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The Direct Ethanol Conversion to Hydrocarbons over Pt-Containing Catalysts

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Here, we present ethanol transformation into hydrocarbons C_4-C_{12} through a one-step catalytic process. A number of industrial Pt-containing catalysts samples (AP-64, R-254, IP-62, Pt-Re/Al_2O_3) were used, as well as an original Pt-Sn/Al_2O_3 catalyst. All the catalytic experiments were carried out at 5 atm and 350°C. After a pretreatment procedure under 50 atm of H_2 at 450 °C during 12 hours, the catalysts improved a enhanced selectivity to hydrocarbons. After about 10 hours on stream, catalytic activity decreased due to coking issues. However, high catalytic performance could be recovered after calcination in air followed by reduction at 450 °C.

In general, the hydrocarbons C_4-C_{12} yield varied from 20 to 50 wt.% over the different catalysts samples. Depending on the support nature, the ethanol was preferentially converted to alkanes or olefins. The effect of metal addition to Pt-containing catalysts was studied on some industrial Pt-Re and one original Pt-Sn samples. Re addition led to high activity for the formation of olefins, of which the yield reached up to 40 wt.%. Sn addition promoted both olefins and oxygenates formation. The most suitable catalyst for obtaining fuel hydrocarbons (gasoline compounds) was found to be the platinum/alumina catalyst AP-64. The structural particularities of this sample were studied using the XAS technique. Relations between the Pt clusters structure and the catalytic properties were identified.

1. Introduction

Nowadays, a significant interest has been concentrated on effective approaches related to renewable biomass conversion to fuels. A number of alcohols, e.g., ethanol, butanol, iso-pentanol and glycerol, produced via the fermentation of biomass or by triglycerides transesterification (glycerol) can be incorporated into gasoline and bio-diesel, either directly or after chemical/catalytic conversion into more effective additives. Bioethanol is an alcohol that can be produced by fermentation of sugarcane, starch, and algae (Hasheminejad et al., 2011). It can be used as a fuel for vehicles (John et al., 2011). However, there are some obstacles to the wide application of alcohol-based biofuels. Using pure bioethanol is not possible without changing the overall engine design and, accordingly, without changing the entire production line. The fuel efficiencies for hybrid cars using the E85 mixture (85% bioethanol, 15% gasoline) are only 75% those of standard cars. Converting bioethanol into common gasoline components (C3+ hydrocarbons) is the most promising way for its application in the transport industry. A reaction of the aliphatic alcohols C_2 – C_5 yielding to the formation of a large amount of branched hydrocarbons was described by Tsodikov et al., 2008:

$$nC_2H_5OH + H_2 \rightarrow C_{2n}H_{4n+2} + nH_2O \quad (1)$$

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The catalytic system for this reaction was a mixture of intermetallic hydride [$TiFe_{0.95}Zr_{0.03}Mo_{0.02}$]$H_{0.36}$ and Pt/Al_2O_3. The hydrogen required for alkane formation (according to reaction 1) was formed through the parallel reaction of partial ethanol dehydration. The products of the alcohol conversion, alkane/alkene fraction C_4 - C_{12+}, can then be used as fuel components. The problem was the low mechanical stability of the intermetallic hydride.

The aim of the present work was the development of Pt-containing catalysts that are suitable for the reaction of ethanol conversion towards hydrocarbons, with proper mechanical stability.

2. Materials and Methods

Chapter 2 For catalytic experiments, industrial Pt-containing catalysts samples (AP-64, R-254, IP-62, Pt-Re/Al_2O_3) were used, as well as an original Pt-Sn/Al_2O_3 catalyst. Both gaseous and liquid organic products in the aqueous and the organic phases were identified by GC-MS. Catalyst testing was performed in a PID Eng & Tech microcatalytic fixed-bed flow reactor unit, equipped with relevant instrumentation and control devices, in order to maintain the pressure at 5 atm, the temperature at 350 °C, and the space velocity at 0.6 h^{-1}. As a substrate, ethanol was used without any further purification.

