

## Full Length Article

New Pt/Alumina model catalysts for STM and *in situ* XPS studies

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## ABSTRACT

The new Pt/alumina model catalysts for STM and *in situ* XPS studies based on thin alumina film formed over the conductive substrate are proposed. Procedure of platinum deposition developed for porous alumina was adapted for the model alumina support. The set of Pt/AlOx-film samples with the different mean platinum particle size was prepared. Capabilities of *in situ* XPS investigations of the proposed catalysts were demonstrated in study of NO decomposition on platinum nanoparticles. It is shown that proposed model catalysts behave similarly to Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and provide the new opportunities for the instrumental studies of platinum catalysts due to resolving several issues (charging, heating, screening) that are typical for the investigation of the porous oxide supported catalysts.

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## 1. Introduction

Advances in understanding catalysts and catalytic reactions are closely related with progress in methods of characterization of catalysts and surface processes. From this viewpoint *in situ* application of such techniques as X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), transmission electron microscopy (TEM), extended X-ray absorption fine structure (EXAFS), etc., are the most promising since they provide unique structure and spectroscopy information under reaction conditions [1–4]. However these studies of industrial ‘real’ catalysts (typically metal nanoparticles deposited on porous oxide) are hindered by methodical problems such as complex composition, non-conducting support, metal screening by substrate, etc. The last

one is principal, for example, for adsorbed layer XPS study when signal contribution of pore located active component and adsorbed species impedes quantitative analysis.

These problems can be overcome by the designing of special model catalysts suitable for instrumental methods [5,6]. Thus using classic model supported catalysts on the base of thin alumina film on NiAl single crystals outstanding fundamental investigations were performed [6]. Nevertheless such systems have some limitations associated with thickness of the films formed on the surface of equimolar alloys. Bridging the gap between ‘real’ and model systems, the new model support, namely, thin alumina film on the surface of FeCrAl alloy was proposed [7–10]. Stable alumina film demonstrates surface morphology and chemical composition similar to porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Nowadays researchers, working in the field of the heterogeneous catalysts, have great expectations for activity and selectivity control by particle size of active component. Size dependences were shown in many catalytic reactions [11–13]. But the origins of these effects are still under discussion. *In situ* techniques can be very helpful for this purpose too. Such investigations require methods of particle deposition which provide narrow size distributions and precise mean particle size control. Soft-landing deposition and atomic-layer deposition techniques look very promising from this point of view [14,15]. Methods of so-called ‘chemical’ active com-

**Abbreviations:** XPS, X-ray photoelectron spectroscopy; STM, scanning tunneling microscopy; TEM, transmission electron microscopy; EXAFS, extended X-ray absorption fine structure; FCA, FeCrAl alloy; SR, synchrotron radiation; BE, binding energy; IR, infrared radiation.

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ponent deposition traditionally used in catalysis are developing in this field also [16,17].

In the present paper to design platinum on alumina models suitable for *in situ* XPS/STM studies and at the same time similar to 'real' catalysts the procedure of Pt deposition from  $H_2[Pt(OH)_6]/HNO_3$  solutions was adapted to model AlOx/FCA supports. Varying mean particle size the set of samples of model catalysts was prepared. Capabilities of *in situ* XPS investigations over proposed model catalysts were demonstrated in study of NO decomposition on platinum nanoparticles.

## 2. Experimental

Thin alumina film formed on the surface of FeCrAl alloy foil [7] was used as support for the preparation of the model Pt/AlOx-film/FCA catalysts suitable for *in situ* XPS/STM study.

Recently the novel procedure of the preparation of Pt catalysts on porous alumina with narrow particle size distribution and precise size control was developed [18–21]. According to this procedure the porous alumina supports are impregnated with aqueous platinum nitrate solutions ( $H_2[Pt(OH)_6]/HNO_3$ ) with different Pt-to- $NO_3^-$  ratios by the incipient wetness method [19]. In the present work this method was used to develop the procedure of the platinum deposition on model planar AlOx-film/FCA samples. Prepared model samples were characterized by XPS and STM.

