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Room temperature epoxidation of ethylene over delafossite-based $AgNiO_2$ nanoparticles

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Sample preparation

Silver oxide was obtained as a result of the precipitation reaction between $AgNO_3$ and NaOH solutions: $2AgNO_3 + 2NaOH \rightarrow Ag_2O + NaNO_3 + H_2O$. The precipitate was washed by repeated decantation with distilled water, filtered, and dried at 90°C for 4 h. To obtain metallic silver, Ag_2O oxide was heated in vacuum directly in the preparation chamber of the photoelectron spectrometer at 500°C for 2 h. Nickel hydroxide was obtained by precipitation during the interaction between $Ni(NO_3)_2$ and NaOH solutions as follows: $Ni(NO_3)_2 + 2NaOH \rightarrow Ni(OH)_2 + 2NaNO_3$. The precipitate was washed by repeated decantation with distilled water, filtered and dried at 90°C for 4 h. To obtain nickel oxide NiO, nickel foil was oxidized in the preparation chamber of the photoelectron spectrometer in oxygen ($P(O_2)$=500 Pa) at 300° C within an hour. In addition, nickel oxide NiO was obtained by thermal decomposition of $Ni(OH)_2$ in vacuum in the preparation chamber during heating at 400°C for 2 h.

Quantitative XPS analysis

The surface composition was determined from the integral peak areas using the next expression [1]:

$$\frac{[E_1]}{[E_2]} = \frac{I_1 \cdot T_2 \cdot \sigma_2 \cdot \lambda_2 \cdot (1+0.5 \cdot \beta_2 \cdot (1.5 \cdot \sin^2\theta - 1))}{I_2 \cdot T_1 \cdot \sigma_1 \cdot \lambda_1 \cdot (1+0.5 \cdot \beta_1 \cdot (1.5 \cdot \sin^2\theta - 1))} = \frac{I_1 \cdot ASF_2}{I_2 \cdot ASF_1}, \tag{1}$$

where I – the signal intensity (peak area), T – the transmission function ($\sim E_{kin}^{-1/2}$), σ – the photoionization cross section, λ – the electron inelastic mean free path, β – asymmetry parameter, θ – the angle between X-ray source and analyzer (90°), ASF – atomic sensitivity factor. The indexes 1 and 2 correspond to elements E_1 and E_2, respectively. The photoionization cross sections (σ) and asymmetry parameters (β) were retrieved from the work of Yeh and Lindau [2]. Inelastic mean free path (λ) was calculated based on TPP-2M expression [3,4] using true density value (ρ=7.2 g/cm^3) extracted from structural data for $AgNiO_2$ (ICSD, CC=73974).

Quantitative MS analysis

Using RGA-200 instrument (SRS, USA) the MS signals with m/z values of 15, 20, 25, 41, 42 и 44 were registered during the catalytic experiment as partial pressures of corresponding ions. Neon was added as the inert reference for precise calculation of the component concentrations in the reaction mixtures. The partial pressure of each determined ions (m/z) was normalized to the partial pressure of Ne (m/z = 20). Molecules of ethylene (Et), ethylene oxide (EtO), acetaldehyde (AcA) and CO_2 are characterized by different contribution to MS signals with above-mentioned m/z ratios. For each compound (Et, EtO, AcA, and CO_2) the set of coefficients for the calculation of MS signal intensity to concentration was defined. As a result the matrix F was built.

$$Y=\begin{pmatrix}P_{15}\\P_{25}\\P_{41}\\P_{42}\\P_{44}\end{pmatrix}=\begin{pmatrix}a_{11}&a_{12}&a_{13}&a_{14}\\a_{21}&a_{22}&a_{23}&a_{24}\\a_{31}&a_{32}&a_{33}&a_{34}\\a_{41}&a_{42}&a_{43}&a_{44}\\a_{51}&a_{52}&a_{53}&a_{54}\end{pmatrix}\begin{pmatrix}Et\\EtO\\AcA\\CO_2\end{pmatrix}=\|F\|\begin{pmatrix}Et\\EtO\\AcA\\CO_2\end{pmatrix}$$

where P_i – the partial pressure of i ion; a_{ij} – corresponding coefficients. Compound concentrations may be determined by minimizing the sum of the squared differences between measured and calculated partial pressures. At the minimum point, the concentration derivatives of the sum of squared differences will be equal to zero. Through mathematical transformations, we obtain a system of linear equations as follows:

$$\sum_{j=1}^{4}\left(\sum_{i=1}^{5}A_{ik}A_{ij}C_j\right)=\sum_{i=1}^{5}A_{ik}Y_i,$$

It may be present in matrix form as $\|B\| \times C = F$, for what:

$$B_{1j}=\sum_{i=1}^{5}A_{ik}A_{ij}$$

$$F_k=\sum_{i=1}^{5}A_{ik}Y_i,$$

where C and Y - concentration and partial pressure vectors, k is changed from 1 to 4.

Finally, the system of equations for the calculation of Et, EtO, AcA, CO_2 concentrations based on the integral intensities of partial pressure of defined ions was obtained as follows:

$$\begin{pmatrix}C_{Et}\\C_{EtO}\\C_{AcA}\\C_{CO2}\end{pmatrix}=\begin{pmatrix}f_{11}&f_{12}&f_{13}&f_{14}&f_{15}\\f_{21}&f_{22}&f_{23}&f_{24}&f_{25}\\f_{31}&f_{32}&f_{33}&f_{34}&f_{55}\\f_{41}&f_{42}&f_{43}&f_{44}&f_{45}\end{pmatrix}\begin{pmatrix}P_{15}\\P_{25}\\P_{41}\\P_{42}\\P_{44}\end{pmatrix}$$

Presented system of equations was tested for quantitative analysis of model reaction mixtures with given concentrations of EtO, Et, AcA, and CO_2. The measurement error was no more than 5 rel.% for Et and CO_2 and 10 rel.% in the case of EtO and AcA.

