Journal of Catalysis 278 (2011) 71–77

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Characterization of the active sites on the surface of Al_2O_3 ethanol dehydration catalysts by EPR using spin probes

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ARTICLE INFO

Article history:
Received 17 August 2010
Revised 13 November 2010
Accepted 20 November 2010
Available online 31 December 2010

Keywords:
Alumina
Acceptor sites
Anthracene
Ethanol dehydration
EPR

ABSTRACT

Several pure and doped alumina samples were characterized by EPR using spin probes and tested in ethanol dehydration. It was found that the concentrations of the electron acceptor sites and the catalytic activity increased when alumina was modified with chlorides and sulfates. Meanwhile, the number of the electron donor sites decreased. A very good correlation between the concentration of the weak acceptor sites and the catalytic activity of the acid-modified catalysts almost passing through the origin of the coordinates was obtained for all the studied samples. Alumina poisoning with sodium resulted in the decrease in the catalytic activity and the concentration of the weak acceptor sites. Therefore, it appears that the weak acceptor sites tested using anthracene are related to the sites active in the ethanol dehydration reaction.

1. Introduction

Light olefins (ethylene, propylene and butylenes) are important intermediates in petroleum industry. Ethylene is the most widely produced light olefin. It is the key precursor for the synthesis of ethylene oxide, polyethylene and styrene.

Today, practically all ethylene is produced by steam cracking of oil and liquefied petroleum gas (propane–butane fraction) [1]. Due to the limited natural oil resources, their irregular distribution in the world and high prices of crude oil, dehydration of lower alcohols, in particular bioethanol and biobutanol, to the corresponding olefins tends to become a competitive and promising approach that attracts significant attention of researchers.

Many solid materials are known to catalyze alcohol dehydration [2–7]. In a number of papers, it was shown that dehydration of alcohols over solid catalysts takes place predominantly on the acid sites. The presence of strong acid sites on alumina catalysts increases the alcohol conversion [8]. However, it was reported that the concentration of the acid sites was a more important factor than their strength because this reaction is not particularly sensitive to the strength of the acid sites [9,10].

Many physicochemical methods can be used for determining the nature, strength and concentration of the surface acid sites. Total acidity can be estimated by potentiometric titration with n-butyl amine [11]. Temperature-programmed desorption (TPD) of ammonia makes it possible to compare the strength and concentration of acid sites on catalysts with substantial differences in acidity [12]. UV–vis spectroscopy using irreversible adsorption of organic bases with different acid strength pK_a, such as pyridine ($pK_a = 5.3$) and piperidine ($pK_a = 11.1$), allows one to determine relative concentrations of the acid sites of different strengths [13]. FTIR spectroscopy of adsorbed bases is probably the most widely used method for determination of the surface acidity. Adsorption of such bases as ammonia, pyridine and CO makes it possible to distinguish Lewis and Bronsted acid sites and determine their strength and concentration [11,14,15].

However, these methods characterize all acid sites, many of which may be absolutely inactive. An alternative method for characterization of the active sites on the surface of acid or base catalysts is EPR using spin probes formed on the surface after adsorption of initially diamagnetic molecules [16–20]. This method is selective only to the active sites initiating the transformation of the adsorbed donor or acceptor molecules to the corresponding radical anions or radical cations.

Oxide catalysts with relatively strong acidity are known to possess surface electron acceptor sites capable of oxidizing adsorbed donor molecules by single electron transfer (SET) mechanism [17,21,22]. This process results in the formation of radical cations from the adsorbed aromatic molecules. In many cases, these radical cations are readily detected by EPR and act as spin probes that are formed on the active acceptor sites. Their concentration characterizes the concentration of the acceptor sites [17]. Meanwhile, the relative strength of the sites can be evaluated using donor molecules with different ionization potentials. This method

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doi:10.1016/j.jcat.2010.11.015

is characterized by easy sample pretreatment using calcination in air, the possibility of studying many samples in one adsorption experiment, and reasonably high precision.

In the current paper, we report on the development of a simple technique for characterization of the weak acceptor sites on alumina-based catalysts using anthracene as the spin probe and demonstrate the existence of a good correlation between the concentration of the acceptor sites measured by this method and the ethylene formation rate during the ethanol dehydration.

2. Materials and methods

A commercial alumina sample supplied by Condea (SA = 210 m^2/g) was used in the experiments on the development of the method for testing weak acceptor sites. According to the chemical analysis data provided by the manufacturer, the sample contained about 20 ppm Na_2O, 100 ppm Fe_2O_3 and 120 ppm SiO_2 as the main impurities.

A commercial aluminum oxide AOK-63-22 (Katalizator, Russia) was used as the starting material for synthesis of chlorinated and sulfated alumina catalysts. Chlorinated aluminum oxides were prepared by incipient wetness impregnation of the commercial Al_2O_3 sample at 20 °C. About 3 g of the 0.5–1.0 mm granules of the Al_2O_3 samples was impregnated with 3.4–3.6 ml aqueous solutions of HCl with concentrations 0.24, 0.48 and 0.96 M, followed by drying at 120 °C for 6 h and calcination at 550 °C for 4 h. The volumes of the solutions used for impregnation were equal to the total pore volume of alumina determined using pure water. The hydrochloric acid concentrations were calculated to yield catalysts containing 1, 2 and 4 wt.% Cl^- ions.