The main part of XPS experiments was performed at High Pressure VG ESCALAB photoelectron spectrometer equipped with a special gas cell which allows acquiring XPS spectra at elevated (up to 0.02 mbar) gas pressures [22]. The non-monochromatic Al K $\alpha$  line at 180–200 W was used as the primary excitation. The spectrometer was calibrated using the Au4f<sub>7/2</sub> (84.0 eV) and Cu2p<sub>3/2</sub> (932.7 eV) peaks from metallic gold and copper foils [23]. Residual gas pressure was better than  $2 \times 10^{-9}$  mbar. Gas phase spectra were recorded following the procedure described in [24]. The second apparatus, consisting of a photoelectron spectrometer with source of synchrotron radiation (SR) at ISISS Beam Station (BESSY II, Berlin), was used for *in situ* XPS experiments on NO adsorption at pressure up to  $\sim 0.15$  mbar. Residual gas pressure was better than  $2 \times 10^{-9}$  mbar as well.

Spectral analysis and data processing were performed with XPS-Peak 4.1. The binding energy values and the areas of XPS peaks were determined after subtraction of Shirley background and analysis of line shapes. Curves were fitted with Gaussian-Lorentzian functions for each XPS region. XPS peak areas were corrected for quantitative analysis with their respective atomic sensitivity factors for spectra collected using the VG ESCALAB spectrometer. The line Fe2p<sub>3/2</sub> (BE = 707.0 eV) [23] of FCA substrate alloy was chosen as internal standard. The metallic iron is the main component of the conductive substrate (alloy foil), so that the spectra of iron don't shift due to the charging [7].

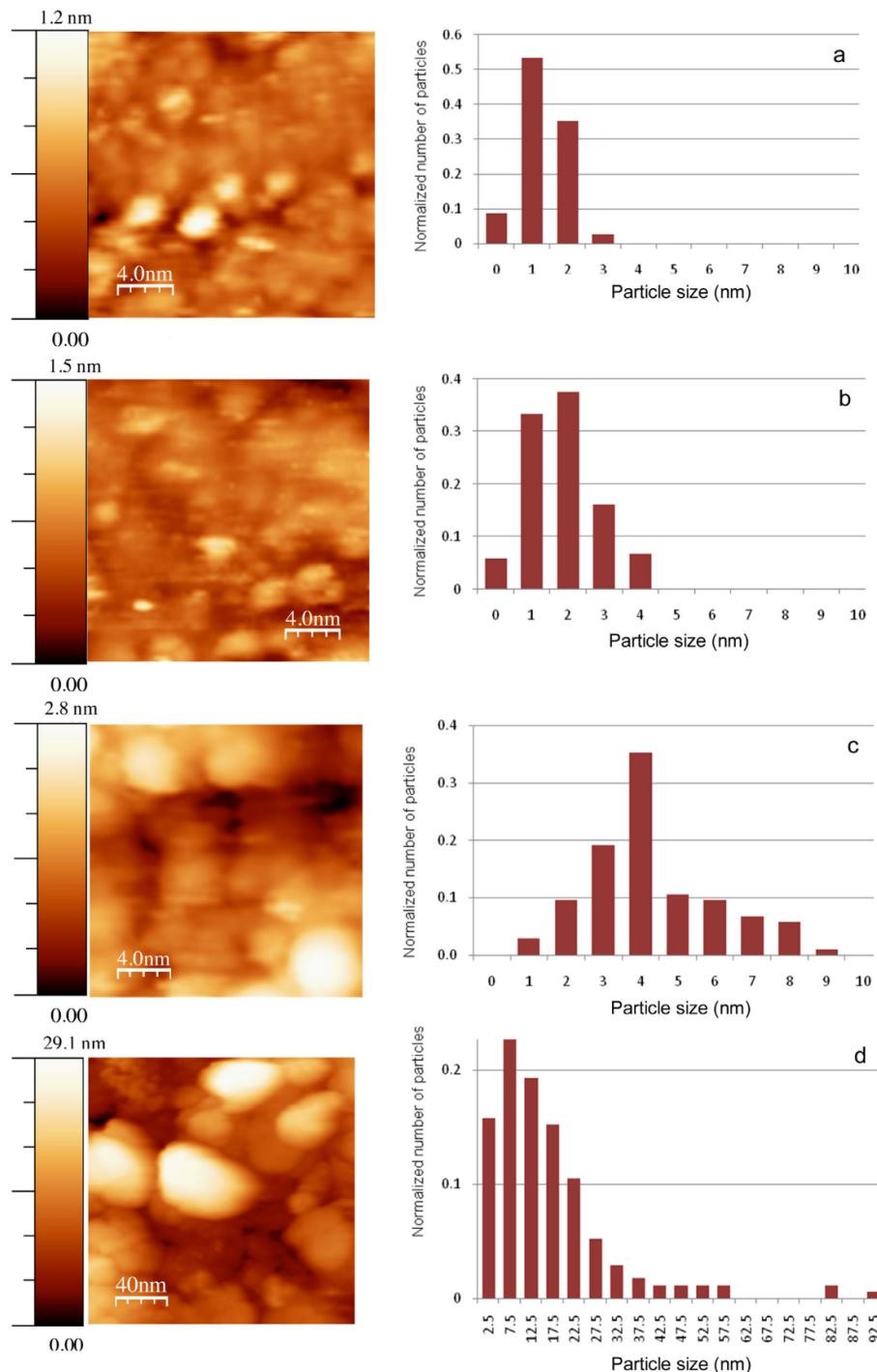
STM study was performed at RHK UHV variable temperature STM instrument (RHK Technology SPM 100). The residual gas pressure in the STM chamber was  $\sim 1 \times 10^{-10}$  mbar. STM images were obtained using cut Pt-Ir tips. The XPMPro 1.2.3.4 software by RHK Technology for SPM100 was used for data acquisition. XPMPro

