Catalysis Today 176 (2011) 369–372

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

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

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ARTICLE INFO

Article history:
Received 21 September 2010
Received in revised form
12 November 2010
Accepted 16 November 2010
Available online 14 December 2010

Keywords:
Spinel catalyst
Potassium promoter
N_2O decomposition
Work function
Cobalt
Manganese
Iron
Oxide

ABSTRACT

The effect of potassium promotion on *de*N_2O 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 *de*N_2O 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 *de*N_2O 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 *de*N_2O reactivity.

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 *de*N_2O 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 *de*N_2O 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 *de*N_2O 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 *de*N_2O 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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doi:10.1016/j.cattod.2010.11.043

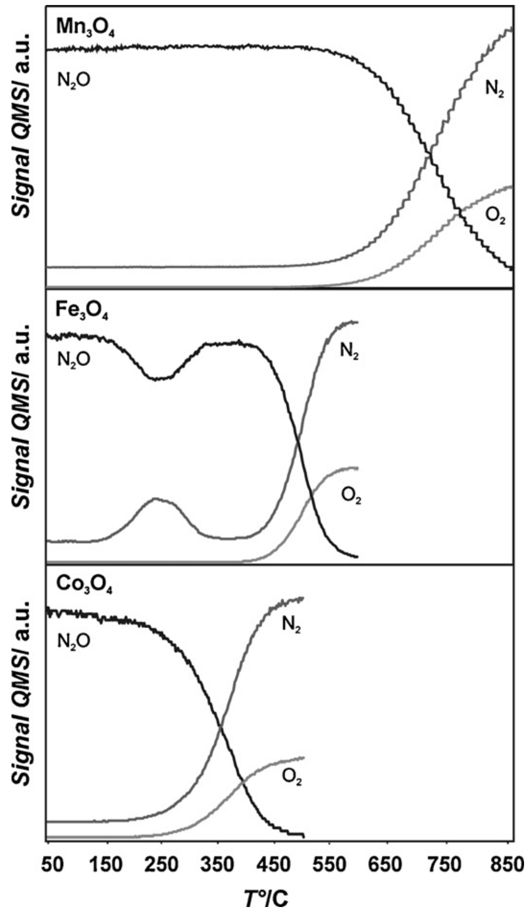

Fig. 1. TPSR results of N_2O decomposition over Co_3O_4, Fe_3O_4 and Mn_3O_4 model catalysts.

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 independent 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.

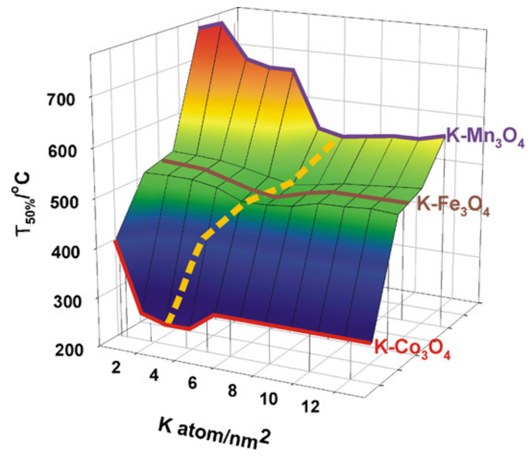

Fig. 2. The changes of half conversion temperature of N_2O decomposition as a function of potassium doping for Co_3O_4, Fe_3O_4 and Mn_3O_4 spinels. Dotted line shows the optimal doping pathway.

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 ($d_{Co^O-O} = 1.0917\,\textbf{Å}$ and $d_{Co^T-O} = 1.924\,\textbf{Å}$) 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 *de*N_2O 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 *de*N_2O 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).

