available at www.sciencedirect.com

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

Article

The role of alkali promoters in enhancing the direct N₂O decomposition reactivity over NiO catalysts

Bahaa M. Abu-Zied^{a,b,c,*}, Abdullah M. Asiri^{a,c}^a Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Jeddah 21589, Saudi Arabia^b Chemistry Department, Faculty of Science, Assiut University, Assiut 71516, Egypt^c Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

ARTICLE INFO

Article history:

Received 5 May 2015

Accepted 21 August 2015

Published 20 November 2015

Keywords:

N₂O decomposition

Greenhouse gas

NiO

Alkali-promotion

Activity enhancement

ABSTRACT

Direct N₂O decomposition has been investigated over bare NiO and a series of its alkali-promoted catalysts. These catalysts were characterized by X-ray diffractometry, X-ray photoelectron spectroscopy (XPS) and field emission scanning electron microscopy. XPS analysis revealed that surface nickel is present in three forms: metal particles, NiO and Ni(OH)₂. It is suggested that nickel(0) valent atoms are essential for the interaction with N₂O molecules at the catalyst surfaces. Bare NiO exhibited a very low N₂O decomposition reactivity. However, the alkali-containing catalysts exhibited a marked activity enhancement.

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

During the last two decades, catalytic decomposition of nitrous oxide (N₂O) has gained more attention, given that N₂O was cited in the Kyoto Protocol of the United Nations Convention on Climate Change (December 1997) as being the second most abundant non-CO₂ greenhouse gas. N₂O has a very long lifetime in the atmosphere (~120 years), and the global warming potential of N₂O is approximately 310 times that of CO₂ [1]. Industrial sources make important contributions to the global atmospheric emissions of N₂O. These include circulating fluidized beds for combustion; automotive exhaust emissions; manufacture of HNO₃, which is used to make synthetic commercial fertilizers; and production of large amounts of adipic acid, which is produced from the HNO₃-promoted oxidation of cyclohexanol-cyclohexanone mixtures for Nylon 6,6 and Nylon 6,12 [1].

Several catalytic methods have been applied to N₂O abatement. These include (i) use of N₂O in the selective oxidation of benzene to phenol [2] and methane to methanol [3], (ii) direct catalytic decomposition of N₂O to N₂ and O₂ [4–27], and (iii) selective catalytic reduction (SCR) of N₂O with ammonia [28–30], carbon monoxide [26,27,31,32] and hydrocarbons [32–37]. Focusing our attention on the direct catalytic decomposition of N₂O, there are many groups of catalysts reported in the literature that exhibit promising activity for this reaction at different temperatures. These include metals, mixed oxides, supported oxides, spinels, perovskites, and zeolite-based catalysts [4–27]. Within the same group of catalysts, the catalytic activity is influenced by several parameters, such as the preparation method, calcination conditions, presence of dopants, and catalyst crystallite size. Focusing our attention on the effect of the dopant, many research papers have been published reporting the use of various promoters, such as alkali, alkali-earth

* Corresponding author. Tel: +96-563737563; Fax: +96-626952292; E-mail: babuzaid@kau.edu.sa, babuzied@aun.edu.eg, babuzied@yahoo.com
DOI: 10.1016/S1872-2067(15)60963-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 36, No. 11, November 2015

and rare-earth cations, to enhance the activity of the de-N₂O catalyst [8,11–14,17–24]. With respect to doping with alkali cations, alkali-cation doping enhances the decomposition of N₂O over CuO- [18], Co₃O₄- [11,12,17], MgCo₂O₄- [8], and Rh/Al₂O₃-based catalysts [13,14], which is an observation that is consistent with the literature. It is believed that the added alkali cations significantly weaken the metal-oxygen bond, facilitating the desorption of the chemisorbed oxygen, thus enhancing N₂O direct decomposition [12,14–17]. However, NiO was reported to exhibit promising activity features in various reactions, such as methanol electro-oxidation [38], degradation of phenol [39], oxidative dehydrogenation of ethane to ethylene [40] and decomposition of ammonium perchlorate [41]. In the literature, there are a limited number of papers that have reported the de-N₂O activity of nickel-based catalysts. Zhang et al. [22] reported the N₂O decomposition activity of a series of Ce_xBa_{1-x}Ni₉ oxide catalysts prepared by a co-precipitation method. Their results revealed that the co-existence of Ba and Ce in NiO leads to a synergic effect, whereas Ce primarily accelerates the dissociation of N₂O and Ba enhances the desorption of O₂ from the catalyst surfaces. Wu et al. [23,24] investigated the effects of the catalyst composition, alkali metal species (Na, K, Cs) and potassium precursors on the N₂O decomposition reactivity over Ni/Al mixed oxides derived from hydrotalcite-like compounds. Their results indicated the superior activity of the K-promoted catalysts compared with that of the Na- or Cs-promoted catalysts. Pasha et al. [15] reported the beneficial effect of NiO doping with cesium ions at Cs/Ni ratios in the range of 0.05 to 0.20 on its de-N₂O activity. Their results indicated that the highest activity was exhibited by the catalyst with a Cs to Ni ratio of 0.1. Therefore, it is still attractive to investigate the role of alkali promotion on the de-N₂O activity of bare NiO. Accordingly, in this paper, we report the results of the influence of alkali cation (Li⁺, Na⁺, K⁺ and Cs⁺) doping on the activity of a bare NiO catalyst toward N₂O direct decomposition. In accordance with the work of Pasha et al. [15], preliminary catalyst screening experiments were carried out on catalysts with alkali/NiO ratios of 0.1. For the most active catalysts, we investigated the effect of changing the alkali cation/NiO molar ratio on the catalytic activity.

