Highly Selective Ce–Ni–O Catalysts for Efficient Low Temperature Oxidative Dehydrogenation of Propane

Yong-Mei Liu · Lu-Cun Wang · Miao Chen · Jie Xu · Yong Cao · He-Yong He · Kang-Nian Fan

Abstract Doughnut-like structured CeNiO, prepared by a novel oxalate gel co-precipitation method, exhibited significantly higher activity in oxidative dehydrogenation of propane at a temperature as low as 275 °C than conventional catalysts such as VMgO. It is suggested that oxygen vacancy formed in CeO_2 lattice due to the incorporating of Ni atoms adsorbs and activates the molecular oxygen to form active oxygen species. The superior performance for propane oxidative dehydrogenation over CeNiO catalyst can be attributed not only to the properties of the CeNiO catalyst but also to its unique doughnut-like structure.

Keywords Nickel · Solid solution · Propane ODH · Oxygen vacancy · Doughnut-like

1 Introduction

Oxidative dehydrogenation (ODH) of propane provides a thermodynamically accessible route to the synthesis of propene [1, 2], one of the most important building blocks in the modern petrochemical industry. Catalyst compositions based on V or Mo oxides have shown to be active and selective for this reaction, but the reaction has to be carried out at a relatively high temperature (above 500 °C), where undesirable combustion pathways leading to limited propene selectivities [3, 4]. With great recent efforts devoted to the design and synthesis of vanadia-based ODH catalysts with more attractive propene yields [5–9], much less attention has been paid to the development of new catalyst systems that can allow the effective conversion of propane at much lower temperatures (below 400 °C). The low-temperature ODH approach is expected to be highly energy efficient, furthermore, it may offer additional opportunity to inhibit the unselective combustion pathways involved in the ODH process.

Recently, ceria-based materials in the presence of transition metal oxides have attracted increasing attention in the area of heterogeneous catalysis due to their unique redox properties [10–12]. Especially in the field of selective oxidation, the essential role of ceria is reported to be the generation and participation of surface oxygen species and anionic vacancies during the catalytic reactions. Lately, Jalowiecki-Duhamel and co-workers reported that catalysts based on Ce-Ni based mixed oxide were active and selective for the ODH of propane at temperature range of 300–350 °C. However, the catalytic results of these catalysts in terms of propane conversion and propene selectivity (<60%) are far from satisfactory [11, 12].

In the present study, a novel Ce–Ni–O catalyst with a doughnut-like morphology has been prepared and proved to be highly selective (>80%) for the ODH of propane at a surprisingly low temperature of 275 °C. The oxalate gel-coprecipitation method, previously established to be an effective technique for the preparation of $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst developed by our group[13], has shown to be particularly useful in regulating the structural and surface redox properties of the Ce–Ni–O catalysts for the ODH of propane. Our results have shown the formation of solid solutions in the as-prepared high surface area Ce–Ni–O catalyst, which can allow the

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favorable creation of active surface oxygen species and anionic vacancies for the selective ODH of propane.

2 Experimental

2.1 Samples Preparation

The Ce_mNi_nO catalysts (m/n denotes the molar ratio of Ce to Ni) were prepared by following a modified procedure involving the gel-coprecipitation of oxalate precursor [13]. Briefly, two alcoholic solutions of mixed nitrates and 30% excess of oxalic acid were combined at room temperature under vigorous stirring. The resultant precipitate of oxalate was then recovered by solvent evaporation at 50 °C under gentle stirring, followed by calcination in air at 500 °C for 2 h. The as-prepared samples were referred as Ce_mNi_nO-OG. For comparison, the pure CeO_2 and NiO were prepared by following the same procedure (see Table 1). The reference samples denoted as Ce_mNi_nO-OC, Ce_mNi_nO-KC and Ce_mNi_nO-imp were prepared by aqueous oxalate coprecipitation, KOH coprecipitation and conventional wet-impregnation methods, respectively.

2.2 Samples Characterization

The BET surface area and the pore volume were determined by N_2 adsorption at 77 K on a Micromeritics TriStar 3000 adsorption apparatus. The morphologies were studied by scanning electron microscopy (SEM, Philips XL 30) and HitachiH600 scan-transmission electron microscope (TEM). The X-ray diffraction (XRD) profiles were collected on a Bruker AXS D8 Advance X-ray Diffractometer with CuK_α radiation. Temperature programmed reduction of the mixed oxide was carried out using 5% H_2 in Ar as reducing agent at a flow 30 ml min^{-1}. The amount of H_2 consumed during the reduction was calculated from the analysis with the thermal conductivity detector. Raman spectra were obtained using a confocal microprobe Raman system (Lab Ram Intensity). The excitation wavelength was 514.5 nm from an internal Ar^+ laser with a power of 8 mW. All the samples were heated to 500 °C in airflow for 2 h before detects. Spectra were recorded with a resolution of 4 cm^{-1}.

