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Catalytic oxidation of CH_2Cl_2 on sodium doped Al_2O_3

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Abstract

Influence of the deposition of Na^+ ions on γ-Al_2O_3 on its surface properties and catalytic activity in oxidation of CH_2Cl_2 by gas phase oxygen has been studied. IR spectra indicate that the concentration of OH groups is significantly reduced and Lewis acidity, related to exposed Al ions, is simultaneously decreased. Therefore, total catalytic activity is strongly depressed, no CH_3Cl is formed as intermediate product, Cl_2 appears in the products which is absent on pure γ-Al_2O_3 and the amount of CO_2 is at all temperatures higher than that of CO. This indicates that parallel to the two mechanisms, operating in case of γ-Al_2O_3 and starting with mono- and bidentate adsorption of CH_2Cl_2 through its chlorine atoms on Lewis sites, a third reaction pathway appears starting with adsorption through hydrogen atoms. ©1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Destruction of halogenated hydrocarbons from flue-gases by catalytic oxidation is recently the subject of considerable attention because of its growing importance in pollution control [1]. The main requirement is the total conversion of chlorine, contained in the organic molecule, into HCl, and oxidation of the organic part into CO_2 and H_2O. The mechanism of the cleavage of C–Cl bond and the formation of HCl is not yet fully understood. Studies of halogen exchange reaction on γ-alumina which can be considered as a measure of the ability of catalyst to cleave the C–halogen bond indicate that Lewis acid sites of a certain strength are responsible for the catalytic activity [2]. Many studies focused on classical acid catalysts as Al_2O_3, TiO_2, SiO_2 and their mixtures [3–4].

In our studies [5] of the oxidation of $CH_2Cl_2$with dioxygen on pure γ-Al_2O_3 and Al_2O_3–SiO_2 we have found that two mechanisms of the reaction operate. At temperatures below 400°C CH_3Cl is formed as an intermediate, with simultaneous evolution of CO, but no HCl appears in the products. This reaction pathway may start from single-site adsorption of CH_2Cl_2 through a chlorine apex at a Lewis site, the adsorbed species transforming by S_N2 reaction to chloromethoxy- and methoxy-species and than by Cannizzaro-type reaction to a formate precursor and finally CO, a hydrogen transfer to chloromethoxy-species giving CH_3Cl. Results of the in situ IR spectroscopic studies are in line with such model. At higher temperatures 100% conversion of CH_2Cl_2 into HCl and CO_2 is observed, this reaction pathway starting from bidentate adsorption of CH_2Cl_2 on exposed Al-ions playing the role of Lewis acid sites. Comparison of catalytic properties with the distribution of acid sites indicates that activity depends on total amount of acid sites, but the selectivity to

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CH_3Cl is related to the concentration of Lewis acid sites. Pure silica shows no activity.

In an attempt to scale-up the process, commercial Al_2O_3 has been used. It has been found that its catalytic performance is different from that of pure Al_2O_3 used in our previous studies. Instead of total conversion of chlorine, contained in the hydrocarbon, into HCl, observed in laboratory experiments at ca. 550°C and higher temperatures, considerable amount of gaseous chlorine was evolved in case of the use of commercial alumina. Whereas our alumina was prepared by hydrolysis of aluminum isopropoxide and therefore was free of any contamination, the commercially available alumina contains important amount of sodium ions as an impurity. It seemed therefore of interest, from both fundamental and applied research point of view to investigate the influence of the presence of sodium ions on the mechanism of interaction of chlorinated hydrocarbon molecules with the surface of γ-Al_2O_3 and hence on its behaviour in catalytic oxidative dehalogenation. Oxidation of CH_2Cl_2 with dioxygen was taken as an example of the catalytic reaction.

2. Experimental

2.1. Materials

Alumina was prepared by hydrolysis of aluminum isopropoxide dissolved in isopropanol. The resulting precipitate was dried at 120°C for 2 h and then calcined at 550°C for 24 h. A part of alumina was impregnated with different amounts of NaOH followed by drying at 120°C for 2 h and then calcined at 550°C for 2 h. The amount of Na ions introduced was 0.5 and 1 wt.%. The samples will be designated as 0.5Na/γ-Al_2O_3 and 1Na/γ-Al_2O_3, respectively. Commercial alumina was Rhone–Poulenc A4.

