

Iron ions supported on oxides: Fe/Al₂O₃ vs. Fe/SiO₂

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(ricevuto il 15 Dicembre 2008; pubblicato online il 17 Febbraio 2009)

Summary. — The effect of the surface structure of the support on the nature and dispersion of iron ions was studied by comparing low-loaded Fe/SiO₂ and Fe/Al₂O₃ catalysts, prepared by the “adsorption-precipitation” method. This method, based on the electrostatic interaction between iron ions and the negatively charged support surface, is effective in the preparation of highly dispersed iron-supported catalysts, active in alkanes selective oxidation reactions. The samples were characterized by DR UV-Vis and IR spectroscopies, coupled with NO adsorption and to temperature programmed reduction (TPR) measurements. DR UV-Vis and TPR show that after calcination in both catalysts mainly isolated Fe³⁺ ions, a minor fraction of 2-d FeO_x dimers/oligomers and a very small fraction of 3-d oxidic particles are present. The results indicate a higher ability of alumina in dispersing iron-supported species. Despite the multiple sites possibly available for hosting iron cations offered by the silica support, only two types of iron species were identified by IR of adsorbed NO, differing for the ability to form mono or trinitrosyl complexes (that evolve into dinitrosyl ones, by decreasing NO pressure). The same technique shows that at least five different types of iron species are formed on the alumina surface, four of them able to form only mononitrosyl complexes and one giving di- or trinotrisylic adducts.

PACS 68.43.Pq – Adsorbate vibrations.

PACS 78.30.-j – Infrared and Raman spectra.

PACS 78.40.-q – Absorption and reflection spectra: visible and ultraviolet.

PACS 82.65.+r – Surface and interface chemistry; heterogeneous catalysis at surfaces.

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1. – Introduction

The development of high-productivity catalysts for the selective oxidation of alkanes represents one of the most challenging topics in heterogeneous catalysis. Alkanes from natural gas are among the world's most abundant and low-cost feedstocks, so that their direct conversion into commodity chemical products would result in significant economic and environmental advantages over current technologies [1, 2]. Due to the low intrinsic reactivity of alkanes and the relatively higher reactivity of the desired products, a close control of the catalysts active centres nature, reactant composition and reaction mechanism need to be pursued [2, 3]. The effectiveness of Fe/SiO₂ catalysts in these reactions has been previously assessed, and the crucial role of the structure of isolated Fe³⁺ sites has been shown [4, 5]. Basic relationships between dispersion and activity pointed to “site isolation” as a key-requirement for the selective oxy-functionalisation of light paraffins [1, 4-6]. Moreover, the influence of the oxide support on the reactivity of iron sites has been ascertained and critical effects of “Me-O-support” bridging functionality and local environment of the active centres have been pointed out [7].

In this respect, some of us developed an effective preparation route—the “adsorption-precipitation” (AP) method—to obtain high dispersion of iron species. Typically the support was “inert” silica matrix, giving low-loaded Fe/SiO₂ catalysts (Fe ≤ 0.5 wt%) with a superior performance in the methane to formaldehyde partial oxidation (MPO) [8, 9]. The AP method is based on a careful pH control, in order to avoid hydroxide precipitation and to favour the electrostatic interaction between iron ions and the negatively charged silica surface. Spectroscopic analysis indicated the speciation of the active phase into isolated Fe³⁺ species, oligomeric 2-d FeO_x patches and 3-d Fe₂O₃ nanoparticles, while their concentration could be evaluated by temperature-programmed reduction (TPR) measurements [4].

In this work the results obtained on Fe/SiO₂ materials (that were the object of previous investigations [4, 5, 9]) are compared with new data about Fe/Al₂O₃ catalysts prepared by the same AP methodology. These catalysts show a different reactivity towards alkanes, being active in the oxidative dehydrogenation of propane (POD). The same investigation techniques employed for the speciation of the active phase in Fe/SiO₂ systems were employed, namely UV-Vis and IR spectroscopies—coupled with the use of NO as probe molecule—and TPR measurements. The results are discussed in terms of the surface properties of the oxide supports by comparing the surface of amorphous SiO₂, which expose (\equiv SiO–)_n rings ($2 \leq n \leq 8$) that when large enough ($n \geq 4$) can exhibit some flexibility, with the rigid surface structure of γ -Al₂O₃.