2. Experimental

Analytical grade chemicals were used in all of the preparations. NiO was obtained by the thermal decomposition of nickel acetate at 500 °C for 3 h, in static air. Alkali-promoted catalysts were prepared by the incipient wetness impregnation of NiO with alkali carbonates (Li₂CO₃, Na₂CO₃, K₂CO₃ and Cs₂CO₃). The alkali metal/Ni molar ratio was adjusted to be 0.10. For the most active catalysts, K- and Cs-promoted NiO, other preparations that had alkali metal/Ni molar ratios in the range of 0.0125 to 0.2 were prepared. The various alkali carbonate-NiO mixtures were dried at 90 °C overnight and then calcined at 500 °C for 3 h in a static air atmosphere.

The XRD patterns of the calcined samples were recorded with the aid of a Philips diffractometer (type PW 103/00). Nitrogen adsorption measurements were carried out using a

Quantachrom (Autosorb iQ series) apparatus. Specific surface area values were calculated using the BET method in the p/p_0 range of 0.05 to 0.25. The composition and chemical bonding of the selected samples were analyzed using a SPECS GmbH X-ray photoelectron spectrometer with a standard dual-anode excitation source emitting monochromatic Al K α (1486.6 eV) radiation operated at 13.5 kV. The working pressure in the analysis chamber was typically 0.05 MPa. The binding energies were determined by computer fitting of the measured spectra, which were referenced to the C 1s peak at 284.6 eV. The composition and chemical state were investigated based on the areas and binding energies of the Ni 2p and O 1s photoelectron peaks. The morphology of the samples was investigated by using a field-emission scanning electron microscope (FE-SEM) on a JEOL model JSM-7600F microscope equipped with an EDX unit. The sample preparation was performed by dispersing the catalyst powder on a carbon film conductor. The images were obtained without gold-sputtering.

N₂O decomposition experiments were performed using an electrically heated quartz tube reactor. The temperature in the reactor was measured using a Cole-Parmer temperature controller (model Digi-Sense 89000-00). Prior to each experiment, 500 mg of the catalyst was heated in N₂ at 500 °C for 1 h. In each experiment, 500 ppm of N₂O was introduced to the reactor inlet with the aid of thermal mass flow controllers (AALBORG, DFC2600) using N₂ as a balance gas at a volume flow rate of 200 cm³/min. Quantitative analyses of the reactor inlet and outlet gases were carried out using a magnetic oxygen analyzer (ABB, AO2020-Magnos 106) and a non-dispersive infrared analyzer for the components, N₂O and NO (ABB, AO2020-Uras 14). Preliminary experiments for the decomposition of N₂O over all of the catalysts showed the absence of NO in the reactor exit gas mixture.

3. Results and discussion

3.1. N₂O decomposition over alkali promoted NiO catalysts

Figure 1 shows the XRD diffractograms of NiO and the various alkali-promoted NiO catalysts. The pattern obtained for the

Fig. 1. XRD patterns of NiO and its alkali-promoted catalysts (M/Ni = 0.10). (1) NiO; (2) Li/NiO; (3) Na/NiO; (4) K/NiO; (5) Cs/NiO.

Table 1 T_{10} , T_{25} , T_{50} and T_{90} values obtained over the alkali-doped NiO catalysts.

Catalyst	T_{10} (°C)	T_{25} (°C)	T_{50} (°C)	T_{90} (°C)	S_{BET} (m ² /g)
NiO	—	—	—	—	24.6
Li/NiO	418	493	—	—	24.7
Na/NiO	331	372	422	—	28.6
K/NiO	304	317	355	419	19.4
Cs/NiO	279	329	359	448	4.2

bare NiO (Fig. 1(1)) reveals the presence of reflections at $2\theta = 37.15^\circ$, 43.23° , 62.80° , 75.37° and 79.39° . These reflections match those of cubic NiO (JCPDS 78-0643, space group Fm3m). Figure 1(1) also shows the presence of a very small reflection at $2\theta = 44.44^\circ$, which could be related to the presence of a trace amount of hexagonal Ni metal (JCPDS 45-1027, space group P63/mmc). In this context, it was reported that the thermal decomposition of nickel acetate in air leads to the concomitant formation of a mixture of NiO and Ni⁰ [42]. Consistent with this result, Mohamed et al. [43] reported that the dehydration of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ takes place in a N₂ flow in the temperature range of 87 °C to 160 °C. In the 300–440 °C range, the anhydrous form, $\text{Ni}(\text{CH}_3\text{COO})_2$, decomposes to yield a mixture of NiO and Ni⁰. For the alkali-promoted catalysts, the intensity of the Ni⁰ peak is approximately zero. In addition, weak reflections appearing at $2\theta = 24.37^\circ$, 29.95° and 31.43° can be observed in the K-doped NiO pattern (Fig. 1(4)). These reflections may be related to monoclinic K₂CO₃ (JCPDS 70-0292, space group C2/c). Another set of weak reflections emerged at $2\theta = 19.58^\circ$, 24.22° , 27.03° and 28.34° in Fig. 1(5), which may arise from the presence of monoclinic Cs₂CO₃ (JCPDS 35-0962, space group P21/c). Table 1 lists the surface area values of NiO and its alkali-promoted catalysts. It is obvious that the NiO and Li/NiO catalysts have similar S_{BET} values. Na/NiO exhibited a slightly higher S_{BET} value. Promoting NiO with potassium and cesium ions leads to a 21.1% and 70.3% reduction of its S_{BET} value, respectively.

