

## Electronic nature of potassium promotion effect in Co-Mn-Al mixed oxide on the catalytic decomposition of N<sub>2</sub>O

L. Obalová<sup>a,\*</sup>, G. Maniak<sup>b</sup>, K. Karásková<sup>a</sup>, F. Kovanda<sup>c</sup>, A. Kotarba<sup>b</sup>

<sup>a</sup>VŠB - Technical University of Ostrava, Faculty of Metallurgy and Materials Engineering, 17. listopadu 15, 708 33 Ostrava, Czech Republic

<sup>b</sup>Jagiellonian University, Faculty of Chemistry, Ingardena 3, 30-060 Krakow, Poland

<sup>c</sup>Institute of Chemical Technology, Prague, Department of Solid State Chemistry, Technická 5, 166 28 Prague, Czech Republic

\*Corresponding author: +420 596 991 532, [lucie.obalova@vsb.cz](mailto:lucie.obalova@vsb.cz)

### Abstract

A series Co-Mn-Al mixed oxides was prepared by thermal treatment of coprecipitated layered double hydroxide precursors modified with different amount of potassium (0-3 wt%) and tested in N<sub>2</sub>O catalytic decomposition. Chemical analysis, XRD, XPS, surface area measurements, SEM, and contact potential difference measurements were used for bulk and surface characterization of the catalysts. The Co-Mn-Al mixed oxide with 1.1-1.8 wt% K exhibited the highest conversion of N<sub>2</sub>O and minimum value of the catalyst surface work function. Direct correlation between the work function values and the activity of the catalysts demonstrates that N<sub>2</sub>O decomposition over K-promoted Co-Mn-Al mixed oxides proceeds via the cationic redox mechanism and controlled modification of surface electronic properties provides the essential factor for catalyst optimization.

**Key words:** Nitrous oxide, Catalytic decomposition, Layered double hydroxides, Mixed oxide catalysts, Potassium promoter, Work function

### 1. Introduction

Nitrous oxide (N<sub>2</sub>O) has a high global warming potential (310 times higher than CO<sub>2</sub>) and contributes to the destruction of stratospheric ozone. As the N<sub>2</sub>O amount emitted from nitric acid production plants (the biggest industrial source of N<sub>2</sub>O emissions) will be taxed from 2013, the attention is focused on development of N<sub>2</sub>O emissions abatement methods. Among them, N<sub>2</sub>O catalytic decomposition to oxygen and nitrogen is the simplest one.

From a big group of tested catalysts, modified cobalt oxides have been found to be very efficient in N<sub>2</sub>O decomposition [1-3]. Promising results were also obtained in the presence of cobalt-containing mixed oxides with a spinel structure prepared from layered double hydroxide (LDH) precursors, e.g. Co-Al [4, 5], Co-Mg-Rh-Al [6], Co-Pd-Al [7], Co-Rh-Al [8, 9] and Co-Mn-Al [10]. In comparison with Co<sub>3</sub>O<sub>4</sub>, mixed oxide catalysts exhibit high thermal stability and large surface area; this makes them promising candidates for industrial application as catalysts for N<sub>2</sub>O decomposition.

The improvement of catalytic activity of Co-Al, Co-Mg-Al, and Co-Mn-Al calcined LDHs by their modification with potassium promoter has been reported [11-13]. The best results were obtained in the presence of Co-Mn-Al mixed oxide with Co:Mn:Al molar ratio of 4:1:1 modified with 0.9-1.6 wt% K [13]. A comparable effect of potassium doping in Co<sub>3</sub>O<sub>4</sub> catalyst for N<sub>2</sub>O decomposition has been observed [14]. It was shown that the beneficial effect of K is mainly of electronic origin as it was found from direct correlation of the catalytic activity with the catalyst surface work function.

In the present work we focused on the elucidation of the effect of potassium doping in Co-Mn-Al mixed oxide catalysts prepared by thermal treatment of LDH precursors. The

changes in the catalytic activity in N<sub>2</sub>O decomposition are discussed in terms of modification of electronic properties upon K-loading, gauged by work function measurements.