Sulfated alumina samples were prepared using a similar procedure. Aqueous solutions of ammonium sulfate with concentrations 0.18, 0.36 and 0.72 M were used for incipient wetness impregnation. The concentrations were calculated to yield samples containing 2, 4 and 8 wt.% SO_4^{2-} ions. Modification of the AOK-63-22 alumina with sulfates and chlorides did not affect much its surface area that remained about 240 m^2/g for all the studied acid-doped catalysts.

Alumina samples with 0, 0.3, 0.6 and 0.9 wt.% Na were prepared using ultrapure aluminum hydroxide (Condea) containing 0.001 wt.% Na_2O and 0.01 wt.% Fe_2O_3 as the main impurities. It was subjected to the incipient wetness impregnation with NaOH solutions of calculated concentrations followed by drying and calcination in air at 550 °C. The synthesized catalysts had the surface areas between 210 and 220 m^2/g and pore volumes 0.42–0.45 cm^3/g.

The surface areas of the samples were determined by the BET method from nitrogen adsorption isotherms at 77 K using a Micromeritics ASAP 2400 instrument. The samples were activated by evacuation at 300 °C for 3 h.

The EPR spectra were recorded at room temperature using an X-band ERS-221 spectrometer at 20 dB attenuation with typical microwave power 3 mW. The spectrometer operation and the analysis of the obtained results were performed using a PC and a software package EPR-CAD developed in our laboratory. The concentrations of the paramagnetic species were determined by numerical double integration with baseline compensation. A DPPH standard was used for calibration.

The experimental procedure was generally similar to the one used earlier for characterization of the donor sites and strong acceptor sites [16]. Before adsorption, the samples were activated in air at 400 °C. Electron donor sites were characterized by adsorption of 1,3,5-trinitrobenzene from 2×10^{-2} M solution in toluene. Strong acceptor sites were characterized using toluene as the donor molecule. Weak acceptor sites were characterized using anthracene adsorption from 4×10^{-2} M solution in toluene. After an activated sample was filled with a desired solution, the ampoule was sealed. The concentrations of the corresponding sites were assumed to equal the maximum concentrations of the radical species obtained after heating the samples with the adsorbed probe solution at 80 °C for 12 h.

The catalytic activity of the samples in ethanol dehydration was determined in a system with a differential flow reactor made of quartz at 330–350 °C and atmospheric pressure. The volume of the loaded catalyst was equal to 1 cm^3 (0.5–1.0 mm fraction), the contact time was 0.5 s. The products were analyzed using a Tsvet-500 gas chromatograph equipped with a flame ionization detector and Porapak S column. The ethylene formation rate at low conversion was used as the measure of the catalytic activity.

3. Results and discussion

3.1. Method for characterization of weak acceptor sites

Until now in our group, we paid most attention to the investigation of the strongest acceptor sites capable of ionizing aromatic molecules with high ionization potentials, such as benzene, chlorobenzene and toluene [17,18,23–27]. Such sites are present in considerable concentrations only on the strongest acid catalysts – high-silica zeolites and sulfated metal oxides. In particular, it was shown that such very strong acceptor sites might be responsible to skeletal isomerization and cracking of light alkanes over sulfated zirconia [18,24,28]. However, the concentration of such sites on conventional acid catalysts, such as Al_2O_3, is very low [16]. As the activity of pure and modified aluminum oxides in alcohol dehydration reactions is relatively high, there is no doubt that the strongest acceptor sites can hardly account for their activity. Meanwhile, it is well known that weaker acceptor sites present in considerable concentrations on the surface of many oxides can be characterized using aromatic molecules with lower ionization potentials, such as anthracene or perylene, as spin probes [29–31]. So, development of a simple method for routine characterization of weak acceptor sites using such probes appeared to be very important. Such method should give quantitative information on the concentrations of such sites on different alumina catalysts and assist in evaluation of their role in the alcohol dehydration reactions.

To find a test donor molecule suitable for characterization of weak acceptor sites on the Al_2O_3 surface, we carried out adsorption of different aromatic compounds on commercial Al_2O_3 sample (Condea). Liquid aromatic compounds were adsorbed in pure form, whereas solid substances were adsorbed from their solutions in p-xylene. The used compositions together with the ionization potentials of the donors and the concentrations of the radical species obtained after activation at 500 °C and 300 °C are reported in Table 1. The obtained data show that the highest concentration

Table 1
Effect of the donor probe and activation temperature on the concentration of radicals (N) observed on Al_2O_3.

