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Characterization and Catalytic Activity of $CuCl_2$-Al_2O_3 Ethylene Oxychlorination Catalysts

Elisabetta Finocchio,* Nicoletta Rossi,* Guido Busca,*,[1] Mario Padovan,†,[2] Giuseppe Leofanti,†,[3]
Barbara Cremaschi,† Andrea Marsella,† and Diego Carmello†

*Istituto di Chimica di Ingegneria, Università, P.le J.F. Kennedy, I-16129 Genoa, Italy; †European Vinyls Corporation Italia, Technological Centre, Via della Chimica 5, 30175 Porto Marghera Venice, Italy
E-mail: icibusca@csita.unige.it

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$CuCl_2/Al_2O_3$ ethylene oxychlorination catalysts have been characterized by using IR spectroscopy of the surface hydroxy-groups and of adsorbed pyridine and CO_2. The ethylene oxychlorination reaction to 1,2-dichloroethane has been investigated by using pulse reactor studies and *in-situ* IR experiments in static conditions. The results allowed emphasizing the negative role of uncovered alumina surface, evidenced by IR experiments, considered to be responsible for the dehydrochlorination of 1,2-dichloroethane with a consequent loss in selectivity that is very important in low Cu-loading samples. © 1998 Academic Press

INTRODUCTION

The heterogeneously catalyzed gas-phase oxychlorination of ethylene to 1,2-dichloroethane (ethylene dichloride, EDC),

$$H_2C{=}CH_2 + 2\,HCl + 1/2\,O_2 \rightarrow Cl\text{-}CH_2\text{-}CH_2\text{-}Cl + H_2O,$$

followed by the dehydrochlorination of EDC represents the main way for the production of vinyl chloride monomer (VCM) and of its polymer polyvinyl chloride (PVC), using HCl as the chlorine source (1, 2) and/or in the balanced processes. The catalysts currently used are based on $CuCl_2$ supported on alumina and doped with other metal chlorides.

Several studies have been devoted to the characterization of the industrial and model catalysts (3–31). Such studies have been mostly devoted to the characterization of the Cu centers, with different techniques: XRD (6, 10–12, 14, 23, 26, 30), EDX (11, 13, 20), EPR (6, 10, 20, 26, 27, 30), UV-VIS DRS (12, 14), IR spectroscopy (10), solubility test (6, 9, 10, 12, 21, 25, 27, 30), and activity test (3, 6, 9, 10, 21, 28).

The existence of two different groups of copper species in copper chloride supported on alumina, has been pointed out. The first species, prevailing at low copper concentration, would be the product of an interaction between copper chloride complexes and the carrier, resulting in a highly (possibly atomically) dispersed copper species. At the present the exact nature of interacting species remains substantially undefined; as a consequence a number of different and often not well defined models have been proposed in the literature (6, 10, 20, 27, 29).

The second species, prevailing at higher copper concentration, would be the product of the precipitation of copper complexes from the impregnating solution. It would not interact with the carrier and would be formed by clusters or small crystals of chlorine containing compounds. About the nature of noninteracting species, copper chloride and/or paratacamite ($Cu_2(OH)_3Cl$) have been found by a few authors. In this case the problem is the definition of the parameters able to affect the existence of different species (i.e., dependence of formation and reciprocal transformation on copper concentration, time, temperature, atmosphere) being difficult to rationalize different published results (4, 10, 12, 16, 17, 22, 31).

Besides the nature of Cu species, the comprehension of the way in which the catalyst works in ethylene oxychlorination requires information on the overall catalyst surface, that is on the dispersion of active phase, on the coverage degree of support surface, and on the chemical characteristics (i.e. acidity) that catalyst surface offers to the reaction environment. No complete information is available in literature on these topics.

The present study is devoted to an IR characterization of the overall catalyst surface in relation to the amount of impregnated copper species and the resulting catalytic activity and represents a further effort to elucidate the catalysts features and the details of the reaction mechanism.

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[1] Corresponding author.

[2] Present address: Via Villa Mirabello 1-20125 Milan, Italy.

[3] Present address: Via Firenze 43-20010 Canegrate (MI), Italy.

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TABLE 1

Characteristics of the Samples under Study and Density of Nucleophilic Sites as Measured from CO_2 Adsorption

Sample notation	Composition	Impregnating salt	Surface area m^2/g	Theoretical monolayer fraction	Relative density of the adsorbed species
A	γ-Al_2O_3	==	174	0.00	1.00
1CuClA	1% Cu/γ-Al_2O_3	$CuCl_2 \cdot 2.5\ H_2O$	188	0.09	0.31
5CuClA	5% Cu/γ-Al_2O_3	“	154	0.50	0.14
9CuClA	9% Cu/γ-Al_2O_3	“	117	0.99	0.15
1CuNA	1% Cu/γ-Al_2O_3	$Cu(NO_3)_2 \cdot 2\ H_2O$	171	0.04	0.50
9CuNA	9% Cu/γ-Al_2O_3	“	154	0.42	0.40
S	SiO_2	==	666	0.00	
14CuClS	14% $CuCl_2$-SiO_2	$CuCl_2 \cdot 2.5\ H_2O$	425	0.46	

METHODS

Some data on the samples under study are summarized in Table 1. Most samples have been prepared by impregnation of a commercial Al_2O_3 sample from Condea (surface area: 174 m^2/g, pore volume 0.50 cm^3/g), but one was prepared by impregnation of SiO_2 obtained from tetraethylorthosilicate (TEOS, $(C_2H_5O)_4Si$) by a sol/gel method (surface area 666 m^2/g, pore volume 0.4 cm^3/g). In all cases incipient wetness method has been used. Two copper compounds have been used: $CuCl_2 \cdot 2H_2O$ and $Cu(NO_3)_2 \cdot 2.5\ H_2O$. After impregnation, all samples have been dried at 393 K for 2 h while only those based on Cu nitrate have been calcined at 773 K for 4 h, in every case in air.

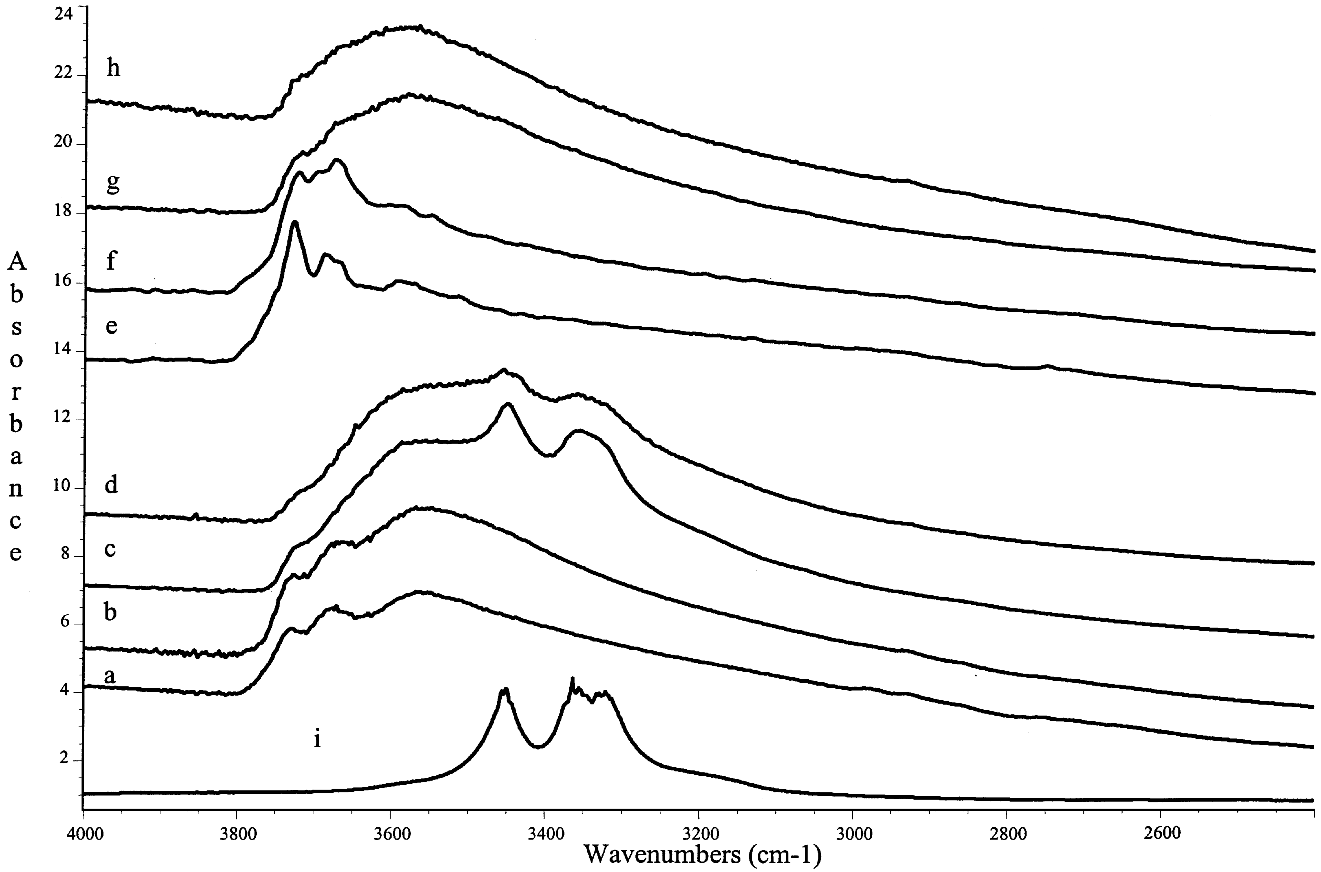

FIG. 1. FT-IR spectra of the following samples: γ-Al_2O_3 (a,e); 1% $CuCl_2/Al_2O_3$ (b,f); 5% $CuCl_2/Al_2O_3$ (c,g); 9% $CuCl_2/Al_2O_3$ (d,h); outgassed at 473 K (a-d); and outgassed at 623 K (e–h), and FT-IR spectrum of bulk paratacamite $CuCl_2(OH)_3$ (i). OH stretching region.