2. – Experimental

Commercial “precipitated” SiO₂ and a γ -Al₂O₃ (Akzo Nobel) were employed for the preparation of low-loaded catalysts by the “adsorption-precipitation” (AP) method [4, 5]. An aqueous suspension of powder oxide, placed into a three-necked bottle, was kept at room temperature under continuous nitrogen flow and stirring to remove oxygen, avoiding any further air admission. Then, an amount of FeSO₄ corresponding to the designed Fe loading (0.5 Fe wt%) was added to the suspension, the pH of which was gradually raised to 7–8 by drop wise addition of a concentrated NH₄OH solution. The suspension was kept at the final pH value (with stirring and N₂ bubbling) for 1 h, during which the quantitative adsorption (> 98%) of Fe²⁺ ions was attained. Afterwards, the solid was filtered and repeatedly washed with bi-distilled water. After impregnation the samples

TABLE I. – *General properties of the studied samples.*

Support	Fe loading (wt %)	SA BET (m ² g ⁻¹)	SSL (Fe _{at} nm ⁻²) × 10 ²
SiO ₂	0.59	592	10.8
γ-Al ₂ O ₃	0.40	185	23.3

were dried at 100 °C and further calcined at 550 °C (Fe/SiO₂) and 600 °C (Fe/Al₂O₃) for 6 h in air.

Volumetric analysis (N₂ adsorption at liquid-nitrogen temperature) was carried out on a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. HRTEM (High Resolution Transition Electron Microscope) images were registered with a JEOL 3010-UHR with acceleration potential of 300 kV. Samples were dispersed on a copper grid covered with a lacey carbon film. The general properties of the samples, that is Fe loading (wt %), BET surface area (SA_{BET}, m² g⁻¹) and specific surface loading (SSL, Fe_{at} nm⁻²) are given in table I.

UV-Vis Diffuse Reflectance (DR UV-Vis) spectra of the powder samples were acquired in reflectance mode using a Perkin-Elmer Lambda 900 instrument equipped with an integrating sphere. The spectra were processed by the “Kubelka-Munk” function. IR measurements were carried out with a Bruker IFS 88 spectrometer with a DTGS detector and running at 4 cm⁻¹ resolution. Spectra of adsorbed NO are reported in absorbance, after subtraction of the spectrum of the sample before NO adsorption (“blank” spectrum). Temperature Programmed Reduction (TPR) analysis was carried out by a “continuous-flow” linear quartz microreactor fed with a 6% H₂/Ar carrier flowing at 30 stp cm³ min⁻¹. All the experiments were run in the range 200–800 °C with a heating rate of 20 °C min⁻¹, while deconvolution of TPR profiles was made by the “PeakFit” software (Jandel Scientific) [4].

3. – Results and discussion

3.1. The support structure. – The surface structure of catalytic aluminas has been deeply studied in the literature, as resumed in the review by Morterra and Magnacca [10]. Catalytic aluminas belong to the group of transition Al₂O₃ phases, that are metastable cubic oxides with the nature of defective spinels. Spinel is a mixed oxide of Al³⁺ and divalent M²⁺ cations, the former occupying half of the octahedral (Oh) sites and the latter one eighth of the tetrahedral (Td) sites in the cubic close-packed array of oxide ions. The defective structure of transition alumina spinels derives from the only presence of trivalent cations, so that some of the lattice positions occupied by cations in the mixed-oxide spinels are empty to guarantee electrical neutrality. These vacancies are usually imagined as randomly distributed between Td and Oh sites [10].