Donor	Ionization potential, eV	N, 10^{16} g^{-1}, T_{act} = 500 °C	N, 10^{16} g^{-1}, T_{act} = 300 °C
Toluene	−8.83	4	2
P-xylene	−8.44	10	1.6
Biphenyl (1 M in p-xylene)	−8.16	8	–
Naphthalene (1 M in p-xylene)	−8.14	10	3.2
Anthracene (0.25 M in p-xylene)	−7.44	40	20

of the radical cations was obtained using anthracene that has the lowest ionization potential among the studied aromatic compounds. Since our goal was to test relatively weak acceptor sites, it seemed to be the most suitable donor for this study.

Fig. 1 presents the EPR spectra obtained after adsorption of toluene, 0.04 M anthracene solution in toluene, which were used for characterization of the strong and weak acceptor sites, respectively, and 0.02 M 1,3,5-trinitrobenzene (TNB) solution in toluene used for characterization of donor sites. The spectra are presented using the same magnification coefficient to show their relative intensities. The spectrum obtained after TNB adsorption can be attributed to its radical anions formed on the electron acceptor sites. The predominant feature of this spectrum is an anisotropic hyperfine splitting on a single nitrogen atom with $A_{zz} = 31$ G. The spectra obtained after adsorption of the donor molecules are singlet lines with $g = 2.003$. They can be attributed to organic radical cations formed by polycondensation of the initial radical cations with neutral molecules on the acceptor sites [17,27]. The mechanism of this process is discussed in more detail below.

Anthracene is a solid compound poorly solvable in organic solvents. So, our second step was to optimize the solvent, anthracene concentration and adsorption procedure to obtain reproducible results. Anthracene adsorption through the vapor phase used in some previous studies was unsuitable for us as it is a slow and too complicated procedure that can hardly be used for routine comparison of many samples. Table 2 summarizes experimental data on the concentrations of the radical species generated after anthracene adsorption on the same commercial Al_2O_3 sample (Condea) activated at 300 °C from solutions of different concentrations in two solvents (toluene and p-xylene) at room temperature and at 80 °C. The latter temperature was previously found to be the most suitable for characterization of the electron donor sites on alumina using 1,3,5-trinitrobenzene as the spin probe [16]. The obtained results show that the concentrations of generated radical cations substantially depend on the anthracene concentration in the solution. Meanwhile, the choice of the aromatic solvent had almost no effect on it. So, we used toluene as the solvent in the subsequent experiments.

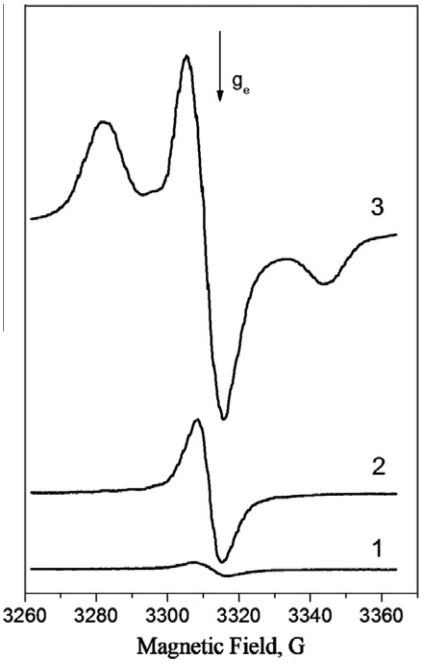

Fig. 1. EPR spectra registered after adsorption of toluene (1), 0.04 M anthracene solution in toluene (2), and 0.02 M 1,3,5-trinitrobenzene (3) solution in toluene on Al_2O_3 activated at 400 °C followed by heat treatment at 80 °C for 12 h.

Table 2
Influence of the probe concentration, solvent, reaction temperature and time on the concentration of the radicals (N) generated after anthracene adsorption on Al_2O_3.

Solvent	Concentration (M)	N, 10^{16} g^{-1}, 2 h at 20 °C	N, 10^{16} g^{-1}, 3 h at 80 °C	N, 10^{16} g^{-1}, 12 h at 80 °C
Toluene	0.25	–	–	22.5
Toluene	0.04	4.4	15.6	21.2
Toluene	0.02	4.6	10.2	14.4
Toluene	0.01	4.6	7.0	7.6
Toluene	0.005	4.7	6.8	6.8
P-xylene	0.025	8.9	13.2	13.6
P-xylene	0.04	–	–	19.8
P-xylene	0.25	–	–	20.0

Apparently, at low concentrations, anthracene did not reach all the active sites. It was adsorbed on other surface sites not capable of generating the radical cations even if the total number of anthracene molecules in solution was more than sufficient. The maximum anthracene solvability in toluene at room temperature obtained by us was about 0.04 M. When we heated the solution to 80 °C, we managed to dissolve more anthracene, reaching 0.25 M concentration. However, the total concentration of the generated radical cations did not change, indicating that 0.04 M concentration was sufficient to detect all the acceptor sites. So, we used the latter concentration in the subsequent experiments as the experimental procedure was much simpler in this case.