provides simultaneous recording of the topography and tunneling current images. The entire apparatus was mounted on air floating legs to achieve vibration isolation. The STM images were analyzed with WSxM software [25]. Particle size analysis was performed manually, for platinum coverage analysis manual approach was supplemented with 'flooding' procedure proposed by WSxM software. To get statistically reliable results particle size distribution histograms were based on the analysis of over 100 particles per each sample, for metal coverage calculations more than 10 regions of the specimen surface were taken into account. For the identification of the particles deposited on the surface of rough support procedure described in [10] was used. This procedure is based on the comparison of the topography and tunneling current STM images of the surface. It was shown that at the some range of the feedback parameters objects having different electron density comparing with background (such as metal particles on the surface of oxide film over conductive substrate) became noisy in tunneling current images. No other features of the sample topography (elements of roughness such as hills, cavities and so on) except regions of with different electron property are visible in tunneling current images. This allows the identification of the particles and lateral size measurement with high accuracy [10].

As a probe reaction the ethylene hydrogenation was chosen. Kinetic measurements were carried out on a combined atmospheric batch reactor attached to the modified RHK UHV STM/AFM instrument (RHK Technology SPM 100). The reaction temperature was continuously regulated by using a temperature controller connected to IR lamp as a heating source and a K-type thermocouple spot-welded to sides of the samples. Before reaction samples were cleaned by the annealing in  $O_2$  at  $1.3 \times 10^{-7}$  mbar at 573 K for 30 min followed by annealing at 13 mbar  $O_2$  and 118 mbar Ar at 453 K for 10 min. The batch reactor was equipped with a gas chromatograph to monitor the hydrocarbon conversion. Research purity ethylene (Matheson, 99.98% purity), hydrogen (Matheson, 99.99% purity) and ultra high purity grade argon (Matheson, 99.9% purity) were passed over a molecular sieve trap before use. During gas input the sample was heated to the reaction temperature. The typical reaction gas mixture consisted of 13 mbar  $C_2H_4$ , 26 mbar  $H_2$ , and Ar make-up gas to bring the total gas pressure to 1 bar. Hydrogen was always introduced first followed by ethylene. Circulation was started after introducing all the gases inside the reactor and whole process took about 2 min which was followed by 10 min of mixing before data collection began. Reaction rates were calculated from the slopes of product accumulation curves as a function of time. Cleaned Pt(111) single crystal was used as reference sample. The apparent activation energy for ethylene hydrogenation over Pt(111) was  $9.9 \pm 0.3$  kcal/mol, reaction rate at 333 K was 9.7 (molecule/surface atom/s), which is in good agreement with literature data [26]. Blank experiments at 333 K using empty sample holder with thermocouple attached to the sample holder body showed negligible rate as the gas chromatography peak area is close to the background and only after two hours the rate can be measured to be less than 5% of the value measured for clean Pt single crystal sample.