The main results of the investigation of the γ-Al₂O₃ support employed in this work are here reported. As shown by TEM (fig. 1) this material is composed by nanosized crystalline particles (around 5 nm in size) of irregular shape. Amorphous regions can be observed at the termination of some of the crystalline patches (white arrows), together with stepped terminations (black arrows). Information on the chemical terminations was provided by the IR spectrum in the OH stretching region (fig. 2). The observed pattern is quite complex, showing six components at 3796, 3770, 3728, 3672, 3632 and 3590 cm⁻¹,

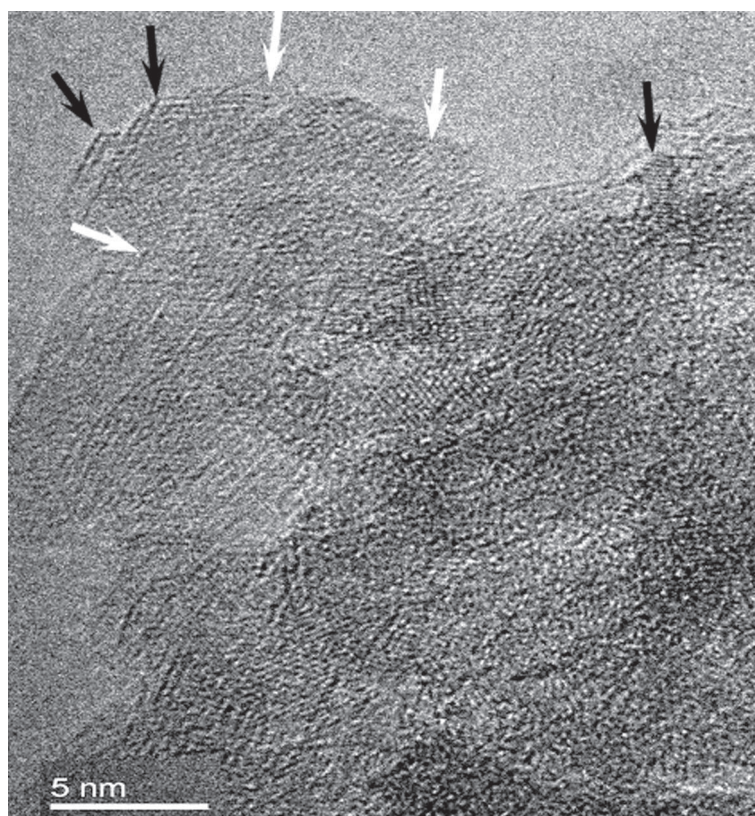


Fig. 1. – TEM image of the γ -Al₂O₃ support. White arrows indicate amorphous regions, black ones stepped termination of the crystals.

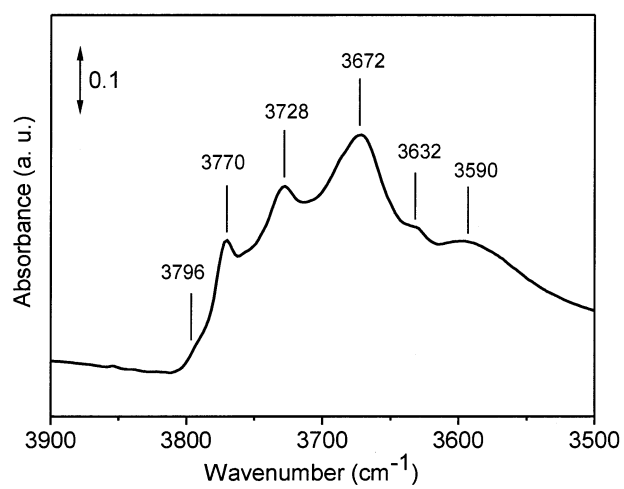


Fig. 2. – IR spectrum in the OH stretching region of the γ -Al₂O₃ support dehydrated at 400 °C.