Figure 2 shows the relation between the N₂O conversion and the reaction temperature over the NiO and its alkali-doped catalysts. It is obvious that bare NiO exhibited a very unfavorable activity pattern. Less than 5% conversion was obtained

Fig. 2. Dependence of the N₂O conversion on the reaction temperature over NiO and its alkali promoted catalysts (M/Ni = 0.10). (1) NiO; (2) Li/NiO; (3) Na/NiO; (4) K/NiO; (5) Cs/NiO. Conditions: 500 ppm N₂O in N₂, total flow 200 cm³/min, 0.5 g catalyst.

over this catalyst at a reaction temperature of 500 °C. The doping of NiO with various alkali cations was accompanied by a sharp activity increase. The onset of the decomposition began at 300, 275, 250, and 200 °C for Li-, Na-, Cs-, and K-promoted catalysts, respectively. The obtained T_{10} , T_{25} , T_{50} and T_{90} values, which are the temperatures at 10%, 25%, 50% and 90% conversion, respectively, are given in Table 1. The results indicate that all of the alkali-promoted catalysts exhibit higher N₂O decomposition reactivity compared with that over the un-promoted NiO. The activity order is un-promoted << Li- << Na- < Cs- < K-promoted catalysts. A similar activity trend was also reported during N₂O decomposition over alkali-doped MgCo₂O₄ catalysts [8]. Table 2 lists the T_{50} values of various catalysts that have recently been reported in the literature for N₂O decomposition. It can be seen that the activity of both Cs- and K-promoted NiO catalysts are comparable with many of these catalysts, which reflects the enhancement effect of the added Cs- and K-ions.

X-ray photoelectron spectroscopy (XPS) is widely used in the investigation of catalysts. It allows for the determination of the elemental composition of a catalyst in the upper layers of

Table 2Comparison of the T_{50} values recently reported in literature for N₂O decomposition.

Catalyst	Feed gas composition and W/F (or GHSV)	$T_{50}/^\circ\text{C}$	Ref.
Rh+K ₂ O (0.08 mol%)/Al ₂ O ₃	1.0% N ₂ O; 4000 h ⁻¹	300	[14]
Rh+Cs ₂ O (0.078 mol%)/Al ₂ O ₃	1.0% N ₂ O; 4000 h ⁻¹	280	[14]
Cs/NiO (Cs/Ni = 0.1)	2500 ppm N ₂ O; 0.5 g s cm ⁻³	200	[15]
Ce _{1.0} Ba _{1.5} Ni ₉	2000 ppm N ₂ O; 0.2 g s cm ⁻³	215	[22]
K-Mn ₃ O ₄ ($n_K = 8$ atoms/nm ²)	5.0% N ₂ O; 7000 h ⁻¹	567±11	[20]
K-Fe ₃ O ₄ ($n_K = 6$ atoms/nm ²)	5.0% N ₂ O; 7000 h ⁻¹	480±9	[20]
K-Co ₃ O ₄ ($n_K = 2$ atoms/nm ²)	5.0% N ₂ O; 7000 h ⁻¹	240±5	[20]
K ₂ CO ₃ /Co ₃ O ₄ (K = 0.2 wt%)	5.0% N ₂ O; 7000 h ⁻¹	304 ± 2	[21]
Pt(K 2 wt%)/Al ₂ O ₃ -(CeO ₂ -La ₂ O ₃)	1000 ppm N ₂ O; 10000 h ⁻¹	365±3	[26]
20 wt% Cu/CeO ₂	1000 ppm N ₂ O; 40000 h ⁻¹	465	[44]
20 wt% Cu/CeO ₂	1000 ppm N ₂ O; 10000 h ⁻¹	430	[44]
Ag/FeAlO ₃	500 ppm N ₂ O; 0.15 g s cm ⁻³	428	[45]
SrCo ₃ /Co ₃ O ₄ (Sr/Co = 0.4)	500 ppm N ₂ O; 0.15 g s cm ⁻³	405	[6]
K/MgCo ₂ O ₄ (K/Co = 0.05)	500 ppm N ₂ O; 0.15 g s cm ⁻³	309	[8]
Ni _{0.75} Co _{0.25} Co ₂ O ₄	500 ppm N ₂ O; 0.15 g s cm ⁻³	263	[9]

Fig. 3. Ni 2p XPS spectra of NiO (1), Li/NiO (2) and K/NiO (3).

its surface, that is, the oxidation number and the electronic interactions between the neighboring elements. Obtaining such information for nickel is of considerable value in understanding the role of the added alkali cations in enhancing the N_2O decomposition over NiO catalysts. For some of the selected Nicatalysts, the Ni 2p and O 1s core-level spectra were recorded. Figure 3 shows the Ni 2p region of NiO and its Li- and K-promoted catalysts pretreated at 500 °C. All of the Ni 2p peaks exhibit doublet Ni 2p_{1/2} and Ni 2p_{3/2} peaks, with a distance of approximately 17.47 eV. The Ni 2p_{3/2} peak of the bare NiO catalyst (Fig. 3(1)) was deconvoluted into three contributions, with binding energies of 853.38, 855.13 and 857.52 eV (Table 3).

This, in turn, indicates that the Ni species on the surface of the NiO catalyst exists in various oxidation states and environments. With the aid of the literature data, the two peaks at 853.38 and 855.13 eV can be attributed to the presence of metallic Ni (Ni⁰) and NiO, respectively [46–51]. The third component, located at 857.52 eV, could be attributed to the existence of either Ni₂O₃ or Ni(OH)₂. Greiner et al. [50] suggested the formation of Ni(OH)₂ rather than Ni₂O₃ on the NiO surface, which was attributed to the higher thermodynamic stability of Ni(OH)₂ compared with Ni₂O₃. Consistent with this hypothesis, Seo et al. [51] reported the formation of Ni(OH)₂ on a carbon fiber Ni film rather than Ni₂O₃. Additionally, the detection of Ni⁰ on the NiO surface indicates the presence of reduction conditions, which could be another cause of the absence of Ni³⁺

Fig. 4. O 1s XPS spectra of NiO (1), Li/NiO (2) and K/NiO (3).