2.2. Methods

X-ray diffraction (XRD) patterns were obtained with a DRON-3.0 diffractometer using Ni-filtred Cu Kα radiation. It has been found that the XRD pattern of alumina was characteristic of γ-Al_2O_3.

The BET surface area was determined from nitrogen adsorption at 77 K. The specific surface area of pure γ-Al_2O_3 sample was 210 m^2/g and that of 0.5Na/γ-Al_2O_3 and 1Na/γ-Al_2O_3 were 190 and 180 m^2/g, respectively.

Catalytic activity was measured in a conventional flow apparatus equipped with a glass reactor of inner diameter 10 mm. The volume of catalytic bed was 0.5 ml. Oxidation of methylene chloride was studied at different temperatures in order to determine light-off curves. Some experiments were carried out after a certain time-on-stream at 250 and 300°C. Before each catalytic experiment samples were standardized at 450°C for 1 h.

Methylene chloride was introduced into the hot stream of air in order to allow its rapid evaporation. The concentration of methylene chloride in air was 2.5 g/Nm^3 of air. G.H.S.V. was 10,000 h^{-1}.

Methyl chloride (CH_3Cl), CO_2, HCl and Cl_2 were the products of the methylene chloride oxidation. CH_3Cl and CH_2Cl_2 were analyzed by an 'on-line' gas chromatograph (SRI 86 10A) with DCQF-1 column. CO and CO_2 were analyzed by Chrom-5 gas chromatograph with TCD and two columns: molecular sieve 5A for CO analysis and HayeSep R for CO_2. HCl was absorbed in water by passing a given volume of the reaction gas. The amount of HCl was determined from the conductivity of HCl solution. Cl_2 was absorbed in KI water solution and then the evolved I_2 was titrated with $Na_2S_2O_3$ solution.

FTIR spectra were registered in the transmission mode at room temperature by using a Nicolet 800 spectrometer. The resolution was 2 cm^{-1}. A thin alumina pellet (12 mg/cm^2) was used.

Before adsorption of pyridine (Fluka AG) alumina was outgassed at room temperature for 0.5 h followed by heating up (5°/min) to 450°C under the pressure of 10^{-6} Torr. Alumina pellet was activated at 450°C for 1 h and then cooled to room temperature. Adsorption of pyridine (several Torr) was carried out for 15 min. Excess pyridine was evacuated for 1 h and FTIR spectrum was registered. Alumina pellet was then heated (10°/min) to 150, 250, 350 or 450°C and kept at each temperature for 1 h under continuous evacuation. From each temperature alumina pellet was cooled to room temperature for acquiring FTIR spectra.

CH_2Cl_2 was adsorbed on alumina pellet activated, as described above, from a stream of dry air containing

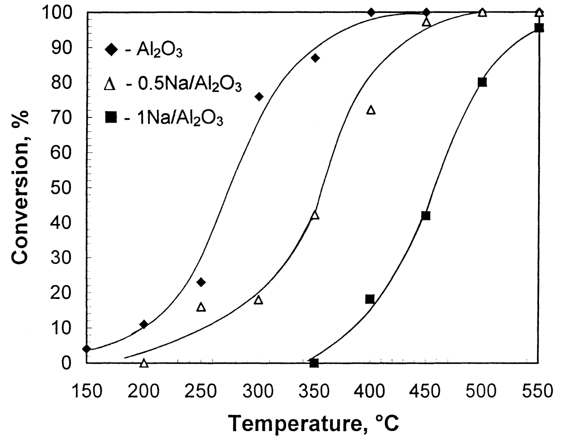


Fig. 1. Conversion of CH_2Cl_2 as a function of the reaction temperature on pure and sodium doped alumina.

10 g of CH_2Cl_2/Nm^3 at 250°C for 0.5 h. The sample was then cooled to room temperature in air and outgassed under pressure 10^{-5} Torr. Alumina pretreated in such way was exposed to pyridine. The spectra of adsorbed pyridine were registered as described above. IR spectroscopic studies are in line with such model.