## 2. Experimental methods

The Co–Mn–Al LDH precursor with Co:Mn:Al molar ratio of 4:1:1 was prepared by coprecipitation of corresponding nitrates. The washed filtration cake was re-suspended in a solution of KNO<sub>3</sub>, the concentration of which was adjusted to obtain a desired concentration of K in the mixed oxide. The product was calcined for 4 h at 500 °C in air; details of preparation are given in [13].

The chemical composition of the prepared catalysts was determined by AAS method using a Spectr AA880 instrument (Varian) after dissolving the samples in hydrochloric acid.

Powder X-ray diffraction (XRD) patterns were recorded using a Seifert XRD 3000P instrument with Co K $\alpha$  radiation ( $\lambda = 0.179$  nm, graphite monochromator, goniometer with the Bragg-Brentano geometry) in  $2\theta$  range from 20 to 120°, step size 0.02°. For refinement of the lattice parameters and estimation of the mean coherence length (approximately equal to crystallite size), DiffracPlus Topas, release 2000 (Bruker AXS, Germany) was used. The structural models were taken from the Inorganic Structure Database (ICSD), Retrieve 2.01 (FIZ Karlsruhe, Germany).

The X-ray photoelectron spectra (XPS) were measured using ESCA 310 spectrometer (Gammadata Scienta, Sweden). The measurements were performed using Al K $\alpha$  radiation for electron excitation. The FWHM of Au 4f<sub>7/2</sub> photoemission line of bulk Au standard was 0.65 eV. The samples were spread on a gold support and spectra were recorded at room temperature and pressure of  $6 \times 10^{-8}$  Pa. The surface static charging of the samples was suppressed by using a Scienta flood gun. Quantification of the elements' concentrations was accomplished by correcting photoelectron peak intensities for their cross-sections [15].

The surface areas of the prepared catalysts were determined by N<sub>2</sub> adsorption/desorption at -196 °C using ASAP 2010 instrument (Micromeritics, USA) and evaluated by BET method. Prior to the measurement, the samples were dried at 120 °C for at least 12 hours.

The contact potential difference ( $V_{\text{CPD}}$ ) measurements were performed by the dynamic condenser method of Kelvin with a KP6500 probe (McAllister Technical Services). The reference electrode was a standard stainless steel plate with diameter of 3 mm ( $\Phi_{\text{ref}} = 4.1$  eV) provided by the manufacturer. During the measurements the gradient of the peak-to-peak versus backing potential was set to 0.2, whereas the vibration frequency and amplitude was set to 120 Hz and 40 a.u. A single  $V_{\text{CPD}}$  value was obtained using two backing potentials (reference voltages generated in preamplifier), each being an average of 20 independent measurements. The final  $V_{\text{CPD}}$  value was an average of 60 independent points. Prior to work function measurements all samples were pressed into the pellets (10 mm in diameter) under the pressure of 8 MPa and heated under primary vacuum ( $10^{-7}$  mbar) to 400 °C, annealed for 15 min to decontaminate and standardize the surface. Actual measurements of the contact potential difference were performed at 150 °C. The  $V_{\text{CPD}}$  values were converted into the work function using a simple relation  $V_{\text{CPD}} = \Phi_{\text{ref}} - \Phi_{\text{sample}}$ .

The catalysts morphology was investigated by a Hitachi S-4700 scanning electron microscope at accelerating voltage of 20 kV. Prior to the SEM-EDX observations the samples were coated with carbon.

Catalytic measurements of N<sub>2</sub>O decomposition were performed in an integral fixed bed stainless steel reactor of 5 mm internal diameter in the temperature range from 300 to 450 °C and atmospheric pressure. Feed to the reactor (100 ml min<sup>-1</sup>) contained 0.1 mol% N<sub>2</sub>O in helium. The amount of catalyst (particle size of 0.160–0.315 mm) used in the catalytic measurements was 0.1 g (GHSV = 40380 h<sup>-1</sup>). The catalytic tests were performed under

kinetic region [18]. A GC/TCD was used to analyze N<sub>2</sub>O concentration and O<sub>2</sub>/N<sub>2</sub> molar ratio at the reactor outlet and inlet. Details of the catalytic experiment and GC analysis were published elsewhere [13].

