

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

On the Ambient Temperature Gas-Solid Interaction of Acetone with Some Silica-Supported d° Metal Oxides

This is the author's manuscript

Original Citation:

Availability:

This version is available <http://hdl.handle.net/2318/87908> since 2017-11-25T16:02:56Z

Published version:

DOI:10.1021/jp1068329

Terms of use:

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)



UNIVERSITÀ DEGLI STUDI DI TORINO

*This is an author version of the contribution published on:
Questa è la versione dell'autore dell'opera:*

On the ambient temperature gas solid interaction of acetone with
some silica-supported d^0 metal oxides

By

Valentina Crocellà and Claudio Morterra

J. Phys. Chem. C, 114, 2010, 18972–18987

DOI 10.1021/jp1068329

*The definitive version is available at:
La versione definitiva è disponibile alla URL:
<http://pubs.acs.org/doi/abs/10.1021/jp1068329>*

On the ambient temperature gas-solid interaction of acetone with some silica-supported d^0 metal oxides

*Valentina Crocellà, Claudio Morterra**

Department of Chemistry IFM and Centre of Excellence NIS, University of Torino,

via P. Giuria 7, 10125 Torino (Italy)

[*] To whom correspondence should be addressed.

Phone: +39 011 6707589; Fax: +39 011 6707855; e-mail: claudio.morterra@unito.it

Abstract

The combined use of adsorption microcalorimetry/gas-volumetry and *in situ* FTIR spectroscopy was employed to investigate qualitative and quantitative/energetic aspects of the ambient (beam-) temperature adsorption of acetone on silica-supported Al, Zr, and Ca oxides. All oxidic systems examined possess strong Lewis acidity, though of different strength ($\text{Al} > \text{Zr} > \text{Ca}$), whereas only the first two mixed oxides present Brønsted acidity of comparable strength. Acetone uptake yields different types of molecular adsorption: - two types of H-bonding interaction with surface silanols, as typical of pure silica systems; - coordinative interaction with Lewis acidic sites, part of which is not vacuum reversible at ambient temperature in the case of Al- and Zr-doped systems; - strong H-bonding interaction with Brønsted acidic centres (when available), a large fraction of which is not vacuum reversible at ambient temperature. In addition, and only on the Ca-doped system, acetone undergoes the aldol condensation reaction yielding, as main reaction product, mesityl oxide that adsorbs, with different strength, at both surface silanols and Lewis acid sites. The occurrence of the aldol condensation reaction on only one of the three mixed oxides examined (whereas it occurs on all of the corresponding pure oxides) is discussed, with conclusions concerning the sites that catalyze the condensation reaction that do not agree with either of two conflicting interpretations present in the literature.

Key words: Acetone adsorption; Silica-supported Al oxide; Silica-supported Zr oxide; Silica-supported Ca oxide; Aldol condensation reaction; Adsorption FTIR spectroscopy; Adsorption microcalorimetry.

1. Introduction

Due to the high covalent character of the Si-O bond (over 50%), silica is commonly considered as the most covalent solid oxide. For this reason, the vacuum cleaned surface of silica-based mixed oxides can somehow be thought of as a dispersion of metal cations and oxide anions (the so called non-bridging oxygens) within a highly covalent and virtually inert silica matrix. The oversimplification hidden in this picture is quite evident, especially for what concerns the possible modifications introduced in the properties of surface Si-OH groups (silanols) by the presence of a more ionic guest oxide. But as a first approximation, this simple picture may turn out to be useful.

The abundant existing literature indicates that silica-based mixed oxidic materials are quite interesting, both *per se* and as reference systems, and are largely used in various fields like, for instance, those of heterogeneous catalysis, solid state physics/chemistry (*e.g.*, see ref. 1), and bioactive materials (*e.g.*, see ref. 2). In the present contribution we have examined the surface acidic/basic and reactivity features of three silica-based mixed oxides, that have been selected following some simple criteria: (i) the cations of the guest oxides have a d^0 configuration, so as to allow to start this study with something simpler, and to avoid any redox activity. For this reason, the three cations we have chosen are Al^{3+} , Zr^{4+} , and Ca^{2+} ; (ii) the guest oxides have one (or more) corresponding pure oxide(s), whose surface features are known and largely understood and agreed upon. For this reason, the corresponding pure oxides can be conveniently adopted (and, in fact, will be adopted) as reference systems; (iii) the mixed oxides are either used as such in some important field of application, or may mimic the characteristics of other mixed oxidic systems of ample application. For this reason: – silicas surface Al-doped by impregnation can simulate some of the surface features of the vast family of amorphous and crystalline silica-aluminas, and can to some extent be compared also with zeolitic materials. The corresponding pure oxides, mainly transition aluminas, are normally considered as typical (Lewis) acidic oxides, with some amphoteric characteristics;³ – sol-gel Zr-doped silica is a system that has been studied, and is still being studied, for some specific catalytic applications.⁴ The corresponding plain oxides, zirconia in either

monoclinic (*m*-ZrO₂) or tetragonal modification (*t*-ZrO₂), have been defined long ago as typical amphoteric oxides;⁵ – silica surface Ca-doped by impregnation is a typical binary reference oxidic system in the study of silica-based bioactive glasses.⁶ The corresponding pure oxide, CaO, is a strongly basic material of very high surface reactivity, as in the case of all basic oxides (*e.g.*, see ref. 7, 8).

The use of acetone (Ac) as a probe for the surface features of silicas has been adopted by several authors⁹⁻¹⁹, and has been recently revisited by us,²⁰ mainly in the optics of a quantitative and energetic adsorption study preliminary to the present contribution. As for the adsorption of Ac on oxidic systems other than silica, its use was discouraged long ago by M. L. Hair²¹ who considered Ac a non-suitable probe for acid sites. Nonetheless, many authors have since used Ac as an adsorbate in the surface study of pure oxides,²²⁻²⁵ mixed oxides,^{26,27} silica-aluminas²⁸ and, above all, zeolitic systems.^{22,29-33}

It is well known that Ac can interact in many ways with the surface of oxidic systems. Limiting ourselves to the forms of specific interaction (*i.e.*, first-monolayer chemisorptive interactions), Ac can yield weak H-bondings with scarcely acidic surface hydroxyl groups (like in the case of Ac uptake on plain silicas, on which two types of H-bonded complexes are usually formed²⁰), or stronger H-bondings with surface hydroxyl groups possessing higher acidity of the Brønsted type.^{22,33} Spectroscopically, the strength of the Ac/OH H-bonds formed can be grossly evaluated on the basis of the red-shift undergone by the C=O stretching frequency ($\Delta\nu_{\text{CO}}$ of the C=O vibrational mode) of the ketonic functionality. Moreover, Ac can coordinate through one of the two O electron lone pairs of the ketonic functionality to coordinatively unsaturated (*cus*) surface cations, acting as Lewis acid centres. Also in this case a red-shift of the $\nu(\text{CO})$ vibrational mode is observed, though relatively small (and comparable to the shift of weak H-bondings) since the surface coordination complexes of Ac are rather weak, much as it has been reported for ketones and aldehydes coordination compounds.³⁴ But probably the most interesting aspect of Ac adsorptive interaction at the surface of oxidic systems is that, in proper conditions, it can undergo the so called aldol

condensation reaction (hereafter referred to as the a.c. reaction). The latter, well known in synthetic organic chemistry, is a reaction in which aldehydes or ketones are condensed to dimeric or higher-membered products. In the case of Ac, the self-condensation reaction leads to the dimeric diacetone alcohol, that readily dehydrates to yield mesityl oxide (hereafter, MO) and, possibly, larger carbonyl compounds like, for instance, the α - β unsaturated cyclic ketone isophorone.²⁶ In homogeneous phase, a.c. reactions have been reported (see for instance ref. 26, and references therein) to be “sometimes catalyzed by transition metal complexes, occasionally by acids, and most frequently by bases”. As for the a.c. reaction of Ac occurring at the surface of either pure or mixed oxides but, above all, at the surface of zeolites and zeolite-like systems, conflicting views seem to exist in the literature. In particular: (i) L. Kubelkova *et al.* ascribe the activation of Ac to Brønsted protonic centres,²⁹ and conclude that the “reactivity of Ac increases with acid strength of skeletal hydroxyls of zeolite adsorbents”; (ii) Unlike that, J. J. Fripiat *et al.* indicate that, on both transition aluminas and zeolitic systems (in both H-form and cation-containing form), strong Lewis acid sites rather than Brønsted sites are responsible for the activation of Ac molecules^{32,33} and for their a.c. conversion to (mainly) adsorbed MO.

The aim of the present contribution is to check what type(s) of adsorption interaction does Ac give at the surface of some typical silica-based mixed d⁰ metal oxides (selected with the criteria reported above) and, in particular, when does the a.c. reaction occur, if at all. In the case that a.c. reaction of adsorbed/gaseous Ac does actually occur to an appreciable extent, the aim of this work is also that to ascertain if either of the two catalytic mechanisms proposed in the literature is likely to cause the reaction or if, when the a.c. reaction products form, neither of them is sufficient to explain the formation of the dimeric diacetone alcohol species and, eventually, of MO.

2. Experimental section

Materials

As reported in the Introduction, the ambient temperature adsorption/desorption of Ac has been studied on three different silica-based mixed oxides.

- 1) Al-modified silica specimens, hereafter referred to as Si/Al(x)-T: (x) indicates the overall Al content (mol %), whereas T represents the temperature (K) at which the sample was vacuum treated before adsorption/desorption experiments (activation temperature). These systems were obtained by adding dosed amounts of an aqueous solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sigma Aldrich) to a dry silica powder (Aerosil 200, a pyrogenic amorphous non-porous silica supplied by Degussa, Frankfurt A.M., Germany; lot.: 1490), and using the so-called “incipient wetness” method (*i.e.*, using an amount of solution just sufficient to wet, but not overwet, all of the support powder). Two Al-modified samples, containing 4 and 8 mol % of Al, respectively, were prepared by contacting 1 g of SiO_2 with 5 ml of aqueous solutions 0.14 and 0.29 M, respectively. The wet powders were dried in air at 373 K (one night), and then calcined at 873 K (2 h) in order to decompose and eliminate the nitrates.
- 2) Zr-modified silica specimens, hereafter referred to as Si/Zr(3)-T: the figure (3) indicates the overall zirconium content (mol %), and T represents the activation temperature (K). This system was synthesized following the sol-gel method, mixing tetramethoxysilane (TMOS) and zirconium propoxide in the amounts necessary to achieve the appropriate composition (*i.e.*, 3% mol in Zr). The detailed preparative procedure has been reported elsewhere.⁴ Unlike the “incipient wetness” method, that deposits all of the selected additive on the silica surface, the sol-gel method is likely to disperse the additive within the whole mass of the resulting solid. For this reason, the surface layer(s) concentration of Zr has been determined by XPS, and a Zr/Si atomic ratio of 1.7/28 was obtained for the as-prepared Si/Zr(3) system. The ratio yields a Zr surface concentration of 6.1%, indicating that the sol-gel preparation leads to an odd distribution of the additive, and to a fair increase of surface Zr species (*i.e.*, twice as much) with respect to the “theoretical” amount.

3) Ca-modified silica systems, hereafter referred to as Si/Ca(4)-T: the figure (4) indicates the overall CaO content (mol %), and T represents the vacuum activation temperature (K). Also this system was synthesized through the “incipient wetness” method, adding dosed amounts of an aqueous solution of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ to a dry silica powder (Aerosil 200, as in the case of Al-doped specimens), as described in detail elsewhere.⁶

In order to gain more information about the behavior of SiO_2 -based mixed oxidic systems, some of the corresponding pure oxides were adopted as reference systems:

- Aluminas. (i) Crystallographically pure $\gamma\text{-Al}_2\text{O}_3$ was obtained by firing in air for 5 h at 773 K a pure commercial pseudo-bohemite precursor (Disperal Alumina, Condea Chemie). Synthesis and structural/morphological features of reference $\gamma\text{-Al}_2\text{O}_3$ have been reported in detail elsewhere³⁵; (ii) Crystallographically pure $\alpha\text{-Al}_2\text{O}_3$ samples were prepared by the oven thermal treatment at 1473 K (in air) of pre-compacted self-supporting pellets of the γ -phase alumina specimen just described. Structural/morphological features of reference $\alpha\text{-Al}_2\text{O}_3$ have been reported elsewhere³⁶.
- Zirconias. (i) Single-phase tetragonal zirconia ($t\text{-ZrO}_2$) was prepared, as reported in detail in ref. 37, by controlled co-precipitation at room temperature from dosed amounts of aqueous solutions of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, so as to yield a final composition of 3 mol% Y_2O_3 . The dried precipitate was then calcined in air at 923K, leading to the so-called yttria-stabilized tetragonal zirconia (YSTZ) system; (ii) Single-phase monoclinic zirconia ($m\text{-ZrO}_2$, baddeleyite) was obtained by the room temperature hydrolysis with pure water of Zr-propoxide, followed by calcinations in air at $T \geq 730\text{K}$, as mentioned³⁷ and described in detail elsewhere³⁸.

