly dependent on the nature of the support[8–10] and since the pK_a of isocyanic acid is 3.46, it was anticipated that the latter could be used as a probe for monitoring the basicity of solid oxides. Moreover, nitromethane being much easier to handle than isocyanic acid, its *in situ* decomposition should provide a friendly route to the basicity probe. In this communication we illustrate this strategy by correlating the results obtained by FTIR spectroscopy with those gained by microcalorimetry of the adsorption of carbon dioxide on five solids featuring acidic, amphoteric or basic character.

The materials used were an ultrastable faujasite zeolite [USY from Uetikon, Si : Al = 3.35, surface area (SA) = 638 $m^2\ g^{-1}$], a γ-alumina (Al_2O_3, prepared by calcination of bohemite at 550 °C, SA = 180 $m^2\ g^{-1}$), magnesium oxide (MgO, prepared by calcination of magnesium carbonate at 550 °C, SA = 168 $m^2\ g^{-1}$) and two mixed magnesium–aluminium oxides (from Kyowa, KW2000, Mg : Al = 2.33, SA = 241 $m^2\ g^{-1}$ and KW2200, Mg : Al = 2.13, SA = 160 $m^2\ g^{-1}$).

FTIR experiments have been carried out in a greaseless IR cell connected to a vacuum line. The self-supported wafers were outgassed at 400 °C for 10 h under 10^{-6} Torr, then cooled to room temperature (RT). Nitromethane (3 Torr, 98% purity, from Lancaster, vacuum distilled) was adsorbed at RT, the excess of gas evacuated and a first spectrum was recorded (Nicolet 320 FTIR spectrometer, resolution $\pm 2\ cm^{-1}$). The cell was then heated under vacuum at increasing temperatures up to 400 °C and a new spectrum recorded at RT at each step. The heats of adsorption of carbon dioxide were determined with a modified microcalorimeter (DSC 111 from SETARAM) using a silica flow reactor placed in the calorimetric cell. After outgassing the samples at 400 °C, the surface was saturated with the probe under He flow at 100 °C and the thermal event recorded and integrated.

Typical results obtained by FTIR measurements during the thermal decomposition of nitromethane on the mixed Mg–Al oxide (KW2200 sample) are shown in Fig. 1 for the spectral range 1100–2500 cm^{-1}. Nitromethane adsorbed at room temperature led to the characteristic signals[11] at 1378 (δ_s CH_3), 1403 (ν_s NO_2), 1430 (δ_a CH_3) and 1562 (ν_a NO_2) cm^{-1} whereas an intense peak at 1272 cm^{-1} (ν_a NO) and a weaker one at 1170 cm^{-1} (ν_s NO) evidenced the formation of the *aci*-anion (Fig. 1, trace *b*).[12,13] The presence of the latter was also identified by additional signals at 1035, 3067 and 3168 cm^{-1}, typical of the sodium salt of nitromethane.[12,13] After desorption at 50 °C (Fig. 1, trace *c*), the peaks due to physisorbed nitromethane disappeared almost completely and those due to the *aci*-anion decreased in intensity. Heating at 110 °C led to a further decrease of the intensity of the *aci*-anion signals (Fig. 1, trace *d*) and to the appearance of a new signal at *ca.* 2200 cm^{-1}. The latter became more evident after outgassing at

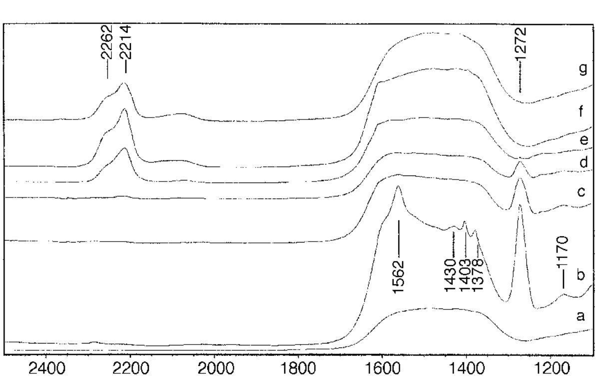

Fig. 1 Infrared spectra recorded during the *in situ* decomposition of nitromethane on a Mg–Al mixed oxide. (*a*) Background spectrum after activation of the IR wafer at 400 °C, (*b*) spectrum obtained after adsorption and desorption of nitromethane at RT, spectra obtained after desorption at (*c*) 50, (*d*) 110, (*e*) 200, (*f*) 300 and (*g*) 400 °C.