### 3. Results and discussion

The Co:Mn:Al molar ratio in the solid determined by chemical analysis corresponded approximately to the ratio of 4:1:1, i.e., to the value adjusted in the nitrate solution used for coprecipitation. The K contents determined in the catalysts are summarized in Table 1. Powder XRD patterns of the precursors showed that the coprecipitated Co-Mn-Al LDH contained a well-crystallized hydrotalcite-like phase together with a slight amount of manganese carbonate (rhodochrosite) admixture (Fig. 1). Trace amounts of KNO<sub>3</sub> were detected in the precursors of the catalysts with high potassium content (2.7% K and 3.1% K). The Co-Mn-Al mixed oxide with spinel structure was found in all prepared catalysts; in addition, trace amounts of birnessite-type oxide, K<sub>x</sub>MnO<sub>2</sub>, were detected in the K-promoted 2.7% K and 3.1% K catalysts (Fig. 1). No statistically significant dependence of crystallite size (7.3 – 10.2 nm, determined as mean coherence length) and the spinel lattice parameter (0.808 – 0.811 nm) on the catalysts composition was found [16].

Surface composition of the catalysts determined by XPS analysis showed that the K concentration on the surface is more than two times higher than in the bulk (Table 1). Almost all potassium is present on the catalyst surface because during the preparation of the catalyst, potassium was added to the coprecipitated Co-Mn-Al LDH precursor and no significant migration to the bulk is expected due to the big cationic radius of K<sup>+</sup>. Specific surface area of prepared samples was nearly the same (89-111 m<sup>2</sup>/g) and no trend was observed with increasing K amount.

The SEM images documenting the morphology of the catalysts are presented in Fig. 2. The prepared Co-Mn-Al mixed oxides modified with K show 5–10 μm aggregates consisting of smaller grains of average diameter of about 100 nm, which, as revealed by XRD measurements, are composed of nanocrystallites (~ 10 nm). The EDX analysis showed the chemical composition of the catalysts similar to that determined by AAS (Tab. 2). XPS analysis showed a higher surface concentration of potassium and aluminum whereas the content of Co on the surface is lower than in the bulk. The elemental mapping of potassium shown in Fig. 2 indicated homogeneous promoter distribution on the catalysts' surface.

Temperature profiles of N<sub>2</sub>O conversion over Co-Mn-Al mixed oxide catalysts with various K content are shown in Fig. 3. The Co-Mn-Al mixed oxides with 1.1-1.8 wt% K were the most active in the N<sub>2</sub>O decomposition. The catalytic activity increased with increasing potassium content up to the optimum value; the further increasing K content resulted in gradual decrease of N<sub>2</sub>O conversion (Fig. 4). Kinetic parameters (rate constant and activation energy) evaluated according to the first rate law  $-r_{N_2O} = k \cdot c_{N_2O}$  by integral method are listed in Table 1. Their values are comparable to the data reported for similar systems [14, 17].

The dependence of catalyst surface work function on K content exhibited similar non-monotonous character (Fig. 4). The low values of work function corresponded to high activity of the catalysts with K loading of 5 - 8 atoms per square nanometer. The promotional effect of K due to its low ionization potential was related to the charge transfer to the catalyst inducing an electric field gradient at the surface generated by the resulting dipole and modification of the density of states characteristics. Such effects are a specially pronounced in the case of heavy alkali atoms because their large ionic radii give rise to large values of the dipole moment ( $\mu_s$  5-10 D) and the associated surface work function changes ( $\Delta\Phi \approx n\Delta\mu_s$ ) [14]. However, the initial lowering of the work function caused by separated surface dipoles was followed by the increase in work function caused by their depolarization [14]. The addition of

alkali evidently also influenced the acid-base properties of the catalysts surface, especially at high K-loadings.

The idea of importance of the Fermi-level electrons and the associated density of states is not new in catalysis [18]. In the frontier orbital picture of bonding to surfaces, the states near the Fermi level play the role of HOMO and LUMO in molecular interactions since their electrons can be rearranged with the least energetic expenses. An analogous approach has been used to account for potassium adspecies ( $K^+$ , KOH,  $K_2O$ ) in activation of  $N_2O$  on the model (100) surface of  $Co_3O_4$  by molecular modeling [14].

