Data Article

Dataset N-doping of alumina thin film support of catalysts

Aleksey M. Dmitrachkov, Ren I. Kvon, Anna V. Nartova*  
Boreskov Institute of Catalysis SB RAS, Lavrentieva Ave., 5, Novosibirsk 630090, Russia

A R T I C L E   I N F O

Article history:
Received 15 July 2021
Revised 13 September 2021
Accepted 15 September 2021
Available online 20 September 2021

Keywords:
N-doped catalyst support  
Model alumina  
XPS  
STM

A B S T R A C T

The search for the ways of thermal stabilization of supported metal catalysts is an important challenge in the modern catalysis. Chemical modification of support seems to be the most versatile approach to stabilize the metal particles against sintering and alter their catalytic performance. Also for such modification nitrogen doping can be used and is considered rather perspective. In a recent manuscript (A.M. Dmitrachkov, R.I. Kvon, A.V. Nartova, N-doping of alumina thin film support to improve the thermal stability of catalysts: preparation and investigation, Appl. Surf. Sci.) we have developed the procedure of N-doping of alumina thin film grown at the surface of metal substrate. Proposed N-doped model alumina support is suitable for catalysis – oriented surface science studies and improves the resistance of supported metal particles against thermal driven sintering. Herein, we provide useful complementary data for the characterization of the prepared materials in the form of: in situ / ex situ XPS (X-ray photoelectron spectroscopy) spectra at every stage of sample preparation, including angle resolved XPS experiments and thermal stability tests; STM (scanning tunneling microscopy) images of supported gold catalysts. Presented data support the proposed mechanism of film formation and modification.

DOI of original article: 10.1016/j.apsusc.2021.150631  
* Corresponding author.  
E-mail address: nartova@catalysis.ru (A.V. Nartova).

https://doi.org/10.1016/j.dib.2021.107383
2352-3409/© 2021 The Author(s). Published by Elsevier Inc. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/)
Specifications Table

| Subject | Materials Science: Surfaces, Coatings and Films |
|---------|--------------------------------------------------|
| Specific subject area | Inorganic Chemistry and Physical Characterization |
| Type of data | Image |
| How data were acquired | X-ray photoelectron spectra were acquired on a VG ESCALAB HP electron spectrometer (basic chamber pressure was $\sim 10^{-4}$ mbar, Bayard-Alpert Type Ionization Vacuum Gauges). Scanning tunneling microscopy images were recorded on an UHV (ultrahigh-vacuum) variable temperature STM VT-7000 (RHK Technology, USA) (basic chamber pressure was $\sim 10^{-10}$ mbar, Gamma Vacuum Ion pump). |
| Data format | Raw Analyzed |
| Parameters for data collection | XPS source – nonmonochromatic Mg Ka ($\hbar \nu = 1253.6 \text{eV}$) X-Ray gun (XR-3 source by VG Scientific) at $\sim 150$ W power (anode voltage of 10 kV and emission current of 15 mA); Hemispheric Analyzer – Constant Analyzer Energy (Fixed Analyzer Transmission) mode with retard grid in front of entrance analyzer slit (i.e., transmission function is constant); Pass Energy = 50 eV (Ag3d peak fwhm = 1.75 eV) used for survey spectra and Pass Energy = 20 eV (Ag3d peak fwhm = 1.34 eV) was chosen for high-resolution spectra; typical angle of analysis ($\theta$) was $30^\circ$ to normal to the sample plane; angle resolved measurements were done in $\theta$ range of $30^\circ$ – $85^\circ$. STM – the cut Pt/Ir tips, topography and tunneling current images were acquired simultaneously. Typical tunneling current of 0.5 nA at voltage in range of $\pm 200$ mV to $\pm 2200$ mV. |
| Description of data collection | XPS – The foil specimens were mounted on spectrometer sample holder by tungsten wire legs spot-welded to the backside of the disks to provide resistive heating to anneal the samples. The sample temperature was measured by K type thermocouple spot-welded directly to the back of samples. The flows of gases were tuned up in by-pass line by leak valves and then switched directly into XPS analytic chamber to carry out in situ XPS experiments. STM – samples were placed on standard sample holder of ST - microscope VT-7000 (RHK Technology, USA), contacts were spot-welded directly to the sample. |
| Data source location | Boreskov institute of catalysts Siberian Branch of Russian Academy of Science (BIC SB RAS), Novosibirsk, Russia. |
| Data accessibility | https://data.mendeley.com/datasets/m7sgtybh5w/draft?a=24aaa0e15-bdb8-491f-8d5f-98add5c78a2f (https://doi.org/10.17632/m7sgtybh5w.1) |
| Related research article | A.M. Dmitrachkov, R.I. Kvon, A.V. Nartova, N–doping of alumina thin film support to improve the thermal stability of catalysts: preparation and investigation, Applied Surface Science 566 (2021) 150631 (https://doi.org/10.1016/j.apsusc.2021.150631) |