X-ray diffraction data

Fig.S1 shows the X-ray diffraction data for the pristine $AgNiO_2$ sample before and after interaction with ethylene. Heating in a C_2H_4+O_2 mixture to 200°C led to the appearance of reflections at $2\theta\approx$ 38.1 and 44.3°, which correspond to the Ag^0 phase, while no additional peaks were observed as a result of the interaction at room temperature. The crystallite size of formed Ag^0 particles was close to15 nm. It should be noted that no additional reflections corresponding to any other nickel-containing crystallized phases other than $AgNiO_2$ were observed according to X-ray diffraction data, as well as no destruction of the initial $AgNiO_2$ structure.

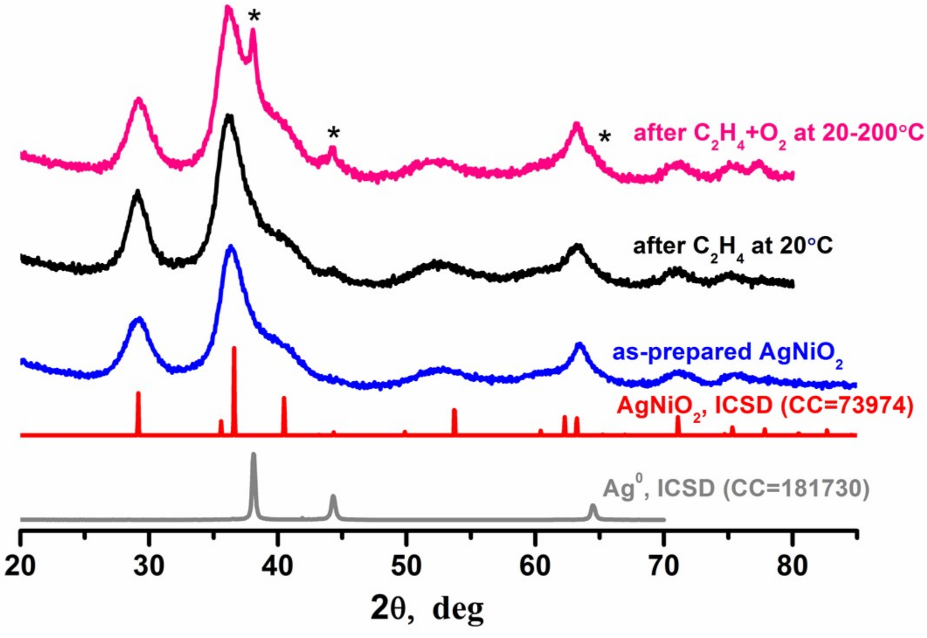

Fig.S1 X-ray diffraction pattern for mixed oxide $AgNiO_2$ before and after interaction with C_2H_4-containing reaction mixtures at room temperature or when heated to 200°C

Fig.S2 shows calculated X-ray diffraction patterns for delafossite models with stacking faults. The crystal model used for the calculation represented layers with a thickness d = 6.207 Å and a diameter of 2 nm, in which the probability of succession of these layers one after another was varied. If the one layer follows another with a shift (1/3, 2/3), then a fragment of the 3R structure without twins is obtained. When each subsequent layer is turned at 180° relative to the previous one, then a fragment of the 2H structure is obtained. It can be seen that the experimental diffraction pattern is best described by the model with a probability of 0.5. This is fully consistent with the model used to simulate the PDF data with a double cell consisting of alternating 2H and 3R layers.

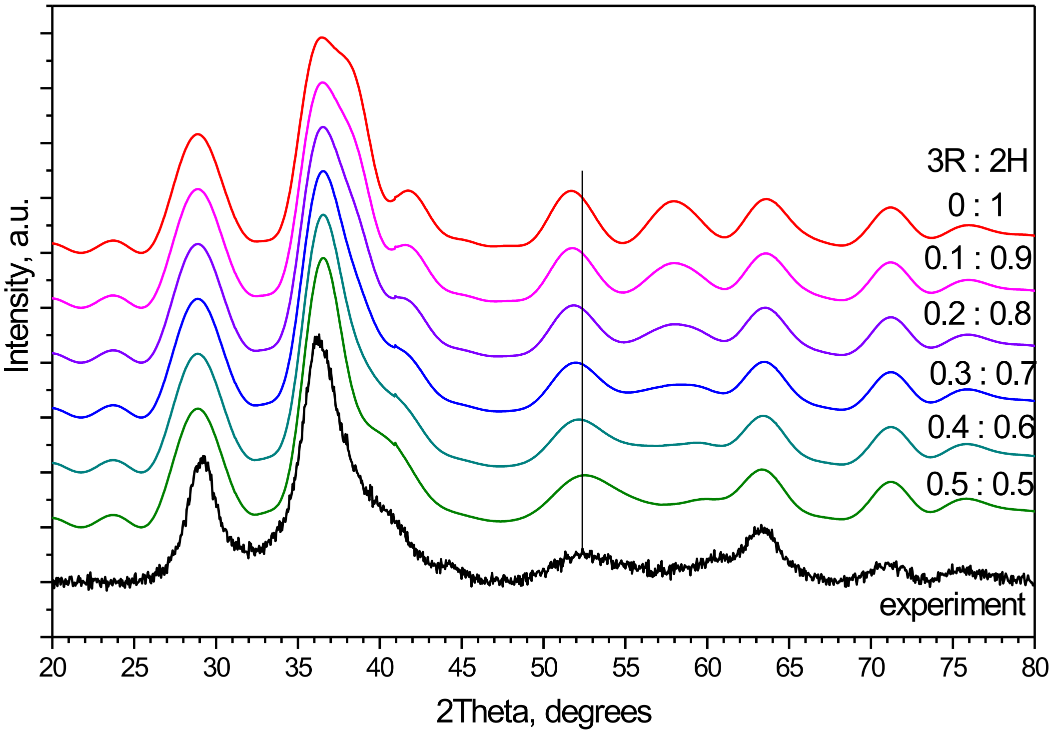

Fig. S2. Calculated XRD patterns based on models with different probabilities of the stacking faults

Table S1. PDF refined structural parameters of deficient model for $AgNiO_2$ delafossite.