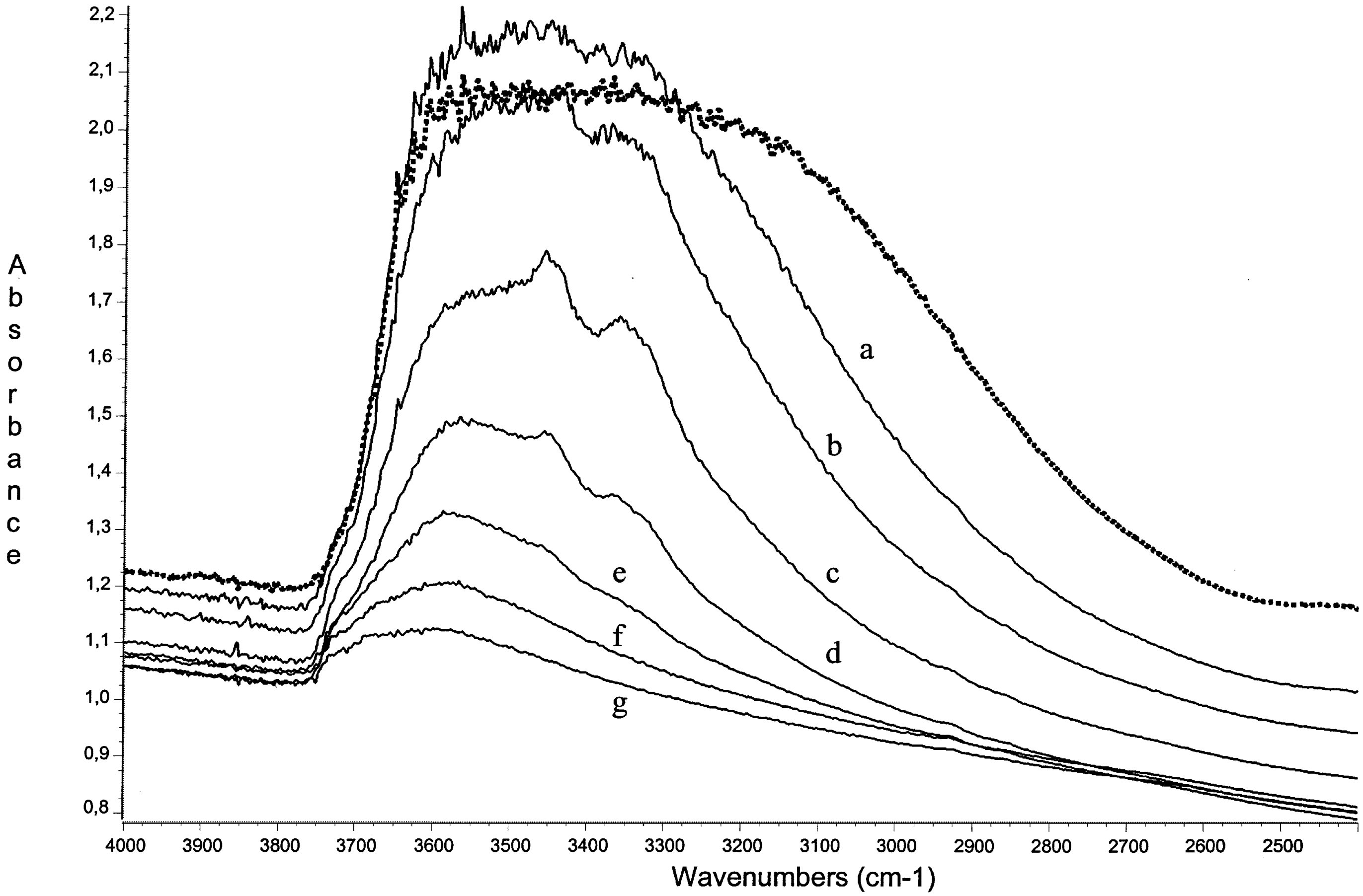

FIG. 2. FT-IR spectra of γ-Al_2O_3/Cu 9% disk outgassed at room temperature (dashed line), at 373 K (a); 423 K (b); 473 K (c); 523 K (d); 573 K (e); 623 K (f); 673 K (g). OH stretching region.

Surface areas have been calculated by applying the BET equation to N_2 adsorption isotherms obtained at 77K using a Micromeritics ASAP 2010 apparatus. The theoretical coverage reported in the Table 1 is expressed as "monolayer fraction," as frequently done in the field of oxides supported on oxides (32), including oxide supported CuO (33). It has been calculated assuming that one $CuCl_2$ molecule covers 0.163 nm^2 (CuCl A and CuCl S samples) and one CuO molecule covers 0.076 nm^2 (CuNA samples). Note that only in the case of the 9CuClA sample the alumina surface could be almost completely covered by Cu-chloride species, while, in the other cases the carrier surface is certainly largely exposed.

FT-IR spectra have been recorded with a Nicolet Magna 750 instrument, using conventional IR cells with NaCl windows, connected to an evacuation/gas manipulation apparatus. All the spectra in the figures are presented using absorbance units as the ordinate axis.

The sample powders were pressed into self-supporting disks, having a medium weight of 10–12 mg, and outgassed (10^{-4} torr) at 523 K for 20 min before the interaction experiments. These procedures, performed before any organic species adsorption experiment, allowed us to obtain a "clean" catalyst surface without adsorbed molecular water, carbonates, or any other adsorbed impurity. The activation temperatures have been chosen considering the process temperature and assuming that adsorbed molecular water desorbs before 473 K. For pure γ-Al_2O_3 outgassing at 823 K has also been performed before some experiments, in order to have a largely dehydroxylated surface.

Catalytic activity tests on the alumina and on the $CuCl_2/Al_2O_3$ catalysts have been carried out using a pulse microreactor system. This system is made of an oven, where a microreactor of a few cubic centimeters of volume is placed (and heated at the reaction temperature) and of a gas chromatograph (Carlo Erba Fractovap 4200) equipped with a packed column, flame detector, and integrator (Shimadzu C-R3A Chromatopac) to detect the reactant and the products of the ethylene oxychlorination reaction.

Ethylene, EDC, ethylchloride, VCM, and other oxychlorination by-products have been analyzed by gas chromatography; the reactants were injected with the following sequence: air, HCl, and ethylene at 523 K and a contact time of 1 s.

RESULTS AND DISCUSSION

(a) Surface Hydroxy Groups

In Fig. 1 we report the spectra in the OH stretching region of pressed disks of the pure γ-Al_2O_3 support and of the catalysts 1 CuClA, 5 CuClA, and 9 CuClA, all outgassed both at 473 K and at 623 K.

In the case of the pure support (Fig. 1a), after the activation at 473 K three main absorption bands can be noticed at 3730, 3680, and 3550 cm^{-1}. These bands have been assigned (34, 35) to different types of surface OH groups, namely to terminal OH over a octahedrally coordinated Al ion, and to bridging and triply-bridging OH, respectively. After outgassing at higher temperatures (Fig. 1e) the components at 3728, 3688, and 3585 cm^{-1} are better resolved and two additional shoulders at 3790 and 3770 cm^{-1} appear, although very weak, assigned to terminal OH's group over two different tetrahedrally coordinated Al ions (34).

The spectra of 1 CuClA (Fig. 1b) are almost the same as the spectra of pure alumina, with three evident components near 3730, 3680, and 3550 cm^{-1} (Fig. 1f). After outgassing at 623 K better-resolved bands appear. The main peak is centered at 3675 cm^{-1}, with minor components at 3722 and 3695 cm^{-1}, and a shoulder at 3790 cm^{-1}.

