Application of Kelvin method and mass spectrometry for investigation of oxide catalyst surface properties

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Many oxides are applied as catalysts for commercially important processes. Recently, decomposition of nitrous oxide into nitrogen and oxygen have became a topic of vital interest for catalytic chemistry. Two possible ways of deN\textsubscript{2}O reaction, low temperature and high-temperature, can be distinguished. Promising results were obtained for spinel oxides which contained cobalt. Because of cationic redox route, triggered by electron transfer, of N\textsubscript{2}O decomposition over these oxides, investigation of their electronic properties was justified. Therefore the work function measurements, using Kelvin method were carried out. Moreover in-situ monitoring of processes occurred at catalyst’s surface was performed using mass spectrometry.

**Keywords:** work function, Kelvin method, mass spectrometry, oxide catalyst, N\textsubscript{2}O decomposition.

**Introduction**
Nitrous oxide is a greenhouse gas with a long lifetime of about 150 years in the atmosphere. This gas has also been recognized as a potential contributor to the destruction of the ozone layer in the stratosphere. It is emitted from natural and anthropogenic sources and its concentration in the atmosphere is continuously increasing with the annual growth rate of about 0.3% [1]. Therefore decomposition of N\textsubscript{2}O into nitrogen and oxygen is a topic of vital interest for catalytic chemistry. The catalytic decomposition of N\textsubscript{2}O has been studied over several catalysts such as noble metals, pure metal oxides or mixed metal oxides [2]. High activity on deN\textsubscript{2}O reaction was observed for mixed oxides with spinel structure. The spinels are compounds of general formulation A\textsuperscript{2+}B\textsuperscript{3+}\textsubscript{2}O\textsubscript{4}. Spinels crystallize in the cubic crystal system, with the oxide anions arranged in a cubic close-packed lattice and the cations A\textsuperscript{2+} and B\textsuperscript{3+} occupying the octahedral and tetrahedral sites in the lattice. If the octahedral holes are occupied by B\textsuperscript{3+} (trivalent cations) and the tetrahedral holes are occupied by A\textsuperscript{2+} (divalent cations) it is normal spinel. A common examples of a normal spinel are Co\textsubscript{3}O\textsubscript{4} or MgAl\textsubscript{2}O\textsubscript{4}. If the tetrahedral holes are occupied by the half of B\textsuperscript{3+} and the octahedral holes are occupied by the second half of B\textsuperscript{3+} and all A\textsuperscript{2+} ions it is inverse spinel. A common examples of a inverse spinel are Fe\textsubscript{3}O\textsubscript{4} or NiFe\textsubscript{2}O\textsubscript{4} [3]. The mechanism of nitrous oxide decomposition over this catalysts involves the cationic redox route, triggered by electron transfer [4]:

\[
\text{N}_2\text{O} + \text{M}^{2+} \rightarrow \text{N}_2 + \text{M}^{3+-\text{O}}^-
\]

\[
2\text{M}^{3+-\text{O}}^- \rightarrow \text{O}_2 + 2\text{M}^{2+}
\]

For that reason the catalytic activity strongly depends on electronic properties of the catalyst’s surface [5, 6]. The electronic properties of the material can be described by the work function which is the amount of energy needed to release electrons from a material’s surface and can be measured using Kelvin method. Moreover in-situ monitoring of processes occurred at surface is enabled when mass spectrometry is used additionally.

**Kelvin method**
The Kelvin method is based on the occurrence of a contact potential difference (V\textsubscript{CPD}) outside the surface of two different materials (electrodes) that have been electrically connected, these being the Kelvin probe (p) and the sample (s) under investigation. The electrodes are placed close to each other to form a capacitor, which collects the related surface charge. The presence of this contact potential difference is the result of having different Fermi level by unconnected Kelvin probe and the sample. At the time of connection, the Fermi level
of the system is equating. The electrons from the higher Fermi level are moving to the other conduction band and shifting from one electrode to the other until the same electrochemical potential is reached in both of them. This movement of charges causes a contact potential difference between the electrodes. The $V_{\text{CPD}}$ values are converted into the work function using simple relation $eV_{\text{CPD}} = \Phi_p - \Phi_s$ [7].