Parameters	**Value**
Cell parameters	a= 2.937 Å c = 24. 545 Å
R-factor	22.5
Particle diameter (Sp_diameter)	39.2 Å
Correlated thermal vibrations (delta) 1	1.87
Atomic thermal parameters	$U_{11}(Ni)=U_{22}(Ni)=U_{33}(Ni)=0.015$ $U_{11}(O)=U_{22}(O)=U_{33}(O)=0.042$ $U_{11}(Ag)=U_{22}(Ag)=0.0096$; $U_{33}(Ag) = 0.021$
Ag site occupancies	0.95

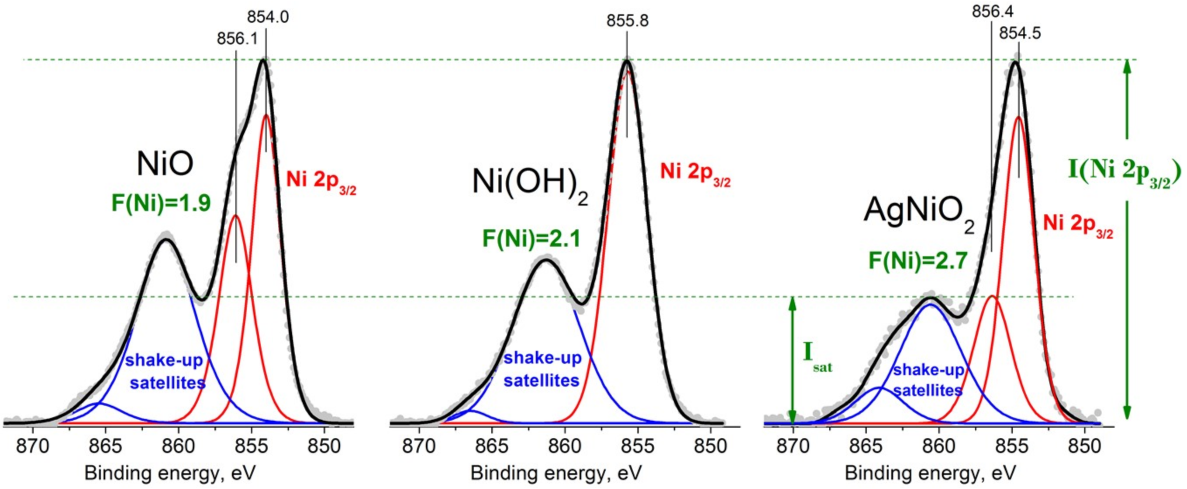

Fig.S3 Curve-fitted Ni $2p_{3/2}$ spectra for NiO, Ni(OH)$_2$ and AgNiO$_2$ compounds in as-prepared state

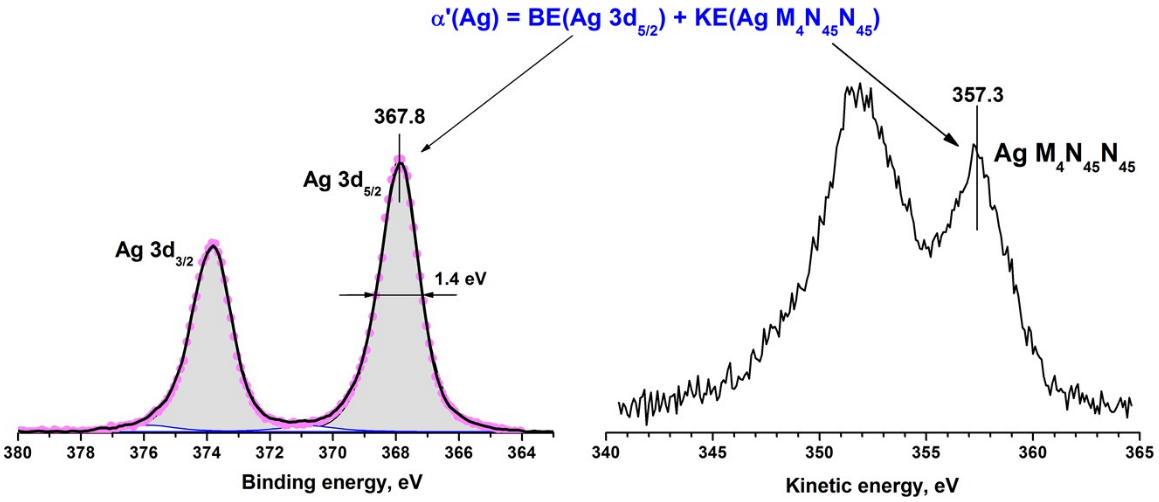

Fig. S4 Photoelectron Ag 3d and Auger Ag MNN regions for pristine AgNiO$_2$ sample