3. Results

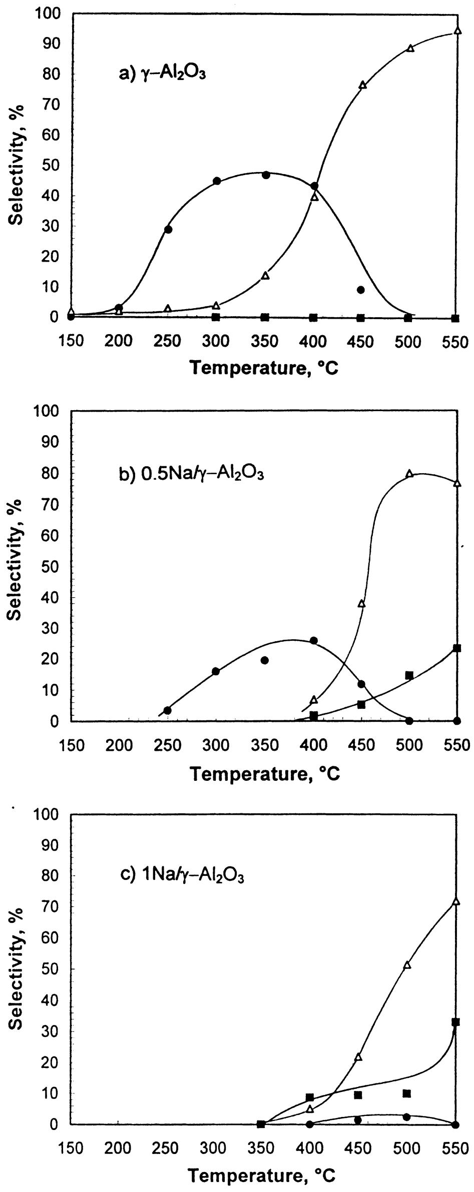


Fig. 2. Selectivity to CH_3Cl (●), HCl (△) and Cl_2 (■) on pure and sodium doped alumina.

Fig. 1 shows the conversion of CH_2Cl_2 as a function of the reaction temperature on pure γ-Al_2O_3, 0.5Na/γ-Al_2O_3 and 1Na/γ-Al_2O_3. It may be seen that the presence of sodium dramatically decreases the catalytic activity, the conversion at 400°C which was 100% in case of pure γ-Al_2O_3, drops to ca. 20% after deposition of 1 wt.% of sodium. Fig. 2(a–c) compares the selectivities to chlorine containing products (CH_3Cl, HCl, Cl_2) on pure and sodium doped samples as a function of the reaction temperature. It is noteworthy, that in the temperature range 250–450°C CH_3Cl is the main product on pure γ-Al_2O_3, its amount decreases after deposition of 0.5 wt.% of Na (sample 0.5 Na/Al_2O_3) and it is practically not formed in the whole investigated temperature range on 1 Na/γ-Al_2O_3. As regards other chlorine-containing products, only HCl is detected in the case of pure γ-Al_2O_3 whereas on sodium containing samples both HCl and Cl_2 appear, the amount of Cl_2 increasing with the increase of Na-loading. Another striking difference between the catalysts is their behaviour in the total oxidation of the hydrocarbon part of the reactant (Fig. 3(a–c)). When pure γ-Al_2O_3 is used as catalyst, CO dominates over CO_2 at lower temperature, at higher temperature mainly the formation of CO_2 is observed. Contrary to that, on 0.5Na/Al_2O_3 and 1Na/Al_2O_3 both CO and