Chapter 3 The local structure and the charge state of platinum were studied by XAFS spectroscopy. The XANES and EXAFS X-ray absorption spectra for two catalyst samples (initial AP-64 alumina–platinum catalyst and the catalyst subjected to reductive treatment in hydrogen at 50 atm and 450°C for 12 h) and for standard materials (platinum foil, and the oxide and chloride derivatives of Pt^{2+} and Pt^{4+}) were measured at the Structural Materials Science station of the Kurchatov Center for Synchrotron Radiation and Nanotechnology. The spectra were recorded in the transmission mode using two ionization chambers filled with argon. A monoblock monochromator with a Si(111) cut was used for the monochromatization of the synchrotron radiation beam. To prepare a sample, catalyst powder was pressed into a 1.5 mm thick pellet in an atmosphere of H_2 or Ar. The pellet was then covered with a thin polymer film and transferred to the spectrometer under anaerobic conditions. For each particular sample, three to four independent measurements were performed to check the reproducibility of the results.

1. Results and Discussion

3.1. Catalytic tests

The results of ethanol conversion over Pt-containing catalysts are presented in Figure 1. The conversion of ethanol was 98 % in all catalytic tests. The industrial AP-64 catalyst (Angarsk catalytic factory) was found to be the most active and selective in the reaction of ethanol conversion towards fuel hydrocarbons. Total yield of the target C_3-C_{12} fraction of hydrocarbons reached 50 wt.%, in which the alkanes content was 90 wt.%, the remainder being olefins.

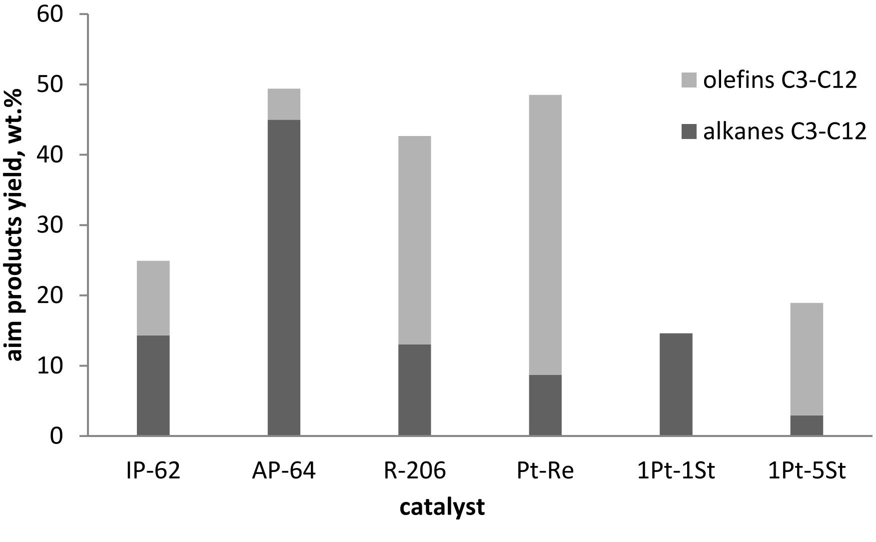


Figure 1: Composition of carbon containing products obtained via a fermentation mixture conversion under optimal conditions

Catalysts samples of R-254 (UOP) and Pt-Re (Angarsk catalytic factory) showed reasonable performances. The target products yields were 43 wt.% and 49 wt.%, respectively. In comparison with AP-64, one can see a selectivity change to the benefit of olefins formation. Olefins content in hydrocarbons fraction over Pt-Re and R-206 was indeed 70-80 wt.%. To use the obtained hydrocarbons as a gasoline additive, higher alkanes concentration are preferre. The catalytic experiments thus showed that the AP-64 catalyst should be the most suitable in that respect.