The spectrum of the 5 CuClA sample outgassed at 473 K (Fig. 1c) presents the component near 3680 cm^{-1} less evident than in the previous cases, but shows also three intense peaks at 3455, 3360, and 3335 cm^{-1}, the last two partially overlapped, that are absent in the samples with lower $CuCl_2$ content. These bands are detected, less intense, also in the spectrum of the 9 CuClA (Fig. 1d) sample outgassed at 473 K. These bands completely disappear after outgassing at 623 K (Figs. 1g and h), the temperature at which, however, a new broad band centered near 3580 cm^{-1} persists, unlike the cases of the sample with lower $CuCl_2$ content.

These data can be interpreted, assuming that on the 5 CuClA and 9 CuClA samples a well-defined and structured species exists after outgassing at 473 K, characterized by peaks at 3455, 3360, and 3335 cm^{-1}. This species decomposes after treating at 623 K, leaving, however, a more disordered species, but still retaining stable H-bonded OH's (band at 3580 cm^{-1}).

In Fig. 1i the spectrum of the compound paratacamite ($Cu_2(OH)_3Cl$), outgassed at 573 K, is also reported for comparison. This compound shows very strong bands at

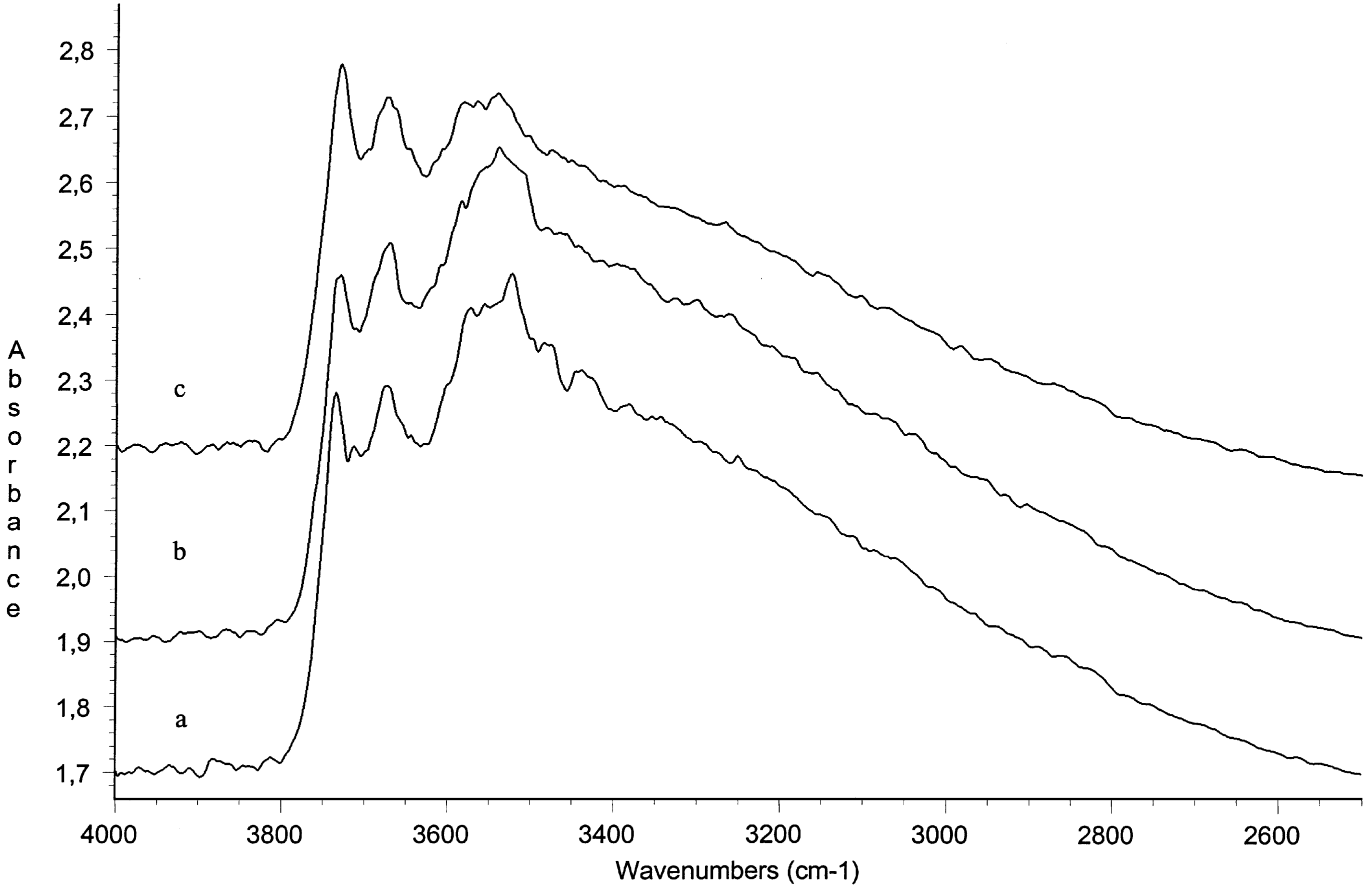

FIG. 3. FT-IR spectra of the 9% Cu/Al_2O_3 catalyst (from $Cu(NO_3)_2$) outgassed at 473 K (a); 523 K (b); 573 K (c). OH stretching region.

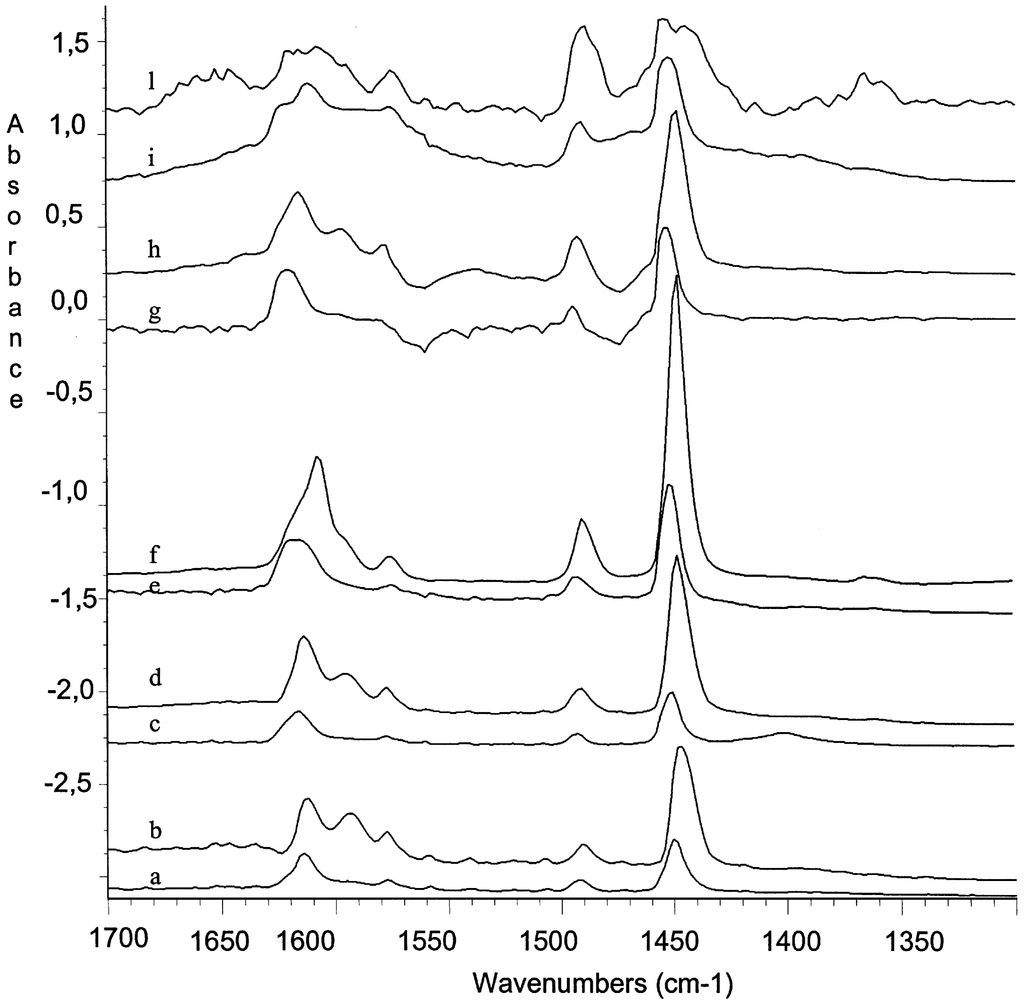

FIG. 4. FT-IR spectra of the surface species arising from the adsorption of pyridine over pure γ-Al_2O_3 at 473 K (a) and at room temperature (b), over 1% $CuCl_2/Al_2O_3$ at 473 K (c) and at room temperature (d); 9% $CuCl_2/Al_2O_3$ at 473 K (e) and at room temperature (f); over pure γ-Al_2O_3 (pretreated with HCl) at 473 K (g) and at room temperature (h); and over 9% $CuCl_2/Al_2O_3$ (pretreated with HCl) at 473 K (i) and at room temperature (l).