It is notable that substantially higher concentrations of the radical species were obtained after activation at 500 °C compared to the activation at 300 °C. The activation at higher temperatures is known to free higher percentage of the surface sites from chemisorbed water. To determine optimum activation temperatures, we studied the dependence of the concentration of the radical cations generated after anthracene adsorption on alumina on the activation temperature (Fig. 2). The concentrations of the strong acceptor sites tested using toluene following the previously reported procedure [16] are also shown for comparison.

One can see that it is possible to detect substantially higher concentrations of the acceptor sites using anthracene as the spin probe. The concentration of the weak acceptor sites tested with anthracene exceeded that of the stronger acceptor sites tested using toluene by more than an order of magnitude. Still, the determined concentration of the weak acceptor sites is below 1% of the monolayer.

Using a donor with a lower ionization potential, such as anthracene, we test the total concentration of the sites capable of ionizing

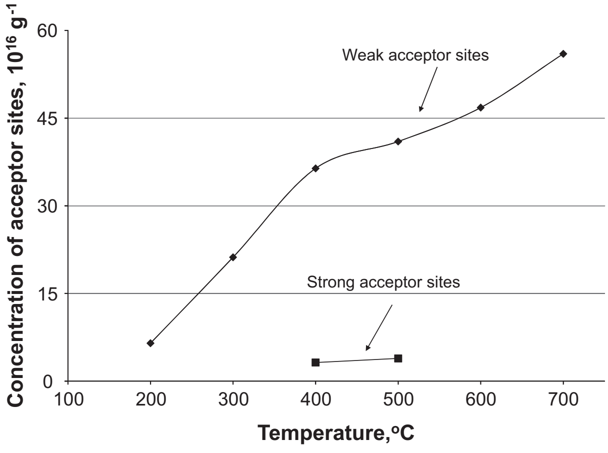

Fig. 2. Effect of pretreatment temperature on the concentrations of weak acceptor sites tested using anthracene and strong acceptor sites tested using toluene.

this donor and possible polycondensation products formed from it. So, this concentration includes the strong sites as well. However, in this study, we shall refer to such sites as weak. Although the sites tested with anthracene are weaker, they are still obviously very active as they are capable of generating the radical cations at moderate temperature and must have the electron affinity close to 7.5 eV.

The measured concentration of the weak acceptor sites increased with the activation temperature in the whole studied temperature range. The highest temperature used in this study was 700 °C as separate experiments showed that the phase composition of the sample could change after prolonged treatment at higher temperatures. Apparently, the activation at higher temperatures leads to deeper purification of the surface from adsorbed water and other impurities. However, it was more important for us to work using lower activation temperatures that are closer to the ones used in the catalytic experiments. The minimum temperature that could be used for testing the strong acceptor sites capable of generating radical cations after toluene adsorption was 400 °C. No strong sites were registered after activation at lower temperatures. Meanwhile, the weak sites tested using anthracene were observed on the alumina surface already after activation at 200 °C immediately after desorption of physisorbed water. This feature may be useful for investigation of the samples prepared by calcination at low temperatures or thermally unstable samples.

The evolution of the measured concentration of the paramagnetic species with time was studied for the alumina sample activated at 400 °C (Fig. 3). The Inset in Fig. 3 shows that a substantial concentration of the radical cations was generated immediately after adsorption. Then, this concentration gradually increased. It was found that the maximum concentration of the radical cations was achieved approximately after 200 h at room temperature and gradually decreased thereafter.

The formation of the primary radical cations on the surface acceptor sites is known to be a fast process taking place without substantial activation energy [17]. So, the concentration of the radical cations observed immediately after adsorption can be attributed to the concentration of the sites capable of ionizing anthracene molecules directly. The subsequent growth in the concentration of the observed radical species can be attributed to gradual polycondensation of the adsorbed aromatic molecules. Previously, it was shown that polycondensation according to Eqs. (1) and (2) is readily observed after benzene adsorption on the strong acceptor sites of H-ZSM-5 zeolites [17,27]. The difference of the ionization potentials is the driving force of such polycondensation that follows the electrophilic substitution mechanism:

$$C_6H_6^+ + C_6H_6 \rightleftarrows C_{12}H_{10}^+ + H_2 \tag{1}$$

$$C_{12}H_{10}^+ + C_6H_6 \rightleftarrows C_{18}H_{14}^+ + H_2 \tag{2}$$

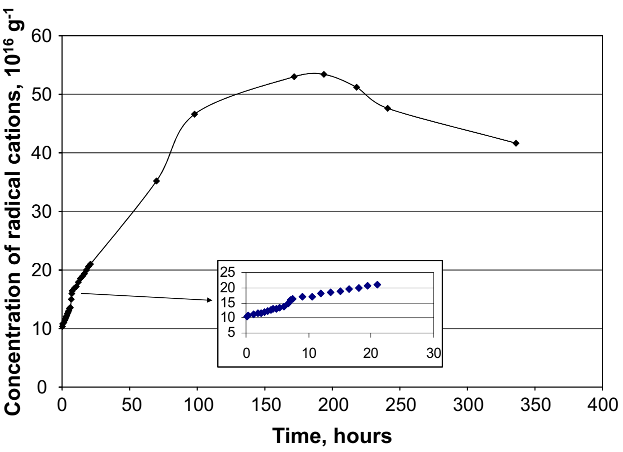

Fig. 3. Dependence of the registered concentration of paramagnetic species on time after adsorption on 0.04 M anthracene solution in toluene at 20 °C on Al_2O_3 (Condea) activated at 400 °C.