Hydrocarbons composition of the target fraction is presented on Figure 2. Alkanes with even number of carbon atoms dominate in the products, which means that the pathway of the carbon chain growth is oligomerization of ethylene formed on the acidic sites of the catalyst support. Formation of alkanes with odd number of carbon atoms may be explained via a cracking process or via carbene formation during decarbonylation or decarboxylation of reaction intermediates.

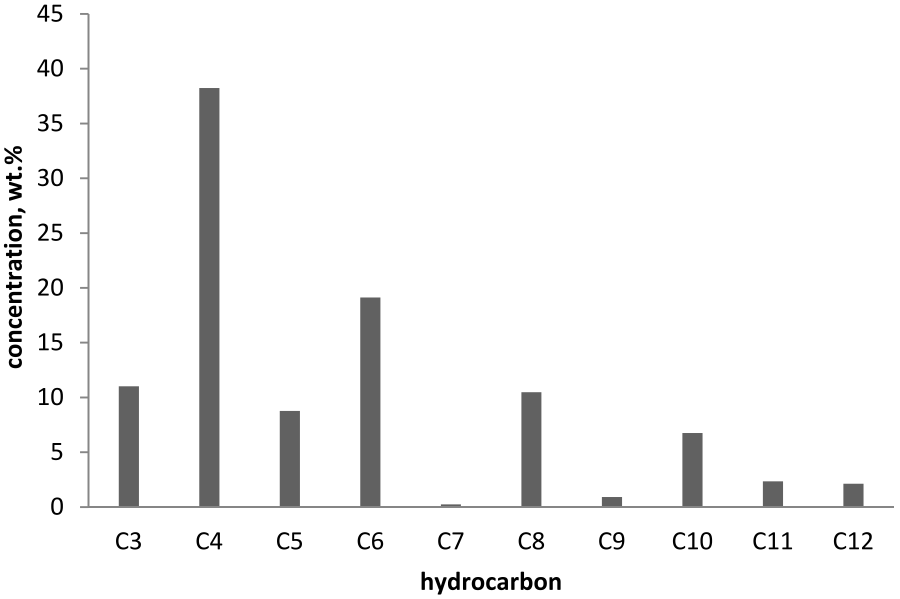


Figure 2: Hydrocarbons concentration in aim fraction obtained from ethanol over the AP-64 catalyst

3.2. Structural investigations

The experimental XANES spectrum (Figure 3a) of the initial AP-64 alumina-platinum catalyst is characterized by a relatively low intensity white line with a spectral maximum at 11,569 eV (the white line in the XANES spectrum at the L3 edge of Pt is formed by dipole-allowed 2*p* 5*d* electron transitions; therefore, its intensity directly correlates with the number of vacancies in the 5*d* valence shell of platinum atoms, that is to say, with the formal oxidation number). The well-known spectra of the oxygen compounds of platinum(II) and platinum(IV) are characterized by much more intense white lines with spectral maximums shifted to higher energies. At the same time, the spectral maximum of platinum metal (see Figure 3a) is even less intense and shifted toward lower energies. Among the well-known spectroscopic standard substances, potassium chloroplatinate(II) is the closest one to the initial AP-64 catalyst in terms of both white line parameters and near edge fine structure over an energy range of 50-70 eV above the absorption edge. Most likely, that is to say that, before catalyst reduction, platinum atoms were mainly surrounded by chlorine atoms, and that the charge state of platinum was close to 2+ (this preliminary conclusion is consistent with EXAFS data). The incomplete coincidence of the XANES fine structure of the initial AP-64 catalyst and K_2PtCl_4 suggests that the coordination polyhedron of platinum atoms in the commercial catalyst is different from a planar square, which occurs in K_2PtCl_4.

