Guidelines for optimization of catalytic activity of 3d transition metal oxide catalysts in N_2O decomposition by potassium promotion

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ABSTRACT

The effect of potassium promotion on deN$_2$O activity of various 3d electron spinels (Mn_3O_4, Fe_3O_4, Co_3O_4) was investigated by TPSR in conjunction with parallel work function measurements. The results were interpreted in terms of a surface dipole model ($K^{\delta+}$–$O_{surf}^{\delta-}$) supported by DFT molecular modelling. The substantial enhancement of deN$_2$O reactivity of Co_3O_4 and Mn_3O_4 upon K addition (decrease of $\Delta T_{50\%}$ by 150 °C) was observed, whereas for Fe_3O_4 the promotional effect was unexpectedly small. The maximum deN$_2$O activity was found for potassium surface coverage of 2, 6, 8 K atoms/nm^2 for cobalt, iron and manganese spinels, respectively. In each case the optimal level of doping was found for the minimum of the measured work function indicating that this parameter can be use for optimization of the catalyst deN$_2$O reactivity.

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1. Introduction

Nitrous oxide is recognized as one of the major contributors to the greenhouse effect and destruction of the ozone layer in the stratosphere [1]. Due to its harmful impact on the environment, catalytic decomposition of N_2O into N_2 and O_2 is a subject of intensive investigations [2]. Among various types of catalysts investigated for the low temperature deN$_2$O reaction the mixed oxides with the spinel structure exhibit the highest activity [3,4]. The most promising performance in nitrous oxide decomposition was observed so far for cobalt spinel based catalysts [5,6]. Modifications achieved by introducing of various metal ions (such as Zn, Ni, Cu, Mn, Al, Mg,) to the Co_3O_4 structure [7–9] can substantially improve its catalytic activity. Recently, several papers have reported the beneficial effect on deN$_2$O activity of oxides catalysts by alkali promotion. It was shown that the effect is present on binary 3d transition metal oxides [10,11] and ternary oxides such as spinels [3–6,12] and more complex systems like hydrotalcites [13,14]. Thus the promotional effect of alkali on catalytic deN$_2$O activity seems to be of a general nature, yet being still debating.

The aim of this work is to elucidate the correlation of the electronic effect of potassium doping gauged by the work function with the deN$_2$O catalytic activity for a series of spinels of various 3d electron counts, such as: Mn_3O_4, Fe_3O_4, Co_3O_4.

2. Experimental

The analytical grade samples of Mn_3O_4, Fe_3O_4 and Co_3O_4 were obtained from Sigma–Aldrich. Potassium doping was achieved by incipient wetness impregnation from KOH by introducing 0.5–2.0 ml of the solution with various concentrations (0.01–0.20 M) onto 1.0 g of the spinel samples. The potassium loading was expressed as number of atoms per nm^2 (n_K). The promoted samples were next calcined at 400 °C for 4 h. For each spinel the series of ten samples with different K-loading (in the range of 0–12 atoms/nm^2) were investigated. The BET measurements, carried out by means of Quntasorb Junior instrument, showed that K-doping did not change the spinels surface area, which were in the range of 22 ± 7 m^2/g.

The Temperature Programmed Surface Reaction (TPSR) measurements of N_2O decomposition in the range of 20–900 °C were performed in a quartz flow reactor using 300 mg of the catalyst (sieve fraction of 0.2–0.3 mm). The flow rate of the feed (5% N_2O in He) of 7000 h^{-1}, and the heating rate of 10 °C/min were used. The progress of the reaction was monitored by a quadruple mass spectrometer (SRS RGA200).

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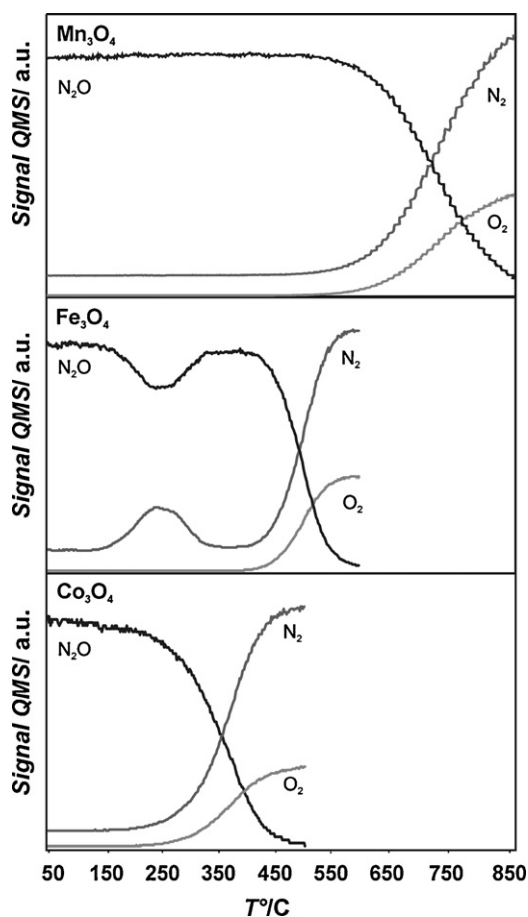E-mail address: kotarba@chemia.uj.edu.pl (A. Kotarba).

Fig. 1. TPSR results of N_2O decomposition over Co_3O_4, Fe_3O_4 and Mn_3O_4 model catalysts.

