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Article

Precursors of active Ni species in Ni/Al₂O₃ catalysts for oxidative dehydrogenation of ethane

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ABSTRACT

Ni/Al₂O₃ catalysts for oxidative dehydrogenation (ODH) of ethane were prepared by impregnation of Al₂O₃ with nickel acetate or nickel nitrate, and by mechanical mixing of NiO and Al₂O₃. The Ni-based catalysts were characterized by N₂ adsorption-desorption, X-ray diffraction, diffuse reflectance UV-visible diffuse reflectance spectroscopy, and temperature-programmed reduction of hydrogen. The results showed that formation of crystalline NiO particles with a size of < 8 nm and/or non-stoichiometric NiO species in the Ni/Al₂O₃ catalysts led to more active species in ODH of ethane under the investigated reaction conditions. In contrast, tetrahedral Ni species present in the catalysts led to higher selectivity for ethene. Formation of large crystalline NiO particles (22–32 nm) over Ni/Al₂O₃ catalysts decreased the selectivity for ethene.

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1. Introduction

Ni-based catalysts are attractive industrial catalysts in many reactions such as hydrogenation [1–3], reforming [4–7], hydrocracking [8–10], and oxidative dehydrogenation (ODH) of light alkanes such as ethane and propane [11]. ODH reactions are thermodynamically favorable, and the presence of O₂ can prevent coking of the catalyst.

Pure bulk NiO is very active in ODH of ethane and is capable of activating ethane at low temperatures [12–16]. Bulk NiO exhibits high conversion of ethane (46% at 350 °C) but low selectivity for ethene (below 50%) [13]. The catalytic activity of NiO was influenced by its textural characteristics. Wu et al. [15] reported that at low temperature, nanosized NiO was more active than its bulk counterpart. Moreover, mesoporous NiO gave higher selectivity for ethene at the same ethane conversion than nanosized NiO [16].

In ODH of ethane, NiO supported on Al₂O₃ [13,17–20] is

more selective for ethene than pure NiO. Nakamura et al. reported that NiO loaded on MgO [21] and ZrO₂ [22] with high surface area showed high performance in ODH of ethane without the need to dilute ethane and O₂ with an inert gas. High activity has also been reported for Ni-Nb-O [12,14], Ni-W-O [20], and Ni-Al-O [23] mixed oxides in ODH of ethane.

The improved catalytic performance of supported NiO catalysts compared with that of pure NiO may be related to the higher dispersion of NiO, which favours partial elimination of the unselective sites of NiO. This is consistent with previous results observed for NiO supported on γ-Al₂O₃ [19], Ni-W-O mixed oxide supported on mesoporous Al₂O₃ [20], and NiO dispersed on mesoporous MgO [21]. Zhang et al. [17] reported that the yield of ethene was approximately proportional to the pore volume/surface area ratio of the catalyst, and that highly dispersed NiO on Al₂O₃ preferentially converted ethane to ethene, whereas large crystallites of NiO on Al₂O₃ tended to convert ethane to CO₂. Heracleous et al. [14] reported that the low

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selectivity of NiO in ODH of ethane resulted from the highly reactive electrophilic single-charged O species present on the surface of NiO. Incorporation of Nb into the NiO lattice by substitution of Ni atoms and/or filling of the cationic vacancies in the defect-rich nonstoichiometric NiO surface can reduce the amount of nonstoichiometric NiO crystals present in pure NiO. Nb removes the unselective electrophilic O species by transforming them into more selective nucleophilic O species. This also resulted in high selectivity for ethylene and enhanced activity for ODH of ethane over Ni-Nb-O mixed oxides [14].

In this study, we focused on the relationship between the Ni species present in as-prepared Ni/Al₂O₃ catalysts and the activity/selectivity of the Ni/Al₂O₃ catalysts in ODH of ethane. That is, we determined the effects of different Ni species on the final catalytic performance of Ni/Al₂O₃ catalysts in ODH of ethane. This research follows on from our previous work investigating the activity of Ni/Al₂O₃ prepared by impregnation with nickel acetate with low Ni loading (0–6 wt%) [18] and Ni-Al-O mixed oxides (30–60 wt% Ni) [23] in ODH of ethane. Here, we mainly focused on the activity/selectivity of tetrahedral (T_d) and octahedral (O_h) Ni and NiO species present in Ni/Al₂O₃ catalysts prepared by impregnation with nickel acetate and nickel nitrate, and by mechanical mixing of Al₂O₃ and NiO. The present investigation also builded on the work of Ren et al. [24], who prepared Ni/Al₂O₃ catalysts from nickel acetate more active in hydrogenation of α -pinene than those prepared from nickel nitrate.