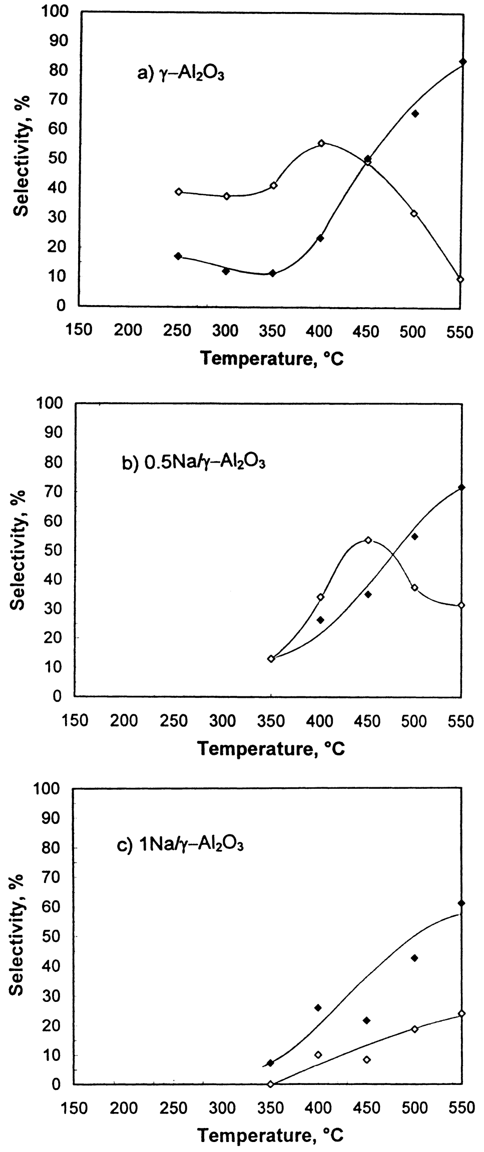


Fig. 3. Selectivity to CO (◇) and CO_2 (◆) on γ-Al_2O_3 and sodium doped alumina.

CO_2 are formed in similar proportions in the whole investigated temperature range. For comparison Fig. 4 summarizes the activity and selectivity data obtained on commercial alumina. It may be seen that considerable amounts of chlorine are formed above 400°C similarly as in the case of sodium containing samples, but at variance with pure Al_2O_3, where chlorine is absent in the whole temperature range.

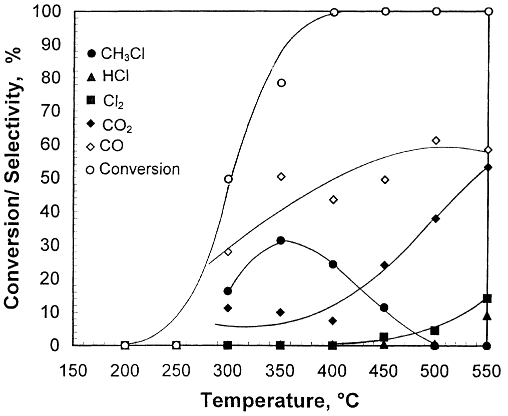
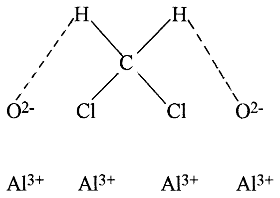


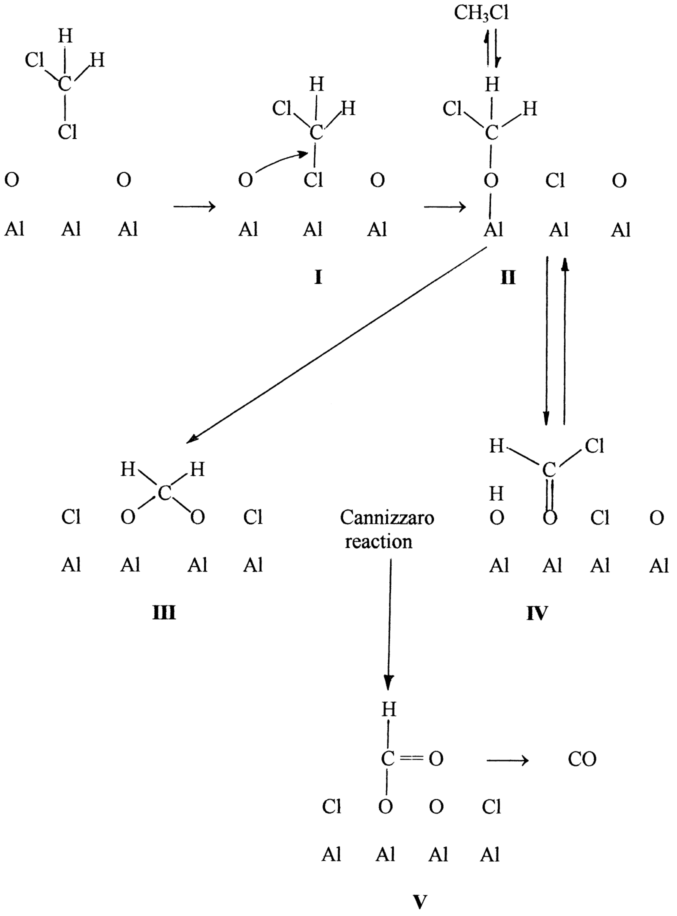
Fig. 4. Conversion of CH_2Cl_2 and selectivity to the reaction products as a function of the reaction temperature on commercial γ-Al_2O_3. Conversion of CH_2Cl_2 (○), selectivity to: CH_3Cl (●); HCl (▲); Cl_2 (■); CO (◇); CO_2 (◆).