**Experimental part**

The contact potential difference ($V_{\text{CPD}}$) measurements were carried out by the dynamic condenser method of Kelvin with a KP6500 probe (McAllister Technical Services). The KP6500 probe was installed in vacuum chamber and the catalyst sample was mounted on a micrometric manipulator holder (Fig. 1).

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. The $V_{\text{CPD}}$ measurements were carried out under the vacuum of $10^{-7}$ mbar with the use of the samples pressed into the pellets (diameter 10 mm, 8 MPa). To standardize the surface the samples were heated to 400°C for 15 min. 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 additional element of this apparatus establish Quadrupole gas analyzer. It is mounted directly on a vacuum chamber so that the entire sensor is at the same pressure as the rest of the vacuum system. In his application residual gas analyzer is used to monitor the processes occurred at surface of examined sample such as temperature programmed desorption of adsorbed chemical individuals (TPD) or surface reaction (TPSR). The temperature programmed experiments were performed with flow rate of the feed (He, 5% N$_2$O/He) of 7000 h$^{-1}$, and the heating rate of 10°C/min in the range of 25–700°C.

Quadrupole mass analyzers use oscillating electrical fields to selectively stabilize or destabilize the paths of ions passing through a radio frequency quadrupole field. Only a single mass/charge ratio is passed through the system at any time, but changes to the potentials on magnetic lenses allows a wide range of m/z values to be swept rapidly, either continuously or in a succession of discrete hops. A quadrupole mass analyzer acts as a mass-selective filter. In mentioned experiments the progress of the processes was monitored by means of a quadruple mass spectrometer (SRS RGA200) by following the m/z = 44 (N$_2$O), 32 (O$_2$), 28 (N$_2$), 30 (NO) and 18 (H$_2$O) lines.

In this work the application of Kelvin method and mass spectrometry to study spinel catalysts dedicated for low-temperature N$_2$O abatement is shown.

**Results and discussion**

The work function measurements were preceded by a heating aimed at removing adsorbed individuals. Desorption of water adsorbed at catalyst’s surface upon temperature raising was monitored in-situ. The typical experimental result of Temperature Programmed Desorption (TPD) of water is presented in Fig. 2. The adsorbed molecules of water are desorbing upon temperature raising, simultaneously the $V_{\text{CPD}}$ value of sample increases therefore the work function value decreases.
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Fig. 2. The influence of adsorbed water molecules on the work function value of cobalt spinel surface.

In Fig. 3 the typical experimental result of Temperature Programmed Surface Reaction (TPSR) measurement of N₂O decomposition over Co₃O₄ is presented. The concentration of N₂O decreases as the reaction temperature increases, whereas corresponding concentrations of products (N₂ and O₂) increases.

The experimental data, expressed as N₂O conversion (X_{N₂O}) versus temperature (T) were fitted with the kinetic model: \( X_{N₂O} = 1 - e^{-kt} \), where k is the rate constant given by the Arrhenius formula \( k = A \cdot e^{-\frac{Ea}{RT}} \) and Ea is an activation energy (kJ/mol), R is the gas constant. From conversion curves the values of half conversion temperature of N₂O decomposition (\( T_{50\%} \)) were determined. In the Fig. 4 the \( T_{50\%} \) values for selected spinels: Co₃O₄, MgCo₂O₄, CoAl₂O₄ were plotted against work function values.

From presented results it can be inferred that the activity of the catalyst in the N₂O reaction strongly depends on electronic properties of the sample.

Conclusions

The experimental results obtained for the spinel catalysts revealed that the catalytic activity of the examined materials is associated with the work function value. The activity of the catalyst increases upon the work function lowering. Moreover it is important to clean the surface of material from adsorbed molecules before the work function measurement to obtain comparable conditions.

Fig. 3. Typical TPSR result of N₂O decomposition in dry atmosphere over cobalt oxide catalyst.

Fig. 4. The half conversion temperature of N₂O decomposition over spinel catalysts versus work function.

References