2.3 Activity Test

The ODH of propane was carried out using a fixed-bed quartz reactor. 0.15 g of the catalyst (60–80-mesh) was loaded in a quartz tubular reactor, and tested under the 14 ml min^{-1} (GHSV ~5,480 h^{-1}) of total gas flow consisting of $C_3H_8/O_2/N_2$ with a molar ratio of 0.7/1/12. The feed and the reaction products were analysed by an on-line gas chromatograph [9].

3 Results and Discussion

The N_2 adsorption data reported in Table 1 indicate that the present oxalate gel-coprecipitation approach can allow the preparation of Ce–Ni–O catalysts with much higher specific surface areas. Figure 1 shows XRD profiles of pure NiO, CeO_2, $CeNi_2O$ samples prepared by different method. The diffraction peaks of NiO (Fig. 1f) are the weakest, and the crystalline diffraction peaks of CeO_2 is very weak and broad. This means that the particles size of both NiO and

Table 1 Catalytic performance of various Ce–Ni–O mixed oxide catalysts for low-temperature ODH of propane

Catalyst	Ce/Ni (molar ratio)	S_{BET} (m^2 g^{-1})	C_3H_8 Conversion (%)	Selectivity (%)		Yield of propene (%)	rC_3H_6 (µmol-C_3H_6-h^{-1} m^{-2})
				C_3H_6	CO_2		
CeO_2-OG	/	53.6	2.3	38.1	61.9	0.9	2.1
NiO-OG	/	34.5	2.1	60.4	39.6	1.3	4.8
Ce_8NiO-OG	8/1	76.9	5.6	66.1	33.9	3.7	6.1
Ce_4NiO-OG	4/1	76.2	7.9	68.1	31.9	5.4	9.1
Ce_2NiO-OG	2/1	73.3	9.7	71.1	28.7	6.9	12.0
$CeNiO$-OG	1/1	65.1	10.1	71.4	28.6	7.2	14.1
$CeNi_2O$-OG	1/2	63.9	12.8	82.7	17.3	10.6	21.2
$CeNi_4O$-OG	1/4	48.1	9.9	73.2	26.8	7.3	19.4
$CeNi_2O$-OC	1/2	28.4	4.2	76.8	23.2	3.2	14.4
$CeNi_2O$-KC	1/2	58.1	55.8	10.1	89.5	5.7	12.5
$CeNi_2O$-imp	1/2	39.3	10.1	40.6	59.4	4.1	13.3

Reaction conditions: temperature ~275 °C; reaction pressure ~1 atm; reaction feed ~$C_3H_8/O_2/N_2 = 0.7/1/12$ (molar ratio); GHSV = 5,478 h^{-1}. Formation of CO was not detected

CeO_2 in $CeNi_2O$-OG is much smaller than other samples. In the case of $CeNi_2O$-imp and $CeNi_2O$-OC, the NiO crystalline diffraction peaks are stronger, and the intensity of CeO_2 crystalline diffraction peaks is similar to that of pure CeO_2, indicating that CeO_2 particles and NiO particles aggregated. This result confirmed that the sample prepared by oxalate gel co-precipitation is better dispersed than other methods. A careful examination of the patterns shows that the addition of nickel affects not only the broadness of the ceria peaks, but also the position. Table 1 reports the difference between the diffraction peak angle of the reference CeO_2 and of the CeO_2 like phase in the mixed oxide. It could be suggested that the Ni^{2+} ions are incorporated into the ceria lattice to form the solid solution [11]. So XRD results show that at least two types of Ni phase existed in the CeNiO catalyst, i.e. small NiO partilce and Ni^{2+} ions incorporated into ceria lattice.

In order to gain an insight into the discrepancies between $CeNi_2O$-OG and $CeNi_2O$-OC, H_2-TPR has been carried out. Figure 2 shows the H_2-TPR profiles of CeO_2, NiO and CeNiO mixed oxides prepared by different methods. As for the reduction of NiO, there is a large difference between pure NiO and the NiO specie in CeNiO catalyst. For pure NiO, there is one reduction peak corresponding to the reduction of NiO at 390 °C. This is named β. The profiles of $CeNi_2O$-imp is similar to that of pure NiO, but the temperure of β peak is lower than that of pure NiO, which indicates a higher dispersion of NiO in $CeNi_2O$-imp. For $CeNi_2O$-OG, $CeNi_2O$-KC and $CeNi_2O$-OC, three hydrogen consumption peaks ($\alpha_1, \alpha_2, \beta$) are observed. The α_1 and α_2 peaks can be ascribed to the reduction of adsorbed oxygen as literature reported [11], but the α_1 peak is very weak.