Direct correlation between the work function value of the examined catalysts and their catalytic activity confirmed that  $N_2O$  decomposition over K-promoted Co-Mn-Al mixed oxides proceeds via the cationic redox mechanism as suggested for similar system of K, Zn-promoted Co-containing spinel-type catalyst [3]. In this mechanism, transition metal ions act as surface electron donor centers stimulating the transfer of electron density for activation of the  $N_2O$  molecule and further as electron acceptor centers of the resultant surface  $O^-$  intermediates. This finding is in agreement with elementary steps of  $N_2O$  decomposition proposed over the Co-Mn and Co-La-Al mixed oxide prepared from LDH precursor (Eq. 1-3) [19, 20].



In these earlier works based on the results of mechanistic kinetic studies, both chemisorption of  $N_2O$  (Eq. 1) and interaction of adsorbed oxygen species with gas-phase  $N_2O$  according to Eley-Rideal mechanism (Eq. 3) were proposed to participate in the overall reaction rate. According to recently published results [21], Eley-Rideal mechanism (Eq. 3) is energetically unfavorable and  $N_2O$  decomposition proceeds only in two elementary steps (1) and (2). Surface oxygen desorption (Eq. 2) via surface diffusion and recombination is the slowest step. The surface oxygen formation can be caused either by  $N_2O$  chemisorption according to Eq. 1 (prevailing at low  $p_{O_2}$ ) or by oxygen adsorption via molecular oxygen according to Eq. 2 (prevailing at higher  $p_{O_2}$ ).

One of the processes well recognized as responsible for the initiation of the catalytic reactions is electron transfer from the catalyst surface to the antibonding orbital of the reacting molecule. In such processes like ammonia synthesis, Fischer-Tropsch or soot combustion alkali promoters can increase the sticking probability and dissociation of the reacting molecules. Owing to its high electron donation ability, potassium is one of the most efficient electronic promoters used for catalyst work function optimization. Although the investigated catalysts exhibit heterogeneous surface, the profile of work function changes with the potassium loading shows the Topping-like behavior observed for alkali on model single crystals in UHV surface science experiments [22]. Since the mechanism of  $N_2O$  decomposition over spinel catalysts involves transfer of the electron density, the adjustment of the catalyst Fermi edge/DOS characteristics can be used for optimization of their catalytic performance. Indeed, in the case of  $N_2O$  decomposition, the strong correlation between the highest catalytic reactivity and the surface work function minimum allows to use this parameter as a convenient guidance for enhancement of the catalysts activity.

#### 4. Conclusions

The promotional effect of K modification of the LDH-related Co-Mn-Al mixed oxide on its catalytic activity in  $N_2O$  decomposition was studied. The direct correlation between the catalytic activity and surface work function was found; the optimum surface concentration of K (5 - 8 K atoms per square nanometer) corresponding to the lowest work function and the

highest N<sub>2</sub>O conversions was determined. Modification of Co-Mn-Al mixed oxide with K did not cause significant changes in surface area and morphology of the catalysts. Therefore, we propose that the impact on electron properties is the main reason of the observed changes in catalytic activity of the K-promoted Co-Mn-Al mixed oxide catalysts in the N<sub>2</sub>O decomposition.

### Acknowledgments

*This work was supported by the Czech Science Foundation (project No.106/09/1664) and Ministry of Education, Youth and Sports of the Czech Republic (project No. 619 89 100 16).*