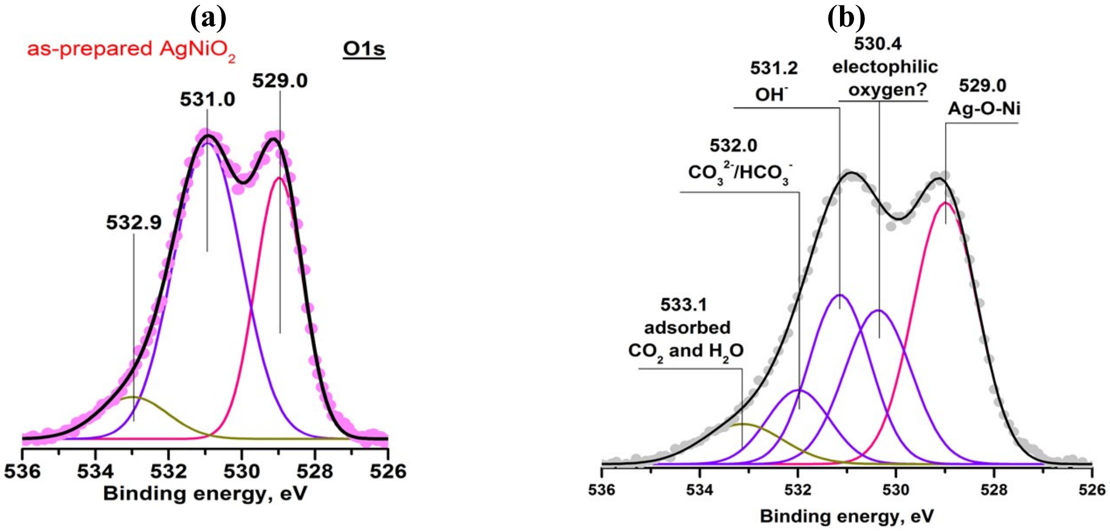

Fig.S5. Curve-fitted O 1s spectrum for as-prepared AgNiO$_2$ using (a) 3 or (b) 5 individual components

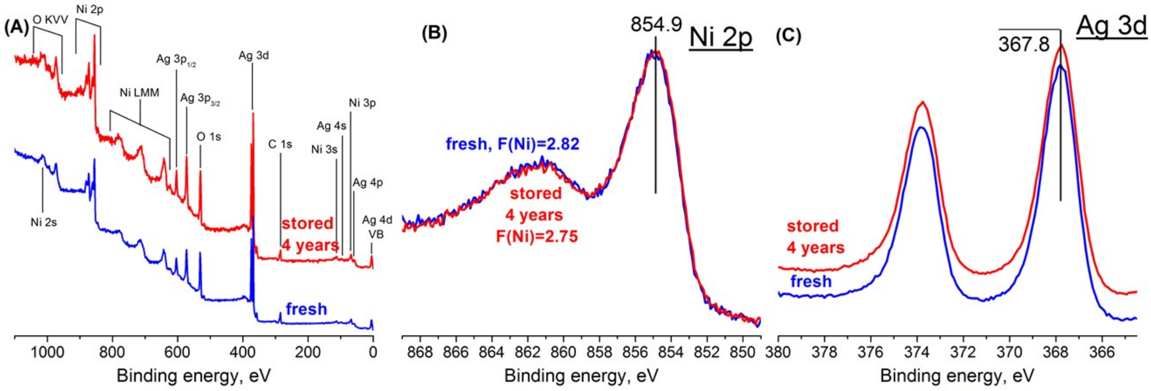

Fig.S6 Normalized spectra for fresh and stored during 4 years samples of $AgNiO_2$*: (A) survey; (B) Ni 2p; (C) Ag 3d*

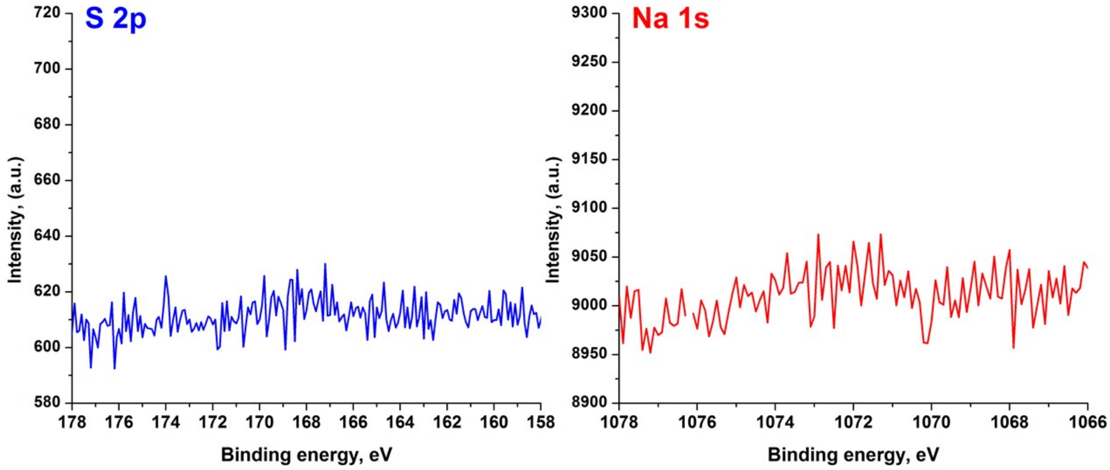

Fig.S7 Spectral regions of S 2p and Na 1s for as-prepared $AgNiO_2$

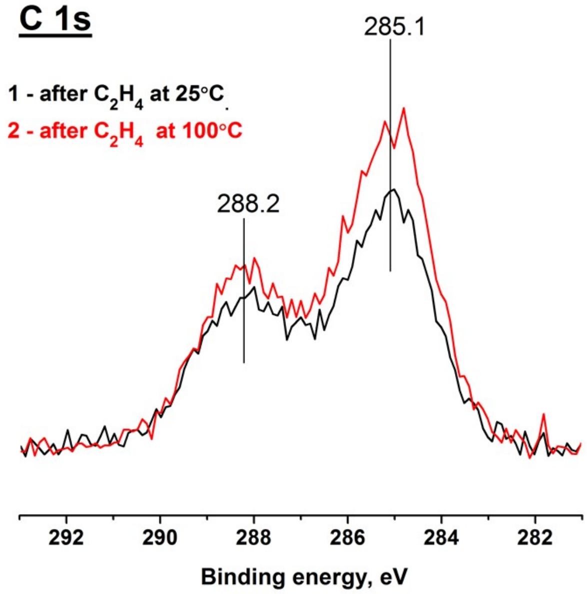

Fig.S8. Curve-fitted C 1s spectrum for $AgNiO_2$ *after interaction with* C_2H_4 *at 25 and 100 °C.*