Aromatic radical cations are strong electrophiles that can participate in such process. Neutral molecules adsorbed on the surface acceptor sites, which are not sufficiently strong to abstract the electron from the adsorbed aromatic molecules but still have substantial electron affinity, are likely to initiate it as well. This reaction yields organic molecules with larger number of aromatic rings having lower ionization potential. The radical cationic species are generated when the ionization potential of the adsorbed polycondensed structure becomes sufficiently low for the molecule to be ionized. Note that such gradual increase in the concentration of the observed radical cations was not observed in the previous studies using zeolites as the adsorbents [27] due to the limited size of the zeolite channels where the radical cations are generated.

Obviously, this process should be characterized by some activation energy. Indeed, the radical generation rate in the first 100 h after anthracene adsorption on Al_2O_3 at room temperature was approximately constant and equal to 3.7×10^{15} g^{-1} h^{-1} (Fig. 3). Then, it decreased as the concentration approached the maximum between 100 and 200 h after adsorption. At 80 °C, the radical cations were formed substantially faster. The concentration of the radical cations generated in 12 h at this temperature was about 4×10^{17} g^{-1}. This is about 80% of the maximum value obtained at room temperature.

As the process is complex and involves sites of different strengths, it is not possible to determine precisely the activation energy. Note that the minimum strength (electron affinity) of the acceptor sites tested by this method is not exactly equal to the ionization potential of the adsorbed donor molecules. Actually, the method tests somewhat weaker sites as well, and their exact strength is unknown. Alternatively, one can use the concentration of the radical cations generated instantly after adsorption as a better approximation of the concentration of the acceptor sites initiating direct ionization of the adsorbed donor molecules. Still, the procedure involving heating of the sample at 80 °C for 12 h appears to be a simple and readily reproducible technique for characterization of the weak acceptor sites. On all studied samples, the concentrations of the weak acceptor sites determined by this procedure were several times higher than those observed immediately after anthracene adsorption.

Based on the results of these preliminary experiments, we selected the optimum conditions yielding quantitative data on the concentration of the weak acceptor sites with good reproducibility (about 10%) and minimum effort that could be used in routine experiments. In all the following experiments, the catalysts were activated in air at 400 °C. This temperature is close to the one used in the catalytic experiments on the ethanol dehydration. Anthracene was adsorbed from 4×10^{-2} M solution in toluene. The concentration of the weak acceptor was assumed to be equal to the concentration of radical cations generated at 80 °C in 12 h after adsorption.

3.2. Electron acceptor sites and catalytic activity of acid-doped alumina

The developed procedure for investigation of the weak acceptor sites was used for characterization of several alumina catalysts doped with chlorine or sulfate ions. In addition, these samples were characterized using the earlier used methods for determination of the concentrations of the electron donor sites and strong electron acceptor sites [16]. The synthesized catalysts were also tested in ethanol dehydration reaction.

It was found that the modification of alumina with chloride and sulfate ions leads to a substantial increase in the catalytic activity in ethanol dehydration (Fig. 4). The addition of both ions is known to increase the alumina acidity. Chlorinated alumina is a widely used acidic catalyst support whereas sulfated alumina is known to have very strong acid sites and was even claimed to be a solid superacid [32].

We used the ethylene formation rate at low ethanol conversion as the quantitative measure of the catalytic activity in the reaction leading to the desired product. The reaction was carried out at 330 °C with 0.5 s contact time. Coking was negligible under these conditions. Modification with sulfates was found to be more efficient than modification with chlorides, producing more active catalysts. For the catalysts containing 2 and 4 wt.% of the anions, the sulfated catalysts were approximately twice more active. Note that the molar weight of the sulfate group is almost 3 times higher than that of the chloride. So, the number of sulfate groups present in the samples with the same weight concentration of the anions is about 3 times lower. This result indicates that the strength of the generated acid sites is important as stronger acid sites are formed over sulfated alumina.

Fig. 5 shows how the concentrations of the donor and acceptor sites depend on the concentration of sulfates. The experimental values were divided by the concentration of the corresponding sites over pure alumina to make the trends resulting from modification with sulfates more evident. These coefficients are shown in the graph. The concentration of the weak acceptor sites tested using anthracene according to the procedure discussed in detail above linearly grows when the concentration of the introduced sulfates increases from 0 to 8 wt.%. After addition of even low concentration of the sulfates (2 wt.%), the measured concentration of the weak acceptor sites significantly increases. Meanwhile, the measured concentration of the strong acceptor sites depends on the sulfate concentration in a substantially different way. It does not increase much until the introduction of 4 wt.% SO_4^{2-}. After introducing 8 wt.% SO_4^{2-}, the concentration of the strong acceptor sites more than doubles.