3455, 3360, and 3335 cm^{-1}, just corresponding to those cited above, present in the spectra of the 5 CuClA and 9 CuClA samples outgassed at low temperature, that can be consequently assigned to paratamite particles. These bands, that are certainly due to the O-H stretchings of hydroxy groups bridging between at least two Cu cations, can consequently be taken as the "fingerprint" of the presence of paratacamite particles.

In Fig. 2 the spectra of the 9 CuClA catalyst sample after increasing outgassing temperatures are reported in the OH stretching region. The surface outgassed at room temperature shows a broad band due to molecularly adsorbed water, while at 473 K (Fig. 2c) the spectrum shows the two main cited peaks at 3455 and 3360 cm^{-1} with the shoulder at 3335 cm^{-1} which is better shown by outgassing at 523 K (Fig. 2d). After outgassing at higher temperatures these bands progressively disappear. This confirms that the paratacamite particles are detectable only up to 573 K, leaving, after decomposition, a copper chloride bulk-like species still present, even after treatment at 623 K, at the highest $CuCl_2$ loading,

In Fig. 3 the spectra of a 9 CuNA catalyst, after outgassing at increasing temperatures are reported. It is evident that, in this case, the bands in the region 3500–3300 cm^{-1} do not exist. This further confirms that they are associated to structures that involve copper, hydroxide ions, and chlorine too, i.e. paratacamite.

It is worth noticing also in the 9 CuClA sample that traces of the OH bands assigned to free alumina OH's (3800–3700 cm^{-1}) persist. This agrees with the formation of bulk copper hydroxychloride particles, so that the real coverage of the alumina support is lower than the theoretical one, that would in principle be sufficient to complete the monolayer.

(b) Characterization of the Surface Sites by Pyridine Adsorption

The IR spectra of pyridine species adsorbed at room temperature on the alumina support preactivated by outgassing at 523 K are shown in Figs. 4a and b. The predominant species after prolonged outgassing at room temperature (corresponding to the IR modes 8a and 19b at 1614 and 1449 cm^{-1}) has been assigned to pyridine bonded to coordinatively unsaturated tetrahedral Al cations, probably located near empty cationic sites (denoted as type II). By increasing the outgassing temperature, namely above 473 K, another component of the 8a mode appears at 1624 cm^{-1} (shoulder) which is typical for the strongest Lewis acid sites of aluminas and is usually denoted as type I (34, 35). Such sites have been identified as coordinatively unsaturated tetrahedral Al cations, probably located in a nondefective environment.

As usual for aluminas, no bands assignable to Brønsted-bonded species (pyridinium ions) can be found.

The spectra of the adsorbed species observed in the same conditions on the 1 CuClA sample are shown in Figs. 4c and d. The spectra are very similar, so that we can only detect in these conditions the adsorbed species located on the bare alumina support. This can be due either to the inactivity of the Cu sites in absorbing alumina, or more probably, to their too low concentration, so we cannot distinguish the features of py-Cu species from those of py-Al species.

The spectra of the adsorbed species observed in the same conditions on the 9 CuClA sample are shown in Figs. 4e and f. In this case, significant differences can be found, with respect to the spectra observed on the pure support. In fact, after outgassing at room temperature a species characterized by a quite strong and pointed 8a band at 1608 cm^{-1} is observed here, unlike that on pure alumina. This species disappears by outgassing at temperatures up to 473 K, when type II and type I species are largely predominant. The detection of the bands of type I and type II species in the spectra of pyridine adsorbed on the catalyst 9 CuClA indicates that the bare alumina surface is likely still present in large amounts despite the nominal near "monolayer" coverage by $CuCl_2$.

To propose an identification of the species responsible for the band at 1608 cm^{-1} we also studied the adsorption of pyridine on the 14 CuClS catalyst. The spectra are reported in Fig. 5. Also in this case, after outgassing at 373 K (Fig. 5b) that allows desorbing the species H-bonded to the silica silanol groups, a species responsible for a 8a and 19b

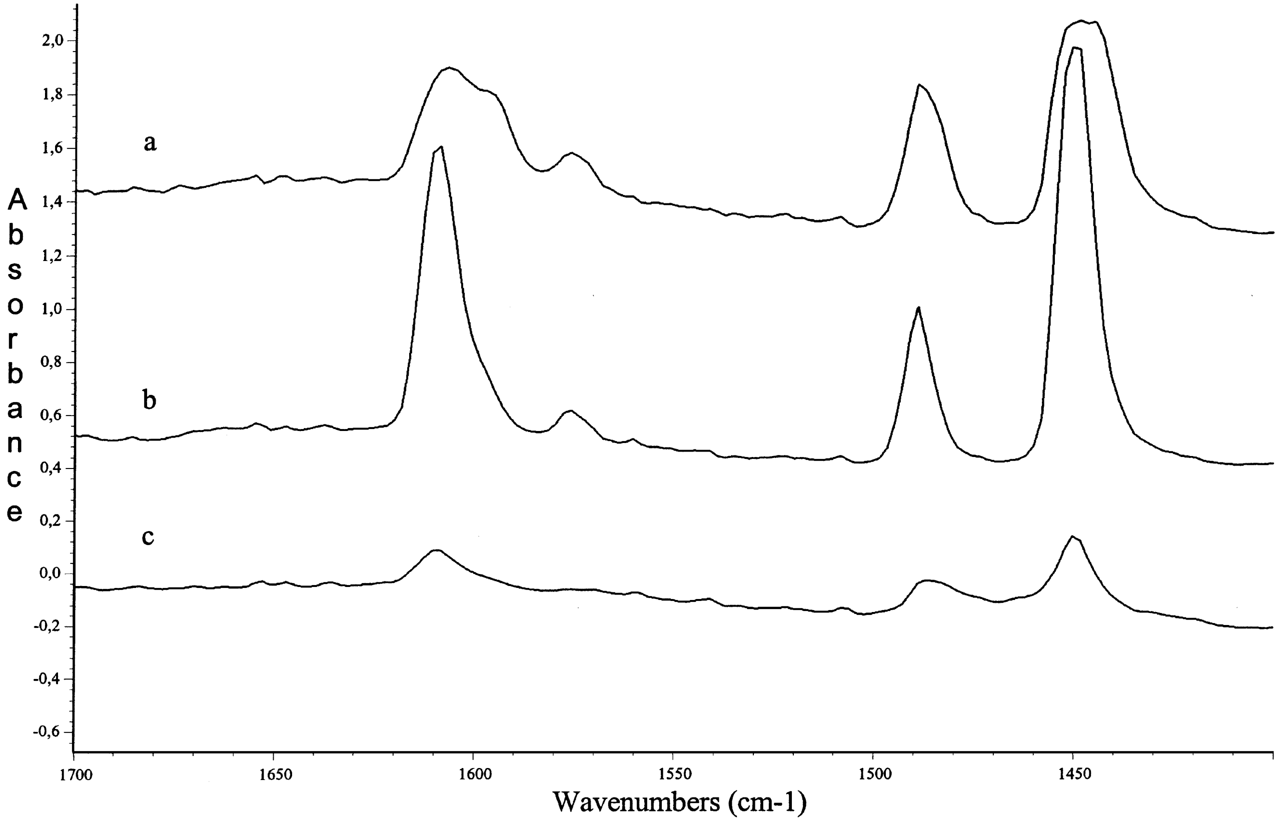

FIG. 5. FT-IR spectra of the surface species arising from the adsorption of pyridine over 14% $CuCl_2/SiO_2$ and at room temperature (a), at 373 K (b), and at 523 K (c).

bands just at 1608 cm^{-1} and 1449 cm^{-1} is detected. This species persists after outgassing up to 573 K. As is well known (and confirmed experimentally by us), silica pretreated in these conditions is not Lewis acidic, because of the lack of any coordinative unsaturation at silicon. So, the pyridine species responsible for the bands at 1608 cm^{-1} and 1449 cm^{-1} is certainly interacting with coordinatively unsaturated Cu centers. This allows us to conclude that also on the 9 CuClA catalyst the species characterized by the 8a mode at 1608 cm^{-1} must be assigned to pyridine interacting with Cu centers. The position of such a band and the remarkable thermal stability of such a species is evidence of a remarkably strong Lewis acidity of such Cu centers.

To have an indication on whether the presence of HCl can modify the picture, we also investigated the interaction of pyridine with the support and with the 9 CuClA catalyst after previous treatment with HCl at 523 K for 3 h, followed by brief outgassing at 423 K. These conditions were chosen to desorb only weakly bound HCl.