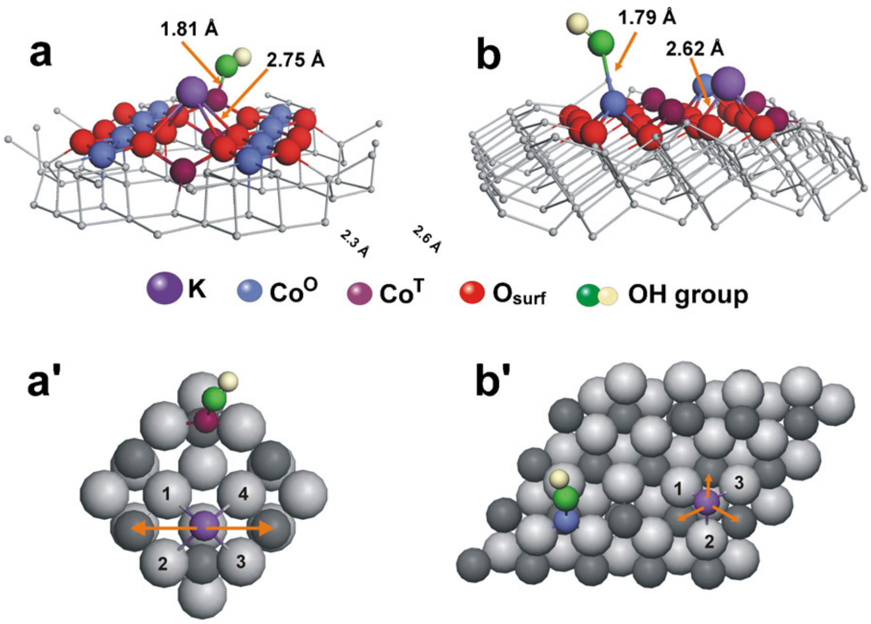

Fig. 3. Perspective view of potassium hydroxide adsorbed on the (1 0 0) and (1 1 1) planes of cobalt spinel (a and b, respectively), together with the corresponding top views (a, b). The calculated values of bond lengths and transfer of electron density from potassium to the adjacent cobalt ions are indicated by the arrows.

manganese spinels are more resistant to oxidation into trivalent oxides as can be inferred from the previous works on surface redox couples for oxide catalysts [23].

The sequence of the *de*N_2O activity of selected spinel catalysts, measured by temperature of 50% conversion ($T_{50\%}$) was found to be correlated with the work function values (Table 1), confirming the electronic character of the catalytic process. This correlation suggests that controlled tuning of the catalytic activity can be achieved by the surface promotion with alkali [6]. The effect of potassium promotion on catalytic activity in N_2O decomposition of the investigated Co_3O_4, Fe_3O_4 and Mn_3O_4 spinels is shown in Fig. 2, where the $T_{50\%}$ values are plotted versus K-loading. For all examined samples $T_{50\%}$ is decreasing upon potassium doping, for Co_3O_4 and Mn_3O_4 the substantial impact of the promoter was observed ($\Delta T_{50\%} > 150\,^{\circ}C$), while in the case of Fe_3O_4 the promotion is rather feeble. Moreover, all curves showed a nonmonotonous behaviour with the minimum located at 2, 6, 8 K atoms/nm^2 for cobalt, iron and manganese spinels, respectively. The observed dependence on potassium surface concentration can be analysed in terms of surface dipoles model ($K^{\delta+}$–$O_{surf}{}^{\delta-}$) manifested by work function lowering upon doping (*vide infra*). For the non-doped samples, and those with the optimal level of potassium promotion, the values of the activation energy for N_2O decomposition were determined by fitting the experimental data, expressed as N_2O conversion (X_{N_2O}) versus temperature (T), using a simple kinetic model: $X_{N_2O} = 1 - e^{-kt_s}$ justified elsewhere [5]. The apparent activation energies together with the corresponding work function values are collected in Table 1.

