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Nitrogen-doped alumina carrier for sintering resistant gold supported catalysts

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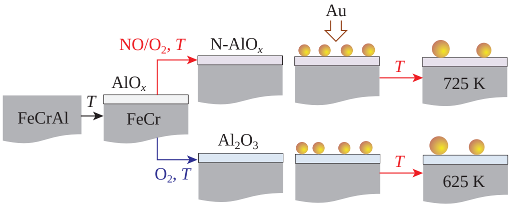
The procedure of alumina support modification by treatment with NO was developed and tested for the improvements in the resistance of supported metal particles against sintering. The stabilization effect caused by a formation of aluminum oxynitrides was clearly demonstrated for the model catalysts bearing supported gold.



Thermal stability of heterogeneous catalysts against the sintering of metal supported particles is among the main problems in the practical catalysis.[1] The resistance of particles against sintering is of great importance for the catalysts showing size effect,[2] especially when any enlargement in the particle size decreases their catalytic activity defined in terms of reaction rate normalized per metal surface atom.[3,4] One of the most prominent examples of such systems is the gold supported catalysts.[3–6] The optimal Au particle sizes are ranged within 2–8 nm depending on the particular reaction. Even a slight sintering of particles leads to the dramatic decrease in their catalytic activity. Thus, the search for the ways of stabilization of supported catalysts is an important challenge for the modern catalysis. The stability can be improved, *e.g.*, *via* a creation of specific sites on the surface of carrier by making special defects[7] or by chemical modification.[8,9] These sites have been proposed in order to stabilize the metal particles against sintering. In the present work, the modification of model alumina support by doping with nitrogen was tested for estimating the effect of this procedure on the thermal stability of systems bearing supported gold.

The procedure of model alumina carrier preparation[10] was further modified by doping with nitrogen.[†] The formation of alumina film was started during the initial annealing *in vacuo*, while the final oxygen treatment was needed only for the improvement of the film.[10] It was also proved that AlO_x/FeCrAl samples can be used for the preparation of model supported catalysts suitable for a surface science study.[5,11]

This procedure was additionally modified by annealing of the sample at 940 K in the flow of NO (for 20 min), which was performed after the primary annealing of the FeCrAl foil *in vacuo*. Subsequent treatment with O_2 ($\sim 3–5\times10^{-7}$ mbar) at 940 K was then applied for the final film improvement. Two different pressures of NO were used to obtain two nitrogen-containing samples: N-AlO_x-1/FeCrAl ($P_{NO} = 1\times10^{-7}$ mbar); N-AlO_x-2/FeCrAl ($P_{NO} = 5.5\times10^{-7}$ mbar). Furthermore, the pure AlO_x/FeCrAl sample was used as the reference.

According to the X-ray photoelectron spectroscopy (XPS) data, Al 2*p* line of all the studied samples is characterized by the binding energy of 74.4 eV. This value is typical of the alumina films obtained under vacuum conditions and, in the case of pure film, similar to α-Al_2O_3.[10] According to the XPS estimations, the film thickness of all the prepared samples was equivalent to the thickness of two layers of alumina, which is close to that of the films described earlier.[10]

Treatment with NO caused a raise of N 1*s* signal with the binding energy of 396.3–396.5 eV (Figure 1). This value is slightly higher than that of aluminum nitride,[12,13] but well corresponded to aluminum oxynitride with the general formula of $Al_xO_yN_z$ (N 1s at 396.3 eV).[14] This assignment is in line with NO introduction into the chamber after treatment of FeCrAl in high vacuum, *i.e.*, while the initial alumina film has already been formed.[10] Although

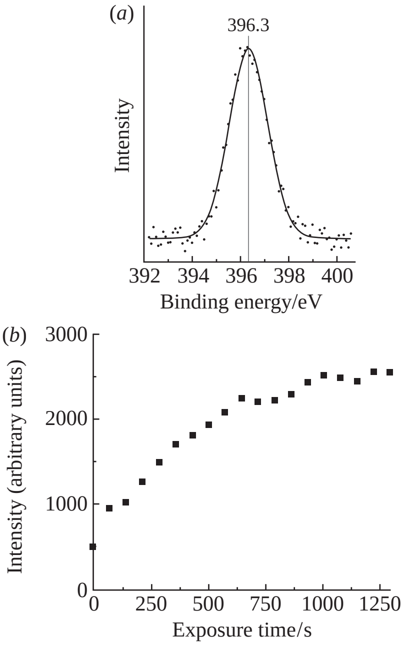


Figure 1 (*a*) Spectrum of N 1s line for N-AlO_x-1 sample and (*b*) intensity of N 1s line during the NO exposition ($P_{NO} = 1\times10^{-7}$ mbar at 940 K).