In the meantime, the concentration of the electron donor sites gradually decreases with the introduction of sulfates. The donor sites are generally associated with the basic rather than acidic properties of solid catalysts. So, the decrease in their concentration when alumina is modified with sulfates reflects the trend for the basicity decrease. As the concentration of the donor sites and the catalyst activity in the ethanol dehydration reaction change in opposite directions on the introduction of sulfates, almost definitely, the donor sites are not related to the sites active in the ethanol dehydration.

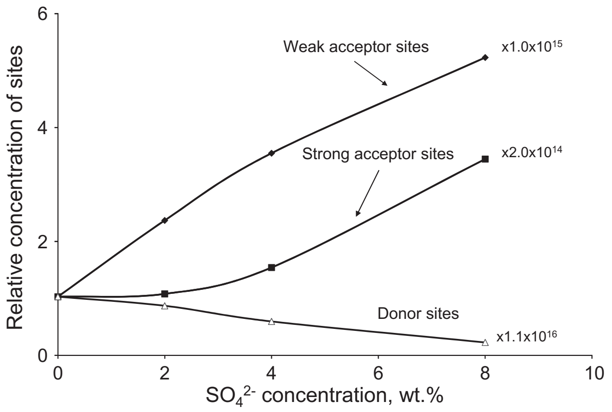

Fig. 5. Effect of the concentration of the sulfates on the concentrations of detected acceptor and donor sites.

Generally, similar trends were observed for the sites of the chloride-doped catalysts (Fig. 6). The concentration of the weak acceptor sites substantially increases after introduction of only 1 wt.% Cl^-. Then, their concentration slowly grows between 1 and 4 wt.% Cl^-. The relative increase in the concentration of the strong acceptor sites after introduction of 1 wt.% Cl^- is not so big compared to that of the weak sites. Then, the growth in the concentration of the strong acceptor sites with the chloride concentration almost parallels that of the weak sites (Fig. 6). Meanwhile, the concentration of the donor sites almost linearly decreases with the addition of the chloride ions.

The obtained data prove that the concentration of the weak acceptor sites correlates with the catalytic activity of the modified alumina catalysts in the ethanol dehydration reaction. Such correlation is illustrated by Fig. 7. It includes data for two commercial alumina samples AOK-62-22 and AOK-78-59 as well as the aluminum oxides modified with chlorides and sulfates. A remarkably good correlation almost passing through the origin of coordinates was obtained for all the studied samples. Therefore, it appears that the weak acceptor sites tested using anthracene are related to the sites active in the ethanol dehydration reaction.

The correlation between the catalytic activity and the concentration of strong acceptor sites was not nearly as good. The obtained results suggest that such strong acceptor sites are not required for alcohol dehydration that can be initiated by much weaker sites present in higher concentration on the surface. This conclusion is quite natural as alcohols can be protonated and undergo dehydration in solutions of strong mineral acids. Meanwhile,

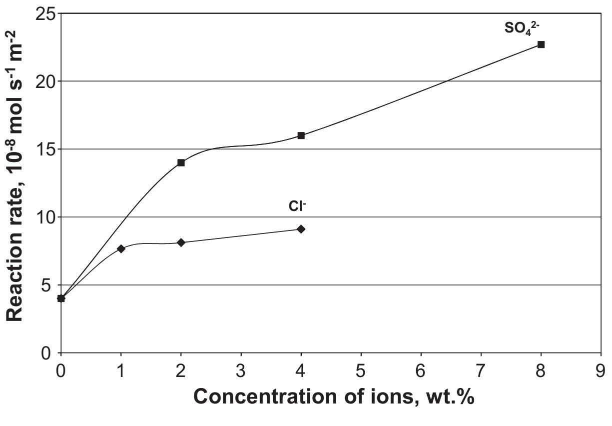

Fig. 4. Dependence of the ethylene formation rate at 330 °C on the concentrations of sulfate and chloride ions.

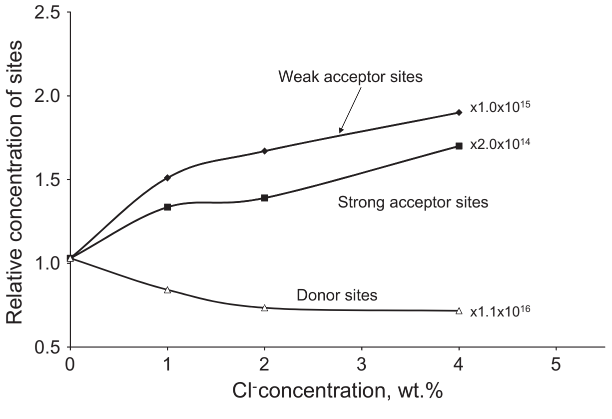

Fig. 6. Effect of the concentration of the chloride ions on the concentrations of detected acceptor and donor sites.