Scheme 1.

4. Discussion

Let us start from the discussion of the reaction of CH_2Cl_2 at lower temperatures, when CH_3Cl is the main intermediate product on pure γ-Al_2O_3, accompanied by the formation of CO and small amount of CO_2, but no HCl appears in the product. The observation that CO dominates over CO_2 indicated that carboxylate-type surface species are formed on interaction of CH_2Cl_2 with the γ-Al_2O_3 surface. IR spectra of pyridine adsorbed on Al_2O_3 revealed the peaks at 1451 and 1498 cm^{-1} (cf. Fig. 6) indicating that only Lewis acid sites are present. They reflect the presence of bare aluminum ions on (1 1 1) planes of γ-alumina mainly exposed by small particles. We have therefore assumed that two types of surface complexes may be formed on adsorption of CH_2Cl_2. When CH_2Cl_2 is introduced at lower temperatures the chlorine atoms fill the vacant oxygen sites above Al ions to form a bidentate species (Scheme 1). This brings the two



Scheme 2.

hydrogen atoms near the adjacent oxide ions of the surface to form OH groups. Two-sites adsorption of CH_2Cl_2 leaves a certain amount of isolated sites unoccupied. Indeed, when the sample of Al_2O_3 after adsorption of CH_2Cl_2 was exposed to pyridine vapour in situ in the IR cell, bands of coordinatively bonded pyridine appeared in the spectrum [5]. The unoccupied Lewis acid sites may be involved in another possible type of CH_2Cl_2 adsorption, namely a single-site adsorption through a chlorine apex (Scheme 2(**I**)).

These species may undergo a nucleophilic attack by adjacent surface O^{2-} ions (analogous to S_N2 reaction) and form surface chloromethoxy groups (species II). This process is equivalent to 'hopping' of the Cl–CH_2 species along the surface [6]. This species may either pick up a surface hydrogen and desorb as CH_3Cl, or its chlorine atom may be now captured by another surface oxygen vacancy and by repetition of a S_N2 reaction a bidentate methoxy species may be formed (species III). It may also undergo a parallel reaction, in which a hydrogen atom may be abstracted from chloromethoxy group to form an OH^- group leaving an adsorbed chloroformaldehyde (species IV). Cannizzaro type reaction between species III and IV will give adsorbed formate precursor (V) which decomposes releasing CO. The formation of surface formate groups is confirmed by IR spectroscopy (Fig. 7). After adsorption of CH_2Cl_2 on Al_2O_3 at 250°C a strong band at 1592 cm^{-1} appears which may be assigned to vibrations of carboxylate structures [10]. The mechanism of the desorption of CH_3Cl is not clear. One of the possibilities could be the hydride transfer from

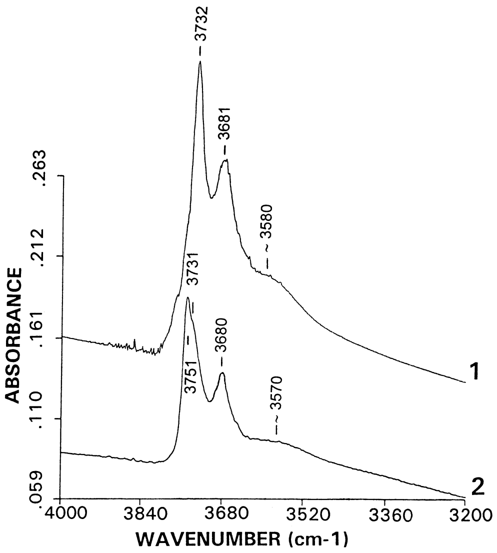


Fig. 5. IR spectra of samples activated in vacuum at 450°C. (1) γ-Al_2O_3, (2) 1Na/ γ-Al_2O_3.

species III to species II instead of IV with the formation of adsorbed formate and desorption of CH_3Cl. This model will account for the simultanous appearance of CH_3Cl and CO in the products of the oxidation of CH_2Cl_2 in the lower temperature range, and the absence of HCl. The chloride ions incorporated into the surface of Al_2O_3 are responsible for deactivation of the catalysts. At higher temperatures the reaction proceeds directly through Scheme 1, the carbon atoms being oxidized by gas phase oxygen molecules to CO_2, and HCl being desorbed from the surface so that only CO_2 and HCl are observed in the products.

