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Potassium Promotion of Cobalt Spinel Catalyst for N_2O Decomposition—Accounted by Work Function Measurements and DFT Modelling

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Abstract The beneficial effect (decrease of the half conversion temperature by 100 °C) of potassium doping, in the range of 0–5 atoms/nm^2, on N_2O decomposition over Co_3O_4 was analyzed by work function measurements and DFT calculations. The optimal potassium surface loading was found to be 1.8 atoms/nm^2. The effect was explained in terms of electronic promotion gauged by lowering of the catalyst work function by 0.48 eV (for K_2CO_3 precursor) and 0.44 eV (for KOH). The promotional effect is discussed in relation to the theoretical and experimental surface dipoles determined from Hirshfeld atomic charges and geometry of the postulated potassium adspecies and from the Topping model, respectively.

Keywords Cobalt spinel · Potassium promoter · N_2O decomposition · Work function · Dipole moment · DFT

1 Introduction

Nitrous oxide is widely recognized as important greenhouse gas and the ozone layer destructor [1]. It is emitted from natural and antropogenic sources and its concentration in the atmosphere is continuously increasing with the annual growth rate of about 0.3% [1]. Because of the harmful effect to environment decomposition of N_2O into N_2 and O_2 is a topic of vital interest for catalytic chemistry [1, 2]. Despite of its thermodynamic instability, N_2O is kinetically inert toward direct decomposition into the constituting elements. Thus, this reaction, to be efficient, requires a catalyst for practical applications, especially in the excess of water and oxygen, usually present in the real conditions [2, 3]. However, none of the many catalysts developed until now exhibit satisfactory performance in real deN_2O process, especially at low temperature regime (below 350 °C) such as those of tertiary abatement in nitric acid plants [3, 4]. So far, many catalytic systems such as noble metals [5, 6], metal oxides [7, 8], ion-exchanged zeolites [9, 10] were investigated for the low temperature deN_2O, but the satisfactory solution in the presence of oxygen and water is still lacking. One of the simple promising systems exhibiting high catalytic activity in such reaction is cobalt spinel [11–13]. Modification by substitution with various transition or alkaline earth metal ions (such as Zn, Ni, Cu, Mn, Al, Mg,) leads to further improvement of the Co_3O_4 catalyst activity [14–16]. Recently it has been found that doping of Co_3O_4 with alkali has also a beneficial effect on the catalytic performance in deN_2O reaction [11–13, 17].

Reported in the literature effect of Co_3O_4 doping with alkali metals has not always been achieved intentionally [13], but resulted form the applied synthesis procedure, where potassium or sodium carbonates or hydroxides are commonly used as precipitating agents. As a result the residual alkali impurities may easily be entrapped in the cobalt hydroxycarbonate precursor of the spinel catalyst [18]. The effect of potassium was associated with enhanced reducibility of Co^{3+} produced upon oxidation of Co^{2+} during N_2O decomposition. This redox conjecture has been

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essentially based on H_2-TPR data only. Another explanation discused the observed promotional effect of alkali in terms of the more speculative reduction of metal-oxygen bond strength which is supposed to facilitate the dioxygen desorption [11]. It was inferred from the studies on the samples deliberately doped by impregnation that even minute amounts of alkali promoter can effectively improved the catalyst performance. Once the alkali addition is further increased the beneficial effect is gradually declining. Such nonmonotonous character with the optimum at low loading may suggest that the electronic promotion is essentially responsible for the observed changes in the cobalt spinel activity in the N_2O decomposition. It is well known that adsorption of alkali promoters on metallic surfaces modifies their electronic properties gauged by the work function. Owing to the exceptionally low ionization potentials of alkali metals, a substantial part of the promotion effect is thought to be related with the charge transfer to the catalyst surface, inducing an electric field gradient at the surface, generated by the resulting dipole moment. Such effects are specially pronounced in the case of heavy alkali atoms because their large ionic radii give rise to large values of the dipole moment and the associated work function changes ($\Delta\Phi \propto n\Delta\mu$) [19]. Such effect is not exclusive for metal surfaces but has been also reported for molybdenum carbide catalyst, where doping of potassium led to strongly nonmonotonous changes in the work function correlated with the analogous changes in the rate constant for indole hydrodenitrogenation [20].