For reasons that will appear clear in the following Results and Discussion section, no reference pure CaO samples were considered to be necessary, and occasionally reference will be made only to some CaO literature data.

Specific surface area (SSA) and porosity morphological features of all the samples of interest, not reported here for the sake of brevity, are summarized in Table 1SM of the Supporting Information section.

Reagents

High-purity liquid acetone (Chromasolv for HPLC, Sigma-Aldrich), mesityl oxide (90%, Sigma-Aldrich), and 2,6-dimethylpyridine (99% GC, Sigma-Aldrich) were used without any further purification, and were rendered gas-free by several “freeze-pump-thaw” cycles.

Carbon monoxide, provided by Praxair (gas purity: 99.9), was dosed from the lecture-bottle onto the samples under study by slowly passing the gas through a cold trap (77K) to prevent any possible contamination with Ni(CO)₄.

Techniques

N₂ adsorption at 77K. SSA, pores volume, and pores size information were obtained from N₂ adsorption/desorption isotherms at 77 K, using a Micromeritics ASAP 2020 analyzer. Prior to N₂ physisorption measurements, all samples were outgassed at 523 K for 12 hours to get rid of physisorbed water and other atmospheric contaminants. SSAs were calculated using the standard BET equation method, and mesopore size distributions were elaborated using the BJH method applied to the isotherms adsorption branch³⁹.

IR Spectroscopy. *In situ* transmission IR spectra were recorded, at a resolution of 4 cm⁻¹, on a FTIR spectrometer (Bruker IFS 113v, equipped with MCT cryodetector) at “beam temperature” (hereafter BT), *i.e.*, the temperature reached by samples in the IR beam. (For self-supporting pellets of insulating white samples, either in vacuo or under a low adsorptive pressure, BT is estimated to be (at least) some 30 K higher than RT).

All powdery samples were compressed in the form of self-supporting pellets (~15-20 mg cm⁻²) and mechanically protected with a pure gold frame. The samples were inserted in a homemade quartz IR cell, equipped with KBr windows and characterized by a very small optical path (~2 mm). The cell was attached to a conventional high vacuum glass line capable of a residual pressure

$<10^{-5}$ Torr. This setting allowed to perform, in strictly *in situ* conditions, both sample thermal treatments (usually 2 hr, at the selected activation temperature), and adsorption-desorption cycles of molecular probes.

The study of surface acidity has been performed using as probes: (i) carbon monoxide uptake at BT, to check strong Lewis acidity; (ii) 2,6-dimethylpyridine (2,6-Lutidine; hereafter, 2,6-Lu) adsorption/desorption at BT and desorption at 423K, to test both total Lewis and Brønsted acidity.

BT CO uptake experiments were carried out by contacting the activated samples with 100 Torr of the adsorptive. The roto-vibrational spectral component, due to CO in the gas phase, was interactively subtracted from the absorbance spectra of adsorbed CO.

2,6-Lu adsorption/desorption tests were carried out as follows: (i) a relatively large amount of the adsorptive (~3 Torr) was first allowed on the activated samples and left in contact at BT for 2 min; (ii) the excess 2,6-Lu was then evacuated at BT for 15 minutes; (iii) a desorption of the strongly bonded 2,6-Lu fraction was eventually carried out at 423 K (15 min).

For what concerns Ac adsorption, all activated samples were first contacted at BT with increasing doses of Ac vapour, usually up to an equilibrium pressure of ~3-5 Torr (the *adsorption run*), and then evacuated at BT for increasing times (up to 1.5 hrs; the *desorption run*), in order to test the desorption spectral response of adsorbed species. At any step of the adsorption/desorption cycles, *in situ* IR spectra were recorded (128 scans). In all IR experiments, the (approximate) equilibrium adsorptive pressure was monitored by a Pirani gauge and a conventional Hg manometer.

Whenever needed, bands resolution was carried out using the FIT routine by Bruker, that allows the interactive research of the best-fit to the experimental absorbance spectral segment examined on the basis of a number of spectral components imposed by the operator. In all of the present experiments, major spectral parameters (*i.e.*, spectral position, half-band width, percent of gaussian profile) were always allowed to float freely.

Adsorption Microcalorimetry/Gas-volumetry. Heats of adsorption of Ac vapour were measured, at 298 K, by means of a heatflow microcalorimeter (Calvet C80, Setaram, France)

connected to a grease-free high-vacuum gas-volumetric glass apparatus (residual $p \approx 10^{-5}$ Torr) equipped with a Ceramicell 0-100 Torr gauge (by Varian), following a well established stepwise procedure, described in detail elsewhere (*e.g.*, see ref. 6, 20, and references therein). This procedure allows to determine, during the same experiment, both integral heats evolved ($-Q_{\text{int}}$) and adsorbed amounts (n_a) for very small increments of the adsorptive pressure.

Adsorbed amounts and integral heats evolved, normalized to the unit surface area, have been plotted vs. pressure in the form of volumetric (quantitative) and calorimetric isotherms, respectively. The adsorption heats observed for each small dose of gas admitted over the sample (q^{diff}) have been finally reported as a function of coverage, in order to obtain the (differential) enthalpy changes associated with the proceeding adsorption process. The differential-heat plots presented here were obtained by taking the middle point of the partial molar heats ($\Delta Q_{\text{int}}/\Delta n_a$, kJ/mol) vs n_a histogram relative to the individual adsorptive doses, prepared as small as possible.

In all quantitative/calorimetric experiments, after the first adsorption run carried out on the bare activated samples (the *primary isotherm*), samples were outgassed overnight at the adsorption temperature (298 K), and then a second adsorption run was performed (the *secondary isotherm*), in order to check whether secondary and primary adsorption runs coincided, or a non-desorbable (irreversible) adsorbed fraction was present.

3. Results and Discussion

Gas-volumetric and micro-calorimetric measurements

In the following, no quantitative/energetic data will be reported for Ac uptake on Si/Ca(4)-T systems, as the presence of long-lasting reaction(s), bringing about the continuous release of reaction heats and of reaction products to the adsorbed/gaseous phases, renders impossible the obtainment of reproducible isotherms of both calorimetric and quantitative type. Unlike that, the easy obtainment of reproducible isotherms for both Al- and Zr-containing oxidic systems, as discussed below, rules out for the latter systems the occurrence at 298K of long-lasting reactions.

These preliminary indications will be then confirmed by *in situ* IR data, despite the fact that the latter are unavoidably obtained at $T > 298\text{K}$, as specified in the Experimental section.

Si/Al systems. Both 4% and 8% Al-modified silica specimens have been examined. As no qualitatively different behavior was exhibited by the two sample series, only quantitative/energetic data relative to the lower-loading system (4%) are here reported, in order to allow a direct comparison between these and integrated absorbance IR spectroscopic data. Also, since the interaction of Ac with the reference pure Al oxides [both α - (corundum structure) and γ - Al_2O_3 (spinel structure)] does not yield a.c. reaction when the oxides are fully hydrated (consistently with the observation that H_2O is a selective poison for a.c. reaction over γ - Al_2O_3 ³³), only thermally activated Si/Al specimens have been studied calorimetrically.

Figure 1 presents, for Si/Al(4)-673, quantitative isotherms [section (a)] and calorimetric isotherms [section (b)]. It is noted that: (i) since a maximum equilibrium pressure of 10.3 Torr was reached ($p/p^\circ \approx 0.045$)⁴⁰, the presence of a liquid-like physisorbed phase can be ruled out, as also indicated by the (still) Type I profile of the isotherms. Still, at the maximum Ac pressure reached, the isotherms are still growing and suggest that the specific (chemisorptive) interaction of Ac with the Si/Al(4)-673 surface is not completed yet; (ii) primary and secondary isotherms are largely non coincident, and indicate the presence of an appreciable fraction of irreversibly adsorbed Ac. The distance between primary and secondary run isotherms indicates that the irreversible amount, that is completed in the earliest uptake stage (p_{Ac} between 2 and 3 Torr; $p/p^\circ \approx 0.009$ – 0.013), accounts for some $0.5 \mu\text{mol m}^{-2}$ (~28% of the overall amount adsorbed within the explored pressure range) and for some 0.04 J m^{-2} (~25% of the overall heat released in that pressure range). Ac adsorption at 298K on the parent non-porous A200 silica, due to carbonyl/silanol H-bonding interactions, is fully reversible,²⁰ and therefore the irreversibly adsorbed Ac fraction must be ascribed entirely to acid/base interactions, of either Lewis or Brønsted type, with sites produced by the introduction of the Al oxidic species.

The inset to section (b) of Figure 1 reports the differential molar adsorption heats for primary and secondary Ac uptake on Si/Al(4)-673. It is noted that: (i) the existence of an irreversible Ac fraction is here monitored by the different coverage (abscissa) range covered by primary and secondary plots. It amounts, as also indicated above, to $\sim 0.5 \mu\text{mol m}^{-2}$; (ii) the two plots have a similar evolution: both q^{diff} curves start high (though at appreciably different q^{diff} values), and decline fast within an overall coverage of $\sim 0.4\text{--}0.5 \mu\text{mol m}^{-2}$ ($q^{\text{diff}} \approx 90\text{--}100 \text{ kJ mol}^{-1}$), after which the two plots become virtually coincident. As the mentioned coverage is reached when the isotherms are still in the steep initial stage (equilibrium $p_{\text{Ac}} \approx 1 \text{ Torr}$), it is deduced that the two q^{diff} plots become flat and virtually coincident when the uptake of the irreversible Ac fraction is roughly only half-way through; (iii) for Ac coverages $n_{\text{a}} > 0.5 \mu\text{mol m}^{-2}$, the virtually coincident q^{diff} plots decline quite slowly and, when the maximum p_{Ac} is reached ($\sim 10 \text{ Torr}$), $q^{\text{diff}} \approx 60\text{--}70 \text{ kJ mol}^{-1}$ (*i.e.*, a molar enthalpy figure roughly corresponding to the strongest fraction of the weaker 1:1 carbonyl/silanol H-bonding interaction observed on the reference silica, and slightly lower than the almost constant $q^{\text{diff}} \approx 75 \text{ kJ mol}^{-1}$ characteristic of the stronger 1:2 form of carbonyl/silanol H-bonding interaction²⁰); (iv) the starting q° figures (*i.e.*, the q^{diff} values extrapolated to zero coverage, representing the limit energetic contribution of the strongest sites fraction) are quite different for the two q^{diff} plots, as expected: $q^{\circ} \approx 325 \text{ kJ mol}^{-1}$ for the primary adsorption run (a medium-high zero-coverage isosteric heat, compatible with the partial irreversibility observed at 298K), and $\sim 200 \text{ kJ mol}^{-1}$ for the secondary adsorption run (a zero-coverage isosteric heat still quite high for a reversible specific uptake); (v) overall, the difference in energetic terms between primary and secondary adsorption runs is relatively small, and limited to the first and more energetic stage of the adsorption process. In this first stage q^{diff} values range between ~ 300 and $\sim 100 \text{ kJ mol}^{-1}$, adsorption enthalpy figures definitely higher than those observed for mere H-bonding interactions in non-porous silicas²⁰, and compatible with irreversible/reversible Ac coordinative interactions of the acid-base type, to be obviously correlated with the presence of Al species in the surface layer.

Si/Zr systems. Since, unlike aluminas, nominally fully hydrated zirconias (*i.e.*, both *m*- and *t*-ZrO₂ merely evacuated at ambient temperature) yield to a moderate extent the a.c. reaction^{41,42}, for a proper comparison with pure Zr oxides both highly-hydrated and medium-activated Si/Zr mixed oxide specimens have been investigated.

