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Alkylpyridines Transformations over Acidic Catalysts. An Example of Radical Reactions on Ionic Surfaces*

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4-Methyl-, 4-ethyl-, and 4-isopropylpyridine, ethyl-, and isopropylbenzene transformations were studied over the series of amorphous silica-aluminas. The main reactions of alkylpyridines were the transformations of the alkyl side chain. The crucial role of one-electron donor (radical) centres in the mentioned reactions was evidenced by the physicochemical characterization of the catalyst surfaces, the apparent correlation of activity *vs.* active centres concentration, and the dependence of product composition upon reaction conditions.

Key words: alkylpiridines transformations, radical reactions on ionic surfaces, activity *vs.* active centres concentration correlation

Oxide systems, even of such simple structure as those of metals of the main groups possess coexisting active surface centres of differentiated chemical properties. Measurements performed using various methods have proved that, for instance, surfaces thought to be solely of acidic character possess centres of Brønsted and Lewis acidic character [1]. Additionally, centres of a specific character can also differ in strength depending on the surrounding environment in the crystal lattice. The ionic centres of surfaces, whose activity is dependent on the ability to donate or accept an electron pair, or proton exchange, are accompanied by one-electron centres capable of catalyzing transformations of the radical type. As already indicated, these centres usually exist on surfaces irrespective of the existence of ionic centres [2–5]. It is known, however, that on the surface of γ-alumina a number of Lewis type acidic centres also exhibit acceptor properties of a single electron [6].

Kolts and Delzer [7] proposed that the remarkable part of the transformations, which take place during catalytic cracking over magnesia deposited iron and manganese oxides, was of radical character, but the origin of radical activity on the surfaces of catalysts was not clearly defined. For a number of years, Malinowski proposed a concept, according to which, the occurrence of deep heterogeneity of the surfaces of oxide ionic systems is related to the coexistence on them of centres of radical activity.

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*Dedicated to the memory of Professor Stanisław Malinowski in appreciation of his outstanding contributions to acid-base catalysis.

He was convinced, that they play a crucial role in various reactions catalyzed by oxides of metals of the main groups in the periodic table. In our earlier works [3,8], we demonstrated that in the alkylaromatic hydrocarbon transformations over magnesia and its superbasic modifications as well as on superbasic γ-Al_2O_3-K systems, a series of reactions such as dehydrogenation and transalkylation, which take place according to the radical mechanism, do so with the participation of one-electron donors.

In these works, we have tried to demonstrate that one-electron donor centres on ionic surface of acidic character, in spite of their occurrence at several times lower concentration than ionic centres, can play a decisive role in the catalytic activity of the surface. The reactions of some commercially important alkylpyridines were carried out over typical acidic catalysts, such as amorphous aluminosilicates and γ-aluminium oxide. It should be emphasized that the strong basic properties of pyridine derivatives make them poisons of acidic centres on surfaces. Parallel transformations of ethylbenzene and isopropylbenzene under the same reaction conditions were performed for comparison purposes. We demonstrated that base-acid interactions of the reactants with the catalyst surface did not inhibit reactions involving the side chain in amine molecules and that these particular reactions were catalyzed by surface one-electron donor centres.

EXPERIMENTAL

Catalysts. All silica-alumina catalysts (containing 11, 24, 50, 74, and 91% of Al_2O_3) were prepared by simultaneous hydrolysis of aluminium triisopropoxide (Aldrich) and tetraethyl orthosilicate (Fluka) with aqueous ammonia. Silica and γ-alumina were obtained by hydrolysis of the respective orthosilicate or isopropoxide. The solid precipitates were washed with distilled water, dried at 60°C for 24 h, and then at 120°C for the next 24 h, and subsequently calcined at 550°C for 20 h in a stream of air. XRD analysis proved all the catalysts to be amorphous. The real composition of the studied silica-aluminas was established by atomic absorption. The catalysts of enhanced electron donor properties (MgO-Zn, γ-Al_2O_3-Na, MgO-Na) were obtained by evaporation of metals according to the procedure described earlier [8,10,11].

Acidic properties. The intensities of the IR bands at 1640 cm^{-1} or 1450 cm^{-1} of adsorbed 4-ethylpyridine were considered as a measure of the relative concentrations of Brønsted acidic centres on the studied surfaces. Respectively, the intensities of the bands at 1625 cm^{-1} or 1540 cm^{-1} were the measure of Lewis acidic centres concentration [13–15]. The IR spectra were recorded using a Specord 80 apparatus after desorption of alkylpyridine at 300°C. For the IR measurements, the catalyst samples were pressed under 2.2×10^3 kNm^{-2} into thin wafers (10 $mg \cdot cm^{-2}$). A wafer was placed in a vacuum cell in which standard treatment was performed. After evacuation at room temperature to 0.1 $N \cdot m^{-2}$ 4-ethylpyridine was adsorbed at room temperature (10.7 kNm^{-2}) over 20 min., and then the wafer was heated to 300°C under vacuum. The IR spectrum was recorded after cooling.

One-electron donor and one-electron acceptor properties. The one-electron donor and one-electron acceptor properties of the catalysts were determined by adsorbing of tetracyanoethylene (TCNE) from 0.1 M solution and perylene from 0.005 M solution, respectively. The ESR signals of corresponding anion radicals and cation radicals were recorded at room temperature using Jeol JMX spectrometer. The spectra of $(\text{perylene})^{\overset{+}{\cdot}}$ cation radicals were recorded under the atmosphere of dry nitrogen containing 5% mol of oxygen, while those of $(\text{TCNE})^{\overset{-}{\cdot}}$ anion radicals in pure nitrogen. The concentrations of the surface ion radicals were established by comparison with the series of DPPH standards.