2. Experimental

2.1. Catalyst preparation

γ -Al₂O₃ (281 m²/g) was supplied by Eurosupport. Reference NiO was prepared by thermal decomposition of Ni(NO₃)₂·6H₂O at 500 °C in air for 10 h. Nickel aluminate precursor (NiAl₂O₄) was prepared by co-precipitating a stoichiometric mixture of Ni(NO₃)₂ and Al(NO₃)₃ from ammonium hydroxide solution with a final pH of 8.0. The precipitated hydroxide precursor was filtered, washed, and calcined at 900 °C in static air for 24 h. Ni-Al₂O₃ catalysts were prepared using different Ni salt precursors; Ni/Al₂O₃ catalysts containing 11.0, 15.8, and 19.6 wt% Ni (denoted Ni-Al-ac-11.0, -15.8, and -19.6, respectively) were prepared by impregnating Al₂O₃ with a solution of Ni(CH₃COO)₄·4H₂O in ethanol. Ni/Al₂O₃ catalysts with 11.7, 15.7, and 19.7 wt% Ni (denoted Ni-Al-NO₃-11.7, -15.7, -19.7, respectively) were prepared by impregnating Al₂O₃ with an aqueous solution of Ni(NO₃)₂·6H₂O. After impregnation, the catalysts were dried at room temperature overnight and then calcined at 500 °C in an air flow for 5 h. A mixture of NiO and Al₂O₃ with 11.8 wt% Ni (denoted Ni-Al-mm-11.8) was prepared by mechanical mixing of NiO and Al₂O₃ that had been calcined at 500 °C in air for 5 h.

2.2. Catalyst characterization

N₂ adsorption-desorption isotherms of samples were determined at liquid N₂ temperature using an adsorption analyser

(ASAP 2020, Micromeritics, USA). Prior to adsorption isotherm measurements, samples were degassed at 300 °C under vacuum for 8 h. The BET method was used to calculate surface areas. Pore size distributions (pore diameter, pore volume, and micropore surface area) were determined by the BJH method using the desorption branch.

X-ray diffractograms (XRD) were recorded with a Bruker AXS D8-Advance diffractometer using Cu K α radiation with a secondary graphite monochromator. The crystallite size of the NiO-like phase in the Ni/Al₂O₃ catalysts was calculated using the Scherrer formula ($D = 0.89\lambda/\beta\cos\theta$) from the full width at half-maximum (FWHM) value of the NiO(200) diffraction line [25,26], where 0.89 indicates a spherical particle, D is crystallite size (nm), λ is the X-ray wavelength (0.154056 nm), β is FWHM (rad), and θ is the diffraction angle (rad).

Ultraviolet-visible (UV-Vis) diffuse reflectance spectra of granulated (0.25–0.50 mm diameter) Ni/Al₂O₃ catalysts were measured using a Cintra 303 spectrometer (GBC Scientific Equipment, Australia) equipped with a Spectralon-coated integrating sphere using a Spectralon-coated disc as a standard. The spectra were recorded in the wavenumber range of 11111 cm⁻¹ (200 nm) to 50000 cm⁻¹ (900 nm); lamps switched at 350 nm. The reflectance was recalculated to absorption using the Schuster-Kubelka-Munk ($F(R_{\infty})$) function, $F(R_{\infty}) = (1-R_{\infty})^2/2R_{\infty}$, where R_{∞} is the diffuse reflectance from a semi-infinite layer.

Hydrogen temperature-programmed reduction (H₂-TPR) profiles were measured by an adsorption analyzer (AutoChem 2920, Micromeritics, USA). A quartz microreactor was charged with 100 mg of Ni/Al₂O₃ catalyst, or 10 mg NiO or NiAl₂O₄. Prior to measurement, all catalysts were pre-treated in O₂ at 450 °C for 1 h with a heating rate of 10 °C/min. The reduction was carried out from 25 to 1050 °C with a temperature gradient of 10 °C/min in a flow of 5% H₂/Ar gas (25 cm³/min). The changes in H₂ concentration were monitored by a thermal conductivity detector.

2.3. Catalyst test

ODH of ethane was carried out in a quartz through-flow microreactor at 500 °C and atmospheric pressure with 50–450 mg of catalyst (0.25–0.50 mm diameter) diluted with 1 cm³ of inert silicon carbide. The catalytic activity of the Ni/Al₂O₃ catalysts was compared at constant conversion of ethane (10%). The reaction mixture (composed of 8.0 vol% C₂H₆, 3.0 vol% O₂, and the balance He) was kept at a total flow of 100 cm³/min. The catalyst was activated in O₂ for 1 h at 450 °C before reaction. Concentrations of CO₂, CO, O₂, and hydrocarbons were analyzed by an online gas chromatograph (Shimadzu GC 17A).

3. Results and discussion

3.1. Characterization of Ni/Al₂O₃ catalysts

3.1.1. N₂ adsorption analysis

Figure 1 shows the N₂ adsorption-desorption isotherm and pore size distribution of Al₂O₃ and representative Ni-Al-NO₃-11.7, Ni-Al-ac-11.0, and Ni-Al-mm-11.8 catalysts. The Ni/Al₂O₃

Fig. 1. N₂ adsorption-desorption isotherms (a) and pore size distributions (b) of Al₂O₃ (1), Ni-Al-NO₃-11.7 (2), Ni-Al-ac-11.0 (3), and Ni-Al-mm-11.8 (4) calcined at 500 °C.

catalysts showed typical type IV isotherms with H3 hysteresis loops, indicating the presence of slit-shaped mesopores in the materials. Table 1 gives the surface area, total pore volume, and average pore size diameter of the catalysts. The specific surface areas (216–227 m²/g) of the Ni-Al-NO₃-11.7, Ni-Al-ac-11.0, and Ni-Al-mm-11.8 catalysts with the same Ni loading, were similar, and lower than that of the Al₂O₃ support (281 m²/g). The total pore volumes of all catalysts and support were similar (0.398–0.454 cm³/g). The Ni/Al₂O₃ catalysts possessed a narrow pore size distribution of 5.6–6.3 nm.