(Ni₂O₃) on the NiO surface. Therefore, it is plausible to relate the peak at 857.52 eV to the presence of the Ni(OH)₂ phase. In this context, the detection of Ni⁰ and Ni(OH)₂ using XPS analysis (Fig. 3) is in contradiction with the XRD results (Fig. 1), which revealed the absence of these two phases from NiO and its alkali-doped catalysts. This could be attributed to the fact that the surface sensitivity of the XPS, which samples the top 8–10 nm of the surface, in contrast to the penetration depth of X-rays during XRD measurements (2–120 μm), or it could be a result of the amorphous nature of large metallic Ni⁰ particles. Such contradictions have been reported for other catalytic systems [52,53]. However, the detected Ni(OH)₂ on the NiO catalyst surface is formed as a consequence of the reaction between the NiO surface and the water vapor in air, whereas the metallic Ni could be formed as a result of the reduction of some of the Ni²⁺ surface ions by the evolved gases accompanying the thermal decomposition of the nickel acetate precursor.

The O 1s spectra collected from the un-promoted NiO and its Li- and K-promoted catalysts are presented in Fig. 4. The obtained spectra were deconvoluted into four components. These components are centered at 527.78, 529.07, 530.92 and 533.00 eV for NiO (Fig. 4(1)). The small peak that appeared at the lowest binding energy (527.78 eV) could be related to the unstable oxygen moiety, the exact chemical nature of which is unknown [54,55]. This peak disappears upon doping NiO with a large amount of K ions (*vide infra*). The peak that appeared at 529.07 eV could be related to oxygen atoms in the crystal lat-

Table 3
Ni 2p_{3/2} binding energies and their relative spectral areas.

Catalyst	Ni ⁰		NiO		Ni(OH) ₂	
	BE (eV)	Area (%)	BE (eV)	Area (%)	BE (eV)	Area (%)
NiO	853.38	24.92	855.13	66.63	857.52	8.45
Li/NiO = 0.1	853.33	24.67	855.06	67.04	857.77	8.29
K/NiO = 0.1	852.77	25.27	854.49	65.44	856.66	9.29
K/NiO = 0.2	852.50	15.75	854.11	65.84	856.03	18.41

tice of NiO [49,56–58]. The peak centered at 530.92 eV has been suggested to arise from the presence of oxygen atoms adjacent to Ni vacancies (defective oxygen) [56,57]; bound hydroxide groups (OH⁻), that is, the Ni(OH)₂ phase [54,57,58]; or the presence of C=O [52] or adsorbed oxygen [58]. The small peak that appeared at 533.00 eV could be related to adsorbed water or oxygen atoms [56,58].

According to the recent nomenclature of Piumetti et al. [59], the two peaks located at 530.92 and 529.07 eV were referred to as O_α and O_β, respectively. Generally, O_α exhibits a higher mobility than O_β and higher O_α/O_β ratios, indicating the presence of higher amounts of surface adsorbed hydroxyls, carbonates and O₂ on the surface of these materials. From Table 4, it appears that bare NiO contains a higher concentration of surface adsorbed species compared with the Li- and K-promoted catalysts (M/NiO = 0.1). The high O_α/O_β ratio of the K/NiO with K/NiO = 0.2 is not surprising because this sample contains a higher amount of potassium carbonate.

The XPS spectra of alkali-promoted catalysts (Fig. 3) reveal the co-existence of metallic nickel, with Ni²⁺ (NiO and Ni(OH)₂) at the surfaces of Li- and K-doped NiO. The quantification of the corresponding proportion of each surface nickel and oxygen species was calculated, and the obtained results are listed in Tables 3 and 4, respectively. It can be seen from Table 3 that doping NiO with Li ions shifts the BE of Ni⁰ from 853.38 to 853.33 eV and that of NiO from 855.13 to 855.06 eV. In the case of K-doped NiO, the shift that occurred is greater, that is, to 852.77 and 854.49 eV. Similar results can be obtained for lattice oxygen atoms. This finding suggests that alkali doping leads to more electrons on both the nickel and oxygen atoms. Such an effect is much more pronounced in the case of K-doped catalyst compared with the Li-doped catalyst.

The reported mechanism of the N₂O decomposition on the surface of several catalysts involves N₂O adsorption onto the catalyst active centers through a charge donation from the catalyst to the antibonding orbitals of N₂O, which is followed by the destabilization of the N–O bond, leading to its scission and the production of an N₂ molecule and an adsorbed oxygen atom. The last step involves the recombination and desorption of two surface oxygen atoms to produce an oxygen molecule [60,61]. Thus, electron transfer occurs from a metal with a low oxidation state to a N₂O molecule, which in turn leads to an increase in its oxidation state. The recoverability of the low oxidation state of the metal is a crucial step for the regeneration of the active centers. Based on the XPS results, it is plausible to suggest that the low oxidation state metal, that is, Ni⁰, represents the active site for N₂O adsorption and subsequent decomposition. This would lead to the formation of Ni²⁺ ions and the production of another electron acceptor molecule, that

is, O₂, which is also adsorbed on the same active sites. Accordingly, the activity of the un-promoted NiO would be decreased because of the accumulation of O₂ molecules on the remaining active sites and the inability to regenerate these sites.

The enhancement effect of alkali and alkali-earth cationic dopants during N₂O decomposition over Co₃O₄ catalysts is well documented in the literature [11–15]. This promotion effect is owing to the electronic interaction induced by the added dopant, which yields an electron-rich cobalt species with a higher electron donation ability to the N₂O molecule. This, in turn, results in the activation of N₂O adsorption and decomposition. Pasha et al. [15] reported, based only on the XRD characterization of the spent catalysts, the development of metallic Ni as a major phase in a Cs-promoted NiO catalyst during the N₂O decomposition in the presence of oxygen and water vapor. Accordingly, they related the high activity of this catalyst to the emergence of the Ni⁰ phase. We performed an XRD-analysis of our spent alkali-promoted NiO catalysts. The obtained results (not shown) revealed the persistence of NiO reflections and the absence of any new reflections arising from the metallic nickel phase.