**Table 1**  
Reduced Pt/AlOx/FCA samples: STM, XPS and ethylene hydrogenation reaction data....

Sample #	BE(Pt4f <sub>7/2</sub> ), eV	Atomic ratio Pt/Al	<d>, nm	$\theta_{STM}(Pt)$ , ML	Reaction data	
					$E_a$ , kcal/mol	$\theta_{react}(Pt)$ , ML
1	72.0	0.029	$1.8 \pm 0.1$	$0.020 \pm 0.008$	–	–
2	71.9	0.050	$2.3 \pm 0.2$	$0.016 \pm 0.010$	$10.0 \pm 2.0$	0.019
3	71.3	0.99	$4.7 \pm 0.3$	$0.94 \pm 0.08$	$9.8 \pm 0.1$	0.89
4	71.1	2.0	$16.8 \pm 2.2$	$0.095 \pm 0.072$	$9.6 \pm 1.0$	0.13



**Fig. 1.** STM images and particle size distribution histograms: (a) sample # 1,  $\langle d \rangle = 1.8 \text{ nm}$  ( $20 \text{ nm} \times 20 \text{ nm}$ ;  $U_t = -1.9 \text{ V}$ ,  $I_t = 0.3 \text{ nA}$ ); (b) sample # 2,  $\langle d \rangle = 2.3 \text{ nm}$  ( $20 \text{ nm} \times 20 \text{ nm}$ ;  $U_t = -2.2 \text{ V}$ ,  $I_t = 0.5 \text{ nA}$ ); (c) sample # 3,  $\langle d \rangle = 4.7 \text{ nm}$  ( $20 \text{ nm} \times 20 \text{ nm}$ ;  $U_t = -1.5 \text{ V}$ ,  $I_t = 0.5 \text{ nA}$ ); (d) sample # 4,  $\langle d \rangle = 16.8 \text{ nm}$  ( $200.4 \text{ nm} \times 200.4 \text{ nm}$ ;  $U_t = -2.0 \text{ V}$ ,  $I_t = 0.5 \text{ nA}$ ).

### 3. Results and discussion

#### 3.1. Model catalyst preparation

The high stability of the proposed alumina films [7] on air and under gas and solution treatments allows application of the chemical methods of active component deposition typically used in practical catalysis.

Before platinum deposition clean AlOx/FCA supports were dried on air at 370 K for 2 h, reproducing procedure of porous alumina pretreatment. For two samples (sample # 3 and sample # 4, see Table 1) glacial acetic acid ( $\text{HOAc}_{\text{glac}}$ ) pretreatment was applied [21]. This pretreatment consists of  $\text{HOAc}_{\text{glac}}$  adsorption for 12 h followed by rinsing in water and drying on air for 2 h at room temperature and for 2 h at 390 K.

At the beginning we had tried to drop a portion of precursor solution on the pretreated surface of the model AlOx/FCA sample, thus modeling impregnation deposition technique [18–21]. The drop of precursor solution diluted with water was dried on air at room temperature for 12 h and at 350 K for 2 h. Resulted sample coating was presumably non-uniform as the obvious painting pattern appeared at the specimen face after the drying. Indeed, STM proved Pt precursor to form huge agglomerates making samples unsuitable for the further use as model catalyst.