Value of the Data

- These data are important for the substantiation of the mechanisms proposed for the formation and N – doping of alumina film on the surface of metal substrate.
- Researchers in surface and materials science and catalysis can find the spectroscopy data, useful for characterizing analogous materials and application of such materials for catalyst designing.
• Reported data can be used for the design of new catalysts based on N-doped alumina supports.

1. Data Description

The data in this article refer to the samples described in “N-doping of alumina thin film support to improve the thermal stability of catalysts: preparation and investigation” [1] and in “Nitrogen-doped alumina carrier for sintering resistant gold supported catalysts” [2].

The survey XPS spectra show presence of main components of foil used as substrate for sample preparation (Fe, Cr, Al, O, Ar) after foil cleaning procedure and before film formation (Fig. 1 (sample # 5, 5_FCA-N_0 [1]) and for successfully grown films (Fig. 2, 0_FCA_1 (non-modified alumina), Fig. 3 (modified sample # 5, 5_FCA-N_1)). In Fig. 4 appearance of N1s signal and N1s line evolution during NO treatment (6_FCA-N_1, 7 × 10⁻⁷ mbar NO exposition at 670°C) are shown. The plots in Figs. 5–7 (5_FCA-N_1) confirms the reproducibility of angular dependences for N–doped films prepared by the proposed procedure. Figs. 8–11 shows evolution of Al2p, O1s, Cr2p and Fe2p lines during N-doped film formation (sample # 3, 3_FCA-N_0 and 3_FCA-N_1 [1]). Both segregation of aluminum and oxygen as well as reduction of FeOx and CrOx due to aluminothermy are well seen (Section 3.2 Mechanism of alumina film formation [1]). In Fig. 12 (6_FCA-N_1), XPS spectra of N1s line before and after NO treatment, when NO presents in residual vacuum, are shown in Fig. 13 (sample Au_FCA-N), the survey XPS spectrum shows presence of Au4f line after vacuum vapor deposition of the gold on N-doped AlOx/FeCrAl. Figs. 14 and 15 shows STM images of gold nanoparticles deposited by vacuum vapor deposition on non-modified AlOx/FeCrAl (Fig. 14, sample Au_FCA) and N-doped AlOx/FeCrAl (Fig. 15, sample Au_FCA-N) samples confirms absence of restrictions for thermal sintering of particles (small particle size (less than 3 nm) and short distance between particles).

In Table 1 see the list of samples mentioned in this article with brief description (sample numbering is the same as used in [1]).

XPS data

![Figure 1](image_url). Survey spectrum of Ar⁺ etched FeCrAl foil (5_FCA-N_0).
Fig. 2. Survey spectrum of sample with non-modified AlOx film over FeCrAl substrate (0_FCA_1).

Fig. 3. Survey spectrum of sample with modified AlOx-N film over FeCrAl substrate (5_FCA-N_1).