Based on Sanderson's approach, the polarity of bonds with alkali cations that have the lowest electronegativity values among the periodic-table elements are considered to be Lewis acids. When a highly electronegative element, such as oxygen (Lewis base), exists in the co-ordination sphere of these cations, it becomes highly basic. Accordingly, electron donation occurs from the highly basic oxygen surrounding the alkali cations towards the surface metal atom (e.g. Co, Ni, Cu), which increases the electron donation ability of these surface metal atoms, and thus their N₂O-decomposition activity. In this respect, Asano et al. [11] reported that doping Co₃O₄ with K-ions leads to a slight shift in the Co 2p_{3/2} XPS-peak towards lower BE values. Such a BE shift was correlated with the increase in the measured N₂O-decomposition reactivity over the K-doped Co₃O₄ catalysts. Similarly, and based on the observed BE of the Ni⁰ shift towards lower values upon alkali cations addition (Table 3), it seems reasonable to attribute the observed enhancement effect of the added alkali cations to their role in the surface-electron-rich Ni⁰ phase formation. This phase has a greater electron donating ability, which initiates N₂O adsorption and subsequent decomposition. In this context, the greater ability of K ions compared with Li ions with respect to enhancing the activity of NiO can be understood in terms of the larger magnitude of the BE reduction, of which is Ni⁰, obtained upon doping with K ions rather than Li ions. The same argument can be proposed for the Cs-doped NiO catalyst.

Regarding the recoverability of the Ni⁰ phase, several research groups demonstrated that the addition of alkali or alka-

Table 4
Quantities of surface oxygen species based on XPS analysis.

Catalyst	Unstable oxygen		Lattice oxygen (O _β)		Adsorbed oxygen (O _α)		O _α /O _β	Adsorbed water	
	BE (eV)	Area (%)	BE (eV)	Area (%)	BE (eV)	Area (%)		BE (eV)	Area (%)
NiO	527.78	3.47	529.07	42.91	530.92	50.04	1.17	533.00	3.58
Li/NiO = 0.1	527.96	4.31	529.00	49.75	530.88	43.35	0.87	532.72	2.59
K/NiO = 0.1	527.18	2.72	528.49	43.66	530.23	41.93	0.96	531.71	11.69
K/NiO = 0.2	—	—	528.26	18.91	530.00	70.32	3.72	532.04	10.77

li-earth cations enhances the regeneration of the active centers of the catalysts, that is, transition-metal atoms with lower oxidation states. For instance, in TPR experiments, Zhang et al. [22] reported that the addition of increased concentrations of Ba to the Ba_xNi_9 catalyst led to a shift of the commencement of H_2 consumption toward lower temperatures. This, in turn, indicates the enhancement role of Ba in the reduction of NiO, that is, the regeneration of the active sites of the catalysts. Based on an XPS investigation, Asano et al. [11] reported a continuous shift in the lattice oxygen O 1s peak towards the lower BE value as a result of adding increasing amounts of K to Co_3O_4 , which indicates that the electronic density of oxygen was increased. In other words, the basicity of the oxygen anion was increased, thus facilitating the oxygen desorption. From the data listed in Table 4, it appears that adding alkali cations to the catalysts shifts the BE of the lattice oxygen O 1s peak towards lower values. This finding is consistent with the previously reported literature data [11,22] that imply that the added alkali cations would facilitate the oxygen desorption and lead to the recoverability of the active centers, that is, Ni^0 phase.

Both K- and Cs-doped catalysts exhibited superior activity compared with the Li- and Na-doped catalysts; therefore, the present investigation was extended to determine the influence of changing the K/Ni and Cs/Ni ratios on their N_2O decomposition reactivity. Figure 5 shows the dependence of the

Fig. 5. Variation of N_2O conversion as a function of M/Ni ratio for potassium- (a) and cesium-doped (b) NiO catalysts at different temperatures. Conditions are the same as those in the Fig. 2.

steady-state conversion of N_2O on the M/Ni ratio at various reaction temperatures. Close inspection of Fig. 5 reveals that the addition of even a small amount of K- and Cs-ions to NiO ($\text{M/Ni} = 0.0125$) is accompanied by a noticeable activity increase. Increasing the M/Ni ratio to 0.1 showed a continuous increase in the N_2O conversion. A further increase in the M/Ni ratio to 0.2 leads to a noticeable decrease in the conversion; however, these catalysts still exhibit much higher activity patterns compared with the un-doped NiO catalyst. These findings indicate the high sensitivity of these catalysts to the change in M/NiO ratio, and the highest activity is exhibited by those with M/NiO ratios of 1. Consistent with this result, for a series of Cs-promoted NiO catalysts, Pasha et al. [15] reported the best activity for the catalyst with a Cs/Ni ratio of 0.1. The dependence of the activity promotion on the concentrations of the added alkali cations was also reported for other catalytic systems. For Co_3O_4 [11] and Co-Al [16] catalysts, the highest N_2O decomposition reactivities were reported for catalysts with K/Co ratios of 0.03 and 0.08, respectively. With respect to K-doped MgCo_2O_4 catalysts, the best performance was obtained over a catalyst with a K/Co ratio of 0.05 [8]. Haber et al. [13,14] reported an optimal value of 0.08% of alkali cations during the N_2O decomposition over $\text{Rh/Al}_2\text{O}_3$ catalysts.