So approach developed in [18–21] was adapted for our purpose. Platinum was deposited on the surface of both clean and pretreated model alumina by adsorption from  $\text{H}_2[\text{Pt}(\text{OH})_6]/\text{HNO}_3$  aqueous solution. Adsorption duration was 48–60 h. The samples were then rinsed with distilled water and dried on air for 12 h at room temperature and for 2 h at 390 K. Using exactly the same regularities as for Pt on porous alumina [21] the set of model samples Pt/AlOx/FCA with various mean particle sizes was prepared. The precursor solution acidity or  $\text{HNO}_3/\text{H}_2[\text{Pt}(\text{OH})_6]$  ratio decreasing as well support pretreatments allowed rising gradually the mean platinum particle size in sample succession # 1 – # 4 (see Table 1) [21,27].

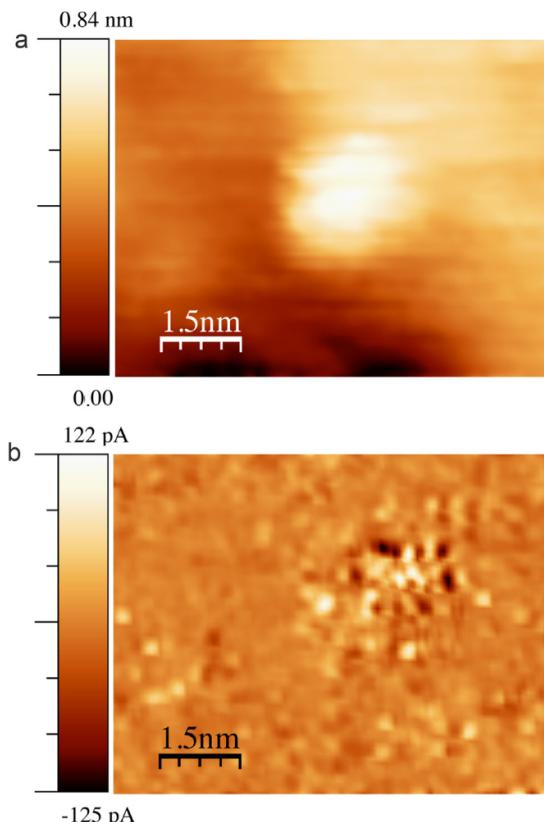
After Pt adsorption on the surface of the samples pretreated with  $\text{HOAc}_{\text{glac}}$  the C1s peak with binding energy of 288.5 eV corresponding to that one of acetic acid residues was still seen. According to our previous experiments on comparative investigation platinum catalysts on  $\gamma$ - and  $\alpha$ -alumina acetic acid residuals adsorb on the surface of  $\gamma\text{-Al}_2\text{O}_3$  only [21]. And no traces of interaction of  $\alpha\text{-Al}_2\text{O}_3$  with  $\text{HOAc}_{\text{glac}}$  were found [21]. So observed interaction of the AlOx/FCA with  $\text{HOAc}_{\text{glac}}$  confirms that proposed model alumina support ‘chemically’ is very close to  $\gamma\text{-Al}_2\text{O}_3$ . Previously similarity of AlOx/FCA and  $\gamma\text{-Al}_2\text{O}_3$  was shown in experiments on  $\text{HNO}_3$  alumina surface treatments [7].

After Pt precursor deposition samples were reduced in preparation chamber of spectrometer by  $\text{H}_2$  at 0.5 bar at 470 K for 2 h, reproducing procedure used for real catalysts. Only traces of the acetic acid residues are seen on the surface of pretreated samples after reduction. The results of STM and XPS study after sample reduction are presented in Table 1.