Files in the data repository are organized in folders according to methods of sample's study: XPS (X-ray photoelectron spectroscopy) and STM (scanning tunneling microscopy). ‘XPS’ folder includes XPS spectrum data files (Excel files). Files are named according to the following convention ‘Fig X spectrum type sample name.xls’, where “X” is the number of the figure (when ‘Fig X-Y...’ file name is used, “Y” is the number of spectrum in figure); “spectrum type” is ‘survey spectrum’ or ‘region spectrum’ (regions are specified commonly for XPS); “sample name” is according to the Table 1. Every file includes description of the sample treatment when XPS spectrum was recorded; MgKa is used radiation; HV50 is HV used for spectrum recording; table
Fig. 4. Evolution of N1s line during NO treatment \( \left( 7 \times 10^{-7} \text{ mbar NO exposition at } 670^\circ\text{C} \right) \) (6_FCA-N_1).

Table 1

| Sample      | Brief description                                                                 |
|-------------|-----------------------------------------------------------------------------------|
| 0_FCA_1     | Sample # 0: non-modified AlOx film over FeCrAl substrate                            |
| 3_FCA-N_0   | Sample # 3: FeCrAl foil after Ar\(^+\) etching                                     |
| 3_FCA-N_1   | Sample # 3: modified AlOx-N film over FeCrAl substrate prepared at \( 1.5 \times 10^{-7} \text{ mbar NO at } 670^\circ\text{C} \) |
| 5_FCA-N_0   | Sample # 5: FeCrAl foil after Ar\(^+\) etching                                     |
| 5_FCA-N_1   | Sample # 5: modified AlOx-N film over FeCrAl substrate prepared at \( 6 \times 10^{-7} \text{ mbar NO at } 670^\circ\text{C} \) |
| 6_FCA-N_1   | Sample # 6: modified AlOx-N film over FeCrAl substrate prepared at \( 7 \times 10^{-7} \text{ mbar NO at } 670^\circ\text{C} \) |
| Au_FCA-N    | Au nanoparticles deposited on N-doped AlOx/FeCrAl support                           |
| Au_FCA      | Au nanoparticles deposited on non-modified AlOx/FeCrAl support                      |

with spectrum (two columns: BE (binding energy) in eV (electron-volt) and intensity in a.u. (arbitrary units). Tables can be used to plot spectrum using any appropriate software (for example, Excel). File Fig. 4 XPS N1s spectra 6_FCA-N_1.xls includes six spectra of nitrogen line at different NO exposition time \( (t = X \text{ s, where } X \text{ is the exposition time in seconds}) \). File Fig. 12 XPS N1s spectra 6_FCA-N_1.xls includes two spectra of nitrogen line before and after NO exposition. ‘STM’ folder includes STM images (JPEG files). Files are named according to the following convention ‘Fig. XX sample name.xls’, where “X” is the number of the figure; “sample name” is according to the Table 1. STM image size is 13.4 nm x 8.5 nm for Fig. 14 Au_FCA.jpg file and 24.0 nm x 14.6 nm for Fig. 15 Au_FCA-N.jpg file.

2. Experimental Design, Materials and Methods

The preparation of all samples is described in principle in “N–doping of alumina thin film support to improve the thermal stability of catalysts: preparation and investigation” [1]. Here we present the extended description of this procedure.
2.1. The choise of proper material

A foil of aluminum-containing heat-resistant steel Fecralloy® alloy (Goodfellow Cambridge Limited, England) in “as rolled” condition was used for the film preparation. The FeCrAlloy foil of this trademark was chosen as commercially available and inexpensive material. Use of such...
Fig. 7. Angular dependence of N/Fe atomic ratio (sample # 5, 5_FCA-N_1).

Fig. 8. XPS spectra of Al2p line before (1) 3_FCA-N_0 and after (2) 3_FCA-N_1 N – doped film formation.
Fig. 9. XPS spectra of O1s line before (1) 3_FCA-N_0 and after (2) 3_FCA-N_1 N-doped film formation.

Fig. 10. XPS spectra of Cr2p line before (1) 3_FCA-N_0 and after (2) 3_FCA-N_1 N-doped film formation (dashed line is (2) spectrum normalized to the intensity of (1) spectra for the comparison purposes).
**Fig. 11.** XPS spectra of Fe2p line before (1) (3_FCA-N_0) and after (2) (3_FCA-N_1) N – doped film formation (dashed line is (2) spectrum normalized to the intensity of (1) spectra for the comparison purposes).