3.1.2. XRD analysis

Figure 2 shows the powder XRD patterns of Ni-Al-NO₃, Ni-Al-ac, and Ni-Al-mm catalysts with those of NiAl₂O₄ and NiO as references. The XRD pattern of the Ni/Al₂O₃ support showed poorly resolved diffraction peaks at 14.4°, 37.6°, 42.5°, 45.8°, and 67° corresponding to γ -Al₂O₃ [27–32]. The peak at 28.2° was assigned to an Al(OH)₃ phase [29]. However, the presence of broad, weak diffraction lines shows that the majority of NiAl₂O₄ is amorphous, with a minor proportion of γ -Al₂O₃. The presence of γ -Al₂O₃ was confirmed in all of the prepared Ni/Al₂O₃ catalysts. Diffraction lines corresponding to NiAl₂O₄ spinel were not observed in all Ni/Al₂O₃ catalysts.

The XRD patterns of Ni-Al-NO₃-11.7, -15.7, and -19.7 only

showed very weak diffraction peaks at $2\theta = 37^\circ$, 43.3° , and 63° corresponding to the (111), (200), and (220) diffraction lines of a cubic NiO-like oxide [19,33,34]. The diffraction patterns of Ni-Al-ac-11.0, -15.8, and -19.6 and Ni-Al-mm-11.8 exhibited intense diffraction peaks at $2\theta = 37^\circ$, 43.3° , 63° , 75° , and 79° corresponding to crystalline NiO. This indicates the presence of large NiO particles with high crystallinity in these catalysts [17,19]. XRD analysis showed that pure NiO crystallizes with NaCl-type fcc structure with a lattice constant a of 0.41762 nm, consistent with reported data [JCPDS 4-835].

The average crystallite sizes of the NiO-like phase in the Ni/Al₂O₃ catalysts calculated using the Scherrer formula are presented in Table 1. Crystalline NiO was not observed in the Ni-Al-NO₃ catalysts, which is possible that NiO crystallites are below the detection limit of XRD [35]. For Ni-Al-ac samples, the average crystallite size of NiO increased with increasing Ni loading in the order Ni-Al-ac-11.0 (8 nm) < Ni-Al-ac-15.8 (24 nm) $\approx$ Ni-Al-ac-19.6 (22 nm), which is comparable with the values reported elsewhere [34,36,37]. Moreover, these values approach those for Ni-Al-mm-11.8 (25 nm) and pure NiO (32 nm).

3.1.3. UV-Vis diffuse reflectance spectra

Figure 3 shows the UV-Vis spectra of Ni-Al-NO₃, Ni-Al-ac,

Table 1

Nomenclature and physicochemical properties of the Ni/Al₂O₃ catalysts calcined at 500 °C.

Catalyst	Ni (wt%)	D_{NiO}^a (nm)	S_{BET} (m ² /g)	Total pore volume (cm ³ /g)	Average diameter (nm)	H ₂ -TPR			
						n_{H_2} (mmol/g)	Δe	T_{max}^b (°C)	Major reducible species ^c
Al ₂ O ₃	0	—	281	0.447	5.3	—	—	—	—
Ni-Al-NO ₃ -11.7	11.7	—	227	0.398	5.6	1.69	1.7	787	Ni(T _d)
Ni-Al-NO ₃ -15.7	15.7	—	—	—	—	2.83	2.1	418, 761	
Ni-Al-NO ₃ -19.7	19.7	—	—	—	—	3.19	1.9	419, 762	
Ni-Al-ac-11.0	11.0	8	224	0.454	6.3	1.69	1.8	447, 824	NiO, Ni(T _d)
Ni-Al-ac-15.8	15.8	24	—	—	—	2.49	1.9	276, 416, 819	
Ni-Al-ac-19.6	19.6	22	—	—	—	3.03	1.8	291, 435, 817	
Ni-Al-mm-11.8	11.8	26	216	0.408	6.3	1.69	1.7	278, 435, 556	NiO
NiO	—	32	—	—	—	16.2	—	230, 400, 506	NiO

^a Ni crystallite size was calculated from the NiO(200) diffraction peak using the Scherrer equation.

^b Numbers in bold are the most intense reduction peaks.

^c Ni(T_d) species could be present as normal NiAl₂O₄ spinel and Ni(T_d) species in the Al₂O₃ lattice.