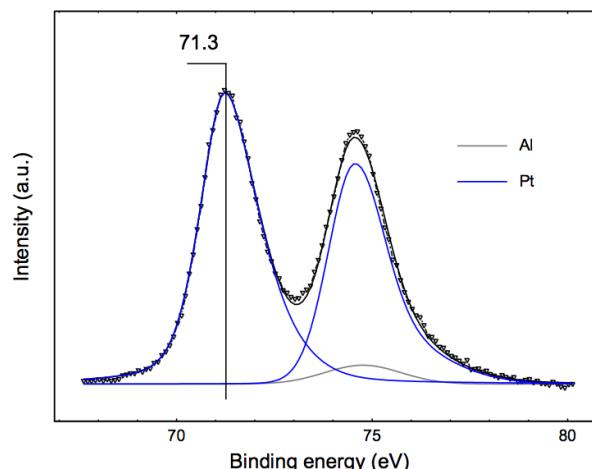
STM images and particle size distribution histograms obtained for prepared samples are shown in Fig. 1. Used model systems Pt/AlOx/FCA with metal nanoparticles on the surface of the thin oxide film on the rough substrate are very arduous task for STM study. For the identification of the platinum particles deposited on the surface of AlOx/FCA special procedure was developed [10]. This procedure is based on the comparison of STM images recorded at the different tunneling currents, topography and tunneling current images of the same surface region and STM images of the surface of Pt deposited samples and surface of the clean alumina films used as support [7,10]. Thus both topography and tunneling current STM images of the platinum particle on the surface of thin alumina film is shown in Fig. 2. Platinum particles are distributed over the surface of the support non-uniformly. So to make calculations presented in Table 1 over a hundred of STM images all over the sample surface were analyzed for each sample to overcome problem of STM locality.

Only one doublet Pt4f peak that can be assigned to metallic platinum was found for all samples after reduction (see Fig. 3). At the same time the exact binding energy of  $\text{Pt4f}_{7/2}$  correlates with mean particle size estimated by STM (Table 1). The particle size decrease is accompanied by XPS line shift towards higher binding energy. This effect is well known in XPS [6]. Hereby STM and XPS are complementary to each other.

Samples # 3 and # 4 were pretreated with  $\text{HOAc}_{\text{glac}}$  before Pt adsorption. Comparing samples with particles of the same size range (# 2 and # 3) the increase of the particle number per alumina surface area (Pt coverage) for pretreated samples was found