IR spectra indicate that pure γ-Al_2O_3, after dehydroxylation at 450°C for 1 h, contains at its surface five different kinds of OH groups. Two of them with stretching frequencies 3681 and 3732 cm^{-1} prevail, other three are visible as shoulders at 3755, 3772 and 3790 cm^{-1}. Deposition of Na leaves the band at 3681 unchanged, but eliminates to a high extent the OH groups responsible for the band at 3732 cm^{-1}, therefore the shoulder at 3751 cm^{-1} becomes the main band (Fig. 5). According to Ivanov et al. [7] this band is generated by the influence of Na^+ cations on adjacent OH groups. Comparison of the frequencies of OH groups observed here with those summarized by Knözinger [8] shows that deposition of Na eliminates the OH groups located between exposed octahedrally and tetrahedrally coordinated Al ions, but does not influence the OH groups located in the centre of three exposed octahedrally coordinated Al^{+3} ions. This could have been expected from the analysis of the structure of sodium aluminate. Namely, in this compound which has a layered spinel structure sodium ions are located above the centre of three oxygen ions linking octahedrally and tetrahedrally coordinated Al ions, because the tetrahedral site has higher negative charge.

Another structural effect should also be mentioned. Sodium deposited at the surface eliminates protons. Therefore, the dehydroxylation by recombination of surface OH groups becomes limited and the concentration of surface oxygen vacancies is decreased. As a result the concentration of exposed Al ions responsible for Lewis acidity is also decreased.

The IR spectra registered after adsorption of pyridine (Fig. 6) indicate that pyridine reacts with all OH groups present at the surface except those responsible for the band at 3680 cm^{-1}, forming H bonds through its aromatic electron system, as indicated by the appearance of the broad band with maximum at 3580 cm^{-1}. Elimination of the OH band at 3731 cm^{-1} by deposition of sodium prevents the formation of H-bonds by pyridine and makes its adsorption much weaker. The IR spectra in the 1300–1700 cm^{-1} range show that on γ-Al_2O_3 Lewis sites formed by exposed Al ions are present and pyridine is adsorbed strongly, remaining even after heating at 450°C, whereas on Na–γ-Al_2O_3 its adsorption is much smaller and disappears almost completely already after heating at temperatures higher than 150°C, the amount adsorbed decreasing with the increasing Na loading. This supports the conclusion that the deposition of sodium significantly reduces the surface concentration of exposed Al-ions.

The IR spectra registered after adsorption of CH_2Cl_2 on γ-Al_2O_3 and Na/γ-Al_2O_3 differ considerably (Fig. 7). In the range of OH stretching vibrations two strong bands at 3010 and 2920 cm^{-1} and a weak band at 2850 cm^{-1} appear in the case of γ-Al_2O_3. They are due to the ν_{as} and ν_s vibrations in the CH_2 group of CH_2Cl_2 adsorbed in a mode showed in Scheme 2(**I**) [9]. In the case of Na/γ-Al_2O_3 a complex spectrum appears with bands at 3005, 2980, 2916, 2852 cm^{-1} and a shoulder ca. 2960 cm^{-1}. It is obvious that besides the surface species showed in Scheme 2(**I**) a second species is formed at the surface,