Figure 2 presents, for Si/Zr(3)-303 and Si/Zr(3)-673, quantitative isotherms [section (a)] and calorimetric isotherms [section (b)] in the same p_{Ac} range used above for Si/Al systems (*i.e.*, up to $p/p^\circ \approx 0.045$). It is noted that: (i) in general terms, both types of isotherm are quite similar to those of the Si/Al system dealt with above. But the adsorption capacity per unit surface area of Si/Zr(3)-673 is appreciably larger than that observed for the corresponding Si/Al(4)-673 system (for instance, at $p_{Ac} \approx 10$ Torr, the primary uptake is $\sim 2.3 \mu\text{mol m}^{-2}$ on the former system, and $\sim 1.8 \mu\text{mol m}^{-2}$ on the latter). Among the various possible causes of the larger activity toward Ac, an important role is supposed to be played by the higher hydration level of a sol-gel silica with respect to a pyrogenic one. Also, the adsorption capacity of the highly hydrated Si/Zr(3)-303 system turns out to be definitely larger than that of Si/Zr(3)-673 (at $p_{Ac} \approx 10$ Torr, on the former system the primary uptake is $\sim 3.2 \mu\text{mol m}^{-2}$, *i.e.*, some 38 percent larger than on the latter one), and the difference is expected to be mainly due, as for pure silica²⁰, to a far larger incidence in the more hydrated material of Ac carbonyl/silanol H-bonding interactions; (ii) both quantitative and calorimetric isotherms indicate the presence of an appreciable amount of irreversible Ac uptake. It accounts, for equilibrium $p_{Ac} > 2\text{--}3$ Torr, for a virtually constant amount of $\sim 0.45 \mu\text{mol m}^{-2}$ and $\sim 0.035 \text{ kJ mol}^{-1}$ on both fully-hydrated and medium-activated samples, meaning that in percent terms the irreversible Ac fraction becomes higher the higher the dehydration stage. This seems reasonable, as the irreversible Ac adsorption is expected to concern, at least in part, acid-base coordination at *cus* surface cationic centres, the concentration of which can only increase with proceeding dehydration, while the incidence of mainly reversible H-bonding interactions is bound to decline.

The inset to Figure 2 reports the differential molar adsorption heats for primary and secondary Ac uptake on both Si/Zr(3)-303 and Si/Zr(3)-673. It can be noted that: (i) larger uptakes on the former

sample are here monitored by the larger coverage ranges covered by the relevant q^{diff} plots (star vs square symbols), whereas the difference between primary and secondary adsorption runs are monitored by the larger coverage ranges covered by empty-symbol plots with respect to the corresponding full-symbol ones; (ii) primary q^{diff} plot of Si/Zr(3)-303 starts at $\sim 300 \text{ kJ mol}^{-1}$ ($q^\circ \approx 330 \text{ kJ mol}^{-1}$), whereas the secondary one starts only somewhat lower (at $\sim 250 \text{ kJ mol}^{-1}$; $q^\circ \approx 270 \text{ kJ mol}^{-1}$). The two star-symbol plots first decline fast and remain separated until, at $q^{\text{diff}} \approx 100 \text{ kJ mol}^{-1}$ and $n_a \approx 1.0\text{--}1.2 \text{ }\mu\text{mol m}^{-2}$ (equilibrium p_{Ac} is around $0.5\text{--}1.0 \text{ Torr}$, *i.e.*, still in the steep initial section of the isotherms), they coincide and proceed declining slowly to $\sim 70\text{--}75 \text{ kJ mol}^{-1}$. Overall, the q^{diff} plot behavior of the highly hydrated Si/Zr(3)-303 sample is quite similar to that of the medium-activated Si/Al(4)-673 one, dealt with above, for which an early prevalence of medium-energy interactions of the acid-base coordinative types was suggested, followed by a relatively long prevalence of the (mainly) reversible 1:2 Ac carbonyl/silanol H-bonding interactions; (iii) Primary q^{diff} plot of the medium-activated Si/Zr(3)-673 system starts quite high (at $\sim 390 \text{ kJ mol}^{-1}$; $q^\circ \approx 410 \text{ kJ mol}^{-1}$), whereas the secondary one starts at definitely lower q^{diff} values ($\sim 240 \text{ kJ mol}^{-1}$; $q^\circ \approx 270 \text{ kJ mol}^{-1}$), that are virtually coincident with those of the secondary plot of the highly hydrated Si/Zr(3)-303 system. Both primary and secondary q^{diff} plots of Si/Zr(3)-673 first decline sharply down to coverage values of $\sim 1.3\text{--}1.4 \text{ }\mu\text{mol m}^{-2}$ (p_{Ac} is around $2\text{--}3 \text{ Torr}$, *i.e.*, at the end of the initial steep section of the isotherms), and heat values as low as $\sim 70\text{--}75 \text{ kJ mol}^{-1}$ (*i.e.*, q^{diff} values lower than those reached by the Si/Zr(3)-303 system at the same coverages). After that, primary and secondary q^{diff} plots keep declining together quite slowly, down to $\sim 60 \text{ kJ mol}^{-1}$. The lower q^{diff} values exhibited by the Si/Zr(3)-673 system (with respect to the corresponding Si/Zr(3)-303 one) for n_a between ~ 1 and $\sim 2.4 \text{ }\mu\text{mol m}^{-2}$ is thought to be due to a lower incidence, on the higher-activated material, of the more energetic 1:2 Ac carbonyl/silanol H-bonding interactions, whereas the much increased initial part (up to $n_a \approx 0.5 \text{ }\mu\text{mol m}^{-2}$) of the primary q^{diff} plot of Si/Zr(3)-673 (still

with respect to the corresponding Si/Zr(3)-303 one) is expected to be due to the creation, upon activation at 673K, of definitely stronger *cus* cationic sites acting as Lewis acid centres.

Most of the deductions based on quantitative/calorimetric data reported in this section ought to be now confirmed by IR spectroscopic data.

IR spectroscopic measurements

Before describing the spectroscopic aspects of Ac adsorption/desorption on the selected SiO₂-based mixed oxides, surface acidity of the systems will be investigated by the IR spectroscopic tool, because surface acidity/basicity is expected to play an important role in Ac adsorption processes and/or in the reaction(s) that Ac may possibly undergo when in contact with the oxidic surfaces.

Surface acidity.

(A) CO adsorption at BT. As it is long known, CO is a weak Lewis base and, upon adsorption at ambient temperature on ionic d⁰ oxidic systems, can yield a weak and usually reversible acid/base coordinative interaction only with highly un-coordinated d⁰ cations, acting as strong Lewis acid centres. Since on some catalytic oxidic systems, like transition aluminas and zeolites, the presence of strong Lewis acid sites has been considered as responsible for the Ac molecule activation that leads to a.c. reaction^{32,33}, the strong Lewis acidity of the SiO₂-supported systems of interest has been preliminarily checked by means of CO adsorption at BT.

Figure 3 reports the spectra of CO adsorbed, under p_{CO} = 100 Torr, on some samples vacuum activated at 673K (*mild-activated samples*). [No spectra are reported relative to BT CO evacuation, as on all systems considered σ -coordinated CO is quickly reversible. Also, no spectra are reported relative to samples vacuum activated at 303K (*hydrated samples*), as no strong Lewis acidity and BT activity toward CO are present yet on both hydrated silica-supported and hydrated reference pure oxide systems]. It is noted that: (i) CO band in spectra (a) and (a'), relative to two Si/Al systems, is constantly sharp and centered at 2225 cm⁻¹, indicating that (as for Ac uptake) also the activity toward CO is quite homogeneous and changes only in mere quantitative terms on varying

Al loading. The ν_{CO} band at 2225 cm^{-1} is the highest- ν CO band observed in this study, meaning that *cus* Al sites created at 673K on Si/Al systems possess the highest Lewis acidity, consistent with the known high Lewis acidity of severely un-coordinated Al sites in incomplete tetrahedral coordination (very strong $^{\text{IV}}\text{Al}_{\text{CUS}}$ sites)⁴³. In particular, the Lewis acidity observed on Si/Al systems is definitely higher and more homogeneous than that evidenced, in the same conditions, on the reference $\gamma\text{-Al}_2\text{O}_3$ system on which a fairly broad band of carbonyl-like species [$\nu_{\text{CO}} = 2198 \text{ cm}^{-1}$; spectrum (b)] is due to anion vacancies either bridging between $^{\text{IV}}\text{Al}$ and $^{\text{VI}}\text{Al}$ ions [$(^{\text{IV}}\text{Al}-^{\text{VI}}\text{Al})_{\text{CUS}}$ sites], or in the coordination sphere of $^{\text{IV}}\text{Al}$ ions located in “regular” (*i.e.*, low-index and extended) crystal planes (medium-strong $^{\text{IV}}\text{Al}_{\text{CUS}}$ sites)⁴³. In fact, on transition aluminas, purely tetrahedral *cus* Al sites located in crystallographically defective configurations, acting as very strong $^{\text{IV}}\text{Al}_{\text{CUS}}$ sites, do form in appreciable amounts only for vacuum activation at $T \geq 800\text{K}$ ^{3,43}. It is interesting to anticipate here that, unlike strongly acidic Si/Al systems, the mild-activated and lower Lewis acidic $\gamma\text{-Al}_2\text{O}_3$ system of spectrum (b) yields, when in contact with Ac at ambient temperature, abundant a.c. reaction; (ii) spectrum (c) shows that, with a sharp CO peak at $\nu_{\text{CO}} = 2191 \text{ cm}^{-1}$, also the Si/Zr(3)-673 system possesses strong Lewis acidity, though definitely lower than that present on the Si/Al systems. In fact, for CO σ -coordination, a ν_{CO} band centered below 2200 cm^{-1} and a downward shift $\Delta\nu_{\text{CO}} \approx -35 \text{ cm}^{-1}$ mean much in terms of the extent of σ -charge release. Comparison with spectra (d) and (d’), relative to the reference samples *t*-ZrO₂ ($\nu_{\text{CO}} = 2194 \text{ cm}^{-1}$) and *m*-ZrO₂ (ν_{CO} band doublet, apparently centered at ~ 2190 and $\sim 2185 \text{ cm}^{-1}$, respectively), indicates that the strong Lewis acidity of mixed and pure Zr oxidic systems is of (almost) equivalent strength. (In fact, the sharper and partly resolved ν_{CO} bands (d) and (d’) of (pure) crystalline zirconias fit within the broader ν_{CO} envelope (c) of the Si/Zr system). It is anticipated here that, unlike the Si/Zr system, in the case of pure crystalline zirconias mildly activated at 673K, the contact with Ac at ambient temperature yields abundant a.c. reaction⁴¹; (iii) in spectrum (e), a broad ν_{CO} peak centered at $\sim 2180 \text{ cm}^{-1}$ indicates that also Si/Ca mixed systems, on which a mild thermal activation produces

surface $\text{Ca}^{2+}_{\text{cus}}$ sites, presents strong Lewis acidity, though of strength further appreciably decreased with respect to the systems described above. No comparison with a reference pure CaO system can be proposed, as on CaO (as well as on other highly basic pure oxides, like MgO) no plain CO σ -coordination occurs at ambient temperature, while dimeric and complex polymeric anions form fast and abundantly^{7c,7d,44}.

(B) The adsorption of 2,6-dimethyl-pyridine (2,6-Lu). IR spectroscopic investigation of 2,6-Lu adsorption/desorption is an useful analytical tool in surface chemistry because: - the strong base can interact, in a molecular form, with both weak and strong Lewis acid sites⁴⁵. The presence of methyl groups in the two α -positions of the heteroaromatic ring renders labile and reversible at BT, or just above that, the species adsorbed on weaker Lewis sites, whereas the species adsorbed on strong Lewis sites are much less labile and can thus be resolved; - the interaction with acid protonic sites (Brønsted acid centres) yields lutidinium ions (LuH^+), whose spectral features can be easily recognized and differentiated from those of all other 2,6-Lu adsorbed species⁴⁵.