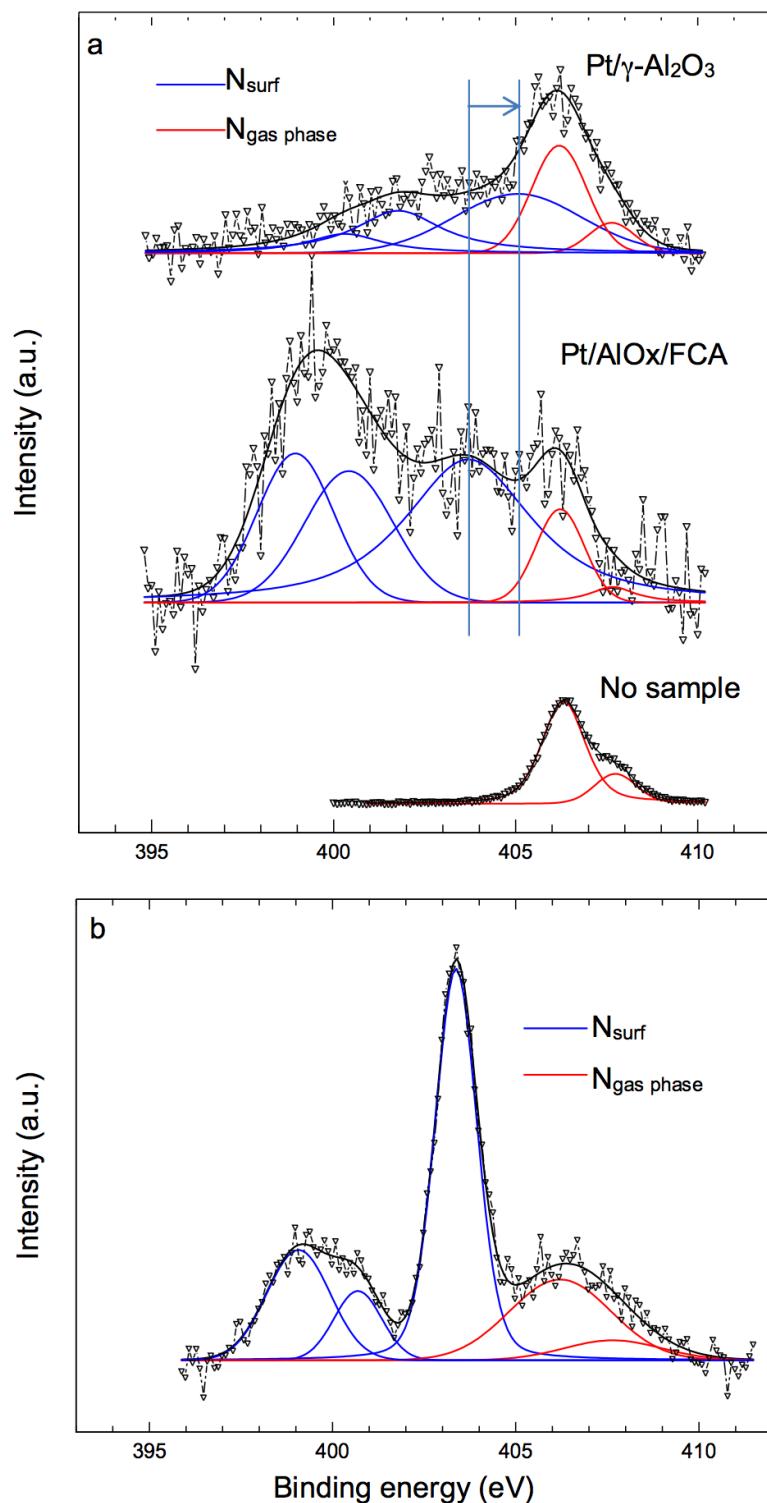
**Fig. 2.** STM image for sample # 1 (8.0 nm × 6.3 nm;  $U_t = -1.9$  V,  $I_t = 0.3$  nA): (a) topography image; (b) tunneling current image.



**Fig. 3.** Pt4f + Al2p XPS spectrum of Pt/AlOx/FCA sample # 3 after reduction.

(see Table 1). Taking into account experiments presented in [21] it can be assumed that adsorbed acetic acid residues unifies alumina surface and provides new adsorption sites for platinum precursor deposition. So in the case of proposed model systems this pretreatment allows to vary the number of platinum particles of the particular size on the surface of the alumina.

So using proposed procedure, metal platinum particles deposited on the surface of thin alumina film were prepared. For samples with small particles (up to ~5 nm) particle size distributions are rather narrow, and mean particle size is well controlled.



**Fig. 4.** *In situ* XPS spectra of N1s region obtained under NO adsorption at 323 K: (a) ESCALAB HP, P(NO) = 0.01 mbar, Pt/γ-Al<sub>2</sub>O<sub>3</sub> (mean particle size is 4.8 nm) and Pt/AlOx/FCA sample # 3 (<4.7> nm); (b) BESSY II, P(NO) = 0.15 mbar, Pt/AlOx/FCA sample # 3 (<4.7> nm).

### 3.2. Hydrogenation of ethylene reaction

All prepared samples were tested on the hydrogenation of ethylene to ethane reaction. The apparent activation energy for ethylene hydrogenation was calculated on the base of the Arrhenius plots.

Results of tests are presented in Table 1. Obtained data are in good agreement with literature [26] pointing on test correctness. Nevertheless for sample # 1 (<1.8> nm) with smallest Pt particles and low Pt coverage the ethylene hydrogenation reaction rate was close to experimental error. So results obtained for this sample exhibit low

reliability. Moreover for this sample we were not able to measure activation energy with required accuracy.