typical of transition aluminas, and its interpretation has been the subject of a lively literature debate [10]. One of the most complete approaches was proposed by Knözinger and Ratnasamy in 1978, who found a correlation between the surface cations coordination and the OH frequencies, proposing that the frequency of the OH group depends upon the net electrical charge at the OH group [11]. This model assumed that the aluminas crystallites are terminated by a limited number of low-index crystal planes, namely the (111), (110) and (100) ones and that the uppermost layer of exposed crystal planes reproduces the anion and cation array of the bulk (thus not considering reconstruction or ion migration as a consequence of thermal treatments). More recently, Busca *et al.* improved the interpretation proposed by Knözinger and Ratnasamy by including in the model the role of cation vacancies [12,13]. On such a basis, the high-frequency bands at 3796 and 3770 cm⁻¹ are related to terminal OH groups linked to two Td surface Al sites (Al_{IV}), the latter being close to a cation vacancy. The band at 3728 cm⁻¹ is assigned to terminal OH groups linked to Oh Al sites (Al_{VI}), with and without vacancy. Both bands at 3672 and 3632 cm⁻¹ can be related to bridged OH groups, and the low-frequency one at 3590 cm⁻¹ to tribridged ones [12]. Notwithstanding the validity of this interpretation, the IR spectra and TEM image here reported and discussed testify of the complexity of the γ -Al₂O₃ support surface, showing a complex hydroxyl population, crystal planes with exposed Al_{IV} and Al_{VI} ions, stepped crystal terminations with defective sites and small amorphous regions.

As regards amorphous silica, many experimental and theoretical studies have been devoted to the elucidation of the surface features of this kind of material [14]. Noticeably, several works [15-17] indicated that the fixation of metal ions on the silica surface is essentially ruled by the presence of the n -fold ($\equiv \text{SiO}-$) _{n} rings, containing both siloxanes (Si-O-Si) and silanols (Si-OH). Unfortunately, it is rather difficult to obtain direct experimental evidence of such rings, and therefore we based our description of the silica surface on the results reported in the literature, mainly based on computational studies [18]. Basically, rings containing a number of silicon atoms ranging from 2 to 9 were proposed and there seems to be a general agreement that 5 and 6 membered rings are the most frequent [18-20]. Additionally, small rings (3 or 4 Si-O units) are expected to be quite rigid, whilst larger rings should exhibit some flexibility.

3.2. Investigation of the ion-support interaction

3.2.1. DR UV-Vis spectroscopy. A basic evaluation of the iron dispersion on the surface of the two catalysts can be made on the basis of the DR UV-Vis spectra of the calcined samples in air (fig. 3). This technique has been widely applied to Fe-based catalysts (mainly zeolites or amorphous SiO₂) as a tool for the speciation of isolated and clustered iron phases [4, 21-23]. Under the experimental conditions here employed Fe ions are expected to be in the +3 oxidation state with Oh coordination (*e.g.*, six ligands corresponding to oxygen atoms of the support and adsorbed water/hydroxyls) [4, 21-23]. The spectra were normalized to the maximum intensity for easier comparison.

The spectrum of Fe/SiO₂ is composed by an intense broad band with maximum at 39000 cm⁻¹ and onset around 33000 cm⁻¹, with a weak tail between 30000 and 25000 cm⁻¹. The main component at 39000 cm⁻¹ can be assigned to a charge transfer (CT) band of isolated Fe³⁺ ions in Oh coordination, that usually show two intense CT components at 41000 and 37000–35000 cm⁻¹ [24, 25]. The remaining part of the adsorption profile at lower frequency (35000–25000 cm⁻¹) suggests the presence of a minor amount of Fe³⁺ species in the form of oxidic dimers/oligomers [4, 21]. It is interesting