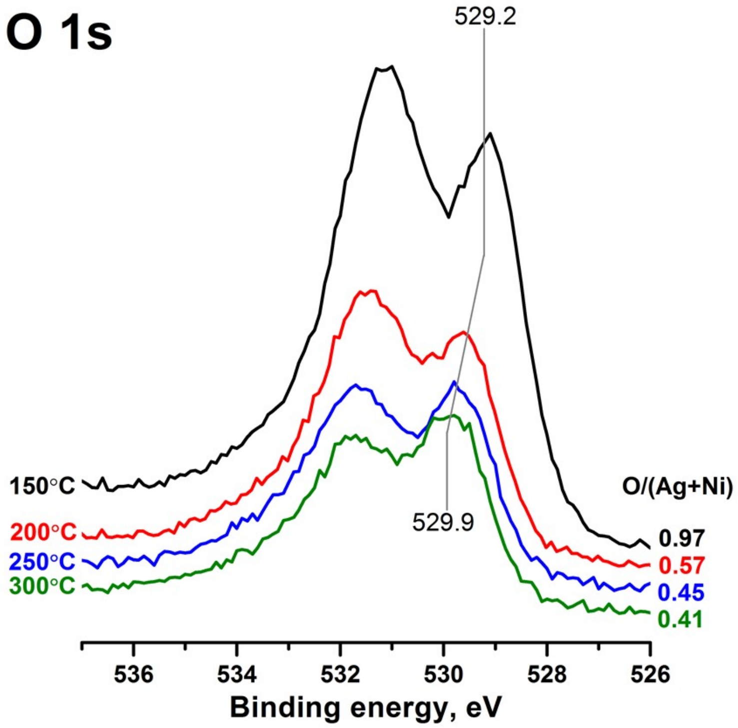

Fig.S9. Normalized O 1s spectra for $AgNiO_2$ after interaction with C_2H_4 at 150-300 °C.

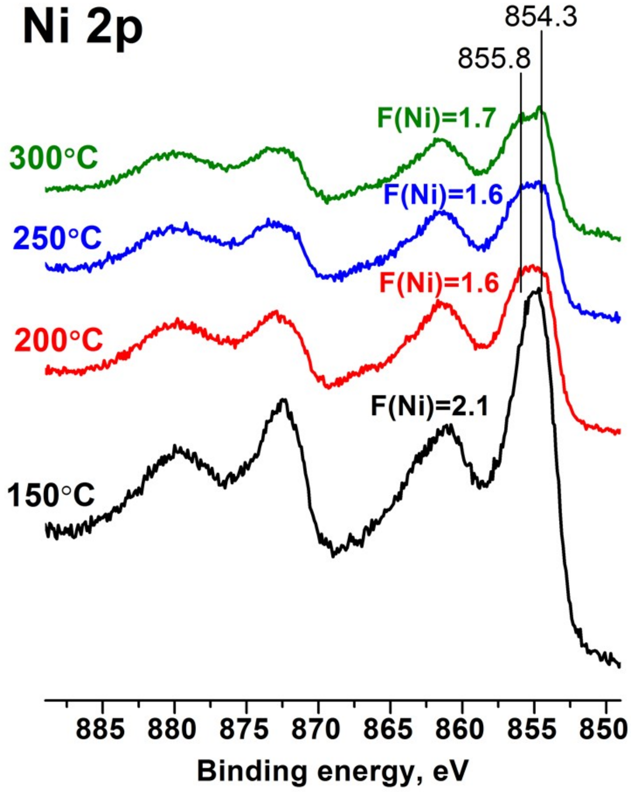

Fig.S10. Ni 2p spectra for $AgNiO_2$ after interaction with C_2H_4 at 150-300 °C

Table S2. The elements ratio on the $AgNiO_2$ surface during the interaction with ethylene at different temperatures

	Ag/Ni	O/(Ag+Ni)	C/(Ag+Ni)	O/Ni	C/Ni	O/Ag	C/Ag
pristine	0.70	0.98	0.36	1.66	0.61	2.38	0.87
T=25°C	0.61	0.96	0.34	1.54	0.55	2.52	0.89
T=60°C	0.60	0.96	0.37	1.54	0.59	2.56	0.98
T=100°C	0.58	1.00	0.41	1.58	0.65	2.74	1.12
T=150°C	0.49	0.97	0.41	1.45	0.61	2.95	1.25
T=200°C	1.40	0.57	0.42	1.38	1.00	0.99	0.72
T=250°C	1.84	0.45	0.34	1.26	0.96	0.69	0.52
T=300°C	2.13	0.41	0.39	1.30	1.23	0.61	0.58

Initially, after interaction with ethylene below 150°C the Ag/Ni ratio decreased noticeably from 0.7 to 0.49. However, when heated above 150°C, a significant increase in the Ag/Ni ratio (up to 2.13) was observed. This may be due to the high dispersion of formed Ag^0 particles or due to the selective interaction of ethylene with the Ni-containing particles formed during the $AgNiO_2$ decomposition. At a reaction temperature above 150 °C, the C/Ni ratio begins to rise, while the C/Ag value falls. This may indicate selective carbonization of the surface of nickel-containing particles. An increase in the O/(Ag+Ni) ratio at temperatures up to 150°C was associated with the accumulation of carbonate-like forms on the oxide surface (E_b(O1s)=531.3 eV) and was consistent with an increase in the C/(Ag+Ni) ratio from 0.36 up to 042. Above 150°C, the value of O/(Ag+Ni) decreased due to the destruction of $AgNiO_2$ to Ag^0 and NiO_x.