### References

- [1] L. Xue, Ch. Zhang, H. He, Y. Teraoka, *Catal. Today* 126 (2007) 449-455.
- [2] N. Pasha, N. Lingaiah, N. Seshu Babu, P. Siva Sankar Reddy, P.S. Sai Prasad, *Catal. Commun.* 10 (2008) 132-136.
- [3] P. Stelmachowski, F. Zasada, G. Maniak, P. Granger, M. Inger, M. Wilk, A. Kotarba, Z. Sojka, *Catal. Lett.* 130 (2009) 637-641.
- [4] S. Kannan, C.S. Swamy, *Catal. Today* 53 (1999) 725-737.
- [5] K.S. Chang, H. Song, Y.S. Park, J.W. Woo, *Appl. Catal. A* 273 (2004) 223-231.
- [6] J. Pérez-Ramírez, J. Overeijnder, F. Kapteijn, J.A. Moulijn, *Appl. Catal. B* 23 (1999) 59-72.
- [7] J. Pérez-Ramírez, F. Kapteijn, J.A. Moulijn, *Catal. Lett.* 60 (1999) 133-138.
- [8] S. Alini, F. Basile, A. Bologna, T. Montanari, A. Vaccari, *Stud. Surf. Sci. Catal.* 143 (2002) 131-139.
- [9] J. Pérez-Ramírez, G. Mul, X. Xu, F. Kapteijn, J.A. Moulijn, *Stud. Surf. Sci. Catal.* 130 (2000) 1445-1450.
- [10] L. Obalová, K. Pacultová, J. Balabánová, K. Jirátová, Z. Bastl, M. Valášková, Z. Lacný, F. Kovanda, *Catal. Today* 119 (2007) 233-238.
- [11] H. Cheng, Y. Huang, A. Wang, L. Li, X. Wang, T. Zhang, *Appl. Catal. B* 89 (2009) 391-397.
- [12] Q. Li, M. Meng, N. Tsubaki, X. LI, Z. Li, Y. Xioe, T. Hu, J. Zhang, *Appl. Catal. B* 91 (2009) 406-415.
- [13] L. Obalová, K. Karásková, K. Jirátová, F. Kovanda, *Appl. Catal. B* 90 (2009) 132-140.
- [14] F. Zasada, P. Stelmachowski, G. Maniak, J.F. Paul, A. Kotarba, Z. Sojka, *Catal. Lett.* 127 (2009) 126-131.
- [15] J.H. Scofield, *J. Electron Spectrosc. Relat. Phenom.* 8 (1971) 128.
- [16] K. Jirátová, J. Mikulová, J. Klempa, T. Grygar, Z. Bastl, F. Kovanda, *Appl. Catal. A* 361 (2009) 106-116.
- [17] F. Kapteijn, J.R. Mirasol, J.A. Moulijn, *Appl. Catal. B* 9 (1996) 25-64.
- [18] J. M. Thomas, W. J. Thomas, *Principles and Practice of Heterogeneous Catalysis*, VCH, Weinheim, 1997.
- [19] L. Obalová, V. Fíla, *Appl. Catal. B* 70 (2007) 353-359.
- [20] H. Dandl, G. Emig, *Appl. Catal. A* 168 (1998) 261-268.
- [21] W. Piskorz, F. Zasada, P. Stelmachowski, A. Kotarba, Z. Sojka, *Catal. Today* 137 (2008) 418-422.
- [22] J. W. Niemantsverdriet, *Spectroscopy in Catalysis*, VCH, Weinheim, 2000.

**Table 1** Chemical analysis of K-promoted Co-Mn-Al mixed oxide and the obtained kinetic parameters for N<sub>2</sub>O decomposition

Catalyst	K content AAS (wt%)	K content XPS (wt%)	$E_a$ (kJ mol <sup>-1</sup> )	$k^a$ (s <sup>-1</sup> )	$k^b$ (mol g <sup>-1</sup> s <sup>-1</sup> Pa <sup>-1</sup> )/10 <sup>-9</sup>
0% K	0	0	123 ± 18	3.3 ± 0.2	8.5 ± 0.4
0.3% K	0.25	0.72	140 ± 15	3.9 ± 0.5	5.3 ± 0.7
0.4% K	0.40	1.35	123 ± 8	4.4 ± 0.6	6.0 ± 0.8
0.6% K	0.60	1.62	128 ± 6	5.2 ± 0.7	7.1 ± 0.9
1.1% K	1.06	3.20	96 ± 6	12.2 ± 1.6	16.5 ± 2.1
1.6% K	1.60	4.37	90 ± 7	11.9 ± 1.5	16.1 ± 2.1
1.8% K	1.76	4.75	79 ± 1	16.2 ± 0.8	21.9 ± 1.1
2.7% K	2.72	7.35	102 ± 1	3.9 ± 0.2	4.8 ± 0.2
3.1% K	3.10	7.78	123 ± 8	2.6 ± 0.3	3.9 ± 0.5