**Fig. 12.** XPS spectra of N1s line before (blue) and after (red) NO treatment (6_FCA-N_1, \(7 \times 10^{-7}\) mbar), when NO presents in residual vacuum.
material as substrate allows reproducible preparation of unrestricted number of samples of supports and catalysts. According to the datasheet, the alloy composition is (wt. %): Fe – 72.8%, Cr – 22%, Al – 5%, Y – 0.1%, Zr – 0.1%. The thickness of the foil (1 mm) was chosen from the offered list to prevent bending of the samples and as result a damage of alumina film continuity during the further manipulations with sample (XPS to STM sample holder transfer and so on).

It is important to use “as rolled” rather than “annealed” foil condition since in this case the amount of dissolved oxygen is enough for formation of the initial alumina film over the surface of steel foil [1]. All the samples were shaped as disks with a diameter of ∼8 mm and a thickness of 1 mm to meet the dimensions of STM sample holder.

2.2. Cleaning protocol

Before the mounting on sample holder loading the samples were cleaned in ultrasound bath (96% ethanol) to remove technical contamination of steel rolling and shape machining.

Prior to the film preparation both sides of the specimens were cleaned by argon sputtering to remove surface contaminations as well as the major part of the surface native oxides. The regimes of argon sputtering (Ar pressure, current and duration) were chosen to achieve Fe/C atomic ratio of ∼5 as a criterion for the quality of cleaning. It should be mentioned that the comparable fractions of metal and oxide aluminum have to be well seen after argon sputtering (see Fig. 8). The purpose of this stage is to remove the mixed oxide barrier which prevents the future diffusion of aluminum to the surface of specimens.

2.3. Alumina film preparation

After cleaning procedure steel foil samples were used for preparation of N–doped alumina thin film support following procedure described in “N–doping of alumina thin film support to improve the thermal stability of catalysts: preparation and investigation” [1], based on sample annealing in vacuum at 670°C followed by NO treatment at 670°C and NO pressure in range of $1 \times 10^{-7}$ mbar – $1 \times 10^{-6}$ mbar.
STM data

![Figure 14](image1.png)

**Fig. 14.** STM image of model catalyst Au/AlOx/FCA (13.4 nm × 8.5 nm) (Au_FCA) and cross section of the surface with gold particle.

![Figure 15](image2.png)

**Fig. 15.** STM images of model catalyst Au/N-AlOx/FCA (24.0 nm × 14.6 nm) (Au_FCA-N).

To use resistive heating to anneal the sample tungsten wire legs (Ø 0.2 mm) on tantalum springs were spot-welded to the backside of the foil disks. Tungsten legs on tantalum springs prevent the distortion of the sample position during the annealing, which is important for precise angle resolved XPS experiments (Scheme 1). The sample temperature was measured by a K type thermocouple spot-welded directly to the back side of samples. Standard water cooling of the XPS spectrometer sample holder was used to cool down the “cold” ends of thermocou-
samples for precise temperature measuring. Resistive heating allowed fast ramping of the sample temperature \((\beta = 1 \text{ C/s, see Fig. 16})\) as well as fast cooling (by turning off the power of power supply).

For all foil samples, a cycle of \(\text{Ar}^+\) sputtering followed by vacuum annealing at 700°C for 20 min and final \(\text{Ar}^+\) sputtering was used as pretreatment to remove possible contaminations with low melting point. After that all the subsequent procedures were carried out at temperature lower than 700°C (except for the temperature stability tests) and 670°C was pointed as the highest recommended temperature of using the samples [1].

The flows of NO and \(\text{O}_2\) were tuned up in a by-pass line by leak valves and then switched directly into an XPS analytic chamber to carry out \textit{in situ} XPS experiments. This allowed controlling NO / \(\text{O}_2\) exposition precisely, which was important for the final film preparation, minimizing the time of NO / \(\text{O}_2\) flow stabilization when leak valve is used. The initial residual gas pressure in the chamber was \(\sim 10^{-9} \text{ mbar}\), rising to \(10^{-8} \text{ mbar}\) between \textit{in situ} experiments. The influence of NO presence in residual vacuum is shown in Fig. 12.