Fig. 2. XRD patterns of Ni-Al-NO₃ (a), Ni-Al-ac (b), and Ni-Al-mm (c). (1) Al₂O₃; (2) Ni-Al-NO₃-11.7; (3) Ni-Al-NO₃-15.7; (4) Ni-Al-NO₃-19.7; (5) Ni-Al-ac-11.0; (6) Ni-Al-ac-15.8; (7) Ni-Al-ac-19.6; (8) Ni-Al-mm-11.8; (9) NiO; (10) NiAl₂O₄.

and Ni-Al-mm catalysts with different Ni loadings. The measured spectra corresponded only to the electron transitions in the Ni particles and were not affected by the presence of Al₂O₃. The Al₂O₃ support did not exhibit any bands. The bands at 13900–14100, 15600–15800, and 16700–16900 cm⁻¹ indicate the presence of Ni(T_d) species [19,24,38–40]. The bands at 13900–14100, 24100, and 26300–26500 cm⁻¹ are attributed to Ni(O_h) in the NiO lattice [19,38]. The bands at 12900–13200 cm⁻¹ and broad band at 21500–27500 cm⁻¹ are attributed to the *d-d* transition of Ni(O_h) ions in the Al₂O₃ lattice [19,24,38,40,41]. The bands above 33000 cm⁻¹ correspond to the charge-transfer transition of both T_d and O_h Ni species. The background in the spectra below 25000 cm⁻¹ could be attributed to the presence of non-stoichiometric NiO species [19].

The UV-Vis spectrum of the mechanical mixture of NiO with Al₂O₃ (Fig. 3(c)) contained bands at 13900, 24050, and 26360 cm⁻¹ corresponding to crystalline NiO particles [24]. The bands at 14080, 15860, and 16830 cm⁻¹ showing the presence of Ni(T_d) species were much more intense over Ni-Al-NO₃-11.7,

-15.7, and -19.7 than that over Ni-Al-ac-11.0, -15.8, and -19.6. This indicates that the relative population of Ni(T_d) species in the Ni-Al-NO₃ catalysts is higher than that in the Ni-Al-ac catalysts. In contrast, Ni-Al-ac-11.0, -15.8, and -19.6 catalysts exhibited intense bands at 13900, 24050, and 26360 cm⁻¹, revealing a high population of Ni(O_h) in the NiO lattice. These bands were not observed in Ni-Al-NO₃-11.7, -15.7, and -19.7 samples. Ni-Al-NO₃-11.7, -15.7, and -19.7 catalysts also show the presence of Ni(O_h) ions in the Al₂O₃ lattice (a band at 12900 cm⁻¹ and broad band at 21500–27500 cm⁻¹). A broad band at 21500–27500 cm⁻¹ was also observed over the Ni₂AlO₄ reference material.

The intensity of the background of the UV-Vis spectra of Ni-Al-NO₃, Ni-Al-ac, and Ni-Al-mm catalysts was higher below 25000 cm⁻¹ than that of the NiAl₂O₄ reference, suggesting the presence of non-stoichiometric NiO species, which give the catalysts their dark grey colour. The intensity of the background increased with Ni loading.

Fig. 3. Diffuse reflectance UV-Vis spectra of Ni-Al-NO₃ (a), Ni-Al-ac (b), and Ni-Al-mm (c). (1) Al₂O₃; (2) Ni-Al-NO₃-11.7; (3) Ni-Al-NO₃-15.7; (4) Ni-Al-NO₃-19.7; (5) Ni-Al-ac-11.0; (6) Ni-Al-ac-15.8; (7) Ni-Al-ac-19.6; (8) Ni-Al-mm-11.8; (9) NiO; (10) NiAl₂O₄.

Fig. 4. H_2 -TPR profiles of Ni-Al- NO_3 (a), Ni-Al-ac (b), and Ni-Al-mm (c). (1) Ni-Al- NO_3 -11.7; (2) Ni-Al- NO_3 -15.7; (3) Ni-Al- NO_3 -19.7; (4) Ni-Al-ac-11.0; (5) Ni-Al-ac-15.8; (6) Ni-Al-ac-19.6; (7) Ni-Al-mm-11.8; (8) $NiAl_2O_4$; (9) NiO.

3.1.4. H_2 -TPR results

The H_2 -TPR profiles of the Ni-Al- NO_3 , Ni-Al-ac, and Ni-Al-mm catalysts with different Ni loadings are presented in Fig. 4 along with that of NiO as a reference material. Table 1 gives the maxima of the reduction peaks. The average Ni oxidation state changes during the H_2 -TPR experiments (Δe) were calculated from the H_2 consumption at 25–1050 °C and are listed in Table 1. The changes in the oxidation state of Ni during the reduction were between 1.7 and 2.1, consistent with reduction of Ni(II) to Ni(0).

Pure NiO exhibited three reduction peaks: one intense reduction peak with a maximum at 400 °C corresponding to crystalline NiO and the other two small reduction peaks at 230 and 506 °C that can be attributed to the reduction of NiO crystals of different sizes. In the literature, the reduction peak of NiO prepared by decomposition of $Ni(NO_3)_2 \cdot 6H_2O$ has been reported to appear at ~220 [42–44], ~330 [16,45,46], and 400 °C above [33,47,48] depending on the experimental conditions. Generally, two reduction peaks of NiO species are present in TPR profiles, one at lower temperature (~245 °C) related to reduction of non-stoichiometric or/and poorly described Ni_2O_3 , which is black in colour and thermally unstable compared with crystalline NiO, and other at higher temperature (418 °C) from crystalline NiO with octahedral coordination [49].