Reactions. The transformations of the studied alkylpyridines, cumene, and ethylbenzene were carried out in the typical fixed bed reactor at HLSV of 1.5 $g/g_{catalyst} \cdot h$ at temperatures between 450 and 550°C. The liquid products of the reactions were analysed by g.c. using 2 m column with Chromosorb 103. Gases were analysed using 50 m capillary column with squalane, hydrogen content was determined using a conductometric detector with 4 m column filled full with molecular sieves 13X. The identification of reaction products was done by GC/MS and by the comparison of the retention parameters with those of standards.

RESULTS AND DISCUSSION

Acidic properties of the catalysts. IR spectroscopic measurements of adsorbed 4-ethylpyridine were used to determine the acidic properties of the tested catalysts. Fig. 1 illustrates the concentration changes of the respective acidic centres in a series of SiO_2, SiO_2-Al_2O_3 of different Al_2O_3 content, and γ-Al_2O_3.

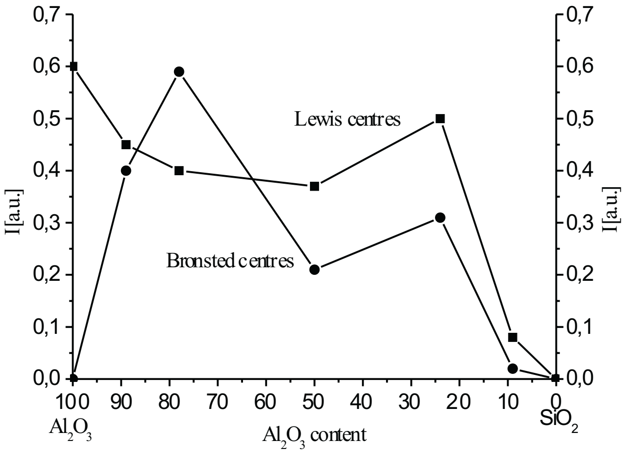


Figure 1. The concentrations of Brønsted and Lewis acidic centers in the series of studied silica-aluminas measured by IR spectroscopy of adsorbed 4-ethylpyridine (bands at 1640 and 1540 cm^{-1}, respectively).

The profile of the concentration of Brønsted type acidic sites in silica-alumina series had two maxima, one corresponding to a system containing 24% of Al_2O_3, and the second to 74% Al_2O_3 content. Pure γ-Al_2O_3 and SiO_2 did not exhibit the presence of Brønsted acidic centres using the adopted determination technique. The concentration of Lewis type acid sites in the series of the tested SiO_2-Al_2O_3 reached a maximum at a 24% content of Al_2O_3. The highest Lewis acidic centres concentration measured by the IR intensity of adsorbed 4-ethylpyridine corresponded to pure γ-Al_2O_3. The sequences of Lewis and Brønsted acidity changes in the studied silica-alumina series were identical to those obtained earlier by Fedoryńska and coworkers [16] by the method of adsorption of Hammett acidity indicators.

One-electron donor and acceptor properties. The one-electron donor and one-electron acceptor properties of the tested catalysts were determined by adsorption of a single electron acceptor which was tetracyanoethylene TCNE, (electron affinity = 2.78 eV), and a single electron donor – perylene (ionization energy = 7.14 eV) and the ESR registration of the signals derived from ion radicals formed on the surface. The adsorption of perylene (Fig. 2) was carried out in the presence of oxygen (4 kNm^{-2}). The intensities of the ESR signal generated by the anion radical (TCNE)$^{\bar{\cdot}}$ and the cation radical (perylene)$^{\dot{+}}$, presented in Fig. 3, illustrated the concentration of surface one-electron donor and one-electron acceptor centres in the series of the studied catalysts. The intensities of the recorded ESR signals corresponded to the concentration of one-electron states equal to 10^{17}–10^{18} spin/g, which has been confirmed by the comparison with the intensities of signals of a series of DPPH standards. The concentrations of radical surface sites were found to be of two orders lower than the concentrations of centres of ionic character. It was observed that only systems with more than 50% of Al_2O_3 content exhibited one-electron donor properties.

Among the investigated silica-aluminas the strongest one-electron donor properties were demonstrated by the catalytic system containing 74% Al_2O_3. Pure γ-Al_2O_3

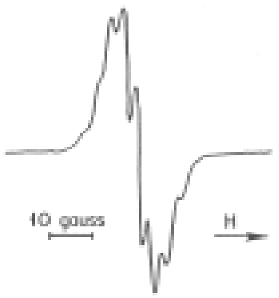


Figure 2. ESR signal of perylene cation radical obtained from silica-alumina (74% Al_2O_3) in the presence of oxygen.

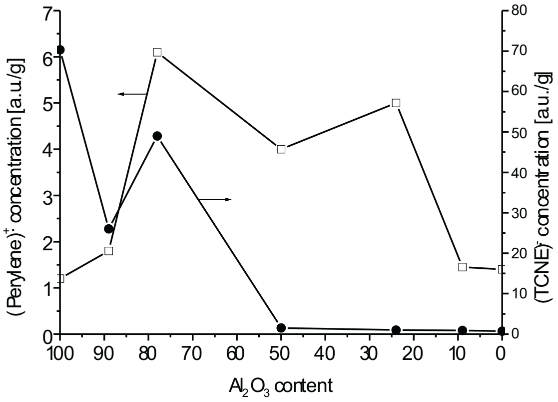


Figure 3. One-electron donor properties (measured by TCNE adsorption) and one-electron acceptor properties measured by perylene adsorption of the studied catalysts.

demonstrated definitely stronger one-electron acceptor properties than the tested silica-aluminas. The profile of the changes of the concentration of one-electron acceptor centres in the series of the tested silica-aluminas was very close to that of the changes of concentration of Brønsted acidic centres although it differed from the changes sequence of Lewis type acidic sites determined by IR spectroscopy. The second observation was a confirmation of our earlier thesis that not all ionic centres with electron pair acceptor or donor properties are also acceptors/donors of a single electron.

Activity of the tested catalysts. The activity of the studied catalysts was investigated by studying the conversion of 4-methylpyridine, 4-ethylpyridine, 4-isopropylpyridine, and for comparison purposes, conversion in ethylbenzene and isopropylbenzene (cumene) transformations. The reactions were performed at the temperature range of 450–550°C.