Figure 4 reports, for the silica-supported oxides of interest, the main analytical spectral features in the region of the 8a–8b ring vibrational modes of 2,6-Lu adsorbed/desorbed (*i.e.*, irreversible) at BT [curves (a)–(c)], and irreversible at 423K [curves (a')–(c')]. No spectra relative to 2,6-Lu uptake on the reference pure Al and Zr oxides are reported, as they have been dealt with elsewhere^{45,46}. It can be noted that: (i) the presence and persistence, in the spectra of Si/Al and Si/Zr systems, of a band doublet at $\nu > 1625 \text{ cm}^{-1}$ [namely, ~ 1645 and $\sim 1630 \text{ cm}^{-1}$ in the better resolved Si/Al spectra (a) and (a')] clearly reveals the presence in these systems of relatively abundant and strongly held LuH^+ species, indicative of a Brønsted acidity that is known to be totally absent in the corresponding pure Al and Zr oxides (and, obviously, in pure silica). Unlike that, no LuH^+ species form on the Si/Ca system, as seems reasonable for a mixed oxidic system in which the added hetero-element should possibly introduce oxygen-basic rather than hydrogen-acidic properties; (ii) the BT spectra of the three systems [curves (a)–(c)] are dominated, at $\nu < 1620 \text{ cm}^{-1}$, by a strong and well resolved band doublet at ~ 1605 and $\sim 1585 \text{ cm}^{-1}$, corresponding for the latter peak to the 8b mode of all

molecularly adsorbed 2,6-Lu species, and for the former peak mostly to the 8a mode of 2,6-Lu H-bonded to surface silanols⁴⁵. But a weak shoulder at $\sim 1617\text{ cm}^{-1}$ in the BT spectrum of the Si/Al system, and an evident asymmetry in the high- ν side of the $\sim 1605\text{ cm}^{-1}$ peak of the Si/Zr system indicate that other minor contributions are also present in the $1600\text{--}1625\text{ cm}^{-1}$ spectral interval. This aspect is rendered quite evident by evacuation of adsorbed 2,6-Lu at 423K [curves (a')–(b')], since much better resolved peaks remain at $\sim 1620\text{ cm}^{-1}$ on Si/Al and at $\sim 1615\text{ cm}^{-1}$ on Si/Zr, to be ascribed to the 8a mode of 2,6-Lu coordinated to a stronger fraction of Lewis acid sites. Note that the 8a bands observed here for strong Lewis-coordinated 2,6-Lu are virtually coincident with those found in the case of the reference systems $\gamma\text{-Al}_2\text{O}_3$ and $t\text{-ZrO}_2$, respectively^{45,46}. As for the Si/Ca system, after evacuation at 423K [curve (c')] no 8a 2,6-Lu bands remain at $\nu > 1610\text{ cm}^{-1}$, to be specifically ascribed to 2,6-Lu coordinated to strong *cus* Ca cations. But a medium-strong peak remaining, after evacuation at 423K, at $\sim 1606\text{ cm}^{-1}$ cannot be ascribed (only, if at all) to residual 2,6-Lu/silanol H-bonding interactions, considering that on pure non-porous silica all 2,6-Lu/silanol H-bonding interactions are eliminated within 423K. So, (at least part of) the residual peak at $\sim 1606\text{ cm}^{-1}$ must be assigned to the Lewis acid/base interaction of 2,6-Lu with some *cus* Ca cationic sites, that are weaker as Lewis acid centres than Al_{cus} or Zr_{cus} sites (on the basis of the lower spectral position of the 8a mode), but strong enough to resist thermal evacuation at 423K; (iii) an appreciable fraction of 2,6-Lu adsorbed at BT on the Si/Ca system is decomposed and/or chemically modified at 423K, as evidenced by strong bands formed at ~ 1560 and $\sim 1540\text{ cm}^{-1}$ (bands that are either absent or only very marginally formed on the other two systems). This high reactivity of 2,6-Lu adsorbed at the surface of the Si/Ca system is not so surprising, considering that on CaO and other strongly basic oxides (*e.g.*, MgO) adsorbed pyridine is easily transformed at mild temperatures into dipyrindyl species^{47,48}.

Ac adsorption/desorption.

(A) The Si/Al system. The ν_{OH} spectral region. Figure 5 reports, in both plain absorbance and differential form (inset), the spectral pattern in the ν_{OH} spectral region relative to the early stages (up to $p_{\text{Ac}} = 3$ Torr) of Ac uptake on Si/Al(4)-673. It is noted that: (i) the mild-activated mixed Si/Al oxide presents only one surface OH species free from H-bonding (sharp free ν_{OH} band centered at ~ 3750 cm^{-1}) and, upon contact with the very first small Ac doses (curves 1–4), the free ν_{OH} band starts declining quite fast. But, unlike what observed in the case of pure silicas (see, for instance, fig. 5 in ref. 20), no specific and discrete bands due to Ac H-bonded OH species are observed yet at $\nu < 3700$ cm^{-1} , where only a diffuse and gradual upward absorbance increase is noted in the first differential spectra (curves 1–4 of the spectral pattern in the inset). Diffuse non-resolved bands of H-bonded hydroxyls have been claimed to be typical of strong Brønsted acidic OH species (like, for instance, in the case of nominally “super-acid” sulfated zirconias)⁴⁹. As for the coincident spectral position at ~ 3750 cm^{-1} for the ν_{OH} vibration of both (free) Brønsted acidic OH (“acidity-enhanced silanol groups” or “pseudo-bridging silanols”) and (free) “regular” terminal silanol groups, this has been observed to be typical of the flexible structure of amorphous silico-aluminas⁵⁰ (unlike the case of the rigid structure of crystalline proton acidic zeolitic systems, in which an additional and specific ν_{OH} band is usually observed at ~ 3590 – 3620 cm^{-1} for (free) bridging Brønsted acidic OH functionalities)^{50a,51}. For the first Ac adspecies formed at low Ac pressures is thus expected, at least in part, a specific interaction of the CO-bearing molecules with Brønsted acidic OH sites, whose existence was clearly evidenced by 2,6-Lu adsorption/desorption; (ii) starting with $p_{\text{Ac}} \approx 0.1$ – 0.2 Torr (curves 5–6 in the spectral patterns of fig. 5), the further fast decrease of the free ν_{OH} band at ~ 3750 cm^{-1} is accompanied by the gradual increase of discrete broad and closely overlapped bands of H-bonded OH species at $\nu < 3700$ cm^{-1} , first centered at ~ 3500 cm^{-1} and then also at ~ 3400 cm^{-1} . These bands have been previously identified as due to the H-bonding interaction of Ac with “regular” silica silanols,²⁰ first in the ratio 1:2 [the corresponding

carbonyl band, centered at $\sim 1695\text{ cm}^{-1}$, was termed the ν_{CO} band (A)], and then also in the ratio 1:1 [yielding the ν_{CO} band termed (B), centered at $\sim 1712\text{ cm}^{-1}$]. The early appearance of the easily recognizable OH bands at ~ 3500 and $\sim 3400\text{ cm}^{-1}$ monitors that, at still quite low Ac coverages ($n_{\text{a}} \approx 0.1\ \mu\text{mol m}^{-2}$), also plain H-bonding adsorption on OH groups of the silica network starts contributing to the overall Ac uptake. This is consistent with the clear but not dramatic difference of q^{diff} plots observed between pure non-porous silica and the Si/Al system(s).

After Ac evacuation at BT, the starting ν_{OH} background spectrum is not fully recovered, as expected of an adsorption/desorption process that, on the basis of quantitative/calorimetric data, was found to be partly irreversible. Note that the after-evacuation residual ν_{OH} spectrum is not explicitly shown in Fig. 5, as it happens to be virtually coincident with the adsorption-run spectrum marked with the number (4), *i.e.*, the last spectrum of the diffuse Ac/OH H-bonding interaction ascribed to Brønsted acidic OH species.

All of the OH-based indications reported here need now to be confirmed, and possibly integrated, by spectral data collected in the specific analytical range of Ac ν_{CO} vibrational mode(s).

The ν_{CO} spectral region. Section (a) of Figure 6 reports, in the spectral range of $\nu_{\text{C=O}}$ and $\nu_{\text{C=C}}$ vibrational modes, the spectral pattern relative to the early stages of Ac uptake on Si/Al(4)-673 (as for fig. 5). Two significant aspects are at first sight evident: **(1)** also at BT (surely $> 298\text{K}$, as reported in the Experimental), no a.c. reaction occurs to any detectable extent on the mild-activated Si/Al system. In fact, the formation of MO (that is the main product of Ac a.c. reaction) could not escape detection, as strong and characteristic features of adsorbed $\text{MO}^{22,52,53}$ would become evident in the extended double-bond spectral range reported in fig. 6. This is demonstrated by the spectra reported, for comparison purposes, in a band-resolved form (for simplicity, only in the low- ν range; see figure caption) in Figure 7(c), showing that: - MO adsorbs reversibly on pure silica [spectral set (3)] yielding, in the ν_{CO} region, a strong band at $\sim 1680\text{ cm}^{-1}$ (band α ; it is the C=O vibration of MO H-bond interacting with surface silanols), and in the $\nu_{\text{C=C}}$ region a strong band at $\sim 1614\text{ cm}^{-1}$ (band

β ; it is the C=C vibration of MO interacting with silanols). [As a reference information, it is recalled that diluted MO solutions in CCl_4 (non-polar solvent) present a strong ν_{CO} band at $\sim 1690 \text{ cm}^{-1}$ (with a weak shoulder at $\sim 1714 \text{ cm}^{-1}$), and a strong $\nu_{\text{C=C}}$ band at $\sim 1620 \text{ cm}^{-1}$ (with a medium-strong shoulder at $\sim 1638 \text{ cm}^{-1}$), whereas solutions in CHCl_3 (polar solvent) present a strong ν_{CO} band at $\sim 1685 \text{ cm}^{-1}$ (with a weak shoulder at $\sim 1708 \text{ cm}^{-1}$), and a strong $\nu_{\text{C=C}}$ band at $\sim 1616 \text{ cm}^{-1}$ (with a medium-strong shoulder at $\sim 1634 \text{ cm}^{-1}$); - upon MO adsorption on Si/Al systems [spectral sets (1) and (2)], the dominant and partly irreversible band β centered at $\sim 1614 \text{ cm}^{-1}$ (MO interacting with silanols) is accompanied by two largely irreversible bands centered at $\sim 1585 \text{ cm}^{-1}$ (band β') and $\sim 1565 \text{ cm}^{-1}$ (band β''), ascribed to the C=C vibration of MO interacting with Lewis acid sites (coordination) and Brønsted acid sites (strong H-bond), respectively. After evacuation, part of the α band (C=O vibrations) associated with the resolved and persistent bands β , β' and β'' , remains weak, quite broad, and still unresolved at $\sim 1674 \text{ cm}^{-1}$ [see spectral set (2) of Fig. 7(c)]. The assignment here proposed for adsorbed MO is consistent with that reported by Panov *et al.*³³ for MO adsorbed at Lewis sites on amorphous sol-gel alumina, and at Brønsted acid sites on USY zeolite, respectively. Not shown in figure 7(c), the relative amount of the Brønsted-bound MO species β'' turned out to be far more sensitive to Al loading [on passing from Si/Al(4) to Si/Al(8)] than the Lewis-bound MO species β' ; (2) the non-reactive BT adsorption/[desorption] of Ac on medium activated Si/Al systems is a rather complex process. Due to the close overlap of several spectral components (at least three in the narrow $1740\text{--}1650 \text{ cm}^{-1}$ interval), only an accurate computer-assisted band resolution effort could allow us to rationalize the complex spectral pattern of fig. 6(a) [and 6(b)].

Band resolution in terms of (up to) three spectral components of the complex Si/Al(4)-673 adsorption spectral pattern of fig. 6(a) resulted in: - the collection, as a function of equilibrium Ac pressure, of the individual major spectral features of each resolved component (and namely: band position, half-band width, integrated absorbance, and percent Gaussian character). The first three of

these data collections, not shown here for brevity, are reported in Table 2SM of the Supporting Information; - a complete set of resolved spectra (some of which are presented in figure 7(a), and are discussed below); - a total spectroscopic adsorption isotherm, resolved in three individual adsorption isotherms. These plots are reported in the inset to figure 6(a).

Moreover, assuming (as we did and discussed for the simpler Ac/silica system)²⁰ that all individual C=O vibrational components of chemisorbed Ac participate in the overall C=O vibrational envelope with roughly equal molar extinction (absorption) coefficients, a multiple-point comparison of the total spectroscopic adsorption isotherm [upper star-symbol curve of the inset to fig. 6(a)] with the corresponding portion of the primary quantitative adsorption isotherm [the upper open-circles curve of fig. 1(a), up to $p_{Ac} = 3$ Torr] allows to find an average absorbance/concentration conversion factor and, consequently, to read the spectroscopic individual adsorption isotherms also in terms of Ac molecules adsorbed per unit surface area. [The molecular-scale of Ac adsorption isotherms is reported, as a plot right-hand ordinate, in the inset of fig. 6(a)]. Note that, in the present case, the assumption of roughly equal molar extinction coefficients for the ν_{CO} vibration of all chemisorbed Ac species is not as straightforward as it could seem in the case of the Ac/silica system²⁰, where only (two) H-bonding interactions occurred. Still, a couple of spectroscopic arguments can possibly justify this useful approximation: (i) all types of interaction are of the dative type, starting from the carbonyl lone-pair electrons. Even if the strength of these dative interactions may be somewhat different, as actually demonstrated by both calorimetric and spectroscopic data, the effect produced by a charge dative release on the (change of) C=O dipole moment, that is actually at the basis of the ν_{CO} extinction coefficient, can be reasonably expected to be quite similar in the various cases; (ii) Fripiat *et al.*, who studied some quantitative aspects of Ac adsorption on amorphous alumina and on several types of zeolites,²² found that the overall specific absorbance of the ν_{CO} band envelope of chemisorbed Ac was much the same for all the systems examined. Considering that both number of Ac adsorption forms, and relative amounts of the various Ac adsorbed species were different for the different systems examined, the result they got

necessarily implies that all individual ν_{CO} components participate in the overall specific absorbance with a (virtually) equal individual absorption coefficient.