### 2.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy study was performed at a VG ESCALAB HP electron spectrometer equipped with retardation grid in front of entry slit of hemispherical analyzer and single channeltron detector [3]. The nonmonochromatic Mg Kα line was used as the primary excitation. The spectrometer was calibrated using the Au4f7/2 (binding energy \(\text{BE} = 84.0 \text{ eV}\), \(\text{Ag3d}_{5/2} (368.3 \text{ eV})\) and \(\text{Cu2p}_{3/2} (932.7 \text{ eV})\) peaks [4]. The position of Fe2p line for metallic iron (\(\text{BE} = 707.0 \text{ eV}\)) has been used as the internal standard for spectra calibration [5]. The binding energy values and the areas of XPS peaks were determined after Shirley background subtraction and analysis of line shapes using XPS peak software [6,7]. Sample holder allows precise adjustment of the angle of photoelectron collection, angle between the surface normal and the analyzer lens axis within the range of \(\theta = 85^\circ - 30^\circ\), for angular resolved XPS measurements (see Scheme 1).
2.5. **Scanning tunneling microscopy**

STM experiments were performed on an UHV (ultrahigh-vacuum) variable temperature STM VT-7000 (RHK Technology, USA). The cut Pt/Ir tips were used for STM measurements. The quality of the tips was tested periodically by achieving the atomic resolution on highly oriented pyrolytic graphite. Both topography and tunneling current images were acquired simultaneously to recognize the regions of the different electron states (film and particles) or to check surface non-uniformity. The STM images were analyzed with WSxM 5.0 Develop 3.3 software [8].

**Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships which have or could be perceived to have influenced the work reported in this article.

**CRediT Author Statement**

Aleksey M. Dmitrachkov: Investigation, Data curation; Ren I. Kvon: Investigation, Writing – review & editing; Anna V. Nartova: Conceptualization, Methodology, Investigation, Data curation, Writing – original draft.

**Acknowledgments**

This work was supported by the *Ministry of Science and Higher Education of the Russian Federation* within the governmental order for Boreskov Institute of Catalysis SB RAS (project AAAA-A21-121011390011-4).

**References**

[1] A.M. Dmitrachkov, R.I. Kvon, A.V. Nartova, N-doping of alumina thin film support to improve the thermal stability of catalysts: preparation and investigation, Appl. Surf. Sci. 566 (2021) 150631–150637, doi:10.1016/j.apsusc.2021.150631.

[2] A.V. Nartova, R.I. Kvon, E.M. Makarov, V.I. Bukhtiyarov, Nitrogen-doped alumina carrier for sintering resistant gold supported catalysts, Mendeleev Commun. 28 (2018) 601–602, doi:10.1016/j.mencom.2018.11.012.
[3] R.W. Joyner, M.W. Roberts, A study of the adsorption of oxygen on silver at high pressure by electron spectroscopy, Chem. Phys. Lett. 60 (1979) 459–462, doi:10.1016/0009-2614(79)80612-0.

[4] J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Kenneth, J. Chastain, R.C. King, Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics, Inc., 1995.

[5] D. Briggs, M.P. Seah, Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, John Wiley & Sons Inc, Chichester, 1983.

[6] A.V. Bukhtiyarov, R.I. Kvon, A.V. Nartova, I.P. Prosvirin, V.I. Bukhtiyarov, In-situ XPS investigation of nitric oxide adsorption on (111), (310), and (533) gold single crystal faces, Surf. Sci. 606 (2012) 559–563, doi:10.1016/j.susc.2011.11.032.

[7] Using XPS PEAK Version 4.1. (November 2000) https://xpspeak.software.informer.com/4.1/.

[8] I. Horcas, R. Fernández, J.M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, A.M. Baro, WSxM: A software for scanning probe microscopy and a tool for nanotechnology, Rev. Sci. Instrum. 78 (2007) 013705–1-013705-8, doi:10.1063/1.2432410.