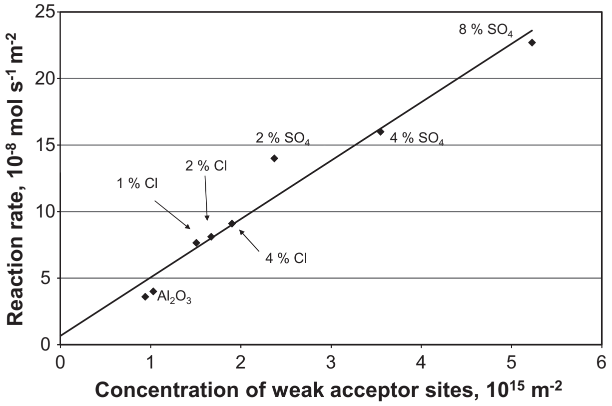

Fig. 7. Dependence of the ethylene formation rate at 330 °C on the concentration of weak acceptor sites on Al_2O_3 and anion-doped Al_2O_3 catalysts.

the strongest acceptor sites of sulfated oxides were earlier suggested to initiate alkane isomerization and cracking at moderate temperatures [24,33]. In the liquid phase, these reactions can be initiated only by superacids [34].

3.3. Electron acceptor sites and catalytic activity of Na-doped alumina

Industrial alumina materials used as the supports, catalysts and sorbents for various processes are known to contain iron, silicon and sodium. The iron and silicon impurities in concentrations below 0.1 wt.% have practically no effect on the catalytic activity. Meanwhile, sodium cations present in concentrations as high as 0.7 wt.% in some industrial alumina samples are known to be poisons for many acid–base catalytic processes. For example, it was shown that the Al_2O_3 with Na concentration 10 ppm was 3–5 times more active in isopropanol dehydration than Al_2O_3 with 180 ppm Na concentration and approximately 180 times more active than the one with 3020 ppm Na concentration [35]. Generally, similar results on the effect of sodium concentrations below 1% were also reported for ethanol dehydration [36]. To study the effect of sodium on the catalytic activity and concentration of the acceptor and donor sites, we prepared a series of alumina samples with sodium concentrations varying from 0 to 0.9 wt.% using ultrapure aluminum hydroxide as the starting material.

The effect of sodium on the concentrations of the weak acceptors sites and the catalytic activity in ethanol dehydration is illustrated in Fig. 8. The ethylene dehydration reaction was carried out at 350 °C with 0.5 s contact time. Slightly higher temperature was selected in this case because the activity of Na-doped samples was lower than that of the anion-doped catalysts. The obtained results indicate that the sodium addition results in a substantial decrease in both the concentration of the acceptor sites and the catalytic activity. Even a small sodium amount about 0.3 wt.% led to the decrease in the catalytic activity by almost a factor of two. Meanwhile, no apparent effect of sodium on the concentration of donor sites was observed.

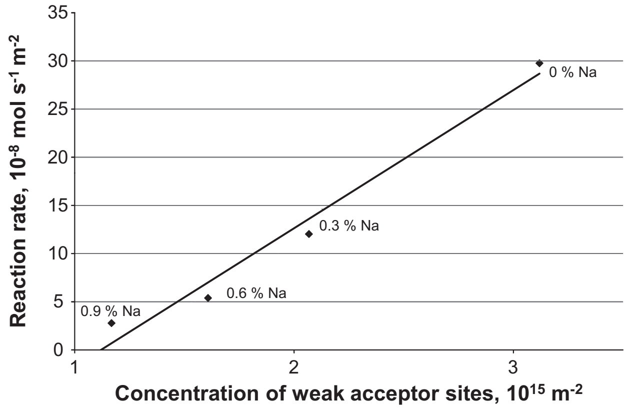

Fig. 8. Dependence of the ethylene formation rate at 350 °C on the concentration of weak acceptor sites on pure Al_2O_3 and Na-doped Al_2O_3 catalysts.

Note that the sodium impurities about 0.2–0.5 wt.% are present in most commercial alumina samples prepared by precipitation or hydration of the hydrargillite thermal activation products. These results clearly indicate that alumina supports with as low sodium concentrations as possible should be used for synthesis of catalysts for ethanol dehydration.

Again, a good correlation between the concentrations of weak acceptor sites tested using anthracene and the dehydration activity of the sodium-doped catalysts was obtained. However, in this case, the linear dependence does not start from the origin of coordinates. These results suggest that some weak acceptor sites are present on the surface of sodium-doped alumina samples with negligible catalytic activity. Most likely, they are formed from the strong Bronsted sites accounting for the weak acceptor sites on sodium-free samples by substitution of the acidic protons with sodium ions.

3.4. The nature of the active sites

The nature of the surface sites accounting for the formation of radical cations after adsorption of aromatic substances on solid catalysts largely remains a mystery despite being known for more than 50 years. It is well known that acceptor sites are observed either in the presence of some transition metals or on acid catalysts [21]. The possibility of ionizing various organic molecules after adsorption on acid catalysts seems to be one of the most intriguing properties of such materials. For instance, benzene with ionization potential 9.2 eV can be ionized after adsorption on high-silica zeolites or sulfated zirconia [17]. No less surprising is the formation of radical cations in substantial concentrations as high as 10^{20} g^{-1} after adsorption of aromatic compounds with low ionization potentials about 7 eV on amorphous alumosilicates [21].