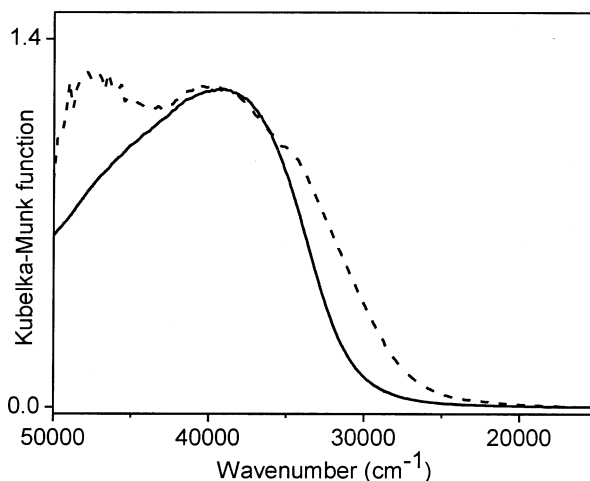


Fig. 3. – DR UV-Vis spectra of calcined Fe/SiO₂ and Fe/Al₂O₃ catalysts in air (full and dashed lines, respectively), normalized to the maximum intensity.

to notice that this DR UV-Vis pattern testifies the higher dispersion of iron species with respect to samples prepared by classical “incipient wetness” (IW), where a larger amount of oxidic dimers/oligomers and the presence of 3-d Fe₂O₃ particles were detected [4, 8].

The DR UV-Vis spectrum of Fe/Al₂O₃ is composed by two main adsorptions with maxima at 47500 and 39500 cm⁻¹, with a shoulder at 35000 cm⁻¹ and a weaker tail from 30000 to 20000 cm⁻¹ (fig. 3, dashed curve). The literature about iron on an alumina matrix is less abundant than that about Fe/SiO₂ systems (also including the very rich data about zeolites, where iron is dispersed in silicate or in aluminosilicate matrices). Octahedral Fe³⁺ ions in corundum Al₂O₃ were reported to have two CT bands at 51000 and 39000 cm⁻¹ [24] so that we can assign the two strong bands at 47500 and 39500 cm⁻¹ to isolated Fe³⁺ ions in Oh coordination also in our sample. By analogy with the literature about Fe/SiO₂ samples, the component with a maximum at 35000 cm⁻¹ and a tail to lower frequency (up to 25000 cm⁻¹) can be assigned to the presence of FeO_x 2-d dimers/oligomers [4, 21]. A very small amount of 3-d Fe₂O₃ particles could be responsible for the very weak adsorption tail between 25000 and 20000 cm⁻¹.

The comparison between the UV-Vis spectra of Fe/SiO₂ and Fe/Al₂O₃ sample deserves further comments. First, UV-Vis data suggest that both samples are mainly formed by isolated Fe species (in a +3 oxidation state and Oh coordination on the calcined sample, with six ligands being oxygen atoms of the support and adsorbed water molecules/hydroxyls), with a minor fraction of 2-d FeO_x dimers/oligomers and probably a very small fraction of 3-d oxidic particles in the case of Fe/Al₂O₃. These results imply that the AP method, based on the electrostatic interaction of iron precursors with the charged support surface, is effective in obtaining high iron dispersion on both matrices.

Secondly, we underline the better band definition when Fe/Al₂O₃ system is concerned. In this case both CT bands expected for Fe³⁺ ions in Oh coordination can be clearly observed, while only a broad adsorption could be seen on Fe/SiO₂ samples. This latter feature should result from a quite wide heterogeneity in the local structure of silica sites hosting iron ions, whilst the narrower bandwidth of the CT absorptions of Fe/Al₂O₃ suggests a more limited number of different local structures sites able to host iron ions.