Conversion of isopropylbenzene. Benzene, ethylbenzene, α-methylstyrene as well as traces of toluene were obtained as the products of cumene reactions. The dependence of the yields of the respective reaction products on the catalysts composition and reaction temperature is illustrated in Figs. 4–7.

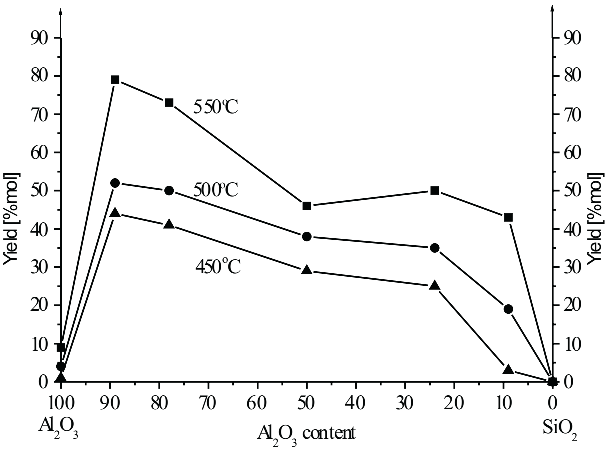
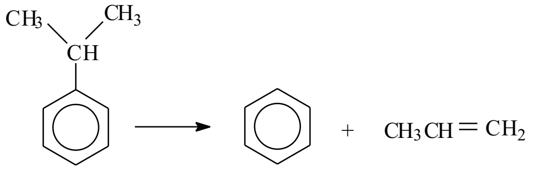


Figure 4. The yields of benzene in isopropylbenzene conversion as a function of catalysts composition.

Benzene obtained as a result of the dealkylation of a cumene molecule according to reaction (1) was the main reaction product over the tested silica-aluminas and pure γ-Al_2O_3 irrespective of the reaction temperature. Silica was completely inactive in cumene transformations.



(1)

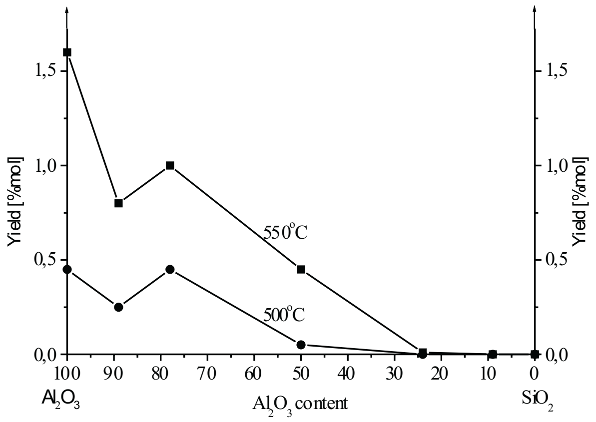


Figure 5. The yields of ethylbenzene in isopropylbenzene conversion as a function of catalysts composition.

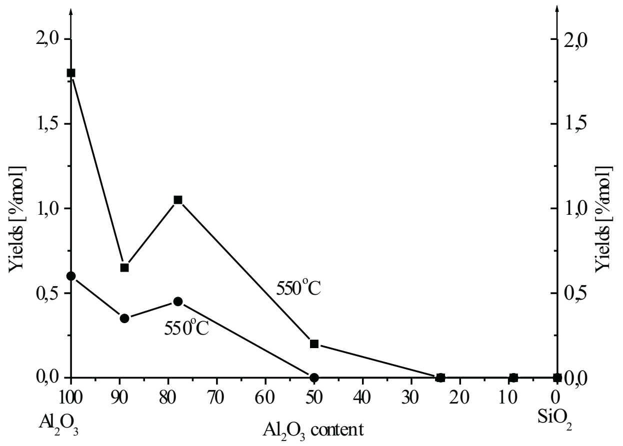
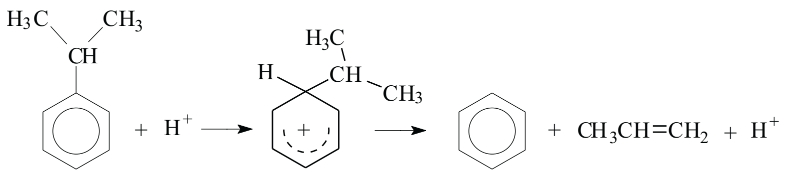


Figure 6. The yields of styrene in isopropylbenzene conversion as a function of catalysts composition.

The yield profile of benzene in the series of tested catalysts (Fig. 4) exhibited a close similarity to the changes in the concentration of Brønsted type acidic centres (Fig. 1) and one-electron acceptor centres (Fig. 3) in the studied silica-aluminas series. Benzene was most probably formed according to the classical electrophilic substitution mechanism (Eq. (2)).



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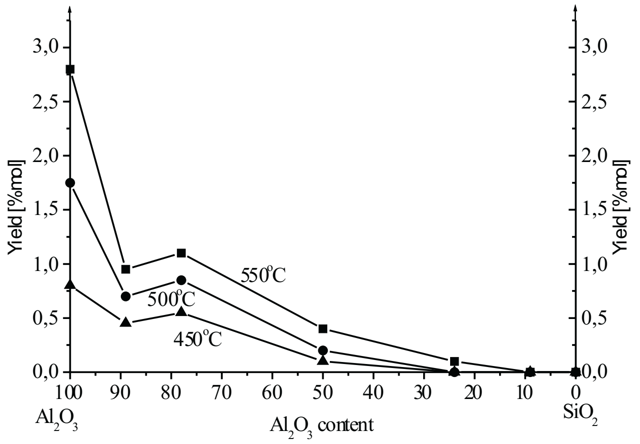
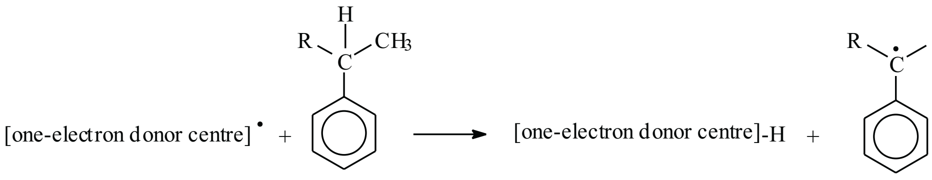


Figure 7. The yields of α-methylstyrene in isopropylbenzene conversion as a function of catalysts composition.