Ni-Al-mm-11.8 exhibited an intense peak at 435 °C and weaker one at 556 °C, which were also observed over pure NiO. The peak at lower temperature corresponds to the presence of NiO species, i.e., to both crystalline NiO particles and non-stoichiometric NiO species. The difference in the maxima of the low-temperature peak in Ni-Al-mm and that of the NiO reference material could be caused by the different NiO particle size and/or by interaction of NiO with Al_2O_3 [17,39,50,51].

Intense reduction peaks at 761–787 °C were observed over Ni-Al- NO_3 -11.7, -15.7, and -19.7 samples (Table 1). Because Ni with tetrahedral coordination is difficult to reduce [52], the reduction of Ni(T_d) species occurs at higher temperature than Ni(O_h) species [2,24,53]. The high-temperature reduction peak

has also been attributed to strongly bound $NiAl_2O_4$ with a spinel-like structure [40,42]. Pure $NiAl_2O_4$ exhibits a high-temperature reduction peak at 878 °C. Therefore, the broad reduction peaks at 761–787 °C over Ni-Al- NO_3 samples may arise from $NiAl_2O_4$ with a spinel-like structure. Slagtern et al. [54] reported that a reduction peak at 771 °C indicated the presence of Ni(II) species, both Ni(T_d) and Ni(O_h), dispersed on Al_2O_3 . In the case of Ni-Al- NO_3 , the peaks at 761–787 °C suggest the presence of Ni(T_d) and Ni(O_h) ions in the Al_2O_3 lattice. Weak reduction peaks at 418 °C were observed in Ni-Al- NO_3 -15.7 and -19.7 samples, which could be related to the presence of NiO species. Although crystalline NiO species were not detected by XRD, the presence of non-stoichiometric NiO species was indicated by the background in the diffuse reflectance UV-Vis spectra.

Ni-Al-ac-11.0, -15.7, and -19.6 samples exhibited reduction peaks at 410–450 and 817–824 °C (Table 1). The reduction peak at higher temperature is attributed to the presence of both Ni(T_d) and Ni(O_h) species in the Al_2O_3 lattice [54]. Because the presence of Ni(O_h) species in the Al_2O_3 lattice of the Ni-Al-ac catalysts was not evidenced by both UV-Vis and XRD results, this reduction peak corresponds to Ni(T_d) species. The intensity of the low-temperature reduction peak (NiO species) increased with the Ni loading in Ni-Al-ac-11.0, -15.8, and -19.6 samples, while the intensity of the high-temperature reduction peak remained approximately constant. Thus increasing the Ni loading in the Ni-Al-ac catalysts from 11.0 to 19.6 wt% mainly increased the relative population of NiO species.

3.2. Ni species present in the Ni/ Al_2O_3 catalysts

Several different Ni species could be present in the Ni/ Al_2O_3 catalysts [55,56]. Based on UV-Vis, H_2 -TPR, and XRD results, the Ni species present in the as-prepared Ni/ Al_2O_3 catalysts are discussed below (Table 2).

Ni-Al- NO_3 -11.7, -15.7, and -19.7 samples mainly contained Ni(T_d) species (Fig. 3(a)). The Ni species with tetrahedral coordination could be present as Ni(T_d) species, which diffused into

Table 2Ni species present in the Ni-Al₂O₃ catalysts.

Ni species		XRD (°)	H ₂ -TPR (°C)	UV-Vis (cm ⁻¹)	Ni/Al ₂ O ₃ catalyst
Ni(T _d)	Diffused into the Al ₂ O ₃ lattice or normal NiAl ₂ O ₄ spinel	—	761–787	14080, 15860, 16830	Ni-Al-NO ₃ -11.7, -15.7, -19.7
		—	810–830	14080, 15860, 16830	Ni-Al-ac-11.0, -15.8, -19.6
Ni(O _h)	Inverse NiAl ₂ O ₄ spinel	—	761–787	12900, 21500–27500	Ni-Al-NO ₃ -11.7, -15.7, -19.7
		—	410–450	background below 25000	Ni-Al-ac, Ni-Al-NO ₃ , and Ni-Al-mm
	Small NiO crystals	37, 43, 63, 75, 79	410–450	13900, 24000, 26400	Ni-Al-ac-11.0
	Large NiO crystals	37, 43, 63, 75, 79	410–450	13900, 24000, 26400	Ni-Al-ac-15.6, -19.6; Ni-Al-mm-11.8

the Al₂O₃ lattice [57], and as normal NiAl₂O₄ spinel [17,58–60], where Ni(II) ions occupy T_d sites and Al(III) ions occupy O_h sites. Although normal NiAl₂O₄ spinel was not detected by XRD (Fig. 2), the presence of these species could not be excluded. Thus, we were unable to distinguish between these two types of Ni species.