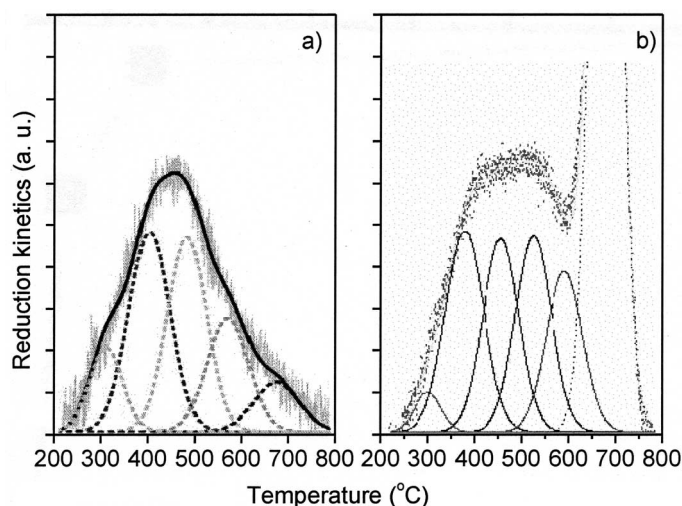


Fig. 4. – TPR profile of a) Fe/SiO₂ and b) Fe/Al₂O₃ catalysts with components calculated by deconvolution analysis. The intense component between 600 and 800 °C (dotted line) is due to sulfate impurities of the support.

Notice that the definition of the bands can be compared with that reported for as-synthesized Fe-silicalite zeolite, characterized by the presence of one single Fe³⁺ species in Td coordination [21]. Finally, when we compare the two samples we have to remember that they have a similar Fe loading but a different surface area; in particular Fe/Al₂O₃ has a surface area three times smaller than Fe/SiO₂ (table I). As a consequence, the higher ability of the alumina support to disperse Fe ions on its surface with respect to silica, when the AP method is employed, is acknowledged.

3.2.2. TPR measurements. The reduction pattern of iron surface species can provide information on their local structure and on the strength of their interaction with the support, and also, by deconvolution analysis, on the concentration of the various surface species [4].

The TPR profiles, and related deconvolutions, obtained for the two catalysts are shown in fig. 4. The reduction pattern of Fe/SiO₂ (fig. 4a) shows five components, indicating the presence of 3-d aggregates, mostly in the form of Fe₂O₃ nanoclusters (peaks at ca. 300 and 400 °C), 2-d (-Fe-O-Fe)_n patches (*i.e.* thin “rafts”) linked to the silica surface by a network of “Fe-O-Si” bonds (peak at ca. 500 °C) and isolated Fe³⁺ ions in a Td-like environment (two peaks at ca. 600 and 700 °C). The two high temperature peaks were explained in terms of isolated Fe³⁺ stabilized by -(Si-O-Si)_n- surface rings of different size, resulting in different stabilization of the anchored ions [4].

The TPR of Fe/Al₂O₃ (fig. 4b) appears dominated by a very intense peak at high temperature that should be due to the decomposition of the residual sulfate groups on the support, and will not be considered further. The remaining part of the pattern was deconvoluted in five components with maxima at ca. 300, 350, 450, 550 and 650 °C. By analogy with the Fe/SiO₂, the same assignments are proposed, that is: i) 3-d Fe₂O₃ nanoclusters (peaks at ca. 300 and 350 °C), ii) 2-d (-Fe-O-Fe)_n patches (peak at ca. 450 °C) and iii) isolated Fe³⁺ ions (peaks at ca. 550 and 650 °C). The slight shift of

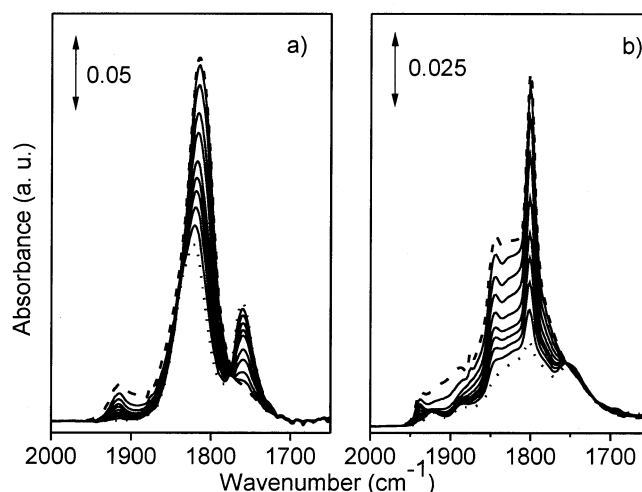


Fig. 5. – IR spectra of decreasing pressure of NO adsorbed at room temperature on a) Fe/SiO₂ outgassed at 400 °C and b) Fe/Al₂O₃ outgassed and oxidized at 400 °C.