The spectra of the surface species arising from pyridine adsorption after these treatments (Figs. 4g–l) are qualitatively very similar to those reported in Figs. 4a, b, e, f, i.e. those of the surface species on the "pure" support and catalysts without HCl pretreatment. In particular, we can note that: the pretreatment with HCl followed by outgassing at 423 K leaves only very small amounts, if any, of Brønsted acidity on the surface, as evidenced by the weakness of a broad absorption at 1550 cm^{-1}, due to pyridinium ions. This indicates that HCl is almost completely dissociated, i.e. neutralized, on the alumina surface. Moreover, the nature of the Lewis acid sites, both Al^{3+} and Cu^{2+} exposed cations, is not substantially changed by chlorination.

(c) Characterization of the Surface Sites by Carbon Dioxide Adsorption

In Fig. 6a the IR spectrum of the alumina support outgassed at 523 K with the adsorbed species arising from the contact with CO_2 gas at room temperature is reported. The spectrum consists of three main bands centered at 1655, 1433, and 1228 cm^{-1}. These bands are typical for bicarbonate species formed on uncompletely dehydroxylated aluminas (36, 37) and are assigned to the asymmetric and symmetric OCO stretching and the COH deformation of such species.

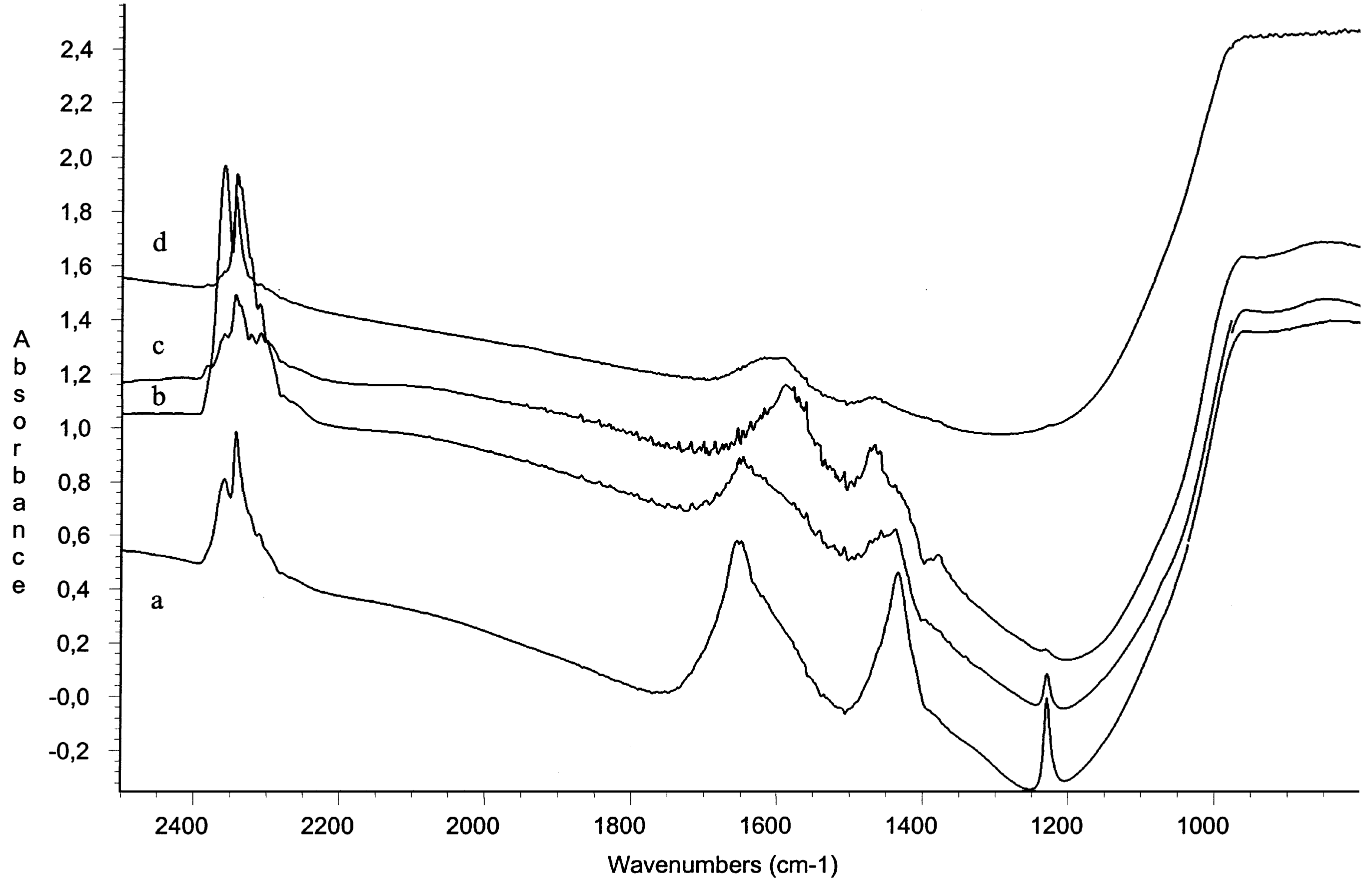

FIG. 6. FT-IR spectra of the catalysts after the contact with CO_2 gas at room temperature: pure γ-Al_2O_3 (a); 1% $CuCl_2/Al_2O_3$ (b); 5% $CuCl_2/Al_2O_3$ (c); 9% $CuCl_2/Al_2O_3$ (d).

Additional components in the range near 1580 and 1350 cm^{-1}, evident as broad shoulders, are assigned to carbonate species (splitting of the asymmetric CO_3 stretching (36)).

The formation of such surface species is evidence of the presence on the alumina surface of nucleophilic centers, i.e. incompletely coordinated hydroxide and/or oxide anions, able to attack the electrophilic carbon atom of the carbon dioxide molecule. For this reason the adsorption of CO_2 can be used to test the presence and the nature of such sites on the surface of the catalyst.

In the same figure the corresponding spectra of the $CuCl_2$-Al_2O_3 samples can be found. It is evident that the spectra observed are quite similar, qualitatively, although the components near 1580 and 1450 cm^{-1} become more evident by increasing the $CuCl_2$ content. However, it is also evident that the intensity of the bands in the 1700–1200 cm^{-1} range decrease progressively by increasing $CuCl_2$ content.

In Table 1 a coarse evaluation of the abundance (or concentration) of the nucleophilic sites on the surfaces, based on the measured relative intensities of the bands near 1230 cm^{-1} (due to bicarbonate species), is reported.

These data suggest that the $CuCl_2$ species deposed by impregnation on the alumina surface covers or interacts with the nucleophilic centers of alumina, neutralising them. The quantitative data suggest also that, however, on the surface of the 1 CuClA already 69% of the nucleophilic sites active in the adsorption of CO_2 have disappeared. On the 9 CuClA catalyst 85% of the alumina surface sites active in CO_2 adsorption are covered or masked by $CuCl_2$, but 15% is still “free.” It is clear that this measure is certainly affected by relevant error. The differences in the dispersion of the active phase for 5 CuClA and 9 CuClA fall certainly in the uncertainty limits.

In Fig. 7 the spectra of the samples produced by impregnation of the alumina support with copper nitrate are also reported, after adsorption of CO_2 at room temperature. The spectra of the adsorbed species are now more complex, showing the same bands found on pure alumina (1650, 1430, and 1230 cm^{-1}) due to bicarbonates on the alumina