Figure 6(a) shows the deconvoluted spectra of the Ni 2p core-level obtained for a K-doped NiO ($\text{K/Ni} = 0.2$) catalyst. Following the same interpretation given during the analysis of the XPS results in Figs. 3 and 4, one can confidently state that the surface of the NiO ($\text{K/Ni} = 0.2$) catalyst is composed of Ni^0 together with Ni^{2+} (NiO and Ni(OH)_2). The deconvoluted O 1s spectra (Fig. 6(b)) clearly show the presence of only three contributions. The first, at 528.26 eV, belongs to lattice oxygen [49,56–58]. The second peak, at 530.00 eV, could be related to bound hydroxide groups (OH^-) [54,57,58] or adsorbed oxygen [58]. The last peak, at 532.04 eV, could be assigned to the adsorbed water or oxygen atoms [56,58].

Inspection of Table 3 reveals that increasing the K/NiO ratio from 0.05 to 0.2 is accompanied by a slight shift of the BE Ni^0 $2p_{3/2}$ peak from 852.77 to 852.50 eV and that of the lattice oxygen O 1s peak from 528.49 to 528.26 eV. This, in turn, implies an increase in the N_2O -decomposition reactivity. Instead, a noticeable activity decrease was obtained, as shown in Fig. 5(a).

Fig. 6. Ni 2p (a) and O 1s (b) XPS spectra of K/NiO ($\text{K/Ni} = 0.2$).

Fig. 7. FE-SEM images and fluorescence spectra of Cs/NiO (K/Ni = 0.05) (a) and Cs/NiO (K/Ni = 0.2) (b) catalysts.

This contradiction can be understood by taking into account the fact that this K-content increase is accompanied by a marked decrease in the area fraction of the Ni^0 phase from 25.27 to 15.75 and lattice oxygen fraction from 43.66 to 18.91 (Tables 3 and 4). In other words, the observed activity decrease, that resulted from the increase in the K/NiO ratio from 0.05 to 0.2, could be ascribed to the sharp decrease in the surface concentration of the Ni^0 phase exposed to the N_2O molecules. The same argument could be proposed for the observed activity decrease that resulted from the Cs/NiO ratio increase from 0.05 to 0.2 (Fig. 5(b)).

Figure 7 depicts the FE-SEM images of the catalysts (Cs/NiO = 0.05 and Cs/NiO = 0.2). It is obvious that the surface of the former catalyst (Fig. 7(a)) consists of a porous network of polydisperse quasi-spherical particles. The size of these particles are in the range of 50 to 150 nm. The corresponding fluorescence spectra indicate the presence of Cs, Ni and O elements. The respective average mass ratios, measured at three different areas, were found to be 4.26:86.26:9.49. Figure 7(b) shows that the catalyst with a higher Cs-content, that is, Cs/NiO = 0.2, exhibits similar morphology. Moreover, EDX analysis of the mass ratios of Cs, Ni and O elements revealed the average values of 21.96:50.21:27.83, respectively. For both Cs-containing catalysts, our EDX analysis revealed the absence of any local concentration of Cs, Ni, or O atoms. This, in turn, suggests an homogeneous distribution of these elements. Accordingly, the observed activity loss (Fig. 5(b)) cannot be related to the presence of agglomerates of cesium carbonate distributed among the nickel oxide particles. This finding reinforces the suggestion that the activity loss observed for the catalysts with the highest M/NiO ratios could be related to the decrease of the Ni^0 phase required for the initiation of the N_2O decomposition reaction.

3.2. Effect of changing the M/NiO and W/F ratios

For the most active catalysts, that is, K/NiO and Cs/NiO that had a M/NiO ratio of 0.1, additional stability tests were per-

Fig. 8. N_2O conversion versus time-on-stream over K/NiO (1) and Cs/NiO (2) (M/Ni = 0.1) at 500 °C.

formed at a reaction temperature of 500 °C. Figure 8 shows the degree of N_2O conversion over these two catalysts measured as a function of time-on-stream. The first data points, which were taken after approximately 120 min on stream, reveal the slightly higher initial activity of the K/NiO catalyst. After 300 min, the degree of N_2O conversion decreases from approximately 100% to 85% over the K/NiO catalyst. However, the Cs/NiO catalyst exhibited a higher degree of stability, and the conversion decreased from approximately 98% to 95%. Both samples remain practically stable afterwards for 720 min on stream.

The influence of changing W/F (mass/feed ratio) value on the catalytic performance was investigated over the most active catalysts, that is, K- and Cs-promoted NiO catalysts having M/NiO ratio of 0.1. Figure 9 shows the dependence of the N_2O

Fig. 9. Effect of W/F on N_2O conversion over the K/NiO (a) and Cs/NiO (b) catalysts. (1) 0.10 g/(cm³·s); (2) 0.15 g/(cm³·s); (3) 0.30 g/(cm³·s). Conditions: 500 ppm N_2O in N_2 .

Graphical Abstract

Chin. J. Catal., 2015, 36: 1837–1845 doi: 10.1016/S1872-2067(15)60963-9

The role of alkali promoters in enhancing the direct N₂O decomposition reactivity over NiO catalysts

Bahaa M. Abu-Zied*, Abdullah M. Asiri
King Abdulaziz University, Saudi Arabia;
Assiut University, Egypt

The N₂O decomposition on alkali-promoted NiO catalysts is investigated. Alkali cations markedly enhance the N₂O decomposition reactivity over NiO. K- and Cs-doped NiO catalysts are shown to have superior activity than Li- and Na-doped catalysts.

conversion on the reactor temperature over these two catalysts at three W/F values. It can be seen that the N₂O conversion profiles shifted to higher temperatures upon decreasing the W/F from 0.30 to 0.10 g/(cm³/s). The obtained *T*₅₀ values of the K-promoted NiO catalyst were 314, 355 and 393 °C at the W/F values of 0.30, 0.15 and 0.10 g/(cm³/s), respectively. The relevant values for the Cs-promoted NiO catalyst were 355, 359 and 427 °C, respectively. This indicates that a temperature higher than 500 °C and a W/F value exceeds 0.15 g/(cm³/s) are required to achieve a complete abatement of N₂O over both catalysts.