Nevertheless, the participation of one-electron acceptor centres exhibiting simultaneously the two-electron acceptor activity (Lewis acidic) in the dealkylation reaction as earlier postulated by Krzywicki and coworkers [17] cannot be ruled out.

The yields of the remaining reaction products of isopropylbenzene transformations – ethylbenzene, styrene and α-methylstyrene were remarkably lower than those of benzene for they did not exceed 3%. Over pure SiO_2 and silica-alumina with 11% Al_2O_3 content none of these products were obtained. It should be stressed that the profiles of the cumene conversion to the mentioned compounds in the series of investigated catalysts were close to the changes of the concentration of one-electron donor sites on the catalysts surfaces. In agreement with our earlier works on the role of one-electron sites in catalysis [3,8,19,20], it could be ascertained that α-methylstyrene and styrene were produced as a result of the dehydrogenation of izopropylbenzene and also of the primarily formed ethylbenzene catalyzed respectively, by one-electron acceptor sites according to the equations (3) and (4).

Ethylbenzene was most probably obtained as a result of the dealkylation of cumene, which was evidenced by the presence of methane in the gaseous reaction products. The radical character of such process was evidenced by Leigh and Szwarc [18]. The transalkylation of the side chain over magnesium oxide cannot be ruled out as earlier observed by us according to the equation (5) [19,20].



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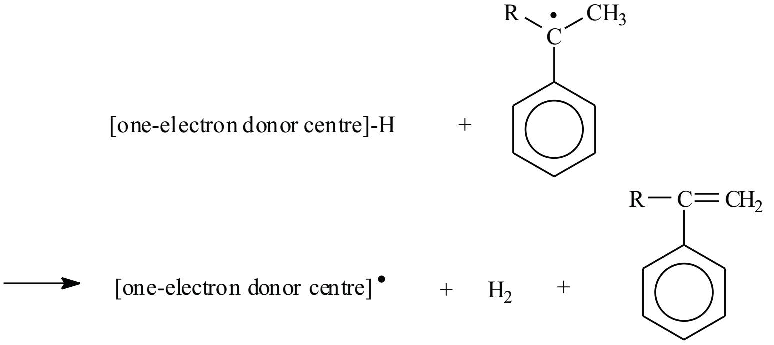

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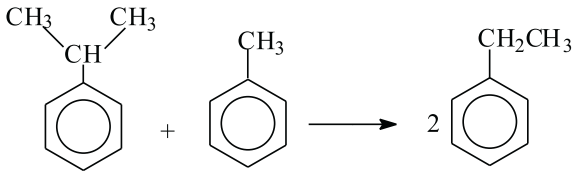


(5)

The occurrence of the reaction above seems to explain the unexpected low toluene content in the reaction products over the tested catalysts.

Ethylbenzene conversion. The main product obtained in ethylbenzene transformations over the tested catalysts was the dealkylation product – benzene (Fig. 8). The changes in benzene yield for the series of tested catalysts were identical to the profile of the changes in the concentration of Brønsted type acidic sites (as well as one-electron acceptor sites) in this series of the studied silica-alumina systems. In the presence of γ-Al_2O_3 or silica-aluminas with 74 and 91% Al_2O_3 content, small amounts of toluene (about 0.2%) and isopropylbenzene (approx. 0.1%) were identified together with the obtained benzene. The content of methane in the reaction products did not exceed 1%. Insignificant amounts of ethane and hydrogen were also identified.

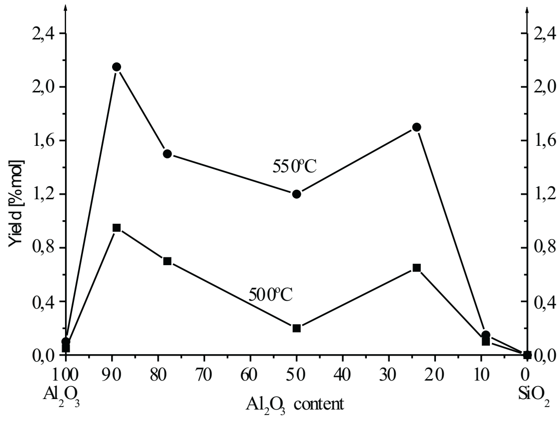
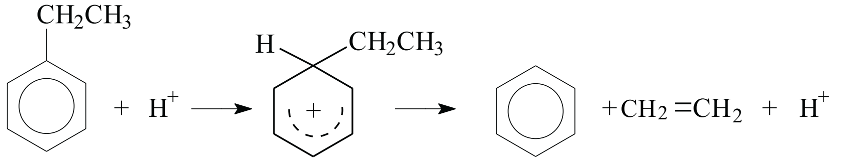


Figure 8. The yields of benzene in ethylbenzene conversion as a function of catalysts composition.

There is no reason to doubt that, as in the case of the dealkylation of isopropylbenzene, benzene formation proceeded according to the electrophilic substitution mechanism:



(6)

Toluene and cumene obtained over the catalysts of the strongest one-electron donor properties (γ-Al_2O_3 and silica-alumina of 74% content) were most likely the products of the disproportionation reaction catalyzed by one-electron donor centres.