Analysis of the resolved spectral pattern of fig. 6(a), and of the resolved isotherms therefrom, indicates that: (i) the very first steps of Ac uptake (up to $p_{\text{Ac}} \approx 0.05\text{--}0.1$ Torr) yield two fast growing ν_{CO} bands, centered at $\sim 1681\text{--}1685$ cm^{-1} and $\sim 1692\text{--}1698$ cm^{-1} , respectively. The former band, broad and of high lorentzian character [see, for instance, the low-lying resolved spectrum (I) in Fig. 7(a)], is not present at any pressure in the Ac/pure-silica system, as shown by the reference resolved spectra of Fig. 7(b), and corresponds well to a ν_{CO} band reported in the literature (~ 1682 cm^{-1}) for Ac interacting with acidic OH species in zeolitic systems.³³ On the basis of these observations and of what is discussed above in the Ac/OH sub-section, this band is assigned to the strong H-bond interaction of Ac with Brønsted acid sites, and is hereafter referred to as the (Br) ν_{CO} band of the Si/Al systems. The (Br) band quickly stabilizes in position (~ 1688 cm^{-1}), grows with a distinct Type I (Langmuir-like) profile³⁹ [see the circle-symbol isotherm trace in the inset to Fig. 6(a)] and, for $p_{\text{Ac}} \approx 0.5$ Torr, reaches a saturation intensity of ~ 0.2 Ac molecules per nm^2 : this figure monitors the complete H-bonding consumption (titration) of Brønsted acid OH sites and, therefore, their surface concentration in the activation conditions adopted. Consistently, 0.5 Torr is also the p_{Ac} range at which, in Fig. 5, the H-bonding consumption of the unresolved free OH groups peak at ~ 3750 cm^{-1} stopped yielding diffuse (*i.e.*, non resolved) upward absorbance increases at $\nu < 3700$ cm^{-1} , and started to yield discrete (resolved) bands of H-bonded silanols at ~ 3500 cm^{-1} [ν_{CO} species (A)] and ~ 3400 cm^{-1} [species (B)]. Note that spectral positions and relative band intensities of the resolved spectrum (IV) of Fig. 7(a), relative to Ac uptake on Si/Al(8)-673, confirm that, on varying the Al loading, only quantitative modifications occur, and indicate that the amount of Brønsted-bound (Br) ν_{CO} species, whose saturation value has become as large as ~ 0.5 Ac molecules per nm^2 , is the most sensitive one to Al loading (as also reported in the case of MO adsorption on Si/Al systems); (ii) the other early-appearing ν_{CO} component (broad band at $\sim 1692\text{--}1698$ cm^{-1}) corresponds in spectral

position, but not in half-band width, to the ν_{CO} band termed (A) for the Ac/silica system [see, for comparison, the two reference spectral sets resolved in fig. 7(b)], and previously assigned to 1:2 carbonyl/silanol H-bonding interactions.^{15,20} The band first appearance at very low Ac pressures, as compared with energetic indications deriving from the earliest stages of the primary q^{diff} plot of Fig. 1(inset), suggests that the broad $\sim 1692\text{--}1698\text{ cm}^{-1}$ band should contain, besides the (A) ν_{CO} component, also other more energetic contributions [as dealt with at point (iv) below]; (iii) at $p_{\text{Ac}} \geq 0.1$ Torr, a third ν_{CO} component appears, constantly centered at $1711\text{--}1712\text{ cm}^{-1}$ and fast growing with Ac pressure [see the high- ν component termed (B) in the resolved spectral sets (II) and (III) of Fig. 7(a)]. This band corresponds in position, half-band width, and pressure behavior [see the square-symbol spectroscopic adsorption isotherm in the inset to Fig. 6(a): a slow- and long-growing Type I (*i.e.*, Langmuir-like) profile³⁹] to the ν_{CO} band termed (B) for the Ac/silica system, and previously assigned to 1:1 carbonyl/silanol H-bonding interactions.^{18,20} The assignment is thus the same, and the band will hereafter be referred to as the (B) ν_{CO} band of the Si/Al systems. Langmuir plot tests indicate that the growth of band (B) does not actually obey the Langmuir isotherm equation (*i.e.*, the growth profile is just qualitatively Langmuir-like), so that it is impossible to evaluate an accurate value for the saturation intensity, that should grossly correspond to not less than ~ 0.4 Ac molecules per nm^2 ; (iv) finally, returning to the broad ν_{CO} component at $\sim 1692\text{--}1698\text{ cm}^{-1}$, it is observed to stabilize in position at $\sim 1700\text{ cm}^{-1}$ and to keep growing, fast up to $p_{\text{Ac}} \approx 0.5$ Torr (integral absorbance of $\sim 10\text{ cm}^{-1}$, corresponding to at least some 0.3 Ac molecules per nm^2) and then far more slowly [see the isotherm with triangle-symbol trace in the inset to Fig. 6(a)]. The isothermal spectral profiles in the inset to Fig. 6(a), and the resolved spectra (II) and (III) of Fig. 7(a)-7(b) indicate that, in the whole p_{Ac} range explored, the relative intensity of the $\sim 1700\text{ cm}^{-1}$ band with respect to that of the ν_{CO} band (B) is, for the Si/Al system(s), definitely higher than that observed for pure silica [compare the present data with, for instance, the isothermal spectral profiles (A) and (B) in Fig. 8(b) of ref. 20]. It is thus deduced that the $\sim 1700\text{ cm}^{-1}$ band of Si/Al systems

does indeed contain another ν_{CO} contribution besides the (A) ν_{CO} one (due to 1:2 CO/silanol interactions). This additional, early starting, and more energetic ν_{CO} component can be identified with the specific Lewis acid/base interaction of Ac with surface Lewis acid sites (namely, *cus* Al surface cations). The $\sim 1700 \text{ cm}^{-1}$ band is, therefore, referred to in the figures and in the following text as the (A+L) ν_{CO} band of the Si/Al systems. Note that the assignment here proposed for the (A+L) ν_{CO} band is consistent with the spectral features of Ac acid/base coordinated onto *cus* Al Lewis acid centres at the surface of: - sol-gel amorphous alumina (1702 cm^{-1} ; 1697 cm^{-1})^{22,33}; - mild-activated crystalline $\gamma\text{-Al}_2\text{O}_3$ [$1695\text{--}1701 \text{ cm}^{-1}$; Lewis acid sites involving *cus* ^{IV}Al cations of the spinel structure, as indicated by the BT CO adsorption of fig. 3(b)]; - $\alpha\text{-Al}_2\text{O}_3$ ($1710\text{--}1712 \text{ cm}^{-1}$; weaker Lewis acid sites due to *cus* ^{VI}Al cations of the corundum structure, that cannot adsorb CO at BT, and cause a lower red-shift of the ν_{CO} mode of Ac).

Spectral patterns relative to Ac adsorption/desorption on reference crystalline γ - and $\alpha\text{-Al}_2\text{O}_3$, and showing the latter assignments for Ac Lewis coordinated on aluminas, are not reported here for brevity, but are shown in Figure 1SM of the Supporting Information. That figure clearly indicates that, besides Lewis coordination, Ac interaction with both γ - and $\alpha\text{-Al}_2\text{O}_3$ yields, though to fairly different extents, also the a.c. reaction.

Section (b) of Figure 6 reports, for the Si/Al(4)-673 system, the spectral pattern of Ac desorption at BT. The relevant spectral features, obtained by the same computer band resolution approach used for the adsorption pattern dealt with above, are reported in Table 3SM of the Supporting Information. The evolution with evacuation time of integrated absorbance for all resolved bands, and of the corresponding surface Ac concentrations, is reported in the inset to Fig. 6(b) in the form of individual desorption spectral profiles. It is noted that: (i) as in the case of pure silica, ν_{CO} band (B) is quickly eliminated (~ 1 min); (ii) the composite ν_{CO} band (A+L) is partly eliminated fast ($\sim 1\text{--}2$ min), and partly declines slowly and eventually contributes (with some 10% of its starting intensity) to the fraction of Ac irreversibly held at BT. The double desorption rate of the (A+L) band confirms

its composite nature, and the presence in it of a strongly held species (*i.e.*, Lewis coordinated Ac) that contributes to the appreciable difference between primary and secondary q^{diff} plots [inset of Fig. 1(b)]; (iii) also the first-formed and most energetic ν_{CO} band termed (Br) presents an appreciable reversible fraction, but after ~ 15 min evacuation it reaches a steady state and contributes with some 30% of its starting intensity (~ 0.06 Ac molecules per nm^2) to the Ac phase irreversibly adsorbed at BT. Note that the percent and surface concentration figures just mentioned are merely indicative, as the spectroscopic evacuation was carried out on samples in the IR beam, and $\text{BT} > 298\text{K}$.

(B) The Si/Zr system. As anticipated in the quantitative/calorimetric section, the overall behaviour of Si/Zr systems is quite similar to that of the Si/Al ones. Still, some peculiarities are worth mentioning in some detail.

The ν_{OH} spectral region. Figure 8 reports, in the ν_{OH} spectral region, the early stages (up to $p_{\text{Ac}} = 1.5$ Torr) of the Ac adsorption pattern on Si/Zr(3)-673. It is noted that: (i) the very first Ac doses induce a diffuse and non-resolved profile modification in the spectral range ($\nu < 3700 \text{ cm}^{-1}$) of still fairly abundant H-bonded hydroxyls (curves 1–5), though not as clearly as in the case of Al-modified systems as a consequence of the complexity of the present ν_{OH} spectrum. Then, when Ac uptake becomes appreciable (from $p_{\text{Ac}} \approx 1.5$ Torr on; see, for instance, curve 9), the first overtone of the ν_{CO} vibrational mode of adsorbed Ac (sharp signal at $\sim 3410 \text{ cm}^{-1}$) starts interfering with the growing band of H-bonded hydroxyls and renders it very complex and hard to read; (ii) after evacuation at BT, the irreversibly adsorbed Ac fraction leaves the ν_{OH} spectral region deeply modified (see the dash-dot trace) with respect to the starting ν_{OH} background (broken line trace). This is a consequence of the persistence of both some residual Ac/OH H-bonding interactions (certainly involving, at least in part, Brønsted acid sites, as in the case of the Si/Al system), and a strong interference with the overtone of the ν_{CO} vibrational mode(s) of irreversibly held Ac

(interference that was not so evident in the case of the Si/Al system). The severe modifications caused by Ac adsorption/evacuation on the starting background ν_{OH} spectrum is quite evident also in the case of the Si/Zr(3)-303 system (see the inset to Fig. 8), where the stepwise Ac uptake (not shown) gradually reduces and eventually eliminates a well-defined ν_{OH} band centered at $\sim 3235\text{ cm}^{-1}$. The band, due to OH-OH H-bonding interactions at the surface of the highly hydrated sol gel material, upon Ac desorption is only marginally restored, confirming that the starting surface hydroxyl situation remains irreversibly modified by the abundant non-reversible fraction of chemisorbed Ac.

The ν_{CO} spectral region. Turning now to the analytical spectral range of the $\nu_{C=O}$ and $\nu_{C=C}$ vibrational modes ($1800\text{--}1500\text{ cm}^{-1}$), two preliminary considerations ought to be introduced: **(1)** there is a close spectroscopic similarity between Si/Zr and Si/Al systems, both in terms of number and nature of species that form upon Ac uptake (as well evidenced by the resolved spectra reported ahead), and of species that do not form. In particular, also with Si/Zr systems no evidence was ever obtained for the occurrence at BT of the a.c. reaction; **(2)** due to both the larger specific adsorptivity of Si/Zr systems (already monitored by the area-normalized quantitative data in Fig. 1 and 2), and the large specific surface area of Si/Zr systems, IR bands in adsorption (and desorption) spectral patterns turn out to present components even more severely overlapped than in the case of Si/Al systems, and to reach intensity saturation at definitely lower Ac coverages. For all these reasons, the use of computer resolved spectra was found to be even more mandatory than in the previous case, and resolved spectra are thus constantly resorted to in the present text.

For reference and comparison purposes, the starting overall adsorption/desorption spectral patterns of Si/Zr(3)-303 and Si/Zr(3)-673 are reported in the Supporting Information section as Figure 2SM. After computer spectral resolution of the adsorption/desorption patterns, the relevant spectral features (some of which were used for the construction of optical adsorption isotherms and

desorption profiles to be presented ahead) have been reported in Tables 4SM – 7SM of the Supporting Information section.