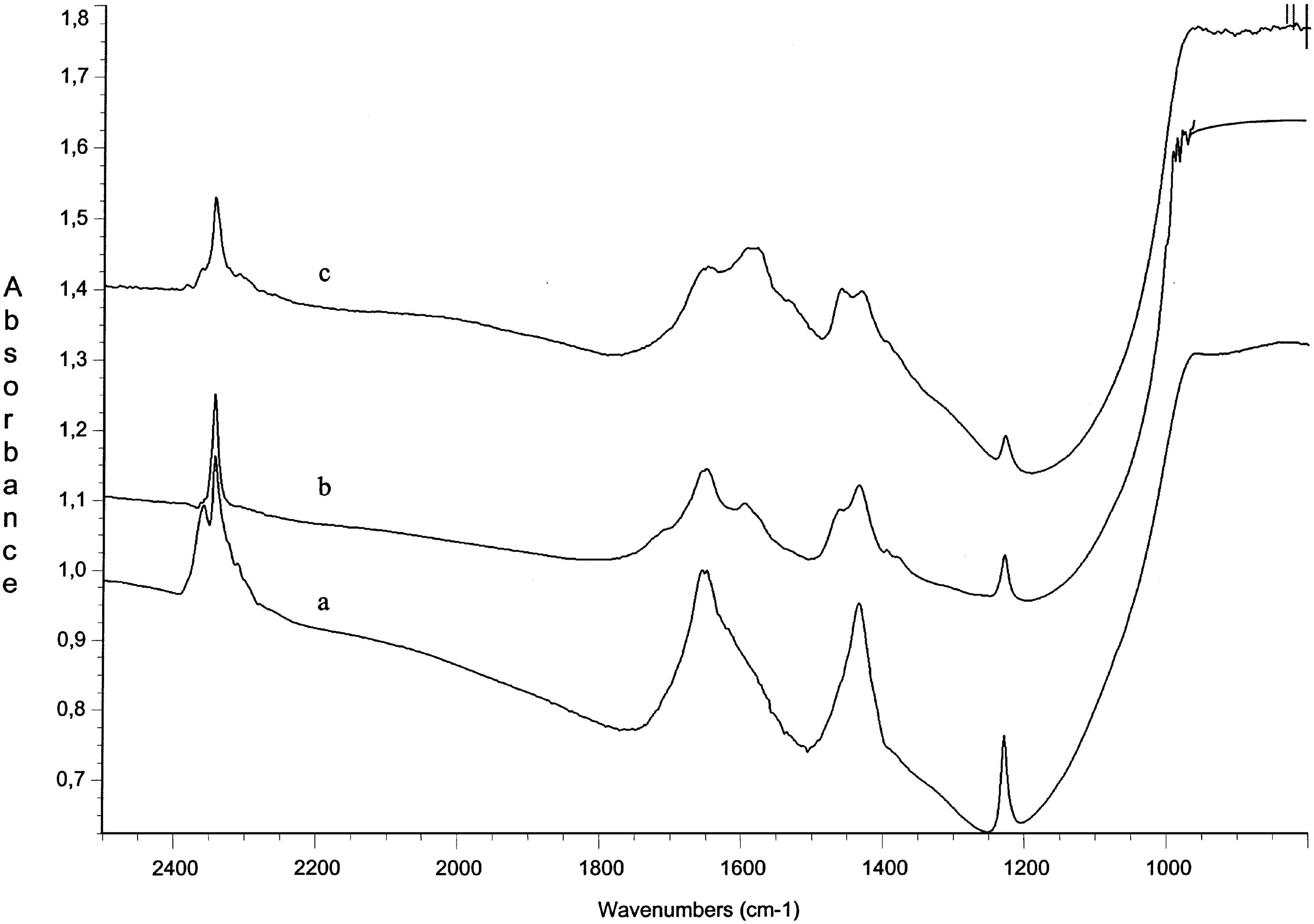

FIG. 7. FT-IR spectra of the catalysts after the contact with CO_2 gas at room temperature: pure γ-Al_2O_3 (a); 1% $Cu(NO_3)_2/Al_2O_3$ (b); 9% $Cu(NO_3)_2/Al_2O_3$ (c).

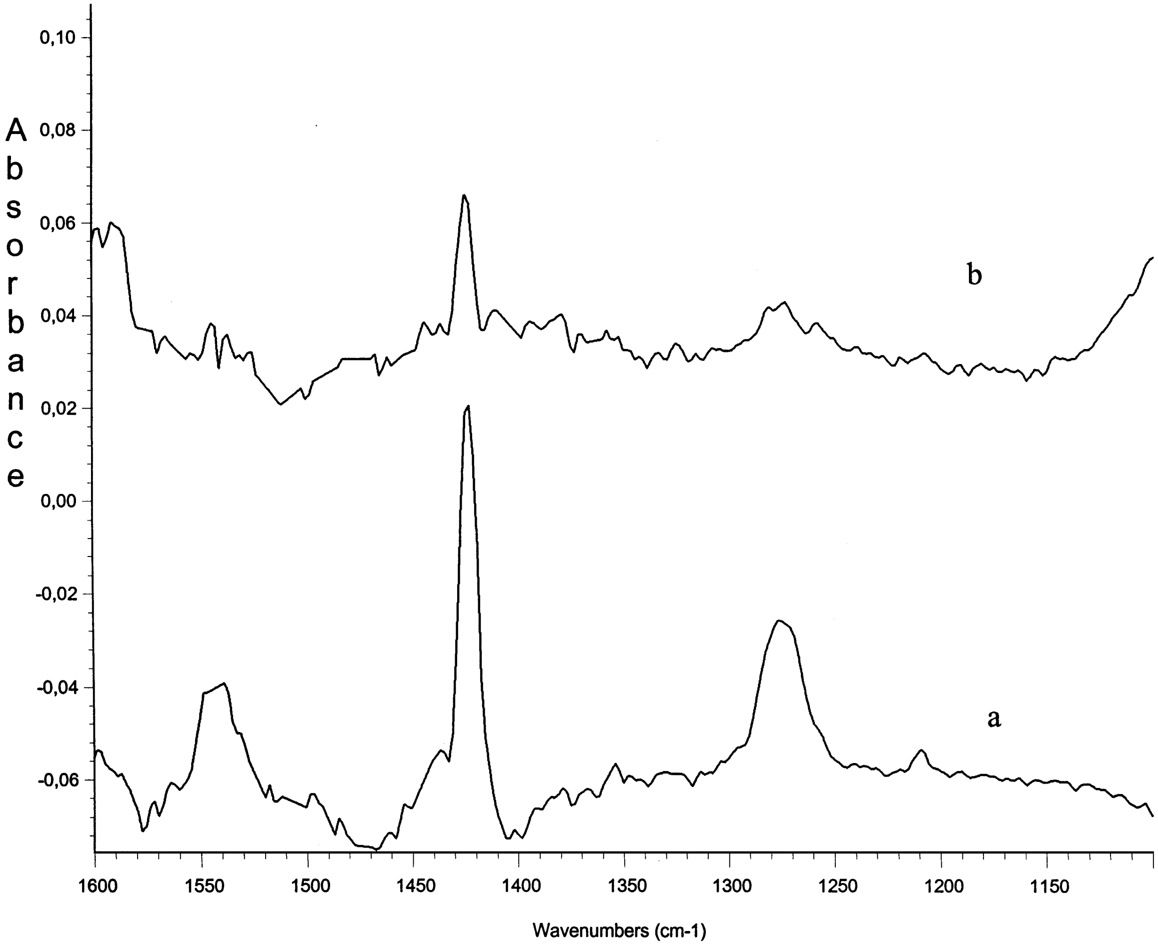

FIG. 8. FT-IR spectra of the 9% $CuCl_2/Al_2O_3$ catalyst surface, activated at 573 K, after the contact with ethylene at room temperature (a), and after evacuation at room temperature (b).

surface and bands at 1580 and 1450 cm^{-1} that grow by increasing the Cu content. Analysis of the relative intensity of such bands shows that the amount of the surface nucleophilic centers decreases also by impregnation with copper nitrate, but much less than on copper chloride. The sample with 9 CuNA has only covered 60% of the alumina surface nucleophilic sites. This result points to a role of the chlorides in "poisoning" the alumina nucleophilic sites.

(d) Catalytic Activity in Ethylene Oxychlorination

The results of pulse catalytic tests are reported in Table 2. This technique was chosen for its simplicity and its usefulness in giving mechanistic information. It is evident that alumina is almost inactive in converting ethylene, as expected indeed. The addition of 1% copper results in the appearance of a relatively weak ethylene oxychlorination catalytic activity, but with moderate selectivity to EDC, giving only a 5% EDC molar yield. By increasing the copper content up to 9% the oxychlorination activity increases while the EDC selectivity becomes very high, giving rise to about 50% EDC yield and 2–3% by-products yield.

The appearance of the oxychlorination activity with the presence of $CuCl_2$-like species on the surface confirms the previous results that indicate, quite obviously, that the species arising from impregnated $CuCl_2$ are the active species in the oxychlorination reaction, alumina being inactive. The almost fivefold increase of ethylene conversion observed on 5 CuClA with respect to 1 CuClA (i.e. when the $CuCl_2$ amount increases nearly five times) can be taken

TABLE 2

Ethylene Conversion and Product Yields and Selectivities in Pulse Catalytic Experiments

Catalyst	C_2H_4 conv.	EDC yield	EtCl yield	VCM yield	Other by-pr. yield	EDC sel.
A	0.09	0	0	0	0.09	0
1CuClA	9.19	5.27	0.20	0.36	3.36	57.34
5CuClA	41.24	38.57	0.01	0.26	2.40	93.53
9CuClA	51.56	49.73	0	0.59	1.24	96.54

Note. Feed: air 0.75 cc, HCl 0.60 cc, C_2H_4 0.30 cc, $T = 523$ K; $\tau = 1$ s.

as evidence that the Cu species present on such catalysts are nearly equivalently active in ethylene conversion. Further enhancement of activity going to the 9 CuClA is in this line, taking into account that Cu-species dispersion is neither complete nor homogeneous, according to the above IR data, with bulk copper chloride particles being formed. This conclusion suggests that the analysis of the $CuCl_2$ active sites and the distinction, deeply discussed in the literature, between highly dispersed and "polymeric" or "bulk" copper chloride species should not be the most important topic to describe the changes in the activity and selectivity behavior of catalysts with different copper chloride loading.