In the literature, the electron acceptor sites have been attributed to Lewis acids sites accepting in this case only one electron instead of an electron pair [37], Bronsted acid sites [38], oxygen radicals formed during the catalyst thermal treatment [39], singlet oxygen [40] and transition metal impurities [31]. However, none of these models has been proven experimentally or theoretically. In fact, no model of surface active sites with the electron affinity approaching the experimental values has been suggested.

In our opinion, the existing close links between the acidity and the electron acceptor ability of acid catalysts seem to indicate that these two generally very different properties are interrelated. So, the observed good correlation between the concentration of the weak acceptor sites and the catalytic activity in ethanol dehydration can help us to understand better the nature of the surface sites accounting for both processes.

Alcohol dehydration in solution can be catalyzed both by acids and bases. Meanwhile, in heterogeneous catalysis, this process is much more efficient over acid catalysts. Apparently, this means that the acid sites of desired strength are much more abundant on the surface of solid catalysts than the active basic sites. This observation seems to indicate that the acid sites have to be rather strong to be active in alcohol dehydration. In any case, we have no reason to believe that this reaction can be initiated by electron transfer on the electron acceptor sites.

The highest dehydration rate was observed when the ratio of Bronsted to Lewis acid sites was as high as possible [41]. H-ZSM-5 zeolite known to possess high concentration of strong Bronsted acid sites and very strong electron acceptor sites was reported to have very high dehydration activity, substantially exceeding that of Al_2O_3 but experiencing fast deactivation due to coking [42]. Alumina modification with sulfates is also known to generate strong Bronsted sites with little effect on the Lewis acid sites. Overall, the analysis of the literature data suggests that the sites active in alcohol dehydration are most likely related to sufficiently strong Bronsted acid sites. However, the contribution of Lewis acid sites that are much more abundant on the Al_2O_3 surface cannot be excluded.

Accurate determination of the active site concentration is a problem for most catalytic processes. The reported concentration of sites active in butanol dehydration on Al_2O_3 determined in poisoning experiments is about $10^{13}\,cm^{-2}$ that is about 1% of the monolayer [43]. Obviously, such poisoning experiments may affect some of the inactive sites in addition to the active ones and can serve as the upper limit of the active site concentration. As this concentration is substantially lower than typical concentrations of the Lewis acid sites or OH-groups determined by FTIR, apparently, only some of them with sufficient strength can initiate this reaction.

The concentration of the weak acceptor sites obtained in our experiments is lower by more than an order of magnitude. Their concentration determined by the developed procedure can be used as the lower limit of the active site concentration. It might be interesting to study other aromatic donors with even lower ionization potentials and compare the results with those obtained in this study using anthracene.

The experimental results obtained in this study seem to support the hypothesis attributing the weak acceptor sites to strong Bronsted acid sites as well. However, only some of such sites are active. Typical concentrations of conventional Bronsted acid sites on acid-doped alumina catalysts are much higher than those of the weak acceptor sites. Furthermore, according to the results of quantum chemical calculations, their electron affinity is very low. Obviously, additional experimental and theoretical studies are required to understand the real meaning of the observed correlations and the true nature of the electron acceptor sites.

4. Conclusions

The developed procedure using anthracene as the spin probe appears to be a simple and readily reproducible technique for characterization of weak acceptor sites by EPR. This method can be used for investigation of the acceptor properties of various catalysts, including thermally unstable ones and the ones obtained after heat treatment at low temperatures.

Modification of Al_2O_3 with sulfate and chloride ions resulted in the increase in the catalytic activity in ethanol dehydration. The concentrations of the weak and strong acceptor sites increased as well. Meanwhile, the concentration of the electron donor sites decreased. This observation suggests that the donor sites are not related to the sites active in the ethanol dehydration. However, a remarkably good correlation between the concentration of the weak donor sites and the catalytic activity of the acid-modified catalysts almost passing through the origin of coordinates was obtained for all the studied samples. So, it appears that the weak acceptor sites tested using anthracene are related to the sites active in the ethanol dehydration reaction. Most likely, both reactions are initiated by sufficiently strong Bronsted acid sites.

A similar correlation may be expected for this reaction over other heterogeneous acid catalysts, including supports other than alumina. It is also very important to study other acid-catalyzed reactions to understand the generality of the suggested approach. The developed method for characterization of the weak acceptor sites can be useful for investigation of the sites active in other catalytic reactions taking place on acid catalysts. We believe that the observed good correlation between the concentration of the weak acceptor sites and the catalytic activity in such typical acid-catalyzed reaction as ethanol dehydration will help to understand better the nature of the surface sites accounting for both processes. Additional experimental and theoretical studies are required to understand the true nature of the catalytically active sites.

Acknowledgment

Financial support by the Russian foundation for Basic Research (Grant 10-03-00691) is acknowledged with gratitude.

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