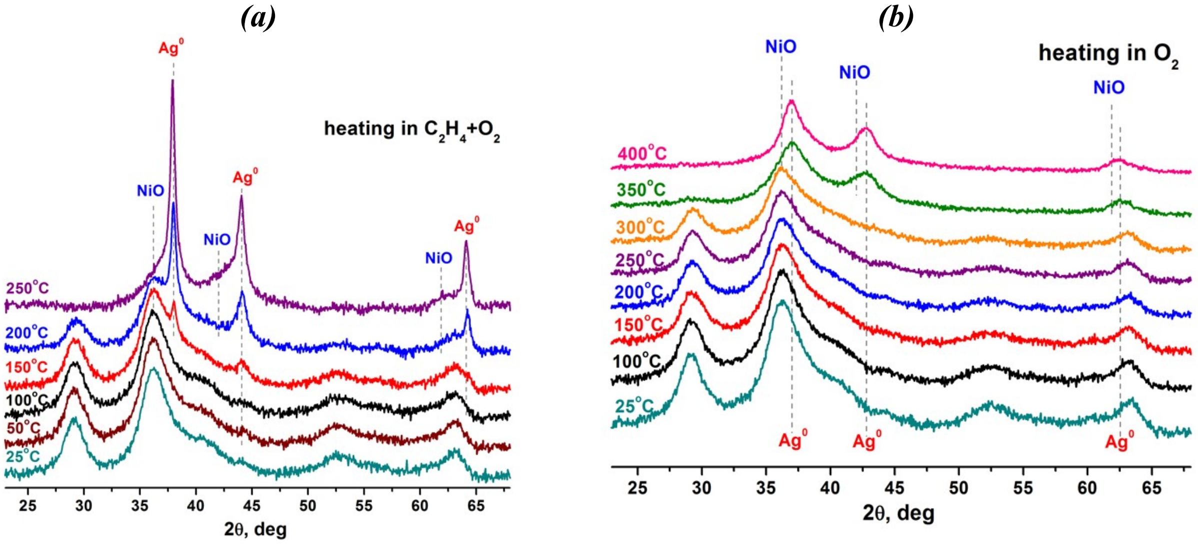

Fig.S11 In situ XRD patterns obtained when $AgNiO_2$ sample was heated (a) during the interaction with a reaction mixture of 2.5%C_2H_4/5%O_2/He or (b) in O_2 flow

The mixed oxide structure was completely destructed during heating in O_2 flow at temperature above 300°C only with the formation of Ag^0 and NiO particles. Below 300°C the heating in O_2 was accompanied by the broadening of $AgNiO_2$ reflections as a result of decrease in crystallite size (down to 1.5 nm). It probably related to amorphization of initial particles surface due to the release of silver from delafossite structure. Under C_2H_4+O_2 conditions the appearance of metallic silver was observed at T>150°C only, while the destruction of delafossite structure occurred at 250°C. Other words, thermal stability of $AgNiO_2$ in the presence of ethylene was found to be decreased by almost 100°C in the comparison with O_2 flow. The size of $AgNiO_2$ crystallites during the silver release from delafossite structure decreased as in the case of O_2 experiment. X-ray pattern obtained at 250°C in C_2H_4+O_2 mixture was simulated using individual reflections. It revealed the anisotropy of formed Ag^0 particles. The size of Ag^0 particles along 111 direction was calculated to be greatly higher, than along 002 direction. It related to silver release from delafossite structure along the specific crystallographic directions.

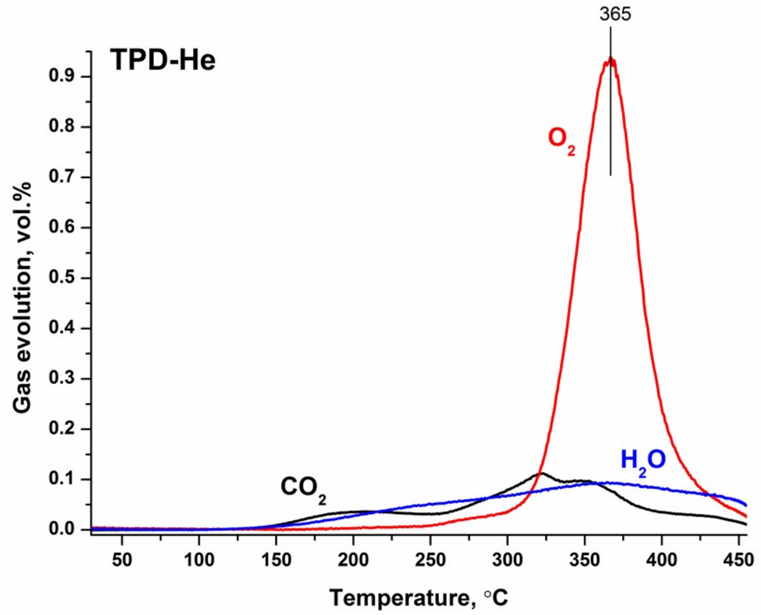

Fig.S12 TPD-He curve for $AgNiO_2$ trained in 20%O_2/He at 100°C (left). In situ XRD patterns obtained during $AgNiO_2$ heating in O_2 flow (right).

Below, the results of TPR-H_2 study are presented in ***Fig.S13***. Before TPR-H_2 experiment, 0.1 g of $AgNiO_2$ was pretreated in 20%O_2/He flow at 100°C for 2 h. Then, sample was heated in a mixture of 5%H_2/He supplied with a rate of 100 cm^3/min. At low temperatures (0-60°C) the interaction of H_2 with weakly bounded oxygen surface species was observed, while the further two-step reduction process was occurred accompanied by the appearance of TPR-H_2 peaks with maxima close to 95 and 163°C. Such maxima relate to the reduction of $AgNiO_2$ into Ag^0/NiO (peak-1) and, further, to the reduction of NiO into metallic nickel (peak-2), respectively.