Reductive treatment resulted in considerable changes in the XANES spectrum of the catalyst: the white line height somewhat decreased. The spectrum shifted by ~2 eV toward lower energies, and the fine structure of the spectrum changed. In this case, the shape of the spectrum approached that observed in platinum metal. Nevertheless, it is beyond reason to consider the complete coincidence of the spectra of the reduced catalyst and platinum metal. For a more detailed analysis of the possible electronic state and structure of platinum in the reduced catalyst, we performed a theoretical simulation of XANES spectra for platinum metal and a Pt_2Al alloy (Chattopadhyay et al., 1976) using the FEFF8 program. Figure 3b shows the results of this simulation. It can be clearly seen that the observed differences between the experimental spectra of Pt and the reduced catalyst were adequately reproduced in the theoretical calculation for the Pt_2Al intermetallide and Pt metal (the most informative regions of the spectra are indicated by arrows in Figure 3b). This result suggests the formation of direct platinum-aluminum contacts in the reduced catalyst.

In addition, more reliably interpreted information on the local atomic environment of platinum in catalysts can be obtained from an analysis of extended X-ray absorption fine structure (EXAFS) spectra. Figure 4 shows the pseudoradial distribution curves obtained by the Fourier transform of normalized EXAFS signals for the parent and reduced AP-64 catalyst samples, and Table 1 summarizes the refined values of local structure parameters. It is most likely that, in the parent AP-64 catalyst, the coordination sphere of platinum atoms mainly contained chlorine atoms. The experimental curve was more consistent with the refined theoretical curve for a model with two nonequivalent Pt-Cl distances of 2.28 and 2.46 E and the total coordination number of ~4. At larger distances (3-5 E), the Fourier transformed spectrum exhibited relatively intense irregularly shaped peaks. This suggests that platinum atoms did not form isolated ion-molecule fragments, but they were incorporated into a sufficiently rigid low symmetry skeleton consisting of heavy atoms.

A possible interpretation is the chemical grafting of platinum to the surface sites of γ-Al_2O_3 through one or two bridging chlorine atoms. The Pt-Cl peak intensity considerably decreased after reductive treatment. Nevertheless, according to EXAFS data, chlorine atoms with an effective coordination number of < 1 were retained in the coordination environment of platinum and oxygen atoms appeared at a Pt-O distance of 1.97 E ($N = 0.4$). Most likely, they suggest the formation of platinum bonds to support oxygen, as chlorine ions were removed. The results of many previous studies (Duplyakin V.K. et al., 1989, Matyshak V.A. et al., 1998, Belyi A.S. et al., 2005) are indicative of the occurrence of oxidized platinum ionic species remaining on the catalyst surface upon reduction.