200 °C (Fig. 1, trace *e*) and consisted, in fact, of two peaks centred at 2214 and 2262 cm^{-1}, assigned to the asymmetric stretching of anionic and covalently bonded isocyanate, respectively, according to Ukisu *et al.*[7] and Yamaguchi.[1] At this desorption temperature the signals of the *aci*-anion form vanished almost completely. The intensity of the isocyanate species reached its maximum intensity in the spectrum after degassing at 300 °C (Fig. 1, trace *f*). At this stage a broad signal at 2050–2100 cm^{-1} appeared, tentatively attributed to CN vibrations in decomposition products.[14,15] The intensity of this broad signal increased after heating at 400 °C (Fig. 1, trace *g*) while that of the isocyanate species decreased with a corresponding broadening of the peaks.

These spectral features, which parallel closely those reported by Yamaguchi for γ-alumina,[1] were reproduced qualitatively on all the samples investigated, except for USY on which no *aci*-anion nor anionic isocyanate species could be detected. However, the relative stability of the adsorbed isocyanate species and the position of the signals was definitely a function of the nature of the solid surface. On the one hand, the isocyanate moieties were totally decomposed after evacuation at 300 °C for 30 min on USY and alumina whereas an oxidation treatment performed at 400 °C was required to clear the surface of the mixed oxides and MgO samples. On the other hand, and more interestingly regarding the objective of the present communication, a unique relationship existed between the position of the isocyanate signals determined at maximum peak intensity and the strength of the basic sites of the surface measured by the heat of adsorption of carbon dioxide at 100 °C. Such a correlation is shown in Fig. 2 where adsorption heats have been expressed on a surface basis owing to the different surface areas of the samples.

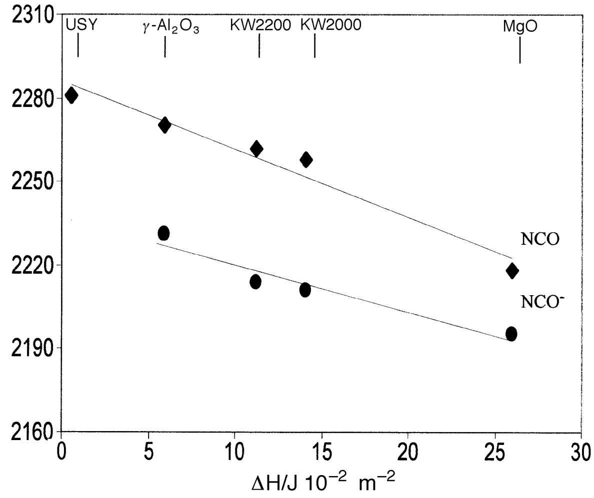

Fig. 2 Correlation between the IR frequencies of the adsorbed isocyanate species and the heats of carbon dioxide adsorption on the various solid samples.

Although the mechanism of nitromethane decomposition, as well as the exact mode of interaction of the isocyanate species with the surface, remain subjects of debate[8–10] and their elucidation will require additional efforts, our data demonstrate that the application of IR spectroscopy to the NCO species generated upon thermal decomposition of nitromethane could prove to be a very efficient and easy method for probing the basic strength of oxides. Moreover, the nature of the adsorption centres (basic OH^- and O_2^- sites, acid–base pairs) at the surface of solid bases is multiple and their distribution is strongly dependent on the preparation and thermal history of the samples. The sensitivity of the position of the infrared signals of the isocyanate species on the nature of the support surface evidenced in this and previous works opens interesting perspectives for the characterization of solid base catalysts. Work in this direction combining microcalorimetric, FTIR and ^{13}C and ^{15}N MAS NMR spectroscopic measurements performed at various stages of surface neutralization is under way.

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