4-Methylpyridine conversion. The only reaction products of 4-methylpyridine conversion at 500–550°C over γ-Al_2O_3 and the series of tested silica-aluminas was almost equimolar mixture of pyridine and 4-ethylpyridine. Pure silica and silica-alumina containing 11% of Al_2O_3 were completely inactive in 4-methylpyridine transformations. The profile of the yield changes of 4-ethylpyridine (Fig. 9) and that of the yield changes in the earlier described transformations of cumene into ethylbenzene, α-methylstyrene and styrene were almost identical and close to the profile of the changes of one-electron donor centres concentration. It was therefore appropriate to suggest that these active sites were responsible for the reaction of 4-methylpyridine, especially because the reactant poisoned the Brønsted and Lewis acidic surface centres as well as, most probably, one-electron acceptor sites.

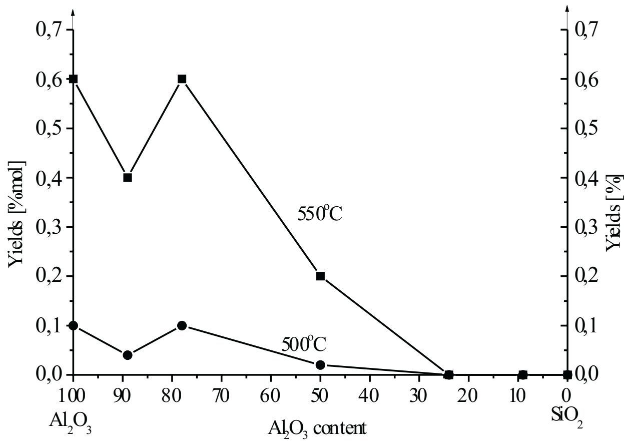
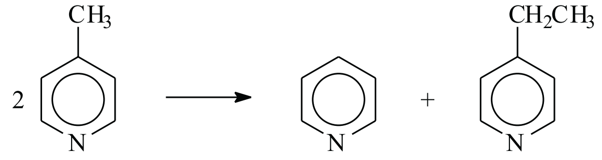


Figure 9. The yields of 4-ethylpyridine in 4-methylpyridine conversion as a function of catalysts composition.

Pyridine and 4-methylpyridine were most probably formed as a result of the disproportionation of the alkyl side chain:



(7)

The occurrence of similar reactions of toluene catalyzed by one-electron donor centres over catalytic systems containing magnesium oxide has earlier been observed by us [3,19,20].

4-Ethylpyridine conversion. The products of 4-ethylpyridine transformations in the presence of the tested silica-aluminas and γ-Al_2O_3 were pyridine, 4-methylpyridine, 4-isopropylpyridine and also 4-isopropenylpyridine [4-(1-methylethenyl) pyridine] (Table 1).

The gaseous products, whose total yield did not exceed 1% mol, were methane, ethylene, propane, propylene, and hydrogen. The reaction products also contained high-boiling condensate and tar of less than 1.5%. Pure silica and silica-alumina containing 11% Al_2O_3 were completely inactive in 4-ethylpyridine transformations. Fig. 10 illustrates the changes in the total conversion of 4-ethylpyridine in the series of the studied catalysts. These changes were close to the changes in yields of the product of the transformations of cumene and 4-methylpyridine obtained, as proposed, in reactions catalyzed by one-electron donor sites as well as to the profile of the changes of the concentration of these centres in the series of tested catalysts. It is therefore appropriate to propose that the observed products of 4-ethylpyridine transformations were obtained likewise as a result of radical reactions catalyzed by one-electron donor centres.

Correlation between catalyst activity and one-electron donor centres concentration. The decisive role of centres of one-electron donor character in 4-ethylpyridine transformations was confirmed by the observed correlation between the conversion of the reactant and the concentration of one-electron donor centres on the surfaces of the tested catalysts (Fig. 11).

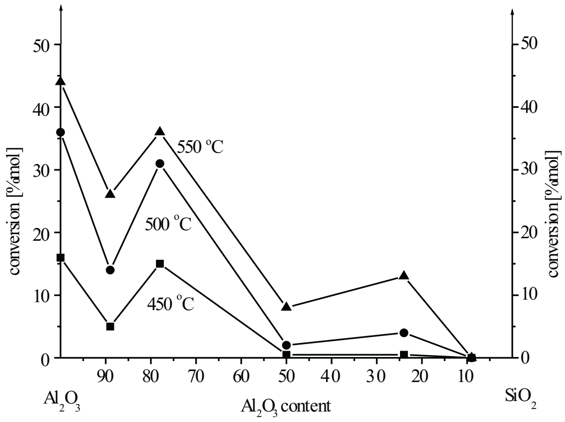


Figure 10. The 4-ethylpyridine conversion as a function of catalysts composition.

Table 1. The yields of products of 4-ethylpyridine transformations over the studied catalysts series.

Catalyst [%Al_2O_3]	Reactant conversion [%]			pyridine yield [%]			4-methylpyridine [%]			4-isopropylpyridine [%]			4-isopropenylpyridine		
	Reaction temperature [°C]														
	450	500	550	450	500	550	450	500	550	450	500	550	450	500	550
Pure Al_2O_3	17.1	37.0	44.1	traces	0.7	2.2	9.3	19.9	29.3	7.5	15.8	11.3	0.1	0.5	1.3
91	4.6	13.4	27.0	traces	0.4	1.6	2.3	7.3	16.4	2.0	5.2	8.2	0.3	0.5	0.8
74	13.6	30.5	36.2	0.2	0.7	1.7	7.5	14.1	23.6	5.8	15.1	10	0.2	0.5	0.8
50	1.0	1.9	7.1	0.1	0.2	0.7	0.5	1.1	4.2	0.3	0.5	1.7	0.1	0.1	0.4
24	0.9	4.3	10.4	0.2	0.6	1.3	0.8	3.7	6.7	traces	0.1	2.4	traces	traces	0.4
11	0.1	0.2	0.8	0.0	traces	0.3	traces	0.1	0.5	0.0	traces	traces	0.0	0.0	traces
Pure SiO_2	0.0	traces	0.4	0.0	0.0	0.1	0.0	traces	0.3	0.0	traces	traces	0.0	0.0	traces