Figure 9 reports some resolved spectra, useful to show the accuracy of the computer-assisted reconstruction of experimental IR data, and to comment some band spectral features. It can be seen that: (i) the ν_{CO} band (Br) of Brønsted-bound Ac is the most constant one in terms of both spectral position ($\nu_{\text{max}} = 1683\text{-}1685\text{ cm}^{-1}$, in both adsorption and desorption runs) and half-band width ($\Delta\nu_{1/2} = 21\text{-}26\text{ cm}^{-1}$), indicating a fairly homogeneous family of adsorbing proton sites, as also confirmed by the high percent Lorentzian character of the band. Moreover, (Br) band is favoured in intensity terms over all other ν_{CO} species in the earliest uptake stages on Si/Zr(3)-303, whereas it is no longer so in the case of Si/Zr(3)-673, owing to the fast decreased overall population of OH species (as also shown by fig. 8) and, within it, of Brønsted acidic ones; (ii) the spectral features of the ν_{CO} band termed (A+L) are more variable. Upon adsorption, ν_{max} gradually moves from $\sim 1691\text{ cm}^{-1}$ to $\sim 1695\text{ cm}^{-1}$ and $\Delta\nu_{1/2}$ varies between ~ 19 and $\sim 27\text{ cm}^{-1}$, whereas the opposite trend is observed upon Ac desorption. This behavior derives from the composite nature of the band, and the different incidence in it, at different coverages, of Lewis-bound and 1:2 OH H-bonded Ac species. The mentioned coverage-dependent trends are less evident in the case of the Si/Zr(3)-673 sample, due to an increased concentration of Lewis acid sites and a decreased probability of having properly spaced silanol pairs that yield the 1:2 H-bonded Ac species (A); (iii) as for the last appearing Ac species termed (B), both ν_{max} and $\Delta\nu_{1/2}$ remain fairly constant upon adsorption/desorption, indicating an homogeneous nature for the 1:1 CO-OH H-bonding interaction, in spite of the intensity and ample heterogeneity of the OH spectral profiles shown in Fig. 8. It is also interesting to note that ν_{max} of band (B), constantly located at $\sim 1705\text{ cm}^{-1}$ in the p_{Ac} range explored, is some 7 cm^{-1} lower than in the case of the Si/Al system, suggesting a non negligible increase of H-bond strength.

Figure 10 reports overall and resolved spectroscopic adsorption isotherms relative to the three ν_{CO} species formed, at low p_{Ac} , on Si/Zr(3)-303 [section (a), left-hand plots] and Si/Zr(3)-673 [section

(b), right-hand plots]. The overall optical adsorption isotherms confirm, for p_{Ac} up to ~ 2 Torr, a higher adsorptivity for the more hydrated Si/Zr(3)-303 system. The spectroscopic isotherms are found to compare well in shape with (the early stages of) the quantitative adsorption isotherms of Fig. 2(a) so that, by applying the multiple-point equating procedure previously adopted for the Si/Al system, average absorbance/concentration conversion factors can be obtained that allow to read the individual spectroscopic isotherms also in terms of Ac molecules adsorbed per unit surface area. [The molecular-scale of Ac adsorption isotherms is reported, as a right-hand ordinate, in the plots of fig. 10(a) and (b)]. It can be noted that the concentration scales of the two plots are slightly different, even if overall (and individual) ν_{CO} extinction coefficients should be the same in the two cases. The reason is that what we actually obtain, by equating quantitative and optical adsorption isotherms, are “apparent” absorption coefficients⁵⁴ that are valid only for each couple of quantitative/optical isotherms, in that Beer-Lambert law is, in principle, not valid for heterogeneous systems.⁵⁵ Also the scattering characteristics of a solid certainly vary on passing from one system to another, and may vary even on the same system when treated (for instance, activated) in different conditions. After the conversion of absorbance-to-concentration scales, the higher overall adsorptivity of the more hydrated Si/Zr(3)-303 system is further evidenced.

As for the resolved optical isotherms of fig. 10, it is noted that: (i) the Brønsted-bound (Br) species, characterized by the lowest ν_{CO} frequency and thus the strongest interaction, grows fast during the first uptake steps and reaches an asymptotic (or quasi-asymptotic) value for $p_{Ac} \approx 2$ Torr. The asymptotic (Br) level is more than twice as large on the highly hydrated Si/Zr(3)-303 system ($\sim 42 \text{ cm}^{-1}$, corresponding to ~ 0.65 molecules per nm^2 , vs ~ 0.3 molecules per nm^2), confirming that a mild vacuum activation at 673 is sufficient to eliminate over 50% of Brønsted acidic OH sites. Moreover, the population of acidic OH sites turns out to be definitely higher on the Si/Zr(3)-673 system than on the corresponding Al-loaded one (fig. 6). Both (Br) isotherms in fig. 10 have an apparent Langmuir-like (*i.e.*, Type I) profile, though neither of them yields a good linear (p/n_a vs p) Langmuir plot. This contradicts somehow the rather homogeneous nature of (Br) sites suggested by

the relevant spectral features (Fig. 9), but certainly agrees with the largely irreversible nature of the Brønsted-bound Ac species, to be shown in next figure; (ii) also the composite (A+L) ν_{CO} band grows fast in the early stages of the uptake process. In the case of Si/Zr(3)-673 (for which higher p_{Ac} values can be reached before saturation of the IR signal), it reaches for $p_{Ac} \approx 2$ Torr an early asymptotic value (~ 40 cm^{-1} , corresponding to ~ 0.55 Ac molecules per nm^2), whereas the corresponding isotherm of the highly hydrated system at $p_{Ac} \approx 2$ Torr is still fast growing and seems to tend to saturation values of at least some 0.7 Ac molecules per nm^2 . [Actually, in the very short (0–2) Torr pressure range, the latter isotherm fits reasonably well the $(p/n_a \text{ vs } p)$ Langmuir plot equation, that would indicate a saturation value (n_m) as high as ~ 1.2 molecules per nm^2 , obviously overestimated]. In any event, the difference of maximum concentration of (A+L) species formed on the two Si/Zr specimens is very large, and is likely to be determined by the relatively limited amount of surface *cus* Zr centres [Lewis acid sites, yielding species (L)] created upon mild activation at 673K, whereas on the highly hydrated system the amount of suitably spaced OH couples yielding the 1:2 CO-OH H-bonded Ac complexes [species (A)] is expected to be quite high; (iii) band (B) of 1:1 CO-OH H-bonded Ac complexes starts appearing on both samples for $p_{Ac} \approx 1$ Torr (*i.e.*, when the adsorption of the stronger-held species is approximately half-way through), and then its initial growth is quite steep (quasi-linear). On the mild-dehydrated system and for p_{Ac} as high as 3–4 Torr ($p/p^\circ \approx 0.01$ – 0.015) it is the only “specific” (chemisorbed) Ac adspecies that is still growing.

Figure 11 shows, for both Si/Zr(3)-303 [section (a), left-hand plots] and Si/Zr(3)-673 [section (b), right-hand plots], the desorption profiles of the band-resolved ν_{CO} components. Some interesting aspects can be evidenced: (i) starting with the weakest-held (B) species, it is noted that it is virtually completely eliminated in 1 hr evacuation from the activated Si/Zr(3)-673 system, whereas in the case of the highly hydrated Si/Zr(3)-303 system some 38% of it still remains (A_{int} varies from ~ 13 cm^{-1} to ~ 5 cm^{-1} , corresponding to surface concentrations of some 0.2 to 0.06 Ac molecules per nm^2).

This different behavior is somewhat surprising, in view of the virtually identical spectral features (*i.e.*, bond strength) of (B) species mentioned above. It is most probably ascribable to kinetic effects, implying the more difficult elimination of Ac from a meso-porous system that still possesses a virtually complete surface hydrated layer. After plain evacuation at RT, the latter is made up of both (abundant) OH groups and (some) coordinated molecular water that, upon Ac adsorption/desorption, may undergo back-and-forth ligand displacement processes; (ii) the desorption of the (A+L) ν_{CO} component starts, in the two samples, from slightly different levels (also in view of the fact that, on Si/Zr(3)-303, the asymptotic uptake saturation was still far from being reached yet), and after ~ 1 hr evacuation the desorption process is still going on slowly while some 0.33-0.35 Ac molecules of the (A+L) type still remain per nm^2 . In the simplifying assumption that this amount may correspond (especially at RT) to the irreversible fraction of the (A+L) species, the latter turns out to account, on both Si/Zr samples, for the largest fraction of total irreversibly adsorbed Ac. Moreover, the virtually constant irreversible amount of (A+L) species indicates that, on the average, the elimination upon activation at 673K of one irreversible 1 : 2 Ac/OH site [the Ac species (A)] yields one irreversible Lewis acid site [the Ac species (L)]; (iii) the desorption profile of the Brønsted-bound Ac species (Br) is quite different for the two Si/Zr systems, in that: - in the case of the activated Si/Zr(3)-673 system, the overall amount of (Br) species remains virtually unchanged (A_{int} varies, in 1 hr evacuation at BT, from $\sim 21 \text{ cm}^{-1}$ to $\sim 19 \text{ cm}^{-1}$, corresponding to a virtually constant concentration of ~ 0.25 Ac molecules, and thus Brønsted acid sites, per nm^2); - in the case of the highly hydrated Si/Zr(3)-303 system, the amount of (Br) species is roughly halved in 1 hr evacuation. In particular, A_{int} varies, in the first 3 sec, from $\sim 42 \text{ cm}^{-1}$ to $\sim 35 \text{ cm}^{-1}$ (~ 0.65 to ~ 0.52 Ac molecules per nm^2), and then falls in 1 hr evacuation to $\sim 19 \text{ cm}^{-1}$ (*i.e.*, ~ 0.27 Ac molecules per nm^2). The fact that the final figure, representing the irreversible fraction of (Br) species, is almost the same in the two cases implies that a (mild) vacuum activation at 673K brings about the elimination of the fraction of Brønsted acid sites that yield, with Ac, reversible (Br)

complexes, and that this fraction accounts for approximately 50% of the overall Brønsted acidity of the nominally fully hydrated Si/Zr(3)-303 system. The BT irreversible amount of (Br) species is found to account for some 40% of the overall irreversible Ac on Si/Zr(3)-303, and for an almost equivalent ~42% in the case of Si/Zr(3)-673.

(C) A preliminary conclusion from the Al- and Zr-loaded systems. Considering that: - both Si/Al and Si/Zr mixed oxides present Brønsted acidity of comparable strength, at least on the basis of the IR response of 2,6-Lu uptake and of the $\Delta\nu_{\text{CO}}$ exhibited by the two (Br) Ac adspecies; - both Si/Al and Si/Zr mixed oxides present Lewis acidity of medium-high and somewhat different strength (Al > Zr), at least on the basis of the IR response of BT CO uptake and of the $\Delta\nu_{\text{CO}}$ exhibited by the two (A+L) Ac adspecies; - neither of the two mixed oxides yields, at RT and/or BT, the a.c. reaction, it can be deduced that: (i) the presence of Brønsted acidity is not, *per se*, sufficient condition for the occurrence of the acid-catalyzed a.c. reaction. Possibly stronger protonic acidity, like the one mentioned by L. Kubelkova *et al.* for the H-form of zeolitic systems²⁹, or that claimed to be present in some anion-doped oxidic systems,⁵⁶ is needed; (ii) the presence of medium-strong to strong Lewis acidity is not, *per se*, sufficient condition for the occurrence of the a.c. reaction. As *cus* ^{IV}Al cationic sites are (among) the strongest Lewis acid sites, the problem does not reside in the strength of the Lewis acidic sites, but rather in the need for the presence (and/or, possibly, the co-presence) of other sites. This conclusion is confirmed by the fact that, on pure Al and Zr oxides (that do not present Brønsted acidity, and possess Lewis acidity of strength comparable to that of the corresponding SiO₂-loaded cations) a.c. reaction proceeds easily. On the other hand, the amphoteric nature of these oxides is well known, and is demonstrated by their capacity of forming various types of surface carbonate-like species upon CO₂ adsorption at ambient temperature.^{3,57,58,59}

(D) The Si/Ca system. As anticipated in a previous section, IR data relative to Ac interaction with the Si/Ca(4)-T systems have no quantitative/calorimetric support, as in all conditions the a.c. reaction takes place to a variable extent, and leads mainly to the slow formation of (adsorbed) MO. For the same reason, no spectra relative to Ac interaction with the Si/Ca(4)-T systems will be reported/described in detail in the ν_{OH} spectral region, as the simultaneous occurrence of Ac adsorption and release/adsorption of a.c. reaction products renders the spectral changes in that region of difficult interpretation and, therefore, of little utility.