The contact potential difference (V_{CPD}) measurements were carried out by the Kelvin method with a KP6500 probe (McAllister Technical Services). The reference electrode was a standard stainless steel plate with diameter of 3 mm ($\Phi_{ref} = 4.1$ eV). 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_{CPD} value was obtained using two backing potentials, each being an average of 20 inde-
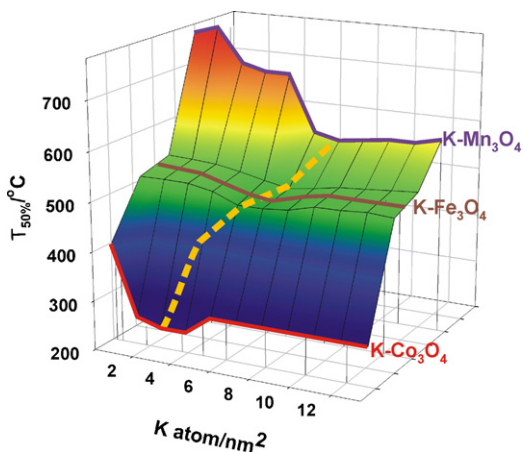

Fig. 2. The changes of half conversion temperature of N_2O decomposition as a function of potassium doping for Co_3O_4, Fe_3O_4 and Mn_3O_4 spinels. Dotted line shows the optimal doping pathway.

pendent measurements. The final V_{CPD} value was an average of 60 independent points. Prior to the measurements the samples were pressed into the pellets (10 mm in diameter) under the pressure of 8 MPa and heated under vacuum of 10^{-7} mbar to 400 °C for 15 min to standardize the surface. The measurements of the contact potential difference were performed at 150 °C.

For all calculations the DFT level of theory was chosen with use of the Vienna ab initio Simulation Package (VASP) [15]. The projector augmented plane wave (PAW) [16] method together with PW91 GGA exchange-functional [17] were employed. All calculations were performed using standard Monckhorst–Pack [18] grid with the cutoff energy of 400 eV. Geometry optimization was performed until the net forces acting upon the ions were smaller than 1×10^{-2} eV A^{-1}. For Bader analysis on a charge density grid an algorithm developed by Tang et al. [19] was employed. Surfaces geometries were constructed by cleaving the solid in the normal $\langle 1\,0\,0 \rangle$ and $\langle 1\,1\,1 \rangle$ directions, with vacuum separation of 15 Å between two periodically repeated slabs. In the adopted computational model both the stoichiometry of the bulk Co_3O_4 ($Co_{30}O_{40}$ and $Co_{48}O_{64}$ for (1 0 0) and (1 1 1) planes, respectively) and the 1:2 ratio between octahedral and tetrahedral ions were preserved. The optimized lattice constant, $a_{PW91} = 8.051$ Å and the u parameter of 0.263 together with Co^O–O and Co^T–O bond lengths ($d_{Co^O-O} = 1.0917$ Å and $d_{Co^T-O} = 1.924$ Å) compare well with the experimental values of 8.082 Å, 0.263, 1.920 Å and 1.935 Å, respectively [20]. More detailed description of the calculation scheme is discussed elsewhere [21].

3. Results and discussion

The TPSR measurements of deN$_2$O reaction over the spinel catalysts presented in Fig. 1 show that the catalytic activity of Mn_3O_4 is much lower than for Fe_3O_4 and Co_3O_4. However, in the case of cobalt and manganese spinels the N_2 and O_2 formation processes are essentially concerted, whereas for iron spinel two separate reaction regimes can be distinguished. In the low temperature range of the N_2O decomposition (150–250 °C) the N_2 formation step is kinetically separated from O_2 formation, indicating that the oxygen atoms produced upon O–N$_2$ bond cleavage stay at the surface of the catalyst [5]. The recombination of the latter, controlled by surface diffusion and subsequent desorption of O_2 starts above 400 °C. As a result the reaction slows down gradually since the active sites are continuously blocked by the intermediate oxygen adspecies accumulated at the catalyst surface. Moreover, the interaction of surface reactive oxygen species with the Fe_3O_4 results in its rather easy transformation into the Fe_2O_3 phase, as can be observed by changes in the iron samples colour from black (magnetite) into brown (hematite) during the deN$_2$O tests. Such phase transformation in iron-oxide catalysts at about 200 °C is often observed in an oxidising environment [22]. In contrast to iron the recombination of oxygen on the cobalt spinel is much easier and follows almost directly the O–N$_2$ bond breaking. The cobalt and

Table 1
The half conversion temperatures, activation energies for N_2O decomposition together with work function values for investigated spinel catalysts.

Sample	$T_{50\%}/$°C	Activation energy/kJ mol^{-1}	Work function/eV
Mn_3O_4	760 ± 15	110.8 ± 0.8	4.40 ± 0.04
Fe_3O_4	520 ± 10	113.2 ± 0.7	3.88 ± 0.03
Co_3O_4	398 ± 8	63.4 ± 0.5	3.81 ± 0.01
[a]K–Mn_3O_4	567 ± 11	57.4 ± 0.4	4.19 ± 0.05
[a]K–Fe_3O_4	480 ± 9	93.7 ± 0.7	3.20 ± 0.04
[a]K–Co_3O_4	240 ± 5	27.6 ± 0.2	3.31 ± 0.01

[a] The samples with optimal level of potassium loading ($n_K = 8$, 6 and 2 atoms/nm^2 for Mn_3O_4, Fe_3O_4 and Co_3O_4, respectively).