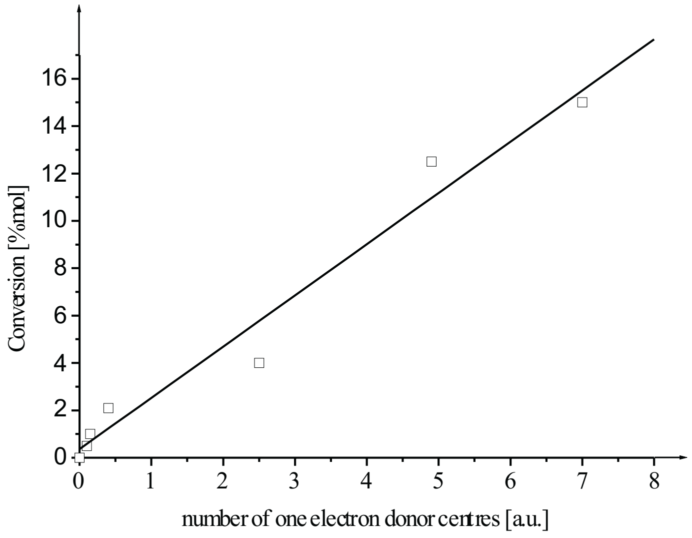


Figure 11. The correlation between 4-ethylpyridine conversion and the number of one-electron donor centers.

The profile of 4-ethylpyridine conversion *vs.* concentration of one-electron donor centres on the catalysts surfaces was in good agreement with the linear dependence of $y = ax$ type. The results of the calculated (least square method) linear dependence for the yields of 4-ethylpyridine products and active centres concentration are presented in Table 2.

Table 2. The values of a in the equation $y = ax$ and the correlation function R^2.

Correlated reaction parameters	Temp. [℃]	(a)	R^2 [%]
4-ethylpyridine conversion [%mol]	450	0.00248	98.8
4-methylpyridine yield	450	0.00135	98.3
4-isopropylpyridine yield	450	0.00108	99.1
4-methylpyridine yield	500	0.00284	98.2
4-isopropylpyridine yield	500	0.00248	97.7
4-ethylpyridine conversion [%mol]	550	0.00697	94.3
4-methylpyridine yield	550	0.00455	95.4
4-isopropylpyridine yield	550	0.00187	92.8
pyridine yield	550	0.00035	79.0

4-Ethylpyridine conversion over catalysts of enhanced one-electron donor activity. In order to confirm the role of the one-electron donor centres in the 4-ethylpyridine transformations, its reactions were performed at 550°C over a series of catalysts known to be of strong, or extremely strong one-electron donor properties: magnesium oxide, zinc oxide doped with metallic zinc, γ-alumina and magnesia doped with sodium (superbasic catalysts). Apart from the γ-Al_2O_3-Na system, the catalysts exhibited insignificant activity in 4-ethylpyridine transformations. The total yields of the obtained products (of the identical qualitative composition to those obtained over the studied γ-Al_2O_3 and silica-aluminas) did not exceed 4% (Table 3). It was only in the case of the superbasic γ-alumina-sodium system did the overall conversion of 4-ethylpyridine attain 30%, which was however remarkably lower than those obtained over unmodified γ-Al_2O_3.

Table 3. 4-Ethylpyridine conversion values over catalysts of enhanced one-electron donor activity at 550°C.

Catalyst	Conversion [%mol]
Al_2O_3	44.0
MgO	1.0
MgO-$Na_{evap.}$	4.0
ZnO	0.4
ZnO-$Zn_{evap.}$	0.9
Al_2O_3-$Na_{evap.}$	30.0

The above observations indicated that the presence of acidic centres on the surface of γ-Al_2O_3 or aluminium cations on the surface of a superbasic catalytic system, acting as adsorption centres of alkylpyridine, could be the condition necessary for reactions of the side chain to take place. The composition of the products of 4-ethylpyridine transformations over γ-alumina and superbasic γ-Al_2O_3 doped with metallic sodium was similar to that of the reactions where the disproportionation of 4-methylpyridine and 4-isopropylpyridine dominated. A larger proportion of the former points to the succeeding cracking type reaction of the initially formed 4-isopropylpyridine to pyridine, 4-ethylpyridine or 4-methylpyridine and also dehydrogenation leading to 4-isopropenylpyridine.

Reactions of 4-ethylpyridine in the presence of ammonia or triethylamine. The reactions of 4-ethylpyridine were carried out over pure γ-Al_2O_3 and silica-alumina containing 74% of Al_2O_3 in the presence of ammonia (flow rate 3 $dm^3 \cdot h^{-1}$) or triethylamine (10 mol%) in the reactant feed. It was expected that the bases stronger ($pK_{\overset{+}{BH}}$ of ammonia = 5, $pK_{\overset{+}{BH}}$ of triethylamine = 3.5) than the reactant ($pK_{\overset{+}{BH}}$ ~8) will undergo a competitive adsorption on acidic sites therefore influencing the diminution in 4-ethylpyridine conversion. Noticeable changes were not observed in the yields of the respective products in the presence of both the added bases. Considering the easier adsorption of the added bases as related to that of 4-ethylpyridine, one can ascertain that adsorption on the acidic sites of the catalyst was not the decisive step on which the overall reaction rate of the selective alkylpyridine side chain transformations was dependent under the adopted conditions.

Reaction of equimolar mixture of ethylbenzene and 4-ethylpyridine. In order to determine the competitiveness between alkylbenzene and alkylpyridine transformations, a series of reactions of equimolar mixtures of ethylbenzene and 4-ethylpyridine over the tested catalysts was performed. The results of these reactions (balanced individually for each reactant) are illustrated in Tables 4 and 5.

Table 4. The yields of benzene from ethylbenzene reaction in the presence of equimolar amount of 4-ethylpyridine.