In this paper we focused our attention on the elucidation of the changes in electronic properties of Co_3O_4 as a function of K-loading using KOH and K_2CO_3 precursors. The experimentally determined work function modifications upon potassium doping were complemented with DFT calculations and correlated with the activity of K-doped Co_3O_4 catalyst in N_2O decomposition.

2 Experimental

The Co_3O_4 samples of 16 m^2/g were obtained from commercial supplier (Fluka). Potassium doping was achieved by incipient wetness impregnation from K_2CO_3 by introducing 1.2 mL of the solution with various concentrations (0.004–0.08 M) onto 1.60 g of the spinel catalyst. In the case of KOH precursor Co_3O_4 samples of 250 mg were prepared by successive addition of 20 μL portions of 0.078 M KOH, to achieved the desired K contant. The potassium loading was expressed as number of atoms per nm^2 (n_K) and the corresponding samples were labelled as n_K-K/Co_3O_4. The promoted samples were next calcined at 673 K for 4 h. The BET measurements carried out by means of a Quntasorb Junior Instrument showed no significant changes in the surface area upon doping procedure.

For the work function measurements the samples were pressed into the pellets (10 mm in diameter) under the pressure of 8 tons. Prior to work function measurements all samples were heated under primary vacuum (10^{-3} mbar) to 673 K, annealed for 15 min to decontaminate and standardize the surface. Actual measurements of the contact potential difference were performed at 423 K.

The Temperature Programmed Surface Reaction (TPSR) measurements of N_2O decomposition in the range of 293–873 K were performed in a quartz flow reactor using 500 mg of the catalyst (sieve fraction of 0.2–0.3 mm), flow rate of the feed (5% N_2O, 5% N_2O + 1% H_2O and 1,500 ppm N_2O + 1% H_2O + 3% O_2 in He (5.0) feed composition were used) of 7,000 h^{-1}, and the heating rate of 10 K/min. The saturation with 1% of water was achieved by means of a thermodynamic saturator connected to a Perkin Elmer cryostat. The progress of the reaction was monitored by means of a quadruple mass spectrometer (SRS RGA200) by following the m/z = 44 (N_2O), 32 (O_2), 28 (N_2), 30 (NO), and 18 (H_2O) lines.

The contact potential difference (V_{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. The reference electrode was a standard stainless steel plate with diameter of 3 mm (Φ_{ref} = 4.3 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_{CPD} value was obtained using two backing potentials (reference voltages generated in preamplifier), each being an average of 20 independent measurements. The final V_{CPD} value was an average of 60 independent points. The V_{CPD} values were converted into the work function using a simple relation $eV_{CPD} = \Phi_{ref} - \Phi_{sample}$.

The unrestricted DFT (Density Functional Theory) calculations were performed with the Dmol^3 package implemented in the Materials Studio (version 2.2) of Accelrys Inc. Double-numerical quality basis set with polarization functions (DNP), semicore relativistic pseudopotentials [21, 22] and generalized gradient-corrected (GGA) functional in parameterization proposed by Perdew, Burke, and Ernzerhof (rPBE) were used in all calculations. A real-space cutoff of 4 Å was used to improve computational performance. For the Brillouin zone sampling the method proposed by Monkhorst-Pack [23], with 2 × 2 × 2 (for bulk calculations) and 2 × 2 × 1 (for slab calculations) resolution, was applied. The geometry optimization

following the BFGS scheme [24] was performed for the unit cell size and all ions position in the bulk model, and for two top layers of the slab model. Three low index (100), (110) and (111) planes of cobalt spinel were chosen for calculations with the vacuum thickness set at 10 Å. The oxide thickness was selected in such a way to ascertain comparable properties of the middle slab and the bulk atoms. Three possible models of surface potassium (potassium hydroxide, surface dissociated hydroxide and oxide species) located on the most stable (100) plane of Co_3O_4 were investigated.