4. Conclusions

Doping NiO with alkali cations significantly enhanced its catalytic activity during N₂O decomposition. A typical activity order obtained was un-promoted << Li- << Na- < Cs- < K-catalyst. XPS investigations clearly indicated the presence of Ni⁰ with Ni²⁺ (NiO and Ni(OH)₂) at the surfaces of the various M/NiO catalysts. Based on the observed shift in the BE of the Ni⁰ phase to lower values, it was suggested that the obtained activity enhancement could be attributed to the change in the electronic properties of the catalysts. This change improves the electron donating ability of nickel, thus facilitating N₂O adsorption and decomposition. Changing the K/NiO and Cs/NiO ratios revealed that the catalysts with a M/NiO ratio of 0.1 exhibited the best performance.

Acknowledgments

The authors are grateful to acknowledge the Center of Excellence for Advanced Materials Research (CEAMR) at King Abdulaziz University for providing facilities. One of the authors, B.M. Abu-Zied, would like to gratefully acknowledge the Deutscher Akademischer Austausch Dienst (DAAD) for the donation of the gas analyzers used in the N₂O decomposition measurements at Assiut University. In addition, Assiut University is gratefully acknowledged for the support of the mass flow controllers used in this investigation.

References

- [1] Pérez-Ramírez J. *Appl Catal B*, 2007, 70: 31
- [2] Yuranov I, Bulushev D A, Renken A, Kiwi-Minsker L. *Appl Catal A*, 2007, 319: 128
- [3] Wood B R, Reimer J A, Bell A T, Janicke M T, Ott K C. *J Catal*, 2004, 225: 300
- [4] Kapteijn F, Rodriguez-Mirasol J, Moulijn J A. *Appl Catal B*, 1996, 9: 25
- [5] Abu-Zied B M, Schwieger W, Unger A. *Appl Catal B*, 2008, 84: 277
- [6] Abu-Zied B M, Soliman S A. *Catal Lett*, 2009, 132: 299
- [7] Abu-Zied B M. *Microporous Mesoporous Mater*, 2011, 139: 59
- [8] Abu-Zied B M. *Chin J Catal* (催化学报), 2011, 32: 264
- [9] Abu-Zied B M, Soliman S A, Abdellah S E. *Chin J Catal* (催化学报), 2014, 35: 1105
- [10] Abu-Zied B M, Soliman S A, Abdellah S E. *J Ind Eng Chem*, 2015, 21: 814
- [11] Asano K, Ohnishi C, Iwamoto S, Shioya Y, Inoue M. *Appl Catal B*, 2008, 78: 242
- [12] Stelmachowski P, Maniak G, Kotarba A, Sojka Z. *Catal Commun*, 2009, 10: 1062
- [13] Haber J, Machej T, Janas J, Nattich M. *Catal Today*, 2004, 90: 15
- [14] Haber J, Nattich M, Machej T. *Appl Catal B*, 2008, 77: 278
- [15] Pasha N, Lingaiah N, Reddy P S S, Prasad P S S. *Catal Lett*, 2007, 118: 64
- [16] Cheng H K, Huang Y Q, Wang A Q, Li L, Wang X D, Zhang T. *Appl Catal B*, 2009, 89: 391
- [17] Pasha N, Lingaiah N, Babu N S, Reddy P S S, Prasad P S S. *Catal Commun*, 2008, 10: 132
- [18] Pasha N, Lingaiah N, Reddy P S S, Prasad P S S. *Catal Lett*, 2009, 127: 101
- [19] Yoshino H, Ohnishi C H, Hosokawa S, Wada K, Inoue M. *J Mater Sci*, 2011, 46: 797
- [20] Maniak G, Stelmachowski P, Zasada F, Piskorz W, Kotarba A, Sojka Z. *Catal Today*, 2011, 176: 369
- [21] Maniak G, Stelmachowski P, Kotarba A, Sojka Z, Rico-Pérez V, Bueno-López A. *Appl Catal B*, 2013, 136-137: 302
- [22] Zhang F F, Wang X P, Zhang X X, Turxun M, Yu H B, Zhao J J. *Chem Eng J*, 2014, 256: 365
- [23] Wu H P, Qian Z Y, Xu X L, Xu X F. *J Fuel Chem Technol*, 2011, 39: 115