Catalyst [%Al_2O_3]	Reaction temperature [°C]		
	450	500	550
	Yield [%mol]		
Pure Al_2O_3	0.2	0.3	0.5
91	traces	0.2	0.3
74	0.2	0.3	0.3
50	0.0	0.3	0.3
24	traces	0.3	0.3
11	0.0	0.1	0.1
Pure SiO_2	0.0	0.0	traces

Table 5. The yields of products of 4-ethylpyridine transformations in the reaction in the presence of the equimolar amount of ethylbenzene.

Catalyst [%Al_2O_3]	Reactant conversion [%]			4-methylpyridine [%]			4-isopropylpyridine [%]		
	Reaction temperature [°C]								
	450	500	550	450	500	550	450	500	550
Pure Al_2O_3	15.3	37.7	46.1	7.5	19.2	32	7.3	17	12.2
91	5.1	13	27.9	2.8	7.1	17.0	1.9	6.0	8.3
74	12.5	26.1	35.3	6.5	12.9	25.7	4.7	12.3	11.3
50	0.5	1.6	8.0	0.1	0.8	5.9	0.3	0.6	1.5
24	0.3	4.3	11.3	0.2	2.1	6.7	traces	1.5	2.4
11	0.2	0.4	0.7	0.1	0.3	0.4	traces	traces	0.1
Pure SiO_2	traces	0.1	0.3	traces	0.1	0.2	traces	traces	0.1

The yields of benzene obtained from ethylbenzene in the mixture with 4-ethylpyridine were a few times lower than those obtained in the absence of alkylpyridine, (Fig. 10) and, apart from that, traces of toluene and isopropylbenzene were not noticed. On the other hand, the composition and yield of 4-ethylpyridine transformation products were comparable to those obtained in the absence of the alkylaromatic compound. Therefore, as expected, 4-ethylpyridine poisoned the acidic centres on the surface that were active in the dealkylation of ethylbenzene and simultaneously underwent transformations of the side chain catalyzed by one-electron donor centres.

4-Isopropylpyridine conversion. The major products of 4-isopropylpyridine transformations carried out in the presence of the catalysts tested were 4-methylpyridine and 4-ethylpyridine. Small amounts of pyridine and 4-isopropenylpyridine were also obtained (Table 6). The main gaseous product was hydrogen accompanied by traces of methane, ethane, propane, ethylene, propylene. The total conversion of 4-isopropylpyridine into gaseous products did not exceed 1%. Tar yield was *ca.* 1.5%.

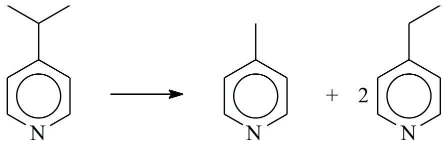
The changes in the yields of the main products over the tested catalysts were in agreement with the change profile of one-electron donor surface properties of the surfaces of this series of catalytic systems. As in the case of 4-methylpyridine and 4-ethylpyridine transformations, this confirmed the participation of one-electron surface sites of the catalysts in 4-isopropylpyridine transformations.

Table 6. The yields of products of 4-isopropylpyridine transformations over the studied catalysts.

Catalyst [%Al_2O_3]	pyridine			4-methylpyridine			4-ethylpyridine			4-isopropenylpyridine		
	Reaction temperature [°C]											
	450	500	550	450	500	550	450	500	550	450	500	550
Pure Al_2O_3	0.2	1.0	3.0	7.5	18.0	26.0	8.0	16.0	12.0	0.5	0.2	1.5
91	0.1	0.5	2.0	6.0	8.0	15.0	4.0	5.0	8.0	0.4	0.3	0.6
74	0.3	1.0	2.5	8.0	14.0	24.0	6.0	14.0	10.0	0.3	0.4	0.5
50	0.2	0.2	1.0	0.8	1.5	4.0	0.2	0.5	2.5	0.2	0.1	0.3
24	0.3	2.0	1.5	1.0	4.0	6.0	0.1	0.2	2.0	0.1	0.1	0.3
11	0.1	0.1	0.3	0.1	0.2	0.3	0.1	0.1	0.1	0.1	0.1	0.1
Pure SiO_2	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1	0.1

Taking into consideration the small amounts of gaseous hydrocarbons formed in the reaction, the insignificant role of cracking type reactions should be ascertained. Thus, it can be proposed that the reactions of the side chain in 4-isopropylpyridine leading to 4-ethylpyridine and 4-methylpyridine were of the subsequent transalkylation character.

Reaction of equimolar mixture of 4-isopropylpyridine and 4-methylpyridine. In order to confirm this thesis, a reaction of an equimolar mixture of 4-isopropylpyridine and 4-methylpyridine was carried out at 500°C over γ-Al_2O_3 which was the most active catalyst in 4-isopropylpyridine transformations. The yields of 4-ethylpyridine and pyridine were several times higher than the yields of products obtained from pure 4-isopropylpyridine under the same reaction conditions (Table 7). The remarkable increase in the obtained 4-ethylpyridine yield compared to the reaction of 4-isopropylpyridine as the only substrate confirmed the transalkylating reactivity of the side chain in pyridine alkyl derivatives according to the reaction:



(8)

Table 7. The yields of pyridine and 4-ethylpyridine from 4-isopropylpyridine and the equimolar mixture of 4-isopropylpyridine and 4-methylpyridine.

Reactant	Yields of reaction products [mol%]	
	pyridine	4-ethylpyridine
4-isopropylpyridine	0.3	0.6
equimolar mixture of 4-isopropylpyridine and 4-methylpyridine	0.6	3.1

Kinetic analysis of 4-ethylpyridine reaction products. Kinetic analysis of 4-ethylpyridine transformation over γ-Al_2O_3 at 500°C was performed according to Wojciechowski's method [21]. By changing the space velocity of the reactant in the range from 5 cm^3/70 s to 5 cm^3/600 s for different weights of catalysts, namely 0.5, 1.2, 2.0, and 4.0 g, a relationship of the yield of product (pyridine, 4-methylpyridine, 4-isopropylpyridine, 4-isopropenylpyridine) *vs*. conversion of the reactant was established (Fig. 12). According to the Wojciechowski method, analysing the shape of the kinetic curves, it can be confirmed that pyridine, 4-methylpyridine (underwent slight consecutive reactions) and probably 4-isopropylpyridine were the stable primary products of the reaction, whereas 4-isopropenylpyridine was an unstable secondary product.