3 Results and Discussion

The typical experimental results illustrating the effect of potassium doping on N_2O decomposition efficiency is shown in Fig. 1, where the TPSR profiles are shown for bare Co_3O_4 (Fig. 1b) and for the most active 1.8-K/Co_3O_4 catalyst (Fig. 1a) together with the blank experiment (Fig. 1c) for dry 5% N_2O/He. The experimental data, expressed as N_2O conversion (X_{N2O}) versus temperature

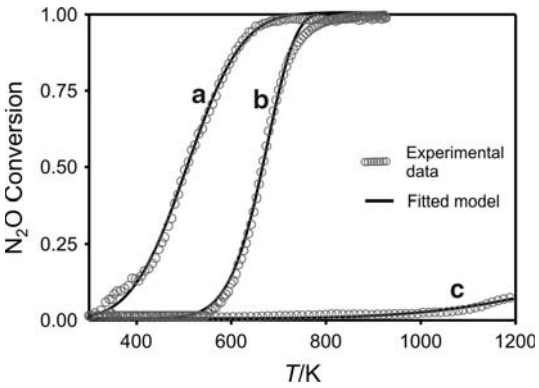

Fig. 1 Typical TPSR results of 5% N_2O decomposition in dry atmosphere over **a** K-Co_3O_4 ($K = 0.23$), **b** bare Co_3O_4, and **c** blank reactor. The doted lines correspond to experimental data whereas the solid lines show the theoretical fit

(T) for the contact time $t_s = 0.39$ s, were fitted with the kinetic model described elsewhere [25]:

$$X_{N_2O} = 1 - e^{-kt_s}$$

with the rate constant given by the Arrhenius formula $k = A \cdot e^{-\frac{E_a}{RT}}$, where E_a, activation energy [kJ/mol]; R, gas constant [J/(mol K)]. The determined values of the activation energies and the rate constants (for $T = 673$ K) for various feed composition and K-loading ($n_K = 0 - 4.8$ atom nm^{-2}) are summarized in Table 1. From comparison of the data, it can be inferred that for all samples the apparent activation barriers are lowered, whereas the corresponding rate constants are significantly increased upon K doping. The most pronounced promotional effect is observed for potassium loading in the range of $n_K = 2 - 4$ atom nm^{-2}. In the presence of the inhibitors (H_2O and O_2) the improvement of catalytic performance though deteriorated was still preserved, reaching 90% conversion at 703 K for the 1.8-K/Co_3O_4 sample.

The activity parameters (E_a and $T_{50\%}$ values) of the K/Co_3O_4 catalysts (impregnated with K_2CO_3) are plotted as a function of potassium loading in Fig. 2 a, b, and compared with the corresponding work function changes (Fig. 2c). All the presented curves showed nonmonotonous behavior of the Φ values with the minimum located at $n_K = 1.8$ atom nm^{-2}, indicating that the activity of K-doped spinel is clearly correlated with the catalyst work function. Additionally in the insert of Fig. 2c the work function variation with n_K for the catalyst obtained by impregnation with KOH is also shown. In this case the $\Delta\Phi$ changes are less pronounced and the broader minimum is shifted towards higher loadings ($n_K = 3.85$ nm^{-2}). Different results observed for KOH and K_2CO_3 suggest that not only the alkali metal itself and its surface concentration, but also the precursor type play an important role in tuning the spinel activity. It can be explained by different nature of the resultant potassium surface species formed upon thermal pre-treatment of the samples. To substantiate this premise the changes in the work function were

Table 1 Apparent activation energies (E_a) and rate constants at 400 °C (k_{400}) for N_2O decomposition over K-doped Co_3O_4 catalysts for various feed compositions