The ν_{CO} spectral region. Before describing the spectral effects of Ac interaction with Si/Ca(4)-T (in two activation conditions), and in order to help the spectral interpretation of the complex double-bond region of reacting Ac, Figure 12 presents in that spectral region the BT adsorption/evacuation of MO on Si/Ca(4)-673. It can be seen that: (i) in the spectral set (a), relative to the BT contact with MO vapour (2 Torr; $p/p^\circ \approx 0.25$)⁶⁰, the formation of two adsorbed MO species is quite evident. A first species, whose double-bond vibrational modes are less perturbed (*i.e.*, less red-shifted) by the adsorption process, is easily assigned to the interaction of MO with surface silanols, in that (using the symbols already adopted in fig. 7) it presents the α band ($\nu_{C=O}$ vibration) at 1682 cm^{-1} , and the β band ($\nu_{C=C}$ vibration) at 1615 cm^{-1} , *i.e.*, at the same wavenumbers reported in fig. 7(c) for the MO/pure-silica interaction. As for the other species, whose double-bond vibrational modes are more perturbed by the adsorption process, it is ascribable to the interaction of MO with surface *cus* Ca ions acting as Lewis acid sites, and presents a strong and well resolvable α' band at 1670 cm^{-1} , and the corresponding β' band at $\sim 1603\text{ cm}^{-1}$. The latter $\nu_{C=C}$ vibration lies at a higher wavenumber ($\sim 20\text{ cm}^{-1}$) than in the case of MO Lewis interacting with *cus* ^{IV}Al sites, as expected in view of the definitely lower Lewis acidity of *cus* Ca sites already evidenced by BT CO adsorption (fig. 3). [Two weaker bands (centered at ~ 1703 and $\sim 1635\text{ cm}^{-1}$, respectively, and not mentioned in the above assignment) correspond to the higher- ν shoulders of the main double-bond bands present in the spectrum of MO, and pertain unresolved to both MO adspecies identified]; (ii) after a prolonged BT

evacuation [see spectral set (b) of fig. 12], the spectrum of adsorbed MO reduces drastically in intensity, and becomes much simpler in that only the double-bond spectral components α' and β' , corresponding to the Lewis coordinated MO species, remain in the spectrum with roughly 40% of the starting integral intensity.

Turning now to the interaction of Ac with the Si/Ca(4) system, the differential spectral pattern reported in Figure 13(a) shows that, even after a plain vacuum treatment at BT, the contact with Ac yields some evidence for the occurrence of the a.c. reaction. It can be noted that: (i) the broad medium-strong δ_{HOH} band centered at $\sim 1635 \text{ cm}^{-1}$ in the background spectrum (broken-line curve 1) clearly indicates that the preliminary *in situ* vacuum activation at 303K (+ further short evacuation at BT, prior to contact with Ac), was not sufficient for the complete removal of molecular water Lewis coordinated to surface exposed *cus* Ca ions; (ii) the contact with Ac produces (see spectrum 2) at least two effects, consisting in the appearance of: - in the higher- ν $\nu_{\text{C=O}}$ region, a broad, strong and non resolved band with apparent maximum at $\sim 1702 \text{ cm}^{-1}$; - a weak shoulder on the low- ν side of the δ_{HOH} band ($\sim 1612 \text{ cm}^{-1}$), to be ascribed to the $\nu_{\text{C=C}}$ vibrational mode [the (β - β') band] of a tiny amount of MO, produced at the surface of the nominally fully hydrated Si/Ca(4)-303 system; (iii) BT evacuation for increasing times (spectra 3–5) causes the gradual downward shift of the weak $\nu_{\text{C=C}}$ shoulder (to $\sim 1604 \text{ cm}^{-1}$), due to a decreasing solvent effect exerted by adsorbed Ac on the $\nu_{\text{C=C}}$ vibration of adsorbed MO, and the gradual resolution, within the $\nu_{\text{C=O}}$ band envelop, of a medium-weak and far more vacuum resistant component centred at $\sim 1704 \text{ cm}^{-1}$. The latter band is to be ascribed to Ac Lewis coordinated to surface *cus* Ca^{2+} ions [*i.e.*, the (L) band; in the starting spectrum 2, the weak Ca-bound (L) component could not be singled out within the strong ν_{CO} band envelop, due to the overwhelming intensity of bands (A) and (B) of the Ac/silanols interactions].

Differential spectra of Figure 13(b) indicate that, on the medium-activated Si/Ca(4)-673 system, the a.c. reaction leading to the formation of adsorbed MO proceeds far more than on the highly hydrated Si/Ca(4)-303 system, since the higher-T thermal dehydration of the support created, as

expected, a more abundant concentration of reactive sites. Still, after a contact time of the order of 1 hr (corresponding here to the strongest spectrum 2 in the figure), the reaction stops and no further increase of MO bands is observed. The reason is that, for each MO molecule produced in the a.c. reaction, one water molecule is also produced in the dehydration of diaceton alcohol to MO, and water brings about a surface rehydration process that, eventually, poisons all residual active centres. The formation of water during the a.c. reaction is quite evident in the evacuation spectral pattern of fig. 13(b). As long as the evacuation is carried out at BT (curves 3-5), the envelope of the bands β - β' of adsorbed MO decreases in intensity and red-shifts for the decreasing solvent effect caused by Ac evacuation/desorption, while the high- ν shoulder of the $\nu_{C=C}$ modes ($\sim 1635\text{ cm}^{-1}$) apparently increases its relative intensity because the δ_{HOH} band of (some of) the newly formed water, probably coordinated at Lewis sites absorbs in that spectral position. Then, when the evacuation is carried out at 423K (see curve 6), all adsorbed Ac and MO are desorbed, whereas a discrete amount of coordinated water still resists at the surface. Spectroscopic evidence for the formation of some molecular water coordinated at Lewis sites (and thus poisoning part of the Lewis sites) allows us to suppose that part of the water formed in the a.c. reaction can also adsorb in a dissociated form and rehydrate the surface, so that *cus* O^{2-} centres are also poisoned and converted into OH groups. Indeed, the differential spectrum II in the inset to fig. 13(b) (dotted line curve) confirms that, after a further evacuation at 523K and complete removal of coordinated molecular water, the material is definitely more hydrated than before contact/reaction with Ac (a sharp negative peak at $\sim 3750\text{ cm}^{-1}$ means less free OH groups, and a broad positive band at $\sim 3550\text{ cm}^{-1}$ means more H-bonded ones).

The presence of the band of coordinated water superimposed on the MO shoulder at $\sim 1635\text{ cm}^{-1}$ renders the $\nu_{C=C}$ spectral range not so convenient for band-resolution and identification of adsorbed MO species. Moreover, the use of that spectral range would possibly allow only the identification of adsorbed MO species, whereas the use of the higher- ν $\nu_{C=O}$ spectral range, though definitely more complex, should allow the identification of both MO and Ac adsorbed species. Computer band-

resolution of the $\nu_{C=O}$ spectral range, at two overall surface coverages, is presented in the two sections of Figure 14.

Spectral set (a) of fig. 14 corresponds to the $\nu_{C=O}$ segment of curve 2 of fig. 13(b) [1 hr contact with ~ 5 Torr Ac; at this (maximum) Ac pressure, no physisorbed Ac is present yet, and no appreciable spectral contribution is expected from the gaseous phase²⁰]. It indicates that: (i) the long-contact spectrum is dominated, in the higher- ν part of the spectral range, by the adsorbed forms of non-reacted Ac. We can distinguish the following bands: - (A), 1696 cm^{-1} , and (B), 1712 cm^{-1} , corresponding with virtually unchanged frequencies to the two forms of CO-OH interaction typical of the silica support; - (L), 1705 cm^{-1} , corresponding to the Lewis coordination of Ac at *cus* Ca^{2+} sites. Note that, unlike the case of Si/Al and Si/Zr systems, here the ν_{CO} modes of Ac species (A) and (L) can be distinguished within the overall envelope, since the lower Lewis acidity of *cus* Ca^{2+} sites brings about a red-shift of the (L) C=O vibration some 10 cm^{-1} lower than for the (A) species. In the present condition of quasi-equilibrium (with a low-pressure Ac gas phase, and a virtually ended a.c. reaction), the (A)/(L) integral intensity ratio is ~ 1.6 , and the (A)/(B) intensity ratio is ~ 1 . In the usual simplifying assumption of constant ν_{CO} molar extinction coefficients, discussed above, these figures yield a rough estimate of the relative populations of Ac-adsorbing sites. (Consider that, on pure non-porous pyrogenic silica activated at 673K and at the equilibrium with 5 Torr Ac, the (A)/(B) intensity ratio was ~ 0.52); (ii) in the lower- ν part of the ν_{CO} spectral range are present two weaker bands: (α), 1680 cm^{-1} , and (α'), 1669 cm^{-1} , corresponding with virtually unchanged frequency, with respect to the reference MO-Si/Ca-673 system of fig.12(a), to the adsorption of MO at surface silanol sites and at *cus* Ca^{2+} sites, respectively. The (α')/(α) integral intensity ratio for adsorbed MO deriving from a.c. reaction is ~ 0.33 , whereas in the direct MO-Si/Ca-673 interaction of fig.12(a), where the (α')/(α) intensity ratio represented the actual Lewis-to-silanol sites ratio under a MO relative pressure of ~ 0.25 , the ratio was ~ 1.1 . In the complex situation created, at the Si/Ca-673 surface, by Ac adsorption/reaction, the much lower MO

$(\alpha')/(\alpha)$ intensity ratio depends on several factors, among which a primary role is certainly played by the competition for Lewis acid sites between Ac, MO, and molecular water.

Spectral set (b) of fig. 14 corresponds to the $\nu_{C=O}$ segment of curve 4 of fig. 13(b), and represents what remains in that spectral range after a short BT evacuation (5 min). It can be noted that: (i) the overall integral intensity of the whole $\nu_{C=O}$ range has decreased dramatically (from ~ 38 to ~ 8 cm^{-1}), and the residual spectrum is no longer dominated by the adsorbed forms of non-reacted Ac; (ii) in the higher- ν part of the spectral range, none of the Ac species has disappeared yet, but both absolute and relative intensities have changed a lot, due to the different reversibility of the various Ac adspecies. In particular, the residual fraction of band (B) is only $\sim 3\%$, that of band (L) is $\sim 10\%$, and that of band (A) is $\sim 18\%$, while the (A)/(L) intensity ratio passed from ~ 1.6 to ~ 2.6 ; (iii) the reversibility of MO adspecies is much lower than that of Ac species, and the (α) - (α') bands envelope now dominates the residual spectrum. In particular, the residual fraction of band (α) is $\sim 45\%$, while in practice no desorption has occurred (yet) for the MO species represented by band (α') and the $(\alpha')/(\alpha)$ intensity ratio has become twice as large as it was before (~ 0.65).

4. Conclusions

At ambient temperature (as well as at BT) Ac adsorbs, readily and abundantly, on all silica-based mixed oxides examined. Ac uptake leads to the formation of both types of H-bonding interaction with surface silanols that are typical of the Ac/pure-silica systems, and their relative amounts depend, as expected,²⁰ on the surface dehydration degree. In addition, other more specific and (in general) more energetic interactions, involving sites whose presence is determined by the presence of d^0 metal species, are also produced. Specific sites are: - Lewis acidic centres, represented by *cus* metal ions formed at the surface in concentrations that depend on the metal-oxide loading and on the vacuum activation temperature (the dehydration degree). *Cus* metal ions, acting as Lewis acid centres, yield coordinative interactions both with Ac [the species called (L)] and, when formed,

with MO which is the main a.c. reaction product [leading to the adspecies whose double-bond bands have been called (α') and (β'), respectively]. When formed, the Lewis interaction of MO is, in general, more vacuum resistant than that of Ac, due to the presence of the C=C functionality; - Brønsted (protonic) acidic centres, yielding with Ac fairly strong and partly non reversible H-bonding interactions [the species called (Br)]. Acidic centres of the former type are formed on all systems examined, and their acidic strength (in the order: Al > Zr > Ca) turns out to depend on the degree of coordinative unsaturation and on the consequent charge-withdrawing capacity of the *cus* metal ions. Unlike that, acidic centres of the second type do not form on all systems examined, and so partly contradict the general rule that ascribes to the different electro-negativity of different elements the formation, in their mixed oxidic systems, of Brønsted acidic OH species. When highly “basic” elements, like Ca and (not considered here) Mg, are introduced to form with silica a mixed oxide, oxygen-basic features rather than proton-acidic ones are developed. And only in these latter silica-based mixed oxides the ambient temperature adsorption of Ac is followed by a (relatively slow) a.c. reaction, leading to the formation of (adsorbed) MO.