The Ni-Al-NO₃ catalysts also contained Ni(O_h) species (Table 2, Fig. 3(a)). The Ni species with octahedral coordination could be present as inverse NiAl₂O₄ spinel, where Ni(II) ions occupy O_h sites and Al(III) ions occupy T_d and O_h sites [17,58,59], and as NiO species. Although inverse NiAl₂O₄ spinel was not evidenced by XRD (Fig. 2), Ni(O_h) ions in the Al₂O₃ lattice were detected by UV-Vis spectrum (21500–27500 cm⁻¹) of Ni-Al-NO₃-11.7 and Ni₂AlO₄ reference material. While crystalline NiO particles were not detected in the Ni-Al-NO₃ catalysts (Fig. 2 and Fig. 3(a)), non-stoichiometric NiO species were observed as the background in their UV-Vis spectra (Table 2, Fig. 3(a)). Non-stoichiometric NiO species have been described as NiO_{1+x} species [51] with an equivalent amount of Ni³⁺ ions and small excess of O²⁻ [61–63]. Because Ni-Al-NO₃-11.7 samples exhibited a background UV-Vis signal but not a reduction peak at 410–450 °C (Fig. 4(a)), it is possible that UV-Vis spectroscopy can detect non-stoichiometric NiO species with higher sensitivity than TPR.

Ni-Al-ac-11.0, -15.8, and -19.6 samples contained higher relative populations of crystalline NiO particles than Ni-Al-NO₃ (Fig. 2 and Fig. 3(b)), and non-stoichiometric NiO species (Fig. 3(b)). Reduction peaks at 400–550 °C indicated the presence of both crystalline NiO particles and non-stoichiometric NiO species. In addition, Ni-Al-ac catalysts also contained Ni(T_d) species (Fig. 4(b) and Fig. 3(b)).

Increasing the Ni loading in the Ni-Al-ac catalysts from 11.0 to 19.6 wt% mainly caused the relative population of crystalline NiO particles and/or non-stoichiometric NiO species to increase. This was clearly seen in the TPR profiles of the Ni-Al-

ac-11.0, -15.8, and -19.6 catalysts (Fig. 4), where the intensity of the reduction peak at 810–830 °C remained constant while that of the reduction peak at 410–450 °C increased with Ni loading. While Ni-Al-ac-11.0 contained small NiO species (crystalline NiO particles with a size of 8 nm), Ni-Al-ac-15.8 and -19.6 contained larger NiO species with a particle size of 22–24 nm (Table 1).

Ni-Al-mm-11.8 sample contained crystalline NiO particles (Fig. 2 and Fig. 3(c)), and non-stoichiometric NiO species (Fig. 3(c)). The intense reduction peak at 435 °C was consistent with the presence of both crystalline NiO particles and non-stoichiometric NiO species (Fig. 4(c)).

3.3. ODH of ethane

The catalytic behavior of the Ni-Al-ac, Ni-Al-NO₃, and Ni-Al-mm catalysts was compared at the same ethane conversion (10%) (Table 3). We selected such a low ethane conversion to suppress the influence of a lack of reactant on the final activity of the catalysts. Ethene was the main product of the reaction, and CO₂ was mainly formed as an undesired by-product. All of the tested Ni/Al₂O₃ catalysts exhibited very low selectivity for CO, and only traces of CH₄ were detected. The activities of the Ni/Al₂O₃ catalysts given in Table 3 were stable for 3 h of time on stream. The effect of time on stream on the catalytic performance of the Ni catalysts over 3 h was not studied. No contribution from homogeneous gas-phase reactions was observed under the studied reaction conditions (independently checked by a blank experiment).

The catalytic behavior of the Ni/Al₂O₃ catalysts strongly depended on their preparation procedures and Ni loadings. Next, the activity of the Ni catalysts is discussed based on both the amount of catalyst used to achieve a constant conversion of ethane and the productivity taking into consideration the amount of catalyst and ethene yield.

Table 3Conversion of O₂, selectivity for products, and yield of ethene obtained over the Ni/Al₂O₃ catalysts at 10% conversion of ethane.

Catalyst	<i>m</i> /mg	<i>X</i> (O ₂)/%	<i>S</i> /%				<i>Y</i> (C ₂ H ₄)/%	Productivity (g(C ₂ H ₄)/g _{cat} ⁻¹ h ⁻¹)
			CH ₄	C ₂ H ₄	CO	CO ₂		
Ni-Al-NO ₃ -11.7	453.8	23.8	0.1	84.2	0.7	15.0	8.5	0.106
Ni-Al-NO ₃ -15.7	143.2	22.9	0.2	86.5	0.9	12.5	8.6	0.340
Ni-Al-NO ₃ -19.7	130.5	23.5	0.1	86.1	0.6	13.4	8.6	0.364
Ni-Al-ac-11.0	87.5	26.0	0.1	80.6	0.9	18.7	7.7	0.486
Ni-Al-ac-15.8	108.0	31.8	0.2	75.4	3.0	21.5	8.6	0.436
Ni-Al-ac-19.6	119.2	30.1	0.2	74.9	0.9	23.9	7.6	0.352
Ni-Al-mm-11.8	205.7	60.0	0.4	36.1	1.1	62.5	3.6	0.100

Reaction conditions: gas composition of 8.0% ethane-3.0% O₂/He, total flow 100 mL/min, reaction temperature 500 °C.