Catalyst	n_k/nm^{-2}	E_a/kJ/mol			k_{400}/s^{-1}		
		5% N_2O	5% N_2O + 1% H_2O	0.15% N_2O + 1% H_2O + 3% O_2	5% N_2O	5% N_2O + 1% H_2O	0.15% N_2O + 1% H_2O + 3% O_2
Co_3O_4	0.00	77.8 ± 0.5	70.8 ± 0.4	81.1 ± 1.6	1.80	0.69	0.22
	0.24	48.6 ± 0.5	–	–	3.55	–	–
	0.48	71.1 ± 0.3	–	–	3.72	–	–
K-Co_3O_4	1.83	27.6 ± 0.2	47.3 ± 0.3	41.5 ± 0.9	8.13	4.10	4.21
	3.71	40.9 ± 0.3	–	–	15.88	–	–
	4.81	48.1 ± 0.4	–	–	10.76	–	–

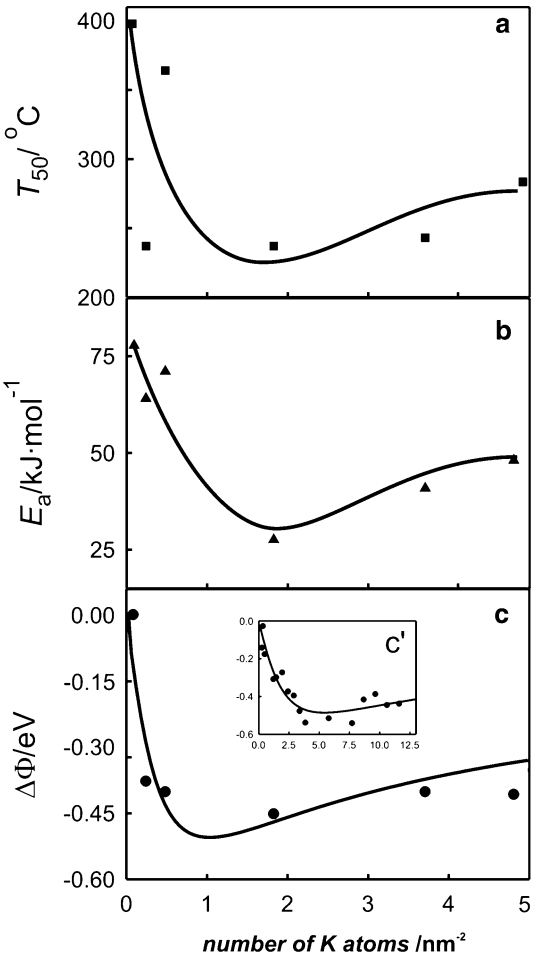

Fig. 2 **a** The half conversion temperature of N_2O (T_{50}%), **b** apparent activation energy (E_a) and **c** work function changes ($\Delta\Phi$) as a function of potassium loading (Θ_K) introduced from K_2CO_3 and (c insert) KOH precursor

analysed within the surface dipole model and corroborated by DFT calculations.

According to Helmholtz [19] at low surface loading, deposited potassium forms positive ions and associated surface dipoles giving rise to linear drop in the work function, as observed in Fig. 2c. When potassium ions come closer with the gradual increase in coverage, mutual depolarization takes place, and after passing the minimum the work function starts to increase with the amount of potassium added. The resultant nonmonotonous character of the work function variation can be analyzed in terms of the Topping equation [26]:

$$\Delta\Phi = \frac{\mu}{\varepsilon_0} \cdot n_K \cdot \left(1 + \frac{\kappa \cdot \alpha \cdot n_K^{3/2}}{4 \cdot \pi \cdot \varepsilon_0}\right)^{-1},$$

where $\Delta\Phi$ is express in eV, n_K in m^{-2}, and $\kappa\alpha$ express in cm^2/V is the product of geometrical factor and polarizability of surface potassium. The κ value varies from 9 to 11 depending on the surface packing which implies that the value of polarizability of surface potassium is in the range $\alpha = 17 - 190$ Å, similar to the data for potassium adsorbed on model surfaces of transition metals [27].

Upon substitution of the numerical values the curve fitting (with *Mathematica* software) of the experimental data for the Co_3O_4 samples impregnated with K_2CO_3 and KOH gives effective surface dipole moment μ equal to 3.73 ± 0.66 and 0.71 ± 0.07 D, respectively. These values confirm that the surface status of the potassium promoter is distinctly different in both cases.