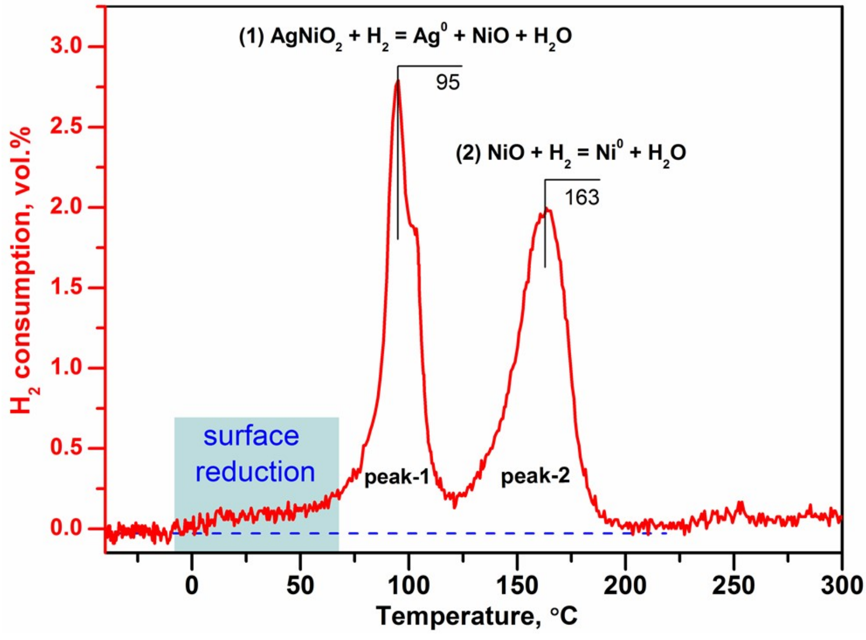

Fig.S13 TPR-H_2 curve for $AgNiO_2$ pretreated in 20%O_2/He at 100°C

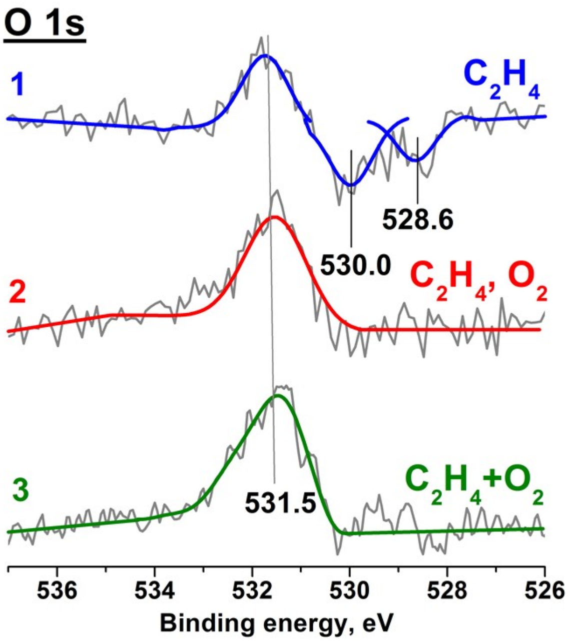

Fig.S14 Difference O 1s spectra obtained for AgNiO$_2$ oxide before and after the interaction with (1) ethylene (P=500 Pa), (2) firstly ethylene (P=500 Pa), and then with O$_2$ (P=1000 Pa), (3) a mixture of ethylene and oxygen (P=500+1000 Pa). In all experiments the interaction temperature was equal to 60°C.

In the photoelectron spectrometer chamber, a sequential treatment of AgNiO$_2$ oxide was performed. Firstly, the sample was treated in ethylene (P=500 Pa, exposure $5.5 \cdot 10^{10}$ L), and then in oxygen (1000 Pa, exposure $3.5 \cdot 10^{11}$ L) at a temperature from 60 to 300°C. We also studied the interaction of AgNiO$_2$ sample with a mixture of ethylene and oxygen (P=500+1000 Pa, total exposure $4 \cdot 10^{11}$ L) when heated up to 400°C. In both cases, at temperatures above 150°C, significant spectral changes were observed (see ***Figs.S15*** and ***S16*** below) indicating the destruction of the mixed oxide structure: (1) a drop in the F(Ni) parameter below 1.8; (2) an increase in the α'(Ni) parameter to ~726 eV; (3) removal of more than 15% surface oxygen. This is in good agreement with *in situ* XRD (***Fig.S11***) showing noticeable structural changes upon heating AgNiO$_2$ in C$_2$H$_4$+O$_2$ at T≥150°C. The most interesting was the temperature range below 100°C, when the mixed oxide structure was still preserved. ***Figure S14*** above shows the difference O 1s spectra, reflecting the changes before and after the interaction of AgNiO$_2$ with only ethylene (*curve 1*), first with ethylene, then with oxygen (*curve 2*) and with a mixture of ethylene and oxygen (*curve 3*) at 60°C. The *curve 1* indicates the titration of oxygen species with E$_b$(O 1s)=528.6 and =530 eV, as well as the accumulation of C-containing species with E$_b$(O 1s)=531.5 eV on the surface of AgNiO$_2$ as a result of interaction with ethylene. In contrast to ethylene, in the case of successive exposure to ethylene and oxygen or exposure to a C$_2$H$_4$+O$_2$ mixture at 60°C, only the accumulation of carbonate-like oxygen species with E$_b$(O 1s)=531.5 eV was observed on the AgNiO$_2$ surface. It was accompanied by an increase in the surface ratio of C/(Ag+Ni) by more than 25% compared to the initial $AgNiO_2$ sample. In this case, the changes in the difference O 1s spectra range of 528-530 eV, which is characteristic for reactive oxygen species, were insignificant. During the heating below 150°C, the F(Ni) parameter did not increase neither in O_2, nor in a reaction mixture $C_2H_4+O_2$, indicating the irreversible reduction of Ni^{3+} to Ni^{2+} during the reaction.