<sup>a)</sup> Kinetic constant at 400 °C evaluated according to 1<sup>st</sup> rate law  $-r_{N_2O} = k \frac{\varepsilon}{1-\varepsilon} c_{N_2O}$  by integral method, where  $\varepsilon = 0.445$  is bed voidage for spherical particles

<sup>b)</sup> Kinetic constant at 400 °C evaluated according to 1<sup>st</sup> rate law  $-r_{N_2O} = k p_{N_2O}$  by integral method

**Table 2** Comparison of the bulk and surface composition of the Co-Mn-Al mixed oxide catalyst modified with 1.1 wt% K

Element	AAS (wt %)	EDX (wt %)	XPS (wt %)
Co	51.1 ± 2.6	53.0 ± 1.7	45.6 ± 9.1
Mn	10.5 ± 0.5	11.7 ± 0.5	10.8 ± 2.2
Al	5.7 ± 0.3	8.7 ± 0.6	8.9 ± 1.8
K	1.1 ± 0.1	0.9 ± 0.2	3.2 ± 0.6

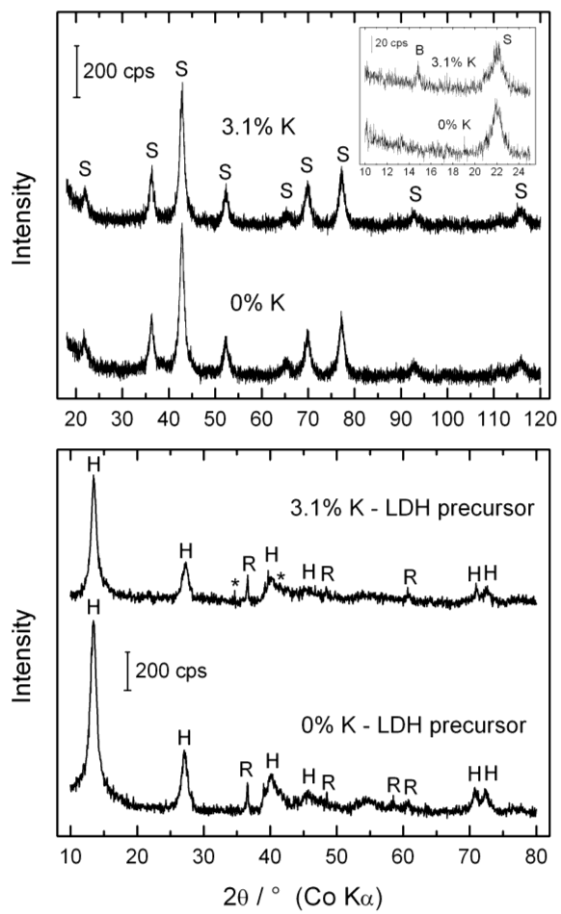
## Figure captions

**Fig. 1** Powder XRD patterns of the LDH precursors and related mixed oxide catalysts prepared by heating at 500 °C. H – hydrotalcite-like LDH; R – MnCO<sub>3</sub> (rhodochrosite); \* – KNO<sub>3</sub>; S – Co-Mn-Al spinel; B – birnessite-like oxide

**Fig. 2** Characteristic SEM image of K-promoted Co-Mn-Al mixed oxide catalyst (1.1% K sample). The dots represent potassium surface distribution