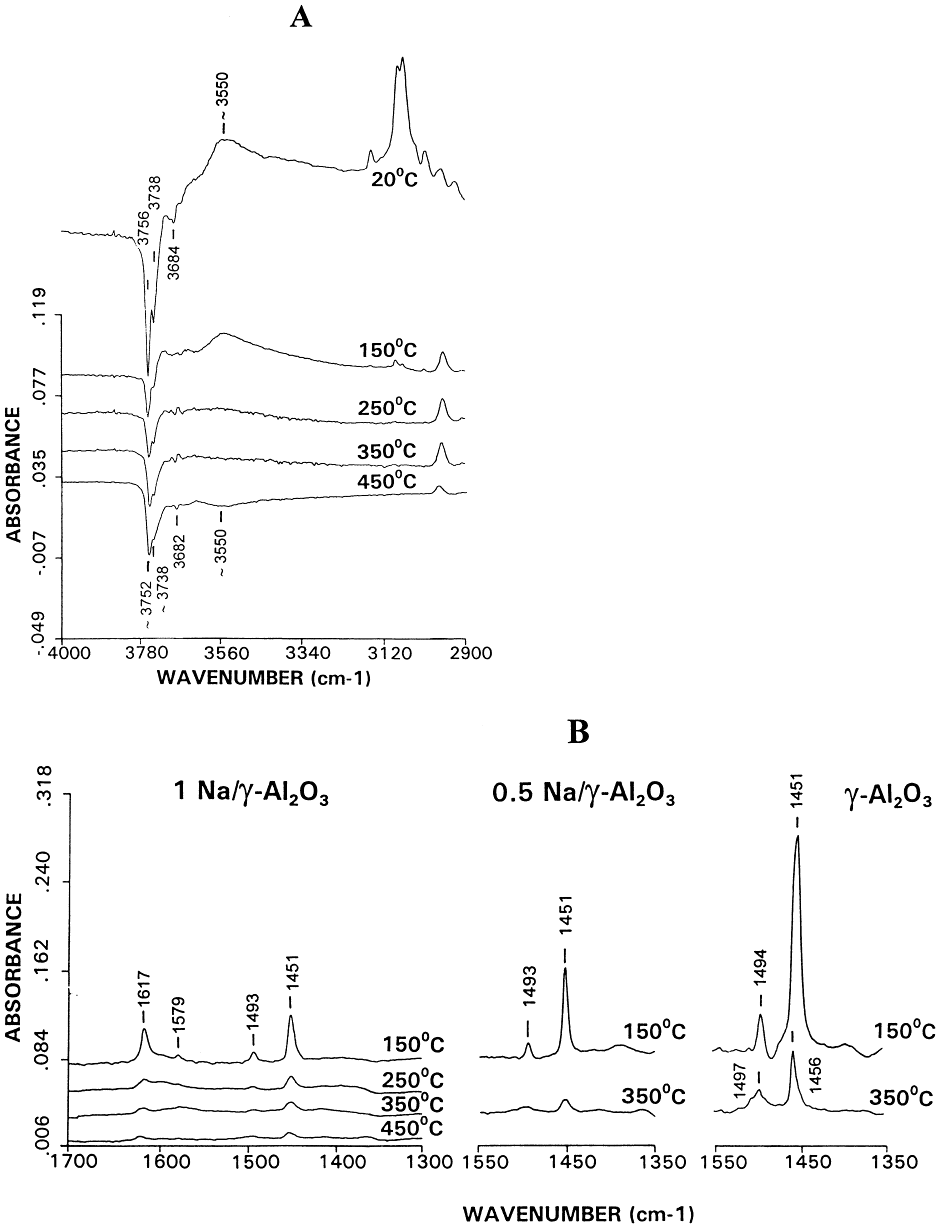


Fig. 6. The difference IR spectra of 1Na/γ-Al_2O_3, 0.5Na/γ-Al_2O_3 and γ-Al_2O_3 after adsorption of pyridine at room temperature and its desorption on heating to 450°C. The spectrum of Al_2O_3 registered before the experiment has been substracted. (A) stretching vibration range, (B) deformation vibration range.

characterized by bands at 2980, 2960 and 2852 cm^{-1}. The bands at 2960 and 2852 cm^{-1} may be assigned to ν_{as} and ν_s of C–H vibrations in the CH_3 group. The strong band at 2980 cm^{-1} may also be due to asymmetric stretching vibrations of C–H bond in CH_3 but in a different chemical surrounding. The presence of CH_3 groups on the surface of Na/γ-Al_2O_3 is confirmed by the analysis of IR spectra in deformation vibrations range of C–H bonds (Fig. 7(b)). Namely, a strong band appears at 1467 cm^{-1} accompanied