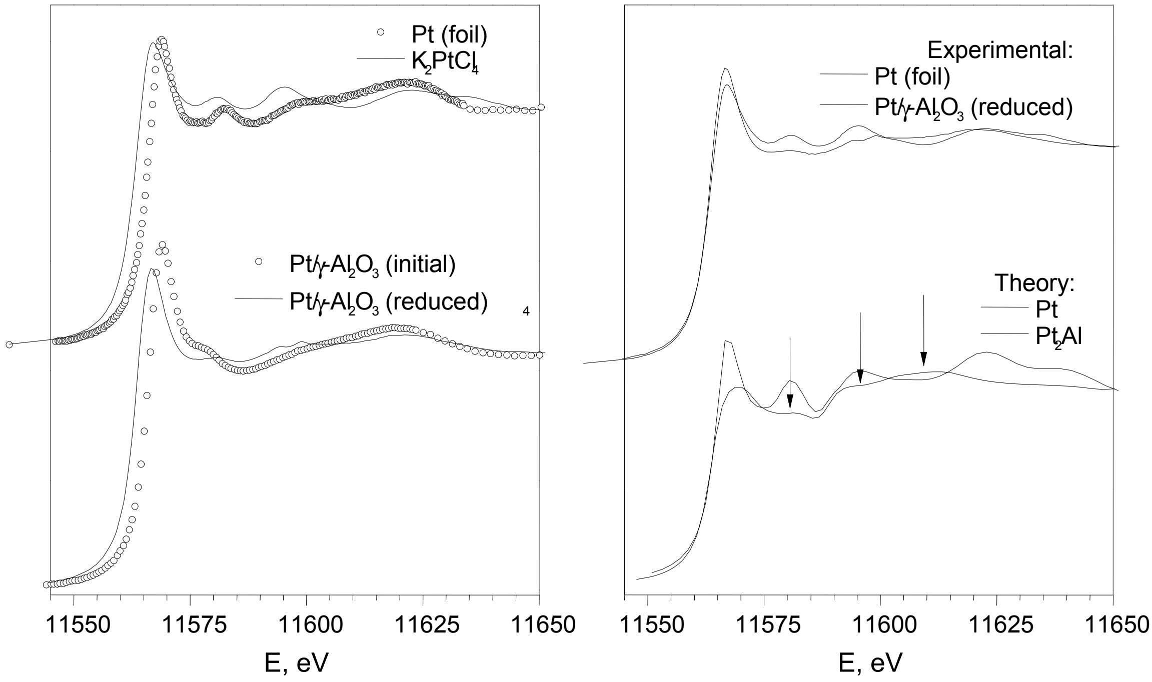
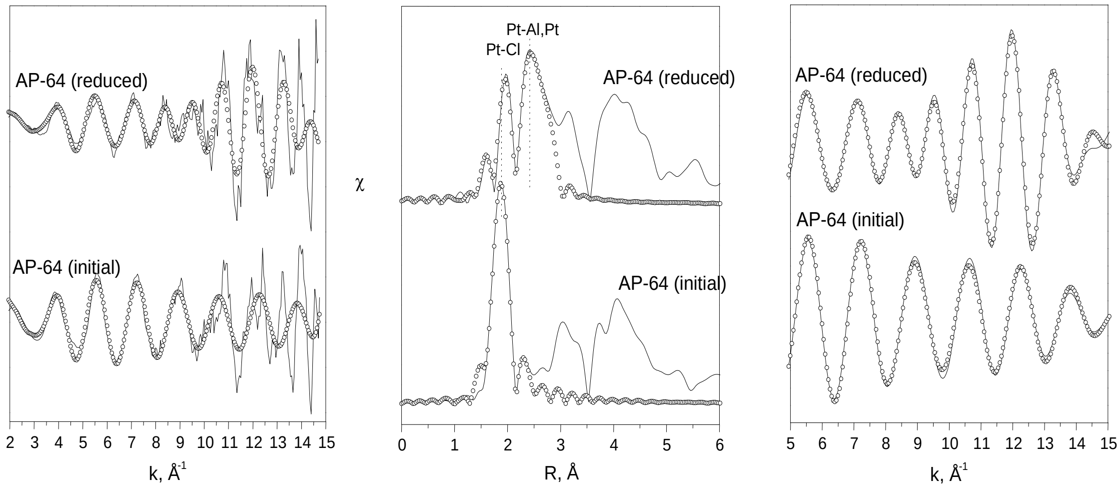


Figure 3: XANES spectra of Pt for (a) initial and reduced AP-64 catalysts and (b) a comparison of the experimental spectrum of the reduced catalyst with the results of theoretical calculations for Pt and Pt_2Al