The much lower selectivity in EDC observed by using the 1 CuClA catalyst, in comparison with those with higher copper content, and the further increase in EDC selectivity going from 5 CuClA to 9 CuClA suggest that the alumina surface, always partly exposed on the catalyst surface, is responsible for the successive transformation of EDC to by-products. In opposition to the strong increase in EDC selectivity we find in fact a significant decrease in the selectivity to VCM and EtCl (ethylchloride), as well as in other by-products, by increasing Cu loading which decreases the exposure of the alumina surface.

Among the main by-products observed by us and cited in the literature (1) VCM, 1,1,2-trichloroethane (TCE), *cis*- and *trans*-1,2-dichloroethylene (DCE) can be assumed to be formed by successive dehydrochlorination/oxychlorination cycles: EDC → VCM → TCE → DCE. We have verified experimentally that, according to its acido-basicity, alumina is very active in performing dehydrochlorination of chloroalkanes. On the other hand, several acid catalysts including modified aluminas have been proposed as catalysts for the catalytic cracking of EDC to VCM (38). This strongly suggests that the above by-products arise from the successive conversion of EDC catalyzed by the free alumina surface. The other main product, EtCl, likely arises from the addition of HCl to ethylene, which can also be catalyzed by alumina. Carbon oxides, due to total ethylene combustion, should instead be produced on the oxidizing Cu sites.

The data shown here suggest that the increase of $CuCl_2$ coverage is favorable just because it "poisons" the alumina sites active in further EDC conversion, more than because of an enhancement of its activity. In other terms, it seems likely that the better selectivity at higher coverages is not necessarily due to a change in the nature of the active sites.

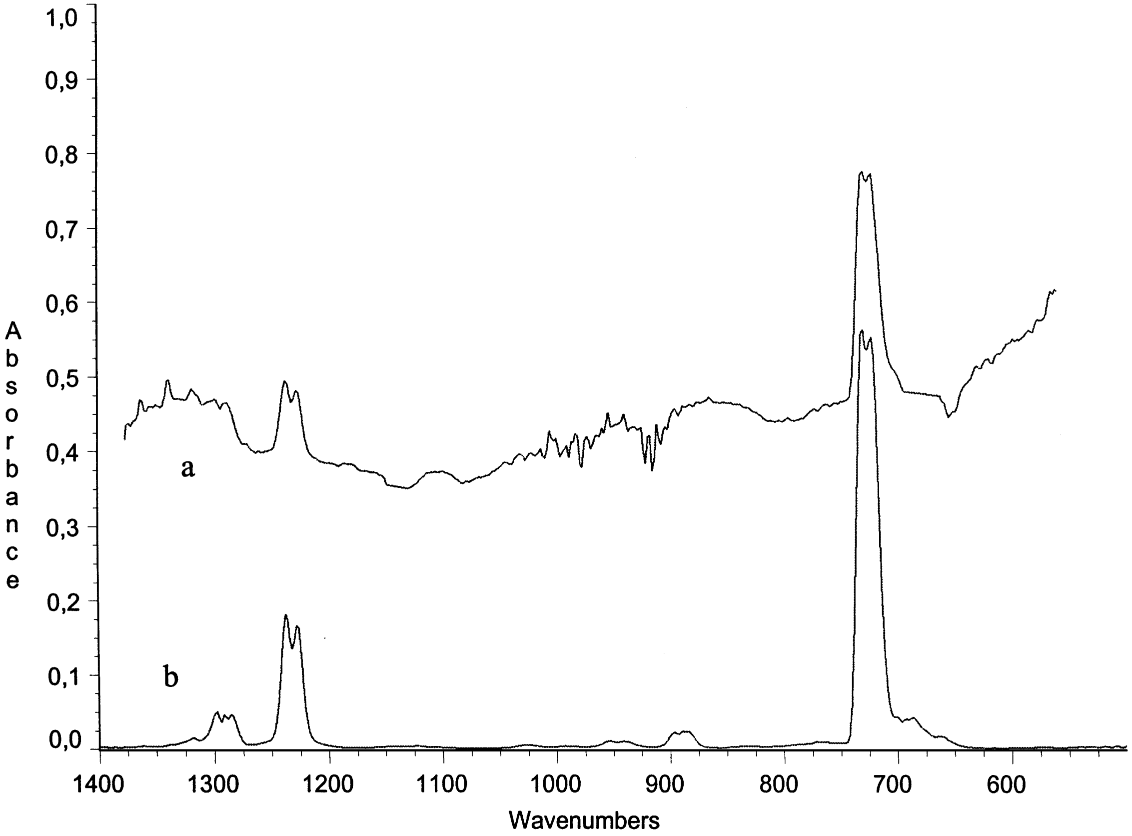

FIG. 9. Gas phase FT-IR spectrum corresponding to the contact between 9% $CuCl_2/Al_2O_3$ pretreated with HCl and ethylene at 573 K for 20 min (a) (gas phase ethylene has been subtracted), in comparison with the FT-IR spectrum of 1,2-dichloroethane gas (b).

(e) FT-IR Study of Ethylene Oxychlorination on 9 CuClA in Static Conditions

The study of the adsorption of ethylene has been performed at room temperature on catalysts pretreated at 573 K. On the pure alumina support we did not find any adsorbed species. On the copper-containing catalysts, instead, the formation of bands due to surface species is observed at 1544, 1424, and 1275 cm^{-1}, as shown in Fig. 8 for 9 CuClA. These bands are typically due to copper-ethylene complexes, like the $C_2H_4 \rightarrow Cu^+$ π-bonded complex (39) and the species adsorbed on Cu/TiO_2 catalysts (40). Evacuation at room temperature for prolonged periods causes the complete disappearance of this adsorbed species.

In the case of samples preactivated at 573 K we observe the disappearance of the bands at 3500–3300 cm^{-1} in the O-H stretching region, showing that paratacamite particles no longer exist as such. However, the interaction of ethylene with the sample previously outgassed at 473 K, where paratacamite particles do exist still, gives the same IR features, due to the formation of a copper chloride-ethylene complex at the surface.

Figure 9a shows the FT-IR spectrum of the gas in contact with the 9 CuClA catalyst pretreated with HCl and ethylene at 573 K. For comparison the spectrum of gaseous 1,2-dicholoro ethane is also shown. The two strongest bands of 1,2-dichloroethane, centered near 1235 and 725 cm^{-1} (present weak in the gas already at 523 K), are evident at 573 K, showing that, in these conditions, the oxychlorination of ethylene did actually occur in our IR cell.

In Fig. 10 the subtraction spectra of the species present on the catalyst surface during the above oxychlorination experiment are shown. After contact of ethylene with the catalyst preactivated in HCl, surface species responsible for bands at 1544, 1423, and 1275 cm^{-1} are present. These bands are those of the $C_2H_2 \rightarrow Cu^+$ π-bonded surface complex (39, 40). The spectrum is fully changed at 573 K (Fig. 10d) when strong bands at 1570, 1390, and 1375 cm^{-1}, which are typical of formate ions likely on Cu sites (41) more than on alumina (42), as deduced by the significant differences in the position of such bands. Weak bands are also observed at 1450 and 1350 cm^{-1} that, together with part of the band at 1570 cm^{-1}, can be assigned to acetate or monochloroacetate species.

The spectra in Fig. 11 are those of the surface species arising from the interaction of ethylene with the same catalyst without previous activation with HCl. Also in this case the $C_2H_2 \rightarrow Cu^+$ π-bonded complex is observed in the range