Since the ethylene hydrogenation is a structure insensitive reaction [26] the reaction turnover rate ideally should allow us to estimate surface platinum coverage by comparing the reaction rate on supported sample with clean Pt(111) single crystal. The results of these estimations are presented in Table 1. Pt coverage calculated on the base of reaction test was compared with estimates made on the base of STM data (see Table 1). It should be noted that rather high error of STM estimations is explained mostly by the locality of STM (scanning range is  $\sim 10^{-12}$ % of sample area) and observed certain non-uniformity of the particle distribution over the surface. Nevertheless taking into account experimental errors coverage estimated both by the reaction and STM match well to each other. At the same time STM allows making some coverage estimations even when reaction does not work.

### 3.3. Application

In Fig. 4(a) the *in situ* XPS spectrum obtained under NO adsorption at 323 K over Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> sample is shown. Grains of catalyst were placed into special designed steel basket with grid bottom for better gas circulation. Thermocouples were attached to the basket. Position of the N1s XPS spectrum of NO in the gas phase is exactly the same in all experiments with or without the sample (Fig. 4a) since this peaks are not affected to the sample differential charging. At the same time it is well seen that the sample charging effect shifts the XPS peaks of surface nitrogen species towards higher binding energy independently from the gas phase peaks (in Fig. 4a peak shift caused by porous alumina charging is marked with arrow), so that N1s peaks from the sample surface overlap with N1s peaks of gas phase. Then spectrum deconvolution needs some additional information.

The same experiments performed over Pt on AlOx-film/FCA under the similar conditions (Fig. 4) resolve charging problems and provide the useful information for the analysis of N1s spectra acquired for the catalysts on the porous supports. The set of the surface nitrogen species is exactly the same both for the model catalysts on AlOx/FCA and for the real catalysts on porous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, although the positions of the nitrogen surface species relative to N1s gas phase are different. All nitrogen species found both on the surface of model and real catalysts are following the same trends depending on sample temperature and gas phase pressure. In absence of screening of Pt by the porous alumina support significant XPS signal of active component (Fig. 3) of model catalysts allows precise and reliable study of the transformations of active component chemical state as well as nitrogen species adsorbed on the platinum particle surface under reaction conditions. The identification of the adsorbed species is currently in progress.

More valuable data can be obtained using SR XPS. It should be noted that SR can't be used for common porous alumina due to the enormous and unstable surface charging. At the same time *in situ* SR XPS over model Pt/AlOx/FCA (see Fig. 4(b)) allows increasing gas phase pressure even more approaching the conditions to 'reality' and improves both 'signal/noise' ratio and photoelectron peak width making spectrum interpretation easier.

### 4. Conclusions

Platinum deposition procedure developed for porous alumina was successfully adopted on model planar alumina supports. In spite of replacement of impregnation on adsorption the particle size distribution over the surface can be controlled in exactly the same way for both types of alumina supports. Behavior of proposed

systems under used treatment conditions confirms that the surface of AlOx-film/FCA 'chemically' is similar to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

At the same time reproducing properties of 'real' catalysts proposed Pt/AlOx-film/FCA systems resolve the set of methodical problems typical for XPS studies of Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts, such as charging issues, sample heating uniformity and active component screening by support. Interpretation of *in situ* XPS spectra obtained for 'open' plane model system "adsorbed layer – metal particles – AlOx-film – conductive substrate" is more unambiguous comparing with real Pt/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and allows studying all aspects of catalytic reaction: composition of the adsorbed layer, chemical state transformation of the catalyst surface, etc. Moreover conductive substrate makes possible to use SR for study of catalysts on alumina which is impossible in the case of 'real' porous supports. Capabilities of *in situ* investigations over our model catalysts were demonstrated in study of NO decomposition on metal nanoparticles. Involving Pt/AlOx/FCA the identification of the N1s peaks was performed. This provided unique information which was difficult to obtain for real catalysts on porous alumina. Application of such model systems in fundamental research allows for full scope study of catalytic behavior.

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