This issue was further addressed by complementary DFT calculations of Co_3O_4 spinel, where three models of surface potassium in the form of KOH_{surf}, $K^+_{surf} + OH^-_{surf}$ and K_2O_{surf}, species where considered (vide infra). They correspond to the presumed state of the promotor deposited from hydroxide precursor upon the catalyst pre-treatment at elevated temperatures. Because of the surface state of the potassium promoter deposited from carbonate is less defined due to enhanced thermal stability of carbonates only the more clear KOH precursor case was taken for the DFT calculations.

For bulk calculations the cubic unit cell ($a = 8.38$ Å) with 24 Co and 32 O ions was chosen [28]. The calculated and experimental geometry (Co–O distances: 1.946–1.948 Å and 1.1914–1.993 Å, O–Co^T–O angle: 109.47° and 109.50°), the band gap (1.42 eV and 1.6 eV) and the magnetic state of cobalt (spin quartet for the tetrahedral and singlet for the octahedral ions) were in good agreement with available experimental data [28], indicating that the calculation scheme was selected properly. The calculated surface energies $\gamma(100) = 1.56$, $\gamma(110) = 1.90$ and $\gamma(111) = 1.71$ Jm^{-2} indicate that the (100) plane is the most stable in agreement with the experiment [29, 30]. The slab model of this plane with KOH_{surf}, $K^+_{surf} + OH^-_{surf}$ and K_2O_{surf} adspecies is shown in Fig. 3a–c. The Co_3O_4 surface can be regarded as a series of the O–Co^{oct}–O strips connected by alternately recessed and exposed the tetrahedral Co ions. Among several surface positions (e.g. on and between O–Co^{oct}–O strips, next to or distant from Co^T) calculated for KOH_{surf}, $K^+_{surf} + OH^-_{surf}$ and K_2O_{surf} the most stable potassium species were found to be in hollow positions between tetrahedral cobalt ions. The energy of potassium in such a hollow position is lower by 30 kcal/mol. This localization is also favourable from the view point of oxygen recombination. Decomposition of N_2O over cobalt spinel can be analysed within the three-step mechanism: activation by abstraction of the oxygen atom ($N_2O \rightarrow N_2 + O_{surf}$), surface diffusion of oxygen adatoms and their recombination into dioxygen molecule [8, 31, 32]. It has been recently shown that recombination of the oxygen atoms via surface diffusion occurs through the cationic and ionic sites along the O–Co^{oct}–O strips (Fig. 3).

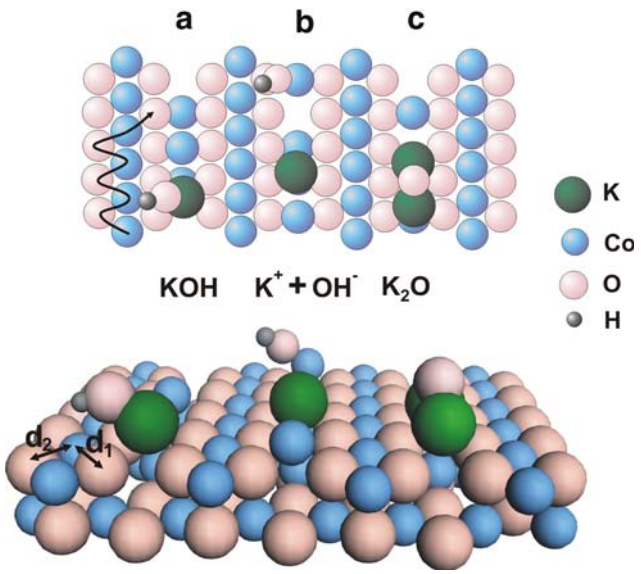

Fig. 3 The model of Co_3O_4 spinel structure with exposed (100) surface. Three most stable potassium adsorption modes: **a** potassium hydroxide, **b** dissociated potassium hydroxide and **c** potassium oxide

This process by involving O^-, O, and O_2^{2-} intermediates is accompanied by the consecutive changes in the oxidation state of the diffusing oxygen adatom [31]. Thus, having a pronounced redox character the recombination process strongly depends on the electronic properties of the catalyst. Indeed, as shown in Fig. 2 by appropriate potassium doping the chemical potential of electrons of the catalyst can be tuned for optimal performance in the implicated redox cycles.