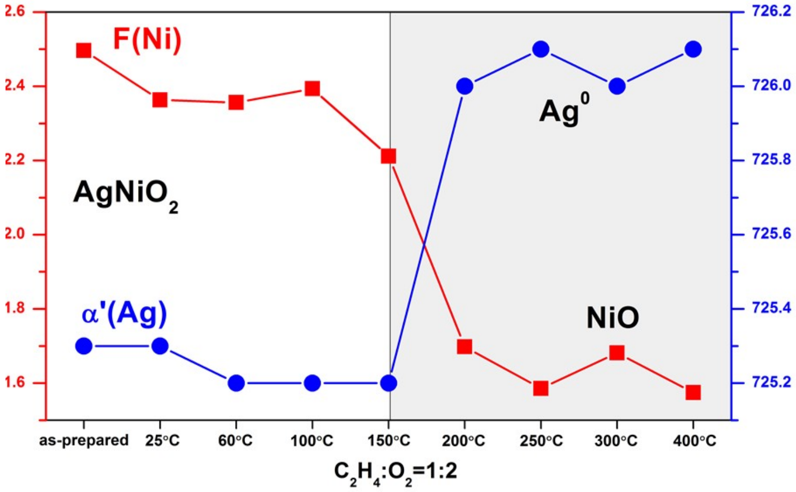

Fig.S15 The evolution of F(Ni) and α'(Ag) parameters during the heating of $AgNiO_2$ in $C_2H_4+O_2$ mixture

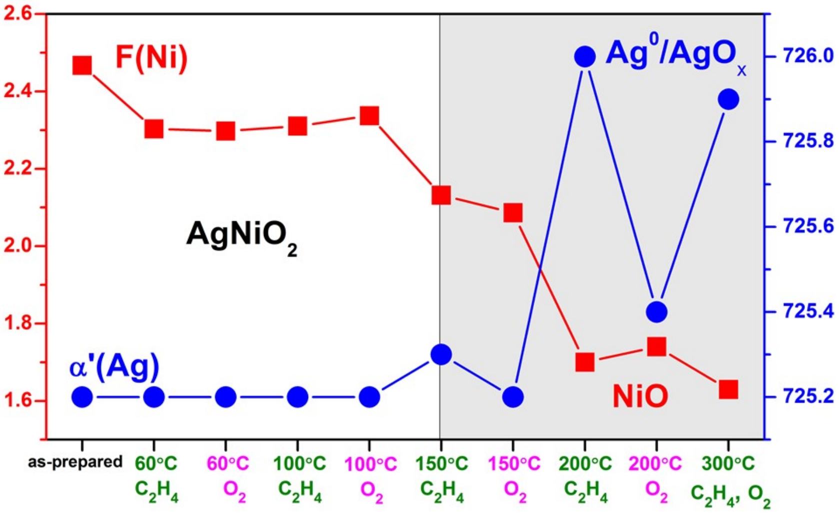

Fig.S16 The evolution of F(Ni) and α'(Ag) parameters for $AgNiO_2$ interacted successively with C_2H_4 and O_2 during the heating from 60 to 300°C

Below, TPR/TPO data for as-prepared $AgNiO_2$ sample is presented in ***Fig.S17.*** Firstly, $AgNiO_2$ sample was treated with a mixture of 2.5%C_2H_4/He at 30°C for more than 2 h. The consumption of ethylene with the formation of mixture of C_2H_4O and CO_2 was observed as it was described in ***Fig.5a*** from manuscript. Then, treated $AgNiO_2$ sample was heated up to 200°C in a mixture of 1%O_2/0.5%Ne/He supplied with a rate of 100 cm^3/min. Obtained TPO curve is presented in ***Fig.S17b*** demonstrating the O_2 consumption in two temperature ranges: (1) 20-100°C and (2) 120-180°C. Such ranges may be related to the activation of oxygen on the $AgNiO_2$ surface through chemisorption of associative species (20-100°C) or through dissociative chemisorption (120-180°C).

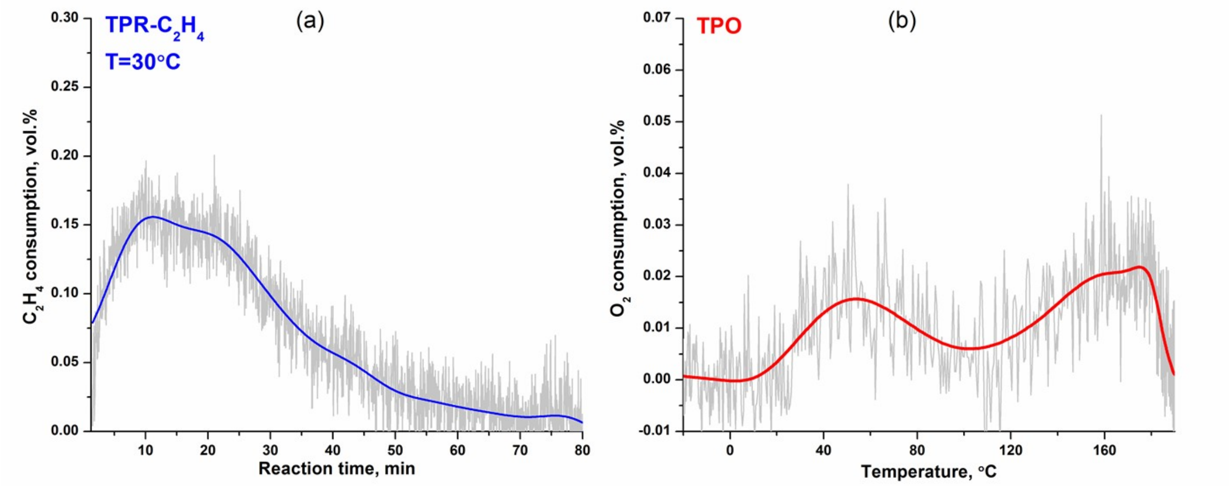

Fig.S17 (a) The curve of C_2H_4 consumption during the interaction of as-prepared $AgNiO_2$ with ethylene at 30°C; (b) TPO curve obtained during the heating of $AgNiO_2$ after the interaction with ethylene at 30°C

References

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