Moreover, in the Fourier transformed EXAFS spectrum of the reduced catalyst, a new intense peak appeared at $R \sim 2.5$ E (with no phase correction), which is characteristic of direct metal-metal contacts (Figure 4). The test of the possible combinations of Pt-Pt, Pt-Al, Pt-Pt, and Al contributions demonstrated that the appearance of this peak can be most likely explained by a combination of the contribution of Pt-Al and Pt-Pt contacts with interatomic distances of 2.57 and 2.72 E, respectively, and a total coordination number of ~3. These interatomic distances and the coordination number ratios N(Pt-Al)/N(Pt-Pt) reliably indicate that the ultradispersed clusters (that, probably, consisted of a few atoms) of an aluminum-platinum alloy structurally similar to Pt_2Al were formed in the catalyst in the course of the severe reductive treatment. Note that the structure of long contacts at distances of 3-5 E for the reduced catalyst differed only slightly from those observed in the parent catalyst. Recently, by a combination of electron microscopy and XAS spectroscopy, it has been demonstrated that metal particles were formed on the surface of γ-Al_2O_3 after supporting the complex $[Pt(NH_3)_4(OH)_2 \cdot H_2O]$ without both thermal treatment and reduction. It was noted that subnanosized platinum particles are characterized by a narrow size distribution. They have the shape of a flattened drop and strongly interact with the support (Kang J.H., et al., 2006). It was found that Pt_8Al_{21} aluminum-platinum alloy particles were formed in the course of reduction of the Pt/γ-Al_2O_3 catalyst at 800°C (Hayek K., 2004, Stadelmann P., 1987, Zhong, X. et al., 2005). Petraszek et al., 2004, used TEM to detect the particles of metastable Al_2Pt intermetallide, which were obtained upon reduction of an alumina–platinum catalyst even at 500°C. At higher temperatures, ordered Pt_8Al_{21} intermetallides with an octahedral structure were also identified (Petraszek et al., 2004). Petraszek et al., 2004, hypothesized that, similarly to Rh ions, platinum was incorporated into the crystal structure of alumina, and, then, it underwent partial reduction. The ionic radius of Pt^{4+} is larger than the ionic radius of Al^{3+}. However, the possibility of this incorporation of platinum ions into the near surface layers of alumina cannot be excluded.



a *b* *c*

Figure 4: EXAFS spectra of Pt (solid lines) and the results of the refining of structural models (points): (a) normalized EXAFS signal k3 χ(k), (b) Fourier transform and (c) inverse Fourier transform

Table 1: Effective coordination numbers (N) and interatomic distances (R) in the nearest environment of palladium atoms in the AP-64 alumina–platinum catalyst before and after reduction (according to EXAFS data)

Sample	Coordination sphere	N	R, Å	ΔE, eV	R^*_f
Initial catalyst AP-64	Pt-Cl	2.6	2.26	15.2	0.004
		1.1	2.43		
Reduced catalyst	Pt-O	0.4	1.97	12.9	0.038
(50 atm H_2, 450 °C, 12 h)	Pt-Cl	0.8	2.29		
	Pt-Al	1.2	2.57		
	Pt-Pt	1.8	2.72		

*Rf is the reliability factor.

Considering the mechanism of formation of platinum-aluminum intermetallides, Petraszek et al., 2004, believed that, in a first step, Pt_{4+} ions could be bound to surface hydroxyl groups. Then, they can interact with aluminum ions at the octahedral positions of β-Al_2O_3. The reduction of Pt^{4+} ions followed by the reduction and clustering of aluminum ions finally results in the formation of cationic vacancies on the surface of aluminum oxide. The atomic radial distribution curves exhibited poorly resolved long-range fine structure peaks around platinum in the range of 3.5-4.5 E (Fig. 4). It is believed that this range consists of a set of interatomic distances in disordered polyhedrons formed by platinum upon its interaction with coordinatively unsaturated sites of aluminum oxide.

4. Conclusions

The industrial AP-64 catalyst was found to be the most active and selective in the reaction of ethanol conversion towards fuel hydrocarbons. Total yield of the target C_3-C_{12} hydrocarbons fraction reached 50 wt.%, in which the alkanes content was 90 wt.%, olefins being the remainder. Experiments on the study of surface structure demonstrated that the long-term reduction results in considerable changes of the catalyst active centers. This facilitates the promotion of reactions leading to the growth of the carbon skeleton in the products. Ethylene produced from ethanol is involved in this process. This results in an increase in the yield of normal alkanes. The recycling of the ethylene-containing gas leaving the reactor through a catalyst bed facilitates the development of this process.

Examination of the literature combined with the present results allowed us to hypothesize that microphase surface changes occur in the course of a long-term treatment with hydrogen at an elevated temperature. Nanosized clusters of a platinum-aluminum intermetallide (Pt_2Al) are formed, and defects like anion vacancies that belong to strong aprotonic acid sites are generated.

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