The DFT calculations allowed for an insight into the changes in the Hirshfeld charges and in interatomic bond lengths in KOH_{surf}, $K^+_{surf} + OH^-_{surf}$ and K_2O_{surf} induced upon adsorption. The changes in total atomic charge of +0.25, +0.28 and +0.59 for KOH_{surf}, $K^+_{surf} + OH^-_{surf}$ and K_2O_{surf}, respectively, were observed, indicating significant electron density donation towards the Co_3O_4 spinel. The most pronounced modification in charge distribution in all potassium adspecies were observed on the oxygen moiety, with $\Delta q = 0.27$, 0.30 and 0.40 for KOH_{surf}, $K^+_{surf} + OH^-_{surf}$ and K_2O_{surf}, respectively. Electron density transfer to the surface was distributed mainly to adjacent surfaces oxygen atoms (four in the case of KOH, and six for K_2O, see Fig. 3) and the nearest octahedral cobalt ions. Both adsorbed KOH_{surf}, and K_2O_{surf} species become strongly bend ($\angle$K–O–H = 113°, and $\angle$K–O–K = 109°) in comparison to isolated linear stable structures. The bond length between potassium and surface oxygen was found to be 2.20 for KOH and 2.25 Å for K_2O. The slight changes in Co-O surface distances were also caused by potassium doping of Co_3O_4. As a result oxygen ions in the vicinity of the adspecies are displaced towards potassium, which leads to the lengthening of d_1 distance between Co^{oct} and O^{2-}(K) (from 1.915 to 1.926 Å) and simultaneous shortening of the distance d_2 between octahedral cobalt and the opposite O^{2-} (from 1.915 to 1.901 Å) (Fig. 3). In the case of dissociative $K^+_{surf} + OH^-_{surf}$ adsorption mode the resultant hydroxyl group can be localized on Co^{tetr} and Co^{oct} sites with the energy lower than for undissociative KOH of 21.4 and 11.2 kcal/mol, respectively. The potassium moiety with an atomic charge of +0.53(5) is situated perpendicularly above the surface oxygen at a distance of 2.14 Å.

Using the Hirshfeld atomic charge and the calculated distances and neglecting the intratomic charge polarization the resultant electric dipole moments for all the potassium adspecies were calculated from the formula $\mu_n = \sum q_i r_{i,n}$, where q_i and $r_{i,n}$ are the Hirshfeld charge and the n-th coordinate of atom i, respectively [33]. The calculated dipole moments were found to be $\mu_{KOH} = 0.44$ D, $\mu_{K2O} = 1.25$ D and for bare potassium in the dissociative mode $\mu_{K+surf} = 1.4(5)$ D. In the latter case inclusion of the adjacent OH^-_{surf} group reduced the resultant dipole moment to 1.1(2) D. The correlation between calculated values are in reasonable agreement with the corresponding average experimental value of $\mu_{KOH} = 0.7$ D, derived from Topping analysis of the work function changes with potassium loading in accordance with the electronic nature of the promotional effect of adsorbed K species.

4 Conclusions

The experimental and theoretical results obtained for the K-doped Co_3O_4 spinel revealed that the beneficial effect of potassium doping is associated with the work function lowering of the catalyst (reaching $\Delta\Phi = 0.5$ eV in the optimal case). This facilitates the redox processes occurring between the catalyst surface and the reaction intermediates produced during the N_2O decomposition. As a result at the optimal potassium loading (1.8 atoms/nm^2), the apparent activation energy for N_2O decomposition could be lowered from 78 to 28 kJ/mol, whereas the temperature of half conversion decreased by 100 K upon the impregnation with potassium carbonate.

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