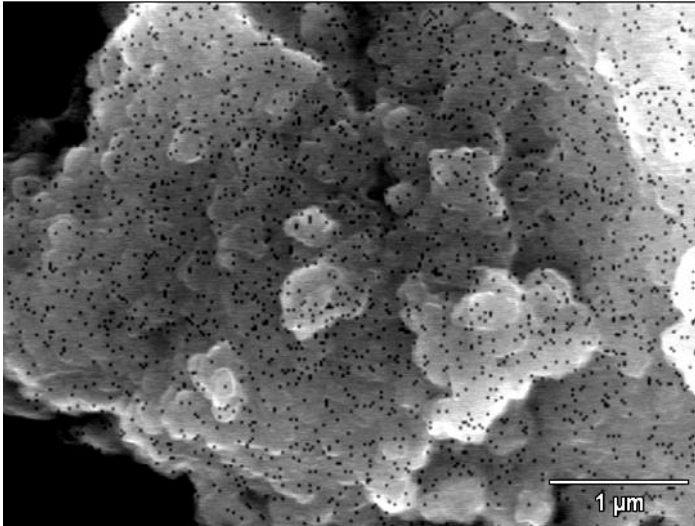
**Fig. 3** Temperature dependence of N<sub>2</sub>O conversion over K-promoted Co-Mn-Al mixed oxide catalysts. Conditions: 0.1 mol% N<sub>2</sub>O in He, GHSV = 60 l g<sup>-1</sup> h<sup>-1</sup>

**Fig. 4** Dependence of N<sub>2</sub>O conversion at 390 °C (a) and catalyst work function (b) on the potassium surface concentration of (K atoms/nm<sup>2</sup>)



**Fig. 1**





**Fig. 2**

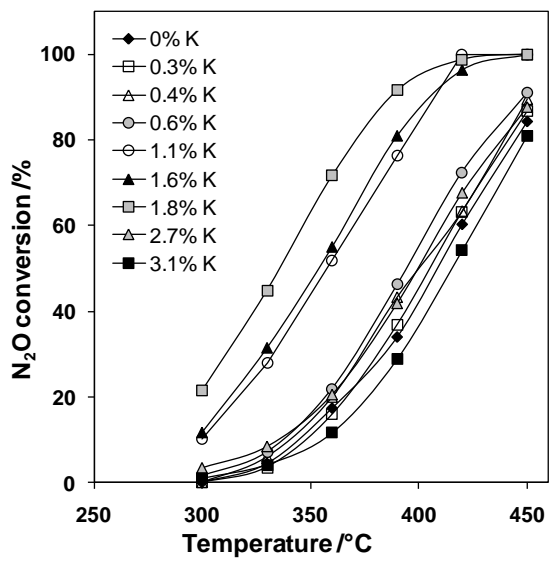


Fig. 3

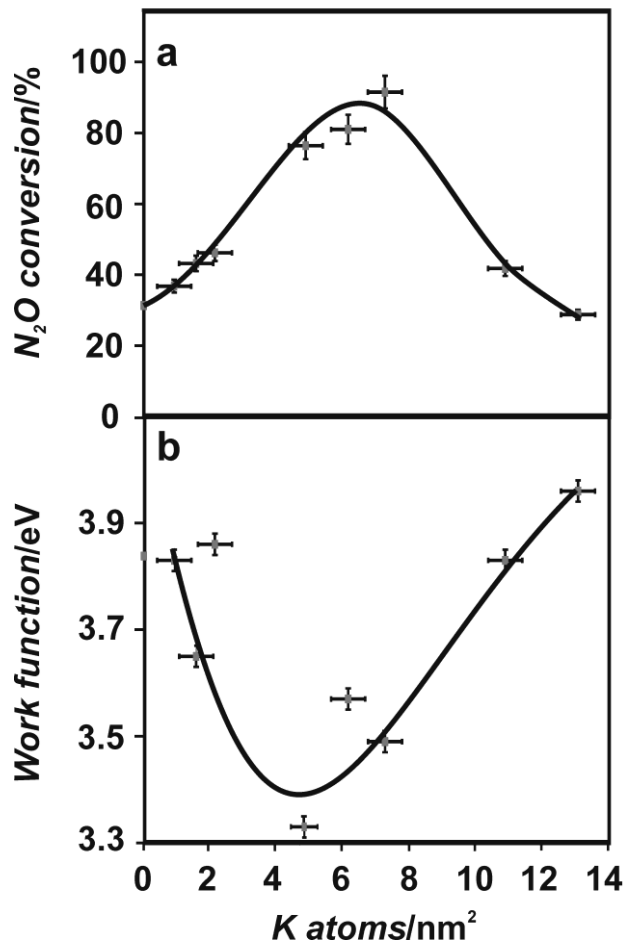


Fig. 4