The Ni-Al-NO₃-11.7, Ni-Al-ac-11.0, and Ni-Al-mm-11.8 catalysts possess the same Ni loading but different populations of Ni species. The activity of these catalysts increased (amount of catalyst decreased) in the order Ni-Al-NO₃-11.7 (453 mg) < Ni-Al-mm-11.8 (206 mg) < Ni-Al-ac-11.0 (87 mg). Moreover, it is clearly seen that Ni-Al-ac-11.0, -15.8, and -19.6 catalysts were more active than the corresponding Ni-Al-NO₃-11.7, -15.7, and -19.7 catalysts. While 87–120 mg of catalyst was required to achieve 10% of ethane conversion for Ni-Al-ac-11.0, -15.8, and -19.6 catalysts, 130–453 mg of catalyst was required to achieve the same conversion by Ni-Al-NO₃-11.7, -15.7, and -19.7 catalysts. While the required amount of Ni-Al-ac catalysts increased with increasing Ni loading (so their activity decreased), the required amount of Ni-Al-NO₃ catalysts decreased (activity increased) with increasing Ni loading.

Besides the effect of preparation method on the activity of the Ni/Al₂O₃ catalysts, they also exhibited different selectivity for ethene. Ni-Al-mm-11.8 showed much lower selectivity for ethene than the Ni-Al-ac and Ni-Al-NO₃ catalysts. This was associated with considerably higher O₂ conversion for Ni-Al-mm-11.8 than that for the Ni-Al-ac and Ni-Al-NO₃ catalysts (Table 3). The Ni-Al-NO₃ catalysts exhibited the highest selectivity for ethene of 84%–86%. The Ni-Al-ac catalysts were slightly less selective for ethene (75%–81%) than the Ni-Al-NO₃ catalysts over the whole range of Ni loading investigated. Moreover, the selectivity for ethene in ODH of ethane with the Ni-Al-ac catalysts decreased slightly with increasing Ni loading, whereas for the Ni-Al-NO₃ catalysts, their selectivity for ethene increased with Ni loading (Fig. 5).

Ni-Al-ac samples exhibited higher ethene productivity (0.35–0.49 g_{C₂H₄} g_{cat}⁻¹ h⁻¹) than the Ni-Al-NO₃ catalysts (0.11–0.36 g_{C₂H₄} g_{cat}⁻¹ h⁻¹). The ethene productivity for the Ni-Al-ac catalysts decreased from 0.49 to 0.35 g_{C₂H₄} g_{cat}⁻¹ h⁻¹ with increasing Ni loading, while the ethene productivity for the Ni-Al-NO₃ catalysts increased with Ni loading from 0.11 to 0.36 g_{C₂H₄} g_{cat}⁻¹ h⁻¹. The ethene productivity was approximately the same for the Ni-Al-NO₃-19.7 and Ni-Al-ac-19.6 catalysts (0.35–0.36 g_{C₂H₄} g_{cat}⁻¹ h⁻¹). Comparing Ni-Al-NO₃-11.7, Ni-Al-ac-11.0, and Ni-Al-mm-11.8 with the same Ni loading, the ethene

productivity increased with the order Ni-Al-NO₃-11.7 ~ Ni-Al-mm-11.8 < Ni-Al-ac-11.0. The highest productivity of ethene in ODH of ethane at 500 °C was achieved using the Ni-Al-ac-11.0 catalyst (0.49 g_{C₂H₄} g_{cat}⁻¹ h⁻¹).

3.4. The effect of Ni species on the ODH of ethane by Ni/Al₂O₃ catalysts

The relationship between the distribution of Ni species in the as-prepared catalysts and their activity/selectivity was compared in two ways. Firstly, Ni-Al-NO₃-11.7, Ni-Al-ac-11.0, and Ni-Al-mm-11.8 possess the same Ni loading, approximately the same amount of non-stoichiometric NiO species (Fig. 3), and similar specific surface areas (Table 1). The ethene productivity of Ni-Al-ac-11.0 was much higher than that of Ni-Al-NO₃-11.7 and Ni-Al-mm-11.8 catalysts. The low ethene productivity of Ni-Al-mm-11.8 is explained by its low selectivity for ethene. Ni-Al-ac-11.0 and Ni-Al-NO₃-11.7 catalysts mainly differed in their population of Ni(T_d) species and crystalline NiO particles. While Ni-Al-ac-11.0 catalyst contained crystalline NiO species of small size ($D_{\text{NiO}} = 8$ nm, Table 1), Ni-Al-NO₃-11.7 did not contain crystalline NiO particles (Table 1). Conversely, Ni-Al-NO₃-11.7 contained a higher relative population of Ni(T_d) species than Ni-Al-ac-11.0 (Fig. 3(a) and (b)).