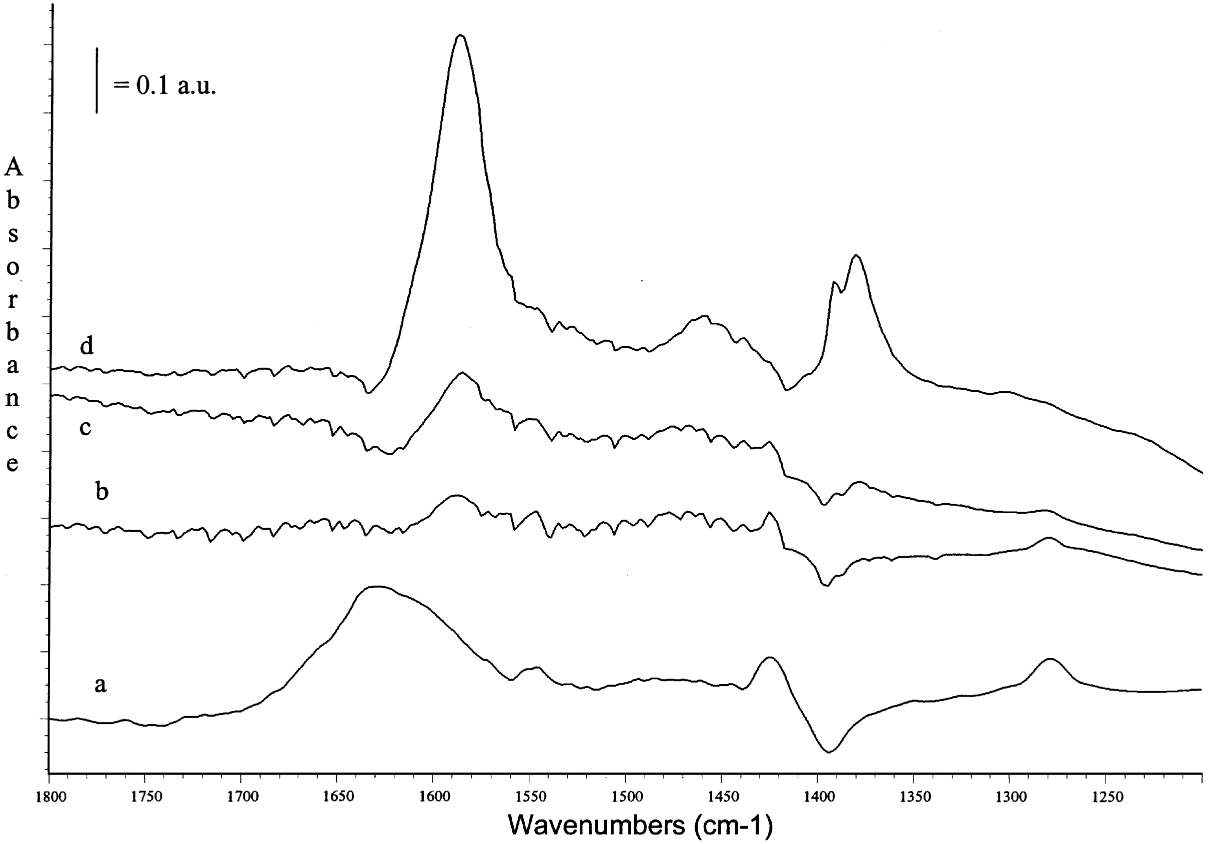

FIG. 10. FT-IR subtraction spectra of the species arising from ethylene adsorption over 9% $CuCl_2/Al_2O_3$ pretreated with HCl at room temperature (a), at 423 K (b), at 473 K (c), at 573 K (d).

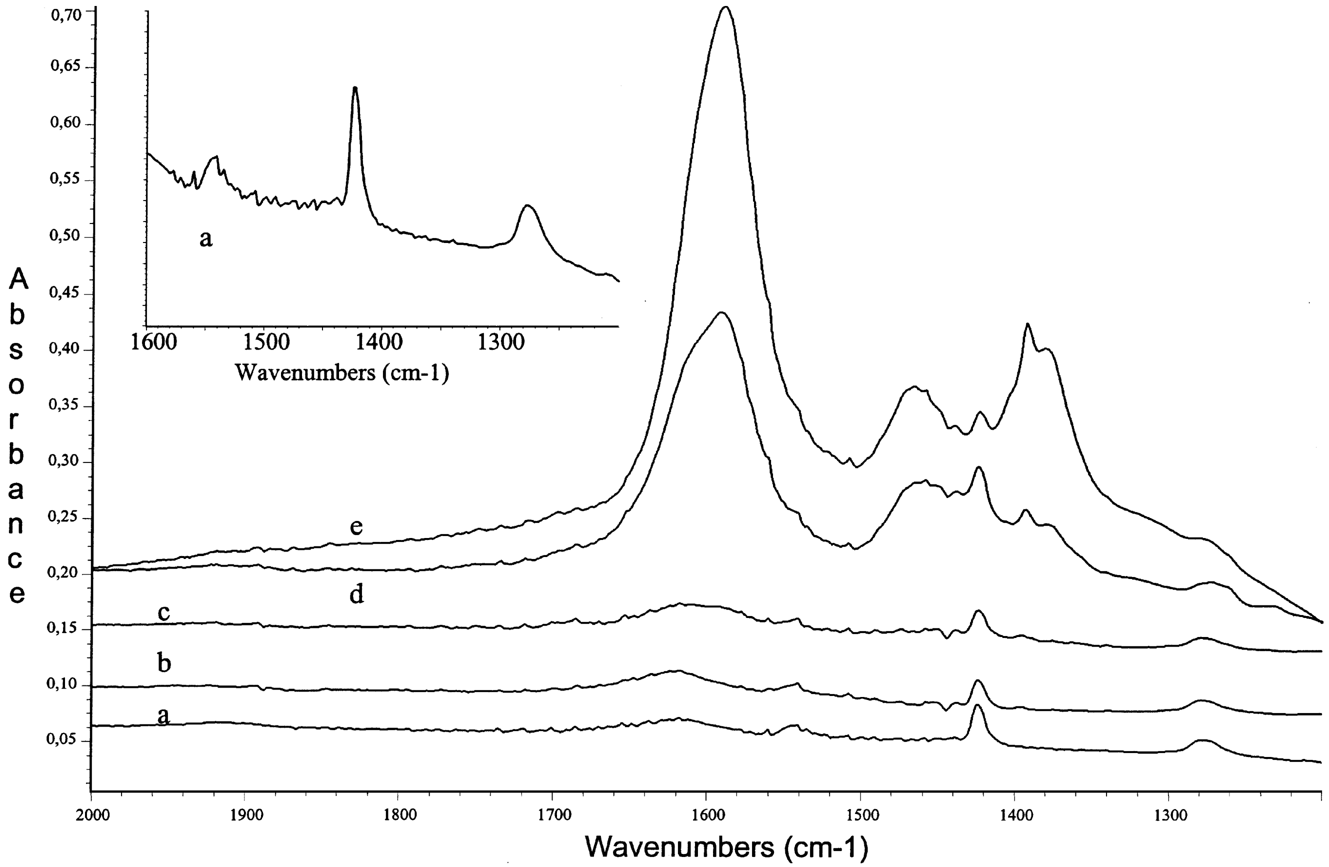

FIG. 11. FT-IR subtraction spectra of the species arising from ethylene adsorption over 9% $CuCl_2/Al_2O_3$ non-pretreated with HCl, at room temperature (a) and in the insert figure; at 373 K (b), at 423 K (c), at 473 K (d), and 523 K (e).

300–423 K, while acetate and formate species are observed at 473 and 523 K. Quite surprisingly, it seems that acetate species are mostly formed at 473 K while formates grow later, at 523 K. Upon this experiment, however, no 1,2-dichloroethane is observed in the gas phase.

These data show that our experimental conditions, although static, can actually be comparable with those of a flow oxychlorination reactor. They also strongly suggest that the π-bonded ethylene species and weakly adsorbed HCl are actually involved in the oxychlorination reaction, while formate species act likely as intermediates in the combustion of ethylene.

CONCLUSIONS

The experiments described above allowed us to come to the conclusions summarized in the following:

(i) alumina surface is still exposed in part on the active oxychlorination catalyst, also in the case of the 9CuClA sample, nominally containing a "full monolayer loading" of $CuCl_2$, as deduced by pyridine and CO_2 adsorption experiments, as well as by the analysis of the surface OH groups.

(ii) fresh catalysts with quite high $CuCl_2$ loadings (5 CuClA and 9 CuClA), which are the most active in oxychlorination, present paratacamite-like particles that decompose in the range 523–623 K, giving rise to a disordered bulk-like copper chloride species.

(iii) surface copper chloride species are medium-strong Lewis acidic, as deduced by pyridine adsorption on CuClA and CuClS catalysts.

(iv) pyridine adsorption also shows that HCl is nearly totally dissociated on the catalyst surfaces and does not give rise to significant amounts of Brønsted acid sites.

(v) impregnation with $CuCl_2$ kills most alumina nucleophilic sites (exposed oxide anions) which does not occur by impregnation with copper nitrate.

(vi) impregnation of alumina with copper nitrate gives rise to surfaces where the alumina sites are present in higher amounts and behave very differently than those obtained by impregnation with $CuCl_2$.

(vii) the oxychlorination reaction could be studied by *in-situ* IR in static conditions. This study allow us to propose a mechanism for the activation and oxychlorination of ethylene over the $CuCl_2/Al_2O_3$ samples that implies a role of the copper-ethylene complex as an intermediate in the selective way and formate species as intermediates in the competitive combustion of ethylene.

(viii) pulse oxychlorination catalytic studies show that alumina is essentially inert towards ethylene conversion and that the sample with very low copper loading, 1 CuClA, is already significantly active, although not very selective to EDC.

(ix) by increasing Cu loading the activity increases, which is likely due to the increased density of active sites, and also the selectivity to EDC strongly increases.

(x) the main conclusion is that the free alumina surface could play a negative role in ethylene oxychlorination, due to its ability to dehydrochlorinate EDC and other chloroalkanes. This is likely the reason why the $CuCl_2$ loading should be increased at a level up to a nominally complete "monolayer" coverage and poisoning the alumina surface active sites. Coupling the data obtained above we can propose that the loss in EDC selectivity must be assigned to the alumina nucleophilic sites involved in EDC dehydrchlorination.

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