[†] The annealing of aluminum-containing heat-resistant steel alloy FeCrAl in a high vacuum at 940 K followed by annealing in O_2 ($\sim 3–5\times10^{-7}$ mbar) at 940 K provided the thin continuous film of pure alumina.

Table 1 XPS data for prepared samples.

Sample	P_{NO}/mbar	Atomic ratio	
		N : Al (±2%)	Au : Al (±2%)
AlO_x	–	0.0030	0.010
N-AlO_x-1	1×10^{-7}	0.042	0.013
N-AlO_x-2	5.5×10^{-7}	0.10	0.013

NO interacts mostly with the alumina surface, some defects capable of activating NO decomposition can still be present at the surface.

The N : Al atomic ratios calculated from the XPS data were used for the comparison of N-content in the films (Table 1). In the case of clean sample, only the traces of nitrogen were observed (due to alloy rolling in the air). At the same time, NO exposition introduced nitrogen into the oxide film, while nitrogen amounts were controlled by the NO pressure during the treatment. In the course of NO exposition at 940 K, N 1s spectra were acquired *in situ* at NO pressure of 1×10^{-7} mbar [see Figure 1(*b*)]. It is clearly seen how the intensity of N 1s line is approaching saturation at this pressure. However, the increased NO pressure in the chamber to 5.5×10^{-7} mbar during the sample treatment at 940 K raised the nitrogen content by ~2.4 times (see Table 1).

The gold particles were prepared by thermal vapor deposition at each support specimen immediately after the film formation. According to the XPS data, Au loading was approximately the same for all samples (see Table 1). The binding energy of Au $4f_{7/2}$ line is 84.0 eV for all the samples, which corresponds to metallic gold.[12]

Once gold was deposited, the thermal sintering of Au particles was studied *in situ*. For this purpose, the samples were step-by-step annealed *in vacuo* at the different temperatures with the simultaneous measurements of XPS spectra in order to calculate the gold to aluminum atomic ratios (Figure 2). The decreased Au : Al atomic ratios at an elevated temperature were used as the indicator of thermal sintering of the supported gold particles. Obviously, the enlargement of the gold particles during the sintering should decrease Au 4*f* intensity due to the gold self-screening inside the particle and increase that of Al 2*p* due to the less attenuation of Al 2*p* signal by gold. Both the factors would diminish the Au : Al atomic ratio.

XPS data (see Figure 2) shows that the enlargement of gold particles on the non-modified alumina starts at the temperatures above 575 K. Further increase of the sample temperature causes the sharp decrease in Au : Al atomic ratio (more than 5-fold at $T > 900$ K) indicating a considerable sintering of Au nanoparticles. This result is in a good agreement with previous combined experiments (XPS and scanning tunneling microscopy), whereby the Au nanoparticles with the sizes in range of 2–7 nm at the surface of non-modified AlO_x/FeCrAl support[5,6] were undoubtedly stable only at the temperatures up to 525 K, thus limiting the temperature range of size effect studies. In the case of modified Au/N-AlO_x samples, the decreased Au : Al atomic ratios were only observed after 675 K (see Figure 2). Analysis of the temperature dependence of Au : Al ratio revealed that the modification of alumina with nitrogen caused the increased thermal stability of gold particles and the shift of sintering temperature to higher values by up to 100 K. Moreover, gold is still clearly observed by XPS even after the annealing at 1025 K for the sample with the higher N-content, indicating the remarkable stability of supported Au particles.

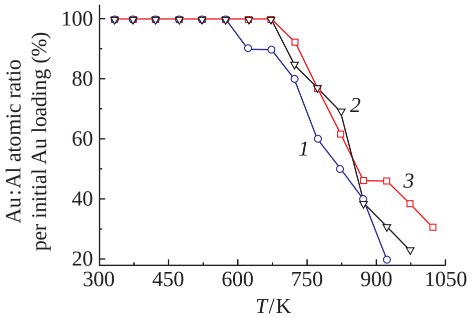


Figure 2 Temperature dependence of Au : Al atomic ratios shown as the fraction of initial Au loading for the samples: (*1*) AlO_x, (*2*) N-AlO_x-1 and (*3*) N-AlO_x-2.

Therefore, we have demonstrated that the treatment of model alumina film AlO_x/FeCrAl with NO during the sample preparation allows one to modify the model support with nitrogen *via* the formation of aluminum oxynitrides. This support modification looks very promising for real practical applications due to the stabilization of supported metal particles against the thermal sintering. In the case of supported gold particles, the proposed modification raises their sintering temperature by ~100 K, which is very important particularly for the gold catalysts since they are completely deactivated due to increase of particle size under high-temperature conditions.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2018.11.012.

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