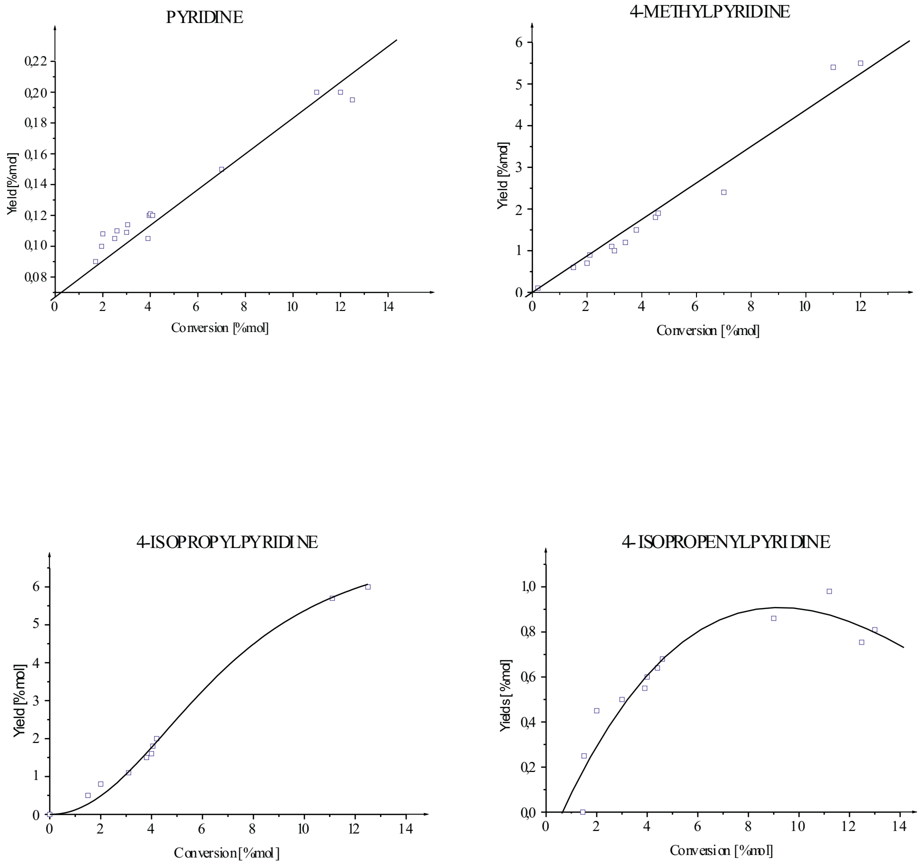


Figure 12. The kinetic analysis of the 4-ethylpyridine products character according to Wojciechowski.

CONCLUSIONS

I. The main transformation of alkyl derivatives of pyridine over the studied silica-aluminas and γ-alumina were side chain reactions of the transalkylation type. The small quantities of gaseous hydrocarbons and coke indicated the limited participation of cracking in the degradation of alkyl side chain. In addition, 4-ethylpyridine and 4-isopropylpyridine underwent dehydrogenation to form the respective alkenyl derivatives.

II. The kinetic analysis of 4-ethylpyridine reaction products carried out according to the Wojciechowski method indicated that pyridine, 4-methylpyridine, and 4-isopropylpyridine were the primary stable products, whereas 4-isopropenylpyridine was an unstable secondary product. The shoulder in the 4-isopropylpyridine yield *vs*. 4-ethylpyridine conversion curve indicated the tendency of the former to undergo further reactions (dehydrogenation) to a little extent.

III. The yield changes of the main alkylpyridines' transformation products in the series of tested catalysts were closely similar to the profiles of the changes in the concentration of one-electron donor sites of these catalysts, which pointed to the decisive role of these sites as the active centres in the observed reactions. The catalytic importance of radical centres was confirmed by the obtained good correlation between one-electron centres concentration on the catalysts surfaces and the conversion of 4-ethylpyridine, or the yield of its transformation products.

IV. The adsorption of the studied alkylpyridines on the surface acidic sites of the catalyst affected the radical reactions of the side chain. As earlier indicated, catalyst systems of very strong (MgO, MgO-Zn), and extremely strong one-electron donor centres (superbasic γ-Al_2O_3-Na, MgO-Na) showed a much lower activity in the observed transformations than γ-Al_2O_3, on whose surface the radical centres coexisted with acidic centres (mainly of Lewis type) of average strength.

V. Furthermore, the absence of a remarkable change in the conversion of 4-ethylpyridine and yields of the main products of its transformation over γ-Al_2O_3 and silica-alumina (74% Al_2O_3) after the addition to the feed of strong bases (NH_3, triethylamine) indicated that the decisive stage for the overall reaction rate was catalyzed by radical centres. The spectacular evidence for the role of the radical centres in alkylpyridines transformations were the results obtained in the reactions of the equimolar mixtures of ethylbenzene and 4-ethylpyridine. The presence of 4-ethylpyridine in the reaction feed caused an almost complete poisoning of ethylbenzene transformations, on the other hand the extent of alkylpyridine conversion and its product composition remain unchanged. Therefore, the poisoning with the aminic reactant of acidic centres exhibiting the cracking activity towards alkylaromatic hydrocarbon, did not hinder the transformation of the side chain of the alkylpyridine molecules.

In conclusion, this work illustrates and confirms the heterogeneity of the surfaces of oxide systems, and the coexistence on them of ionic centres (acidic), and radical ones (acceptor and donor). The role of the latter in the transformations of organic molecules could, in some cases be deciding. However, the condition under which reactions are catalyzed effectively by one-electron centres is probably a joint activity (in adsorption) with Lewis acidic centres.

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