As implied by the results presented in Fig. 1 and Table 1 the most pronounced effect of potassium doping was observed for cobalt spinel. In order to elucidate the surface status of the promoter and its impact on the work function the DFT modelling was performed. The calculated surface energies of the bare (1 0 0) and (1 1 1) surfaces of cobalt spinel were found to be 1.39 and 1.48 J/m^2, respectively. The resultant morphology with the dominant exposition of these planes (and a minor contribution of the (1 1 0) plane) revealed by Wulff construction is consistent with the TEM observations [21]. For the modelling of the (1 0 0) plane the constructed slab model exhibits the following surface composition $\{1Co^{T}_{2c}, 4Co^{O}_{5c}, 2Co^{T}_{4c}, 6O_{3c}, 2O_{4c}\}$, whereas in the case of (1 1 1) it consists of $\{4Co^{T}_{3c}, 2Co^{O}_{3c}, 10O_{3c}, 6O_{4c}\}$. The subscripts indicate the coordination number of the exposed surface ions. Surface potassium was modelled as the most stable dissociated K^+, OH^- pair of adspecies (Fig. 3). On the (1 0 0) plane the hydroxyl group is linked to highly unsaturated $Co^{T}{}_{2c}$ ion (with the Co–OH distance of 1.81 Å). The optimal location of potassium corresponds to K^+ species bound to four surface O_{3c} ions giving rise to adsorption energy of 67.4 kcal/mol. The bond lengths between potassium and the surface oxygen are quite similar (2.75–2.81 Å). The total change in surface atomic Bader charge of the KOH upon adsorption is +0.31, indicating a pronounce transfer of the electron density to the surface. The corresponding variation of the partial charge of the Co^{O}_{5c} ions, connected with the potassium via surface O_{3c}, was about −0.11 (the direction of the charge flow is presented in Fig. 3a). The remaining part of the electron density is accumulated on the oxygen ions (−0.06 on each) directly linked to the K^+ adcation. In the case of the (1 1 1) plane the hydroxyl group were placed on the Co^{O}_{3c} ions forming the bond of 1.79 Å in length. The most stable K localization ($\Delta E_{ad} = 58$ kcal/mol) corresponds to a hollow position surrounded by the three O_{3c} anions with the K–O_{3c} bond lengths of 2.59 Å. The change in the total surface partial charge of KOH after adsorption is +0.29 and the most pronounced modifications (0.09 of the Bader unit) were localized at the two Co^{O}_{6c} (fully coordinated) and one Co^{T}_{3c} (Fig. 3b). The calculated maps of the surface electrostatic potential revealed that the $K^{\delta+}$–$O_{surf}{}^{\delta-}$ dipoles weakened the interfacial potential, which along with the increase in the Fermi energy leads to the decrease of the spinel work function by 0.45 eV. This value is in a remarkable agreement with the experimentally determined $\Delta\Phi = 0.5$ eV (Table 1), confirming the proposed surface status of potassium promoter, revealed by DFT calculations. Since the work function can be correlated directly with the spinel catalyst activity in *de*N_2O reaction we can assigned the promotional effect of potassium doping to the formation of the $K^{\delta+}$–$O_{surf}{}^{\delta-}$ surface dipoles. Facilitating the electron shuttling between the reacting species and the surface by tuning the electron properties of the catalyst at optimal loading they do not block the active sites leaving the octahedral cobalt centers intact (Fig. 3).

4. Conclusions

The effect of potassium promotion on *de*N_2O activity of Mn-, Fe-, Co-spinels was examined by TPSR and work function measurements, supported by DFT molecular modelling. For Co_3O_4 and Mn_3O_4 the substantial impact of K promoter was observed ($\Delta T_{50\%}$ lowers by 150 °C), while in the case of Fe_3O_4 the promotion was rather weak. A nonmonotonous behaviour of the activity with the maximum located at 2, 6, 8 K atoms/nm^2 for cobalt, iron and manganese spinels respectively was paralleled by the work function changes. Thus the latter can be used as a guiding parameter for tuning the optimal performance of the spinel catalysts.

Acknowledgement

The authors are grateful to the financial support from COST action the Grant No. 299/N-COST/2008/0.

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