The increased ethene productivity of the Ni-Al-NO₃ catalysts with Ni loading (Table 3) can be explained by the absolute amounts of Ni(T_d) species and non-stoichiometric NiO species increasing with Ni loading (Fig. 3(a)). In contrast, the decreasing ethene productivity of Ni-Al-ac catalysts with increasing Ni loading (Table 3) could only be connected with the increasing relative population of crystalline NiO particles (Fig. 3(b) and 4(b)) of larger size (Table 1).

Thus, it can be assumed that small NiO species and/or non-stoichiometric NiO species led to more active species in ODH of ethane than Ni(T_d) species under the investigated reaction conditions. The lower activity of the Ni/Al₂O₃ catalysts with a higher population of Ni(T_d) species (Ni-Al-NO₃) is consistent with our previous reports, where we focused on Ni-Al mixed oxides (30–60 wt% Ni) [23] and Ni-Al₂O₃ (0–6 wt% Ni) [18] prepared from nickel acetate. We found that increasing thermal pre-treatment of both types of catalysts caused the Ni species in as-prepared catalysts to redistribute, increasing the relative population of Ni(T_d) species and decreasing activity. As the behavior of the Ni species was not tested under in situ conditions, it is not possible to conclude that Ni(T_d) species are less active in ODH reactions. However, it is possible to state that Ni(T_d) species present in the as-prepared Ni/Al₂O₃ catalysts formed less active Ni species under the reaction conditions than the larger NiO species.

Secondly, the effect of Ni loading on the distribution of Ni species and catalytic behavior was studied. It should be stressed that Ni-Al-mm-11.8, which possessed the largest relative population of crystalline NiO particles (Fig. 2–4), exhibited the lowest selectivity for ethene (Table 3). The higher selectivities of the Ni-Al-ac-11.0 and Ni-Al-NO₃-11.7 catalysts compared with that of Ni-Al-mm-11.8 (Fig. 5) could be explained by the absence of large crystalline NiO particles with a size of ~20–25

Fig. 5. Selectivity for ethene as a function of Ni content under iso-conversion conditions (ethane conversion of 10%) for Ni-Al-NO₃, Ni-Al-ac, and Ni-Al-mm in ODH of ethane at 500 °C

nm. The presence of the particles led to CO_x formation and was associated with high oxygen consumption.

The Ni-Al-ac-15.8 (NiO 24 nm) and -19.6 (NiO 22 nm) catalysts containing crystalline NiO particles were less selective for ethene than Ni-Al-ac-11.0 catalyst (NiO 8 nm) and Ni-Al-NO₃ catalysts lacking crystalline NiO particles (Figs. 2–4). Moreover, the selectivity of the Ni-Al-ac catalysts for ethene decreased with increasing relative population and size of crystalline NiO (Fig. 2, Table 1). In addition, the Ni-Al-NO₃-11.7 catalyst containing too small NiO particles detectable by XRD exhibited the lowest O₂ conversion (Table 3).

Ni/Al₂O₃ catalysts are often prepared by impregnation of an Al₂O₃ support with Ni(NO₃)₂, which leads to a catalyst with a dominant population of Ni(T_d) species. Thus, the preparation of Ni/Al₂O₃ catalysts using nickel acetate would be more profitable in processes where Ni(O_h) species are more desirable. Previously, Ren et al. [24] did not observe the formation of NiO species in Ni-Al-ac catalysts. This is in agreement with our previous result, where we also did not observe the formation of NiO species in Ni-Al-ac catalysts up to 6 wt% Ni. The formation of NiO species started at high Ni loading (11–19 wt% Ni), as discussed here. The formation of NiO species in Ni-Al-ac catalysts and their absence from Ni-Al-NO₃ catalysts could be explained by the different abilities of solutions of nickel nitrate and nickel acetate to disperse in the Al₂O₃ support [64].

4. Conclusions

Ni/Al₂O₃ catalysts with different distributions of Ni species were prepared by impregnation of Al₂O₃ with nickel acetate and nickel nitrate and by mechanical mixing of Al₂O₃ and NiO. The results showed that Ni-Al-ac and Ni-Al-mm contained high relative populations of NiO species, while Ni-Al-NO₃ mainly contained Ni(T_d) species. While formation of crystalline NiO particles with $D_{\text{NiO}} \leq 8$ nm and/or non-stoichiometric NiO species in the as-prepared Ni-Al₂O₃ catalysts led to more active species in ODH of ethane under the investigated reaction conditions, Ni(T_d) species present in the as-prepared catalysts led to higher selectivity for ethene. Formation of large crystalline NiO particles ($D_{\text{NiO}} = 22$ –32 nm) in the as-prepared Ni/Al₂O₃ catalysts decreased their selectivity for ethene. Ni-Al-ac was more active than Ni-Al-NO₃, but showed slightly lower selectivity for ethene. The presence of large NiO particles formed in the Ni-Al-ac catalysts at high Ni loading dramatically decreases the selectivity of ethene.

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Graphical Abstract

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Precursors of active Ni species in Ni/Al₂O₃ catalysts for oxidative dehydrogenation of ethane

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In oxidative dehydrogenation of ethane, small and/or non-stoichiometric NiO species present in the catalyst led to more active species, tetrahedral Ni species increased selectivity for ethene, and large crystalline NiO particles decreased selectivity for ethene.

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