All these observations, together with the preliminary conclusion anticipated in a previous section, lead to the conclusion that: (i) unlike what one would expect on the basis of previous literature on (mainly) zeolitic systems, Brønsted-acid catalyzed a.c. reaction may possibly occur only in the presence of very strong acid protonic sites, if at all. (This contradictory aspect is presently being investigated,⁴¹ and will be dealt with elsewhere); (ii) unlike what suggested by Fripiat *et al.* in their works on aluminas and zeolites, in silica-based mixed oxides (and a zeolite can be also regarded as a sort of silica-based mixed oxide) the presence of Lewis acidic sites that can coordinate Ac may possibly be a necessary condition for a.c. reaction to occur, but certainly is not a sufficient condition. What turns out to be actually necessary for Ac a.c. reaction is the presence of *cus* oxide sites of basicity sufficient to lead to the extraction of a proton from one of the CH₃ groups of an Ac molecule, possibly coordinated at a nearby Lewis acid site. But since Ac can adsorb also in other forms besides Lewis coordination [and (L) is actually not the strongest form of Ac adsorption on the

Si/Ca system], there is no evidence that Ac Lewis coordination is necessarily the (only) precursor for proton extraction and the rest of the a.c. reaction.

As for the basicity of the *cus* oxide sites that can extract the proton and catalyze the a.c. reaction, we can conclude that it does not need to be very strong. In fact, it has been shown⁶¹ that Si/Ca systems of various Ca contents (used as model systems for the study of silica-based bioactive glasses) cannot form carbonate-like surface species by mere contact with gaseous CO₂ [*i.e.*, their basicity is not sufficient to promote the reaction/equilibrium $O^{2-}_{cus} + CO_2^{gas} \rightarrow (CO_3)^{2-}_{ads}$], whereas they do form carbonate-like surface species if the co-presence of H₂O and CO₂ pre-forms the (CO₃)²⁻ ion. Unlike that, all of the pure reference oxides of the elements considered in this contribution, and not only the very basic CaO, do form surface carbonate-like species of various types by plain contact with gaseous CO₂ and, as expected, yield readily and abundantly the a.c. reaction.

Acknowledgements

This work is part of the Ph. D. research activity of one of the authors (V. C.), and has been partly financed with funds of the Italian Ministry MIUR (Project PRIN-2006, Prot. 2006 032335). Thanks are due to Prof. Claudia Bianchi (University of Milan) for carrying out XPS analyses.

Supporting Information Available

Additional information as noted in the text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) Xu, Z.; Gan, L.; Jia, Y.; Hao, Z.; Liu, M.; Chen, L. *J. Sol-Gel Sci. Techn.* **2007**, 41, 203-207.
- (2) (a) Cerruti, M.; Morterra, C.; Ugliengo, P. *J. Mater. Chem.* **2004**, 14, 3364-3369; (b) Cerruti, M.; Morterra, C.; Ugliengo, P. *Chem. Mater.* **2005**, 17, 1416-1423.
- (3) Morterra, C.; Magnacca, G. *Catal. Today* **1996**, 27, 497-532.
- (4) Morandin, M.; Gavagnin, R.; Pinna, F.; Strukul, G. *J. Catal.* **2002**, 212, 193-200.
- (5) (a) Yamaguchi, T.; Sasaki, H.; Tanabe, K. *Chem. Lett.* **1973**, 1017; (b) Tanabe K. *Mater. Chem. Phys.* **1985**, 13, 347-364.
- (6) Bolis, V.; Busco, C.; Aina, V.; Morterra, C.; Ugliengo P. *J. Phys. Chem. C* **2008**, 112, 16879-16892.
- (7) (a) Coluccia, S.; Garrone, E.; Guglielminotti, E.; Zecchina, A. *J. Chem. Soc., Faraday Trans. I* **1981**, 77, 1063-1073; (b) Zecchina, A. *Mater. Chem. Phys.* **1985**, 13, 373; (c) Garrone, E.; Zecchina, A.; Stone, F. S. *J. Catal.* **1980**, 62, 396-400; (d) Zecchina, A.; Coluccia, S.; Spoto, G.; Scarano, D.; Marchese, L. *J. Chem. Soc. Faraday Trans.* **1990**, 86, 703-709.
- (8) Zecchina, A.; Stone, F. S. *J. Catal.* **1986**, 101, 227-237.
- (9) Folman, M.; Yates, D. J. C. *Proc. Roy. Soc. London A* **1958**, 246, 32-51.
- (10) Davydov, V. Ya.; Kiselev, A. V.; Kuznetsov, B. V. *Zh. Fiz. Khim.* **1965**, 39, 2058-2064.
- (11) Young, R. P.; Sheppard, N. *J. Catal.* **1967**, 7, 223-233.
- (12) Hertl, W.; Hair, M. L. *J. Chem. Phys.* **1968**, 72, 4676-4682.
- (13) Elkington, P. A.; Curthoys, G. *J. Phys. Chem.* **1968**, 72, 3475-3482.
- (14) Davydov, V. Ya.; Kiselev, A. V.; Kuznetsov, B. V. *Russian J. Phys. Chem.* **1970**, 44, 1-5.

- (15) Griffiths, D.; Marshall, M. K.; Rochester, C. H. *J. Chem. Soc. Faraday Trans. I* **1974**, 70, 400-410.
- (16) Busca, G.; Lamotte, J.; Lavalley, J. C.; Lorenzelli, V. *J. Am. Chem. Soc.* **1987**, 109, 5197-5202.
- (17) Allian, M.; Borello, E.; Ugliengo, P.; Spanò, G.; Garrone, E. *Langmuir* **1995**, 11, 4811-4817.
- (18) Okunev, G.; Paukshtis, E. A.; Aristov, Y. I. *React. Kinet. Catal. Lett.* 1998, 65, 161-167.
- (19) Kachurovskaya, N. A.; Zhidomirov, G. M.; Aristov, Y. I. *J. Mol. Catal. A: Chemical* **2000**, 158, 281-285.
- (20) Crocellà, V.; Cerrato, G.; Magnacca, G.; Morterra, C. *J. Phys. Chem. C* **2009**, 113, 16517-16529.
- (21) Hair, M. L. *Infrared Spectroscopy in Surface Chemistry*: M. Dekker: New York, **1967**, p. 149.
- (22) Panov, A.; Fripiat, J. J. *Langmuir* **1998**, 14, 3788-3796.
- (23) Hanson, B. E.; Wieserman, L. F.; Wagner, G. W.; Kaufman, R. A. *Langmuir* **1987**, 3, 549-555.
- (24) Busca, G.; Lorenzelli, V. *J. Chem. Soc., Faraday Trans. I* **1982**, 78, 2911-2919.
- (25) El-Maazawi, M.; Finken, A. N.; Nair, A. B.; Grassian, V. H. *J. Catal.* **2000**, 191, 138-146.
- (26) Reichle, W. T. *J. Catal.* **1980**, 63, 295-306.
- (27) Lercher, J. A. *Zeit. Phys. Chem. N. F.* **1982**, 129, 209-218.
- (28) Zaki, M. I.; Hasan, M. A.; Al-Sagheer, F. A.; Pasupulety, L. *Langmuir* **2000**, 16, 430-436.

- (29) Bosacek, V.; Kubelkova, L. *Zeolites* **1990**, 10, 64-65.
- (30) Kubelkova, L.; Cejka, J.; Novakova, J. *Zeolites* **1991**, 11, 48-53.
- (31) Biaglow, A. I.; Sepa, J.; Gorte, R. J.; White, D. *J. Catal.* **1995**, 151, 373-384.
- (32) Panov, A. G.; Fripiat, J. J. *J. Catal.* **1998**, 178, 188-197.
- (33) Panov, A. G.; Fripiat, J. J. *Catal. Letters* **1999**, 57, 25-32.
- (34) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, J. Wiley & Sons: New York, **1986**, p. 231.
- (35) Morterra, C.; Bolis, V.; Magnacca, G. *Langmuir* **1994**, 10, 1812-1824.
- (36) (a) Morterra, C.; Magnacca, G.; Del Favero, N. *Langmuir* **1993**, 9, 642-645; (b) Morterra, C.; Magnacca, G.; Cerrato, G.; Del Favero, N.; Filippi, F.; Folonari, C. *J. Chem. Soc., Faraday Trans.* **1993**, 89, 135-150.
- (37) Morterra, C.; Cerrato, G.; Meligrana, G.; Signoretto, M.; Pinna, F.; Strukul, G. *Catal. Letters* **2001**, 73, 113-119.
- (38) (a) Bensitel, M.; Saur, O.; Lavalley, J. C.; Mabilon, G. *Mater. Chem. Phys.* **1987**, 17, 249-258; (b) Morterra, C.; Aschieri, R.; Volante, M. *Mater. Chem. Phys.* **1988**, 20, 539-557.
- (39) Gregg S. J.; Sing, K. S. W. *Adsorption, Surface Area, and Porosity*: Acad. Press: London, **1982**.
- (40) www.s-ohc.com/Acetone_cal.html
- (41) Morterra C. *et al.*, in preparation: the interaction of Ac with variously dehydrated zirconias has been studied, and compared with the interaction of Ac with the corresponding sulfated zirconia catalytic systems.

- (42) Yu, H.; Fang, H.; Zhang, H.; Li, B.; Deng, F. *Catal. Comm.* **2009**, 10, 920-924.
- (43) (a) Marchese, L.; Bordiga, S.; Coluccia, S.; Martra, G.; Zecchina, A. *J. Chem. Soc., Faraday Trans.* **1993**, 89, 3483-3489; (b) Morterra, C.; Bolis, V.; Magnacca, G. *Langmuir* **1994**, 10, 1812-1824.
- (44) Babaeva, M. A.; Bystrov, D. S.; Kovalgin, A. Y.; Tsyganenko, A. A. *J. Catal.* **1990**, 123, 396-416.
- (45) Morterra, C.; Cerrato, G.; Meligrana, G. *Langmuir* **2001**, 17, 7053-7060.
- (46) Morterra, C.; Meligrana, G.; Cerrato, G.; Solinas, V.; Rombi, E.; Sini, M. F. *Langmuir* **2003**, 19, 5344-5356.
- (47) Iizuka, T.; Tanabe, K. *Bull. Chem. Soc. Japan* **1975**, 48, 2527-2537.
- (48) Coluccia, S.; Hemidy, J. F.; Tench, A. J. *J. Chem. Soc. Faraday I* **1978**, 74, 2763-2770.
- (49) Ward, D. A.; Ko, E. I. *J. Catal.* **1995**, 157, 321-333.
- (50) (a) Busca, G. *Chem. Rev.* **2007**, 107, 5366-5410; (b) Chizallet, C.; Raybaud, P. *Chem. Phys. Chem.* **2010**, 11, 105-108.
- (51) Lercher, J. A.; Gründling, C.; Eder-Mirth, G. *Catal. Today* **1996**, 27, 353-376.
- (52) El-Maazawi, M.; Finken, A. N.; Nair, A. B.; Grassian, V. H. *J. Catal.* **2000**, 191, 138-146.
- (53) Davydov, A. A. *Molecular Spectroscopy of Oxide Catalyst Surfaces*: N. T. Sheppard, J. Wiley & Sons Ltd.: Chichester (U.K.), **2003**, p. 443.
- (54) Morterra, C.; Magnacca, G.; Bolis, V. *Catalysis Today* **2001**, 70, 43-58.
- (55) Morterra, C.; Garrone, E.; Bolis, V.; Fubini, B. *Spectrochim. Acta A* **1987**, 43, 1577-1582.

- (56) (a) Hino, M.; Arata, K. *J. Chem. Soc. Chem. Comm.* **1980**, 851-852; (b) Misono, M.; Okuhara, T. *CHEMTECH*, November (1993) 23.
- (57) Morterra, C.; Cerrato, G.; Ferroni, L. *J. Chem. Soc. Faraday Trans.* **1995**, 91, 125-132.
- (58) Bachiller-Baeza, B.; Rodriguez-Ramos, I.; Guerrero-Ruiz, A. *Langmuir* **1998**, 14, 3556-3564.
- (59) Pokrovski, K.; Young, K. T.; Bell, A. T. *Langmuir* **2001**, 17, 4297-4303.
- (60) www.thegoodscentcompany.com/data/rw1035971.html
- (61) Cerruti, M.; Morterra, C. *Langmuir* **2004**, 20, 6382-6388.