the reduction temperatures of each of these species, with respect to the corresponding components found for Fe/SiO₂ monitors the different strength of their interaction with the two supports. More importantly, the reported results show a higher relative concentration of isolated Fe³⁺ ions (the most resistant to reduction) for Fe/Al₂O₃ than for Fe/SiO₂.

3.2.3. IR spectroscopy of adsorbed NO. IR spectra of adsorbed NO are often employed to study Fe-based catalysts due to the strong affinity of NO for dispersed Fe ions, resulting in stable nitrosyls with high coefficient extinctions [23,26,27]. The spectra obtained upon adsorbing different NO pressure on Fe/SiO₂ and Fe/Al₂O₃ are reported in fig. 5, parts a) and b), respectively. Before probe molecules adsorption, catalysts are usually outgassed at the desired temperature and oxidized in O₂ in order to clean the surface. The catalysts were then outgassed at 400 °C, and this treatment resulted to the autoreduction of almost all Fe³⁺ ions into Fe²⁺ [28].

The NO spectra obtained on Fe/SiO₂ sample (fig. 5a) are similar to those already reported and deeply discussed in the literature [23,26,27]. At high NO coverage (dashed curve) two main bands at 1924 (weak) and 1814 cm⁻¹ (strong) dominates the spectrum. By stepwise reduction of the NO coverage the two bands gradually decrease, while two other grow at 1840 cm⁻¹ (shoulder of the main band at 1820 cm⁻¹) and 1760 cm⁻¹. This evolution has been explained with the 1 : 1 transformation of Fe²⁺(NO)₃ complexes (bands at 1914 and 1814 cm⁻¹ due to the symmetric and antisymmetric stretching modes, respectively) into Fe²⁺(NO)₂ ones (bands at 1840 and 1760 cm⁻¹, same assignment). Moreover, the presence of Fe²⁺(NO) species can be appreciated at low NO coverage, giving the band with maximum at 1820 cm⁻¹ (dotted curve). These bands have been explained with the presence of Fe²⁺ ions with one coordinative unsaturation (forming only mononitrosyl complexes) and of Fe²⁺ ions with a higher degree (two- and/or three-fold) of coordinative unsaturation at the surface of Fe/SiO₂ systems [8]. Despite the multiple sites possibly available for hosting iron cations offered by the silica support,

only two types of iron species were identified by IR of adsorbed NO. This feature can be the result of the combination of a higher abundance of ($\equiv \text{SiO}-$)_n rings with a certain number of members with a possible selectivity of iron ions towards some specific family of such rings.

Noticeably, the IR spectra of NO adsorbed on Fe/Al₂O₃ (fig. 5b) are significantly different with respect to those obtained on Fe/SiO₂ and on Fe-zeolites [23, 26, 27]. At high NO coverage (dashed spectrum) at least five components can be discerned at 1936 and 1890 (weak), 1844 and 1825 (medium), 1800 cm⁻¹ (strong, with an asymmetric tail down to 1700 cm⁻¹). By decreasing the NO coverage the narrow peaks at 1936 and 1800 cm⁻¹ gradually became less intense and almost completely vanish, while the broad ones at 1844 and 1825 cm⁻¹, though diminishing, show a higher stability. In the low coverage spectrum (dotted curve) components can now be better appreciated at 1920 and 1890 cm⁻¹, together with the already described bands in the 1850–1800 cm⁻¹ range and a new component growth at 1752 cm⁻¹.