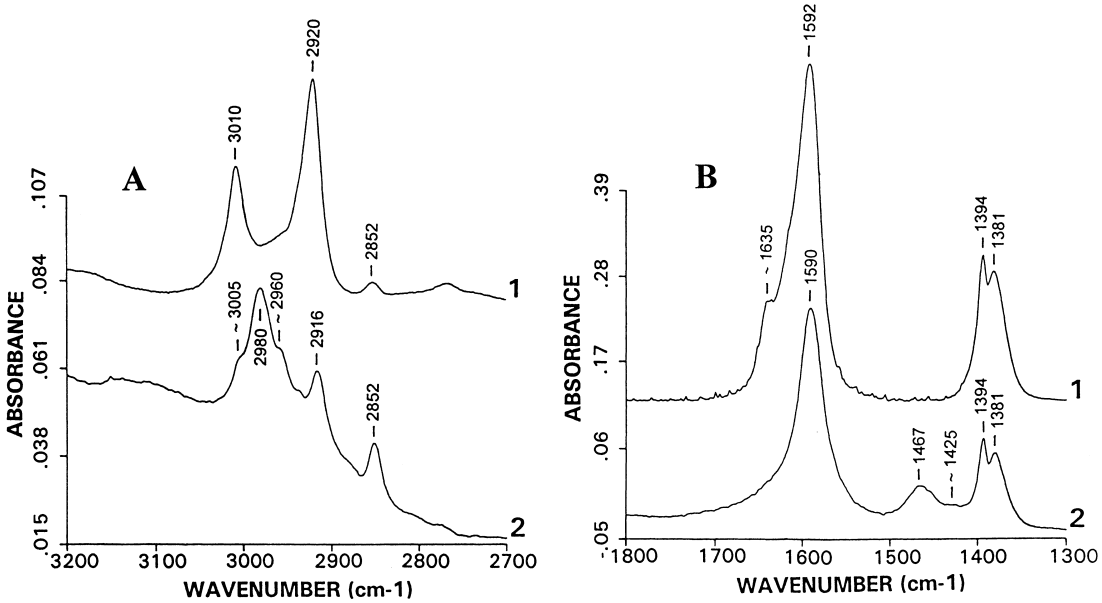


Fig. 7. The difference IR spectra of CH_2Cl_2 after adsorption on γ-Al_2O_3 (curve 1) and 1Na/γ-Al_2O_3 (curve 2) and outgassing at 250°C for 5 min (the spectra of Al_2O_3 and 1Na/γ-Al_2O_3 substracted, respectively). (A) stretching vibration range, (B) deformation vibration range.

by a shoulder at ca. 1425 cm^{-1} after adsorption of CH_2Cl_2 on Na/γ-Al_2O_3, which are not present in the case of CH_2Cl_2 adsorption on pure γ-Al_2O_3. These bands can be assigned to C–H deformation vibrations in CH_3 group linked to oxygen.

It may be thus concluded that the surface of γ-Al_2O_3 on which Na^+ ions have been deposited contains a much smaller concentration of oxygen vacancies, and hence its Lewis acidity, related to exposed Al ions, is also strongly decreased. Simultaneously, protons become substituted by Na^+ ions and the concentration of OH groups is significantly reduced. This has a dramatic effect on catalytic behaviour. Four main differences between the catalytic properties of Na/γ-Al_2O_3 and pure γ-Al_2O_3 should be mentioned:

- total catalytic activity of Na/γ-Al_2O_3 is strongly reduced in comparison to pure γ-Al_2O_3;
- no CH_3Cl is formed, which is the main intermediate product on γ-Al_2O_3 in the temperature range 250–450°C;
- Cl_2 appears in the products, which is absent on γ-Al_2O_3, its amount increasing with temperature;
- at all temperatures the amount of CO_2 is larger than CO at variance with γ-Al_2O_3, where the amount of CO dominates at lower temperatures, whereas that of CO_2 dominates at higher temperatures.

These differences seem to indicate that parallel to the two mechanisms operating at the surface of γ-Al_2O_3 at lower and higher temperatures, respectively (Scheme 2(**I** and **II**)), a new reaction pathway opens when sodium is deposited at the surface. As discussed earlier, on pure γ-Al_2O_3 containing higher concentration of exposed Al ions with Lewis acid properties, the reaction starts by adsorption of CH_2Cl_2 through chlorine atoms, which fill the oxygen vacancies. One can speculate that on the surface with small concentration of oxygen vacancies, exposing mainly oxygen ions of basic properties, the reaction would start by adsorption of CH_2Cl_2 through its hydrogen atoms. Further studies are required to elucidate the mechanism of transformations of such species, resulting in evolution of free chlorine molecules.

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