- [24] Wu H P, Li W J, Guo L, Pan Y F, Xu X F. *J Fuel Chem Technol*, 2011, 39: 550
- [25] Pachatouridou E, Papista E, Iliopoulou E F, Delimitis A, Goula G, Yentekakis I V, Marnellos G E, Konsolakis M. *J Environ Chem Eng*, 2015, 3: 815
- [26] Konsolakis M, Aligizou F, Goula G, Yentekakis I V. *Chem Eng J*, 2013, 230: 286
- [27] Konsolakis M, Drosou C, Yentekakis I V. *Appl Catal B*, 2012, 123–124: 405
- [28] Sugawara K, Nobukawa T, Yoshida M, Sato Y, Okumura K, Tomishige K, Kunimori K. *Appl Catal B*, 2007, 69: 154
- [29] Zhang X Y, Shen Q, He C, Ma C Y, Cheng J, Hao Z P. *Catal Commun*, 2012, 18: 151
- [30] Colombo M, Nova I, Tronconi E, SchmeiBer V, Bandl-Konrad B, Zimmermann L. *Appl Catal B*, 2012, 111–112: 106
- [31] Debbagh M N, Bueno-López A, de Lecea C S M, Pérez-Ramírez J. *Appl Catal A*, 2007, 327: 66
- [32] Debbagh M N, de Lecea C S M, Pérez-Ramírez J. *Appl Catal B*, 2007, 70: 335
- [33] Kögel M, Mönnig R, Schwieger W, Tissler A, Turek T. *J Catal*, 1999, 182: 470
- [34] Nobukawa T, Sugawara K, Okumura K, Tomishige K, Kunimori K. *Appl Catal B*, 2007, 70: 342
- [35] Pophal C, Yogo T, Yamada K, Segawa K. *Appl Catal B*, 1998, 16: 177
- [36] Yamada K, Kondo S, Segawa K. *Microporous Mesoporous Mater*, 2000, 35–36: 227
- [37] Pekridis G, Kaklidis N, Konsolakis M, Iliopoulou E F, Yentekakis I V, Marnellos G E. *Top Catal*, 2011, 54: 1135
- [38] Barakat N A M, Abdelkareem M A, El-Newehy M, Kim H Y. *Nanoscale Res Lett*, 2013, 8: 402/1
- [39] Farzaneh F, Mehraban Z, Norouzi F. *Environ Chem Lett*, 2010, 8: 69
- [40] Zhou D S, Yan A F, Wu Y, Wu T H. *Indian J Chem A*, 2013, 52: 51
- [41] Wang Y P, Zhu J W, Yang X J, Lu L D, Wang X. *Thermochim Acta*, 2005, 437: 106
- [42] Hussein G A M, Nohman A K H, Attyia K M A. *J Therm Anal*, 1994, 42: 1155
- [43] Mohamed M A, Halawy S A, Ebrahim M M. *J Anal Appl Pyr*, 1993, 27: 109
- [44] Konsolakis M, Carabineiro S A C, Papista E, Marnellos G E, Tavares P B, Moreira J A, Romaguera-Barcelay Y, Figueiredo J L. *Catal Sci Technol*, 2015, 5: 3714
- [45] Abu-Zied B M. *Appl Catal A*, 2008, 334: 234
- [46] Zhai X L, Cheng Y H, Zhang Z T, Jin Y, Cheng Y. *Int J Hydrogen Energy*, 2011, 36: 7105
- [47] Guil-López R, La Parola V, Peña M A, Fierro J L G. *Int J Hydrogen Energy*, 2012, 37: 7042
- [48] Lin W W, Cheng H Y, Ming J, Yu Y C, Zhao F Y. *J Catal*, 2012, 291: 149
- [49] Kaichev V V, Gladky A Y, Prosvirin I P, Saraev A A, Hävecker M, Knop-Gericke A, Schlögl R, Bukhtiyarov V I. *Surf Sci*, 2013, 609: 113
- [50] Greiner M T, Helander M G, Wang Z B, Tang W M, Lu Z H. *J Phys Chem C*, 2010, 114: 19777
- [51] Seo H O, Nam J W, Kim K D, Sim J K, Kim Y D, Lim D C. *J Mol Catal A*, 2012, 361–362: 45
- [52] Abu-Zied B M, Asiri A M. *Thermochim Acta*, 2014, 581: 110
- [53] Roy B, Artyushkova K, Pham H N, Li L, Datye A K, Leclerc C A. *Int J Hydrogen Energy*, 2012, 37: 18815
- [54] Rodríguez J L, Valenzuela M A, Poznyak T, Lartundo L, Chairez I. *J Hazard Mater*, 2013, 262: 472
- [55] Rocca M, Savio L, Vattuone L, Burghaus U, Palomba V, Novelli N, Buatier de Mongeot F, Valbusa U, Gunnella R, Comelli G, Baraldi A, Lizzit S, Paolucci G. *Phys Rev B*, 2000, 61: 213
- [56] Liu Y M, Wang T, Sun X, Fang Q Q, Lü Q R, Song X P, Sun Z Q. *Appl Surf Sci*, 2011, 257: 6540
- [57] Payne B P, Biesinger M C, McIntyre N S. *J Electron Spectrosc Relat Phenom*, 2012, 185: 159
- [58] Biesinger M C, Payne B P, Lau L W M, Gerson A, Smart R St C. *Surf Interf Anal*, 2009, 41: 324
- [59] Piumetti M, Bensaid S, Russo N, Fino D. *Appl Catal B*, 2015, 165: 742
- [60] Yamashita T, Vannic A. *J Catal*, 1996, 161: 254
- [61] Pietrzyk P, Zasada F, Piskorz W, Kotarba A, Sojka Z. *Catal Today*, 2007, 119: 219

碱金属助剂对N₂O直接分解催化剂NiO活性的促进作用

Bahaa M. Abu-Zied^{a,b,c,*}, Abdullah M. Asiri^{a,c}

^a阿卜杜勒阿齐兹国王大学高级材料杰出研究中心, 吉达21589, 沙特阿拉伯

^b艾斯尤特大学理学院化学系, 艾斯尤特71516, 埃及

^c阿卜杜勒阿齐兹国王大学理学院化学系, 吉达21589, 沙特阿拉伯

摘要: 考察了一系列碱金属促进和未促进的NiO催化剂上N₂O直接分解反应性能, 并采用X射线衍射, X射线光电子能谱(XPS)和前场扫描电镜对这些催化剂进行了表征. XPS结果表明, 催化剂表面的Ni以金属颗粒, NiO和Ni(OH)₂三种形式存在. 研究发现, 在催化剂表面主要是Ni⁰原子与N₂O分子发生相互作用. 未促进的NiO催化剂表现出非常低的催化N₂O分解活性; 碱金属的加入使得NiO催化剂活性大大提高.

关键词: 一氧化二氮分解; 温室气体; 氧化镍; 碱金属促进; 活性增加

收稿日期: 2015-05-05. 接受日期: 2015-08-21. 出版日期: 2015-11-20.

*通讯联系人. 电话: +96-563737563; 传真: +96-626952292; 电子邮箱: babuzaid@kau.edu.sa, babuzied@aun.edu.eg,

babuzied@yahoo.com

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).