Additional studies aimed to elucidate such a complex pattern, involving the use of ¹⁴NO-¹⁵NO mixture, are in progress. However, some interesting features can be drawn from the comparison of the present data with the results obtained for Fe/SiO₂. First, the number of species detected by NO on Fe/Al₂O₃ is higher than that monitored on Fe/SiO₂, so that at least five distinct Fe surface sites can be discerned. Secondly, the definition of the bands in terms of width is also higher, suggesting a higher homogeneity in the local environment of Fe sites, in agreement with UV-Vis results. Finally, the couple of bands at 1936 and 1800 cm⁻¹ closely resembles those assigned on Fe/SiO₂ to Fe²⁺(NO)₃ complexes. In this case however the usual decrease of the couple of bands is only in part accompanied by the growth of the component at 1752 cm⁻¹, assigned to the antisymmetric stretching mode of Fe²⁺(NO)₂ complexes on Fe/SiO₂ and Fe-zeolites [8, 23]. A similar behaviour was reported for NO adsorbed on Fe-ZSM-5 samples with high aluminum content [29]. Additional experiments must be performed in order to properly explain this phenomenon.

Summarizing, the reported results indicate the presence of at least five distinct Fe sites on the surface of the alumina support. Four sites show only one coordinative unsaturation, forming distinct mono-nitrosyl complexes at 1825, 1844, 1890 and 1920 cm⁻¹, with different sensitivity to pressure changes. On the base of their location the first two can be assigned to NO adsorbed on Fe²⁺, while the other two might be due to Fe³⁺(NO) adducts. The presence of two types of ferrous and two types of ferric centers able to form mono-nitrosyls agrees with the heterogeneity of supported iron species revealed by TPR and with the complexity of the surface of defective structure of γ -Al₂O₃. Finally, the presence of isolated Fe²⁺ sites, with a higher coordinative unsaturation (two- or three-fold) is also proposed on the basis of the bands at 1936 and 1800 cm⁻¹.

4. – Conclusions

The AP method was employed to prepare low-loaded Fe-based catalysts by employing two different supports: the amorphous silica and the crystalline γ -alumina. Fe species were grafted on the surface of the two oxides by exploiting the electrostatic interaction between positively charged ions and the negatively charged support surface. This method was already employed with success to prepare highly dispersed Fe/SiO₂ catalysts and has been now applied to an alumina matrix with a smaller surface area.

The main features of the supports are resumed, showing that the surface structure of Al₂O₃ is more complex, with a complex hydroxyl population, crystal planes with

exposed Al_{IV} and Al_{VI} sites, stepped crystal terminations with defective sites and small amorphous regions. On the contrary the surface of amorphous silica is characterized by $(\equiv SiO)_n$ rings of different size, without coordinative defects.

UV-Vis and TPR results show that both samples after calcination are composed by a large fraction of isolated Fe^{3+} ions, with a minor fraction of 2-d FeO_x dimers/oligomers and of 3-d Fe_2O_3 nanoparticles, showing an overall good dispersion of Fe phases. Since alumina has a smaller surface area with respect to silica, this implies that it has a higher ability to disperse and stabilize Fe ions. Despite the multiple sites available for hosting iron cations offered by the silica support, only two iron species were identified by IR, able to form mono or trinitrosyl complexes (that evolve into dinitrosyl ones, by decreasing NO pressure). On the contrary, the same technique shows that at least five different species are formed on the alumina surface, four of them able to form only mononitrosyl complexes and one giving di- or trinotrisyls. A more precise assignment of the observed nitrosyl complexes in terms of surface sites will be the subject of further investigations.

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The University of Turin is acknowledged for funding the Post-Doc grant of Dr. M. T. NECHITA through the Internationalization Project "World Wide Style". The authors would like to thank Dr. G. GATTI for fruitful discussion and the support on studying the Fe/SiO_2 catalyst.

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