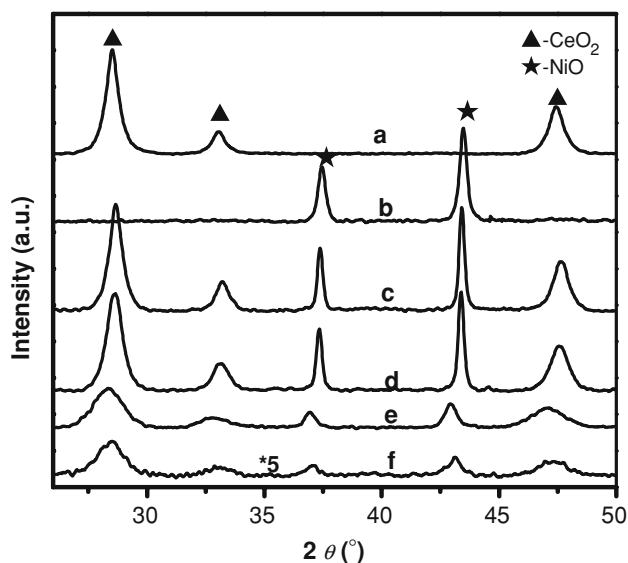Generally, it was proposed that the formation of the solid solution of Ce–Ni–O by the incorporation of Ni^{2+} ions into ceria lattice leads to the generation of oxygen vacancies, which adsorb oxygen easily. Therefore, very reactive oxygen species are formed, which are reduced easily by H_2 at low temperature. The relative intensity of α_2 peak in Fig. 2d is obviously stronger than that in Fig. 2c and e. This fact further confirms that Ni^{2+} ions in $CeNi_2O$-OG sample is easier incorporating into CeO_2 lattice to form solid solution than in $CeNi_2O$-OC and $CeNi_2O$-KC sample. But there are great difference among β peaks of different profiles. The temperature of the β peaks in Fig. 2d is the lowest, and the temperature of β peaks in Fig. 2c is the highest. Thus, the present XRD and TPR results show evidence the significant modification of the redox properties and an easier incorporation of nickel into ceria lattice in the oxalate gel-co-precipitated samples, pointing to the highly dispersed nature of NiO_x species and formation of a higher concentration of low temperature active surface oxygen species over the $CeNi_2O$-OG sample.

More interestingly, the SEM image (Fig. 3a) reveals that the $CeNi_2O$-OG sample consists of well-defined doughnut-like macrostructures with uniform size of ca. 14 μm, which is totally different from the ones prepared by other techniques. But the morphology of $CeNi_2O$-OC (Fig. 3b) revealed a worse and asymmetric appearance, which indicated that the NiO species is highly dispersed in the $CeNi_2O$-OG sample, but it couldn't dispersed so well in the $CeNi_2O$-OC sample. And the TEM image revealed that one cannot distinguish between the surface of a large particle
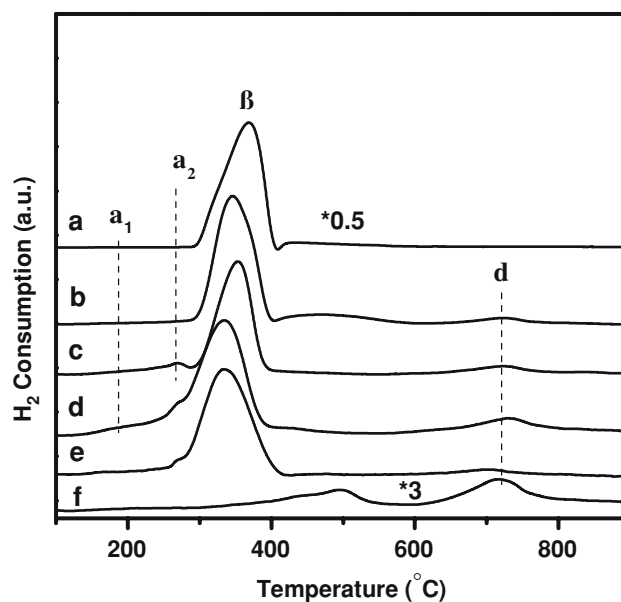

Fig. 1 The XRD patterns of different catalysts: a CeO2, b NiO, c CeNi2O-imp., d CeNi2O-OC, e CeNi2O-KC, f CeNi2O-OG

Fig. 2 H_2-TPR profiles of CeO_2 and NiO and $CeNi_2O$ prepared by different methods: a NiO, b $CeNi_2O$-imp., c $CeNi_2O$-KC, d $CeNi_2O$-OG, e $CeNi_2O$-OC, f CeO_2

Fig. 3 SEM and TEM image of Ce-Ni-O catalysts: **a** SEM image of CeNi$_2$O-OG, **b** SEM image of CeNi$_2$O-OC, **c** TEM image of CeNi$_2$O-OG, **d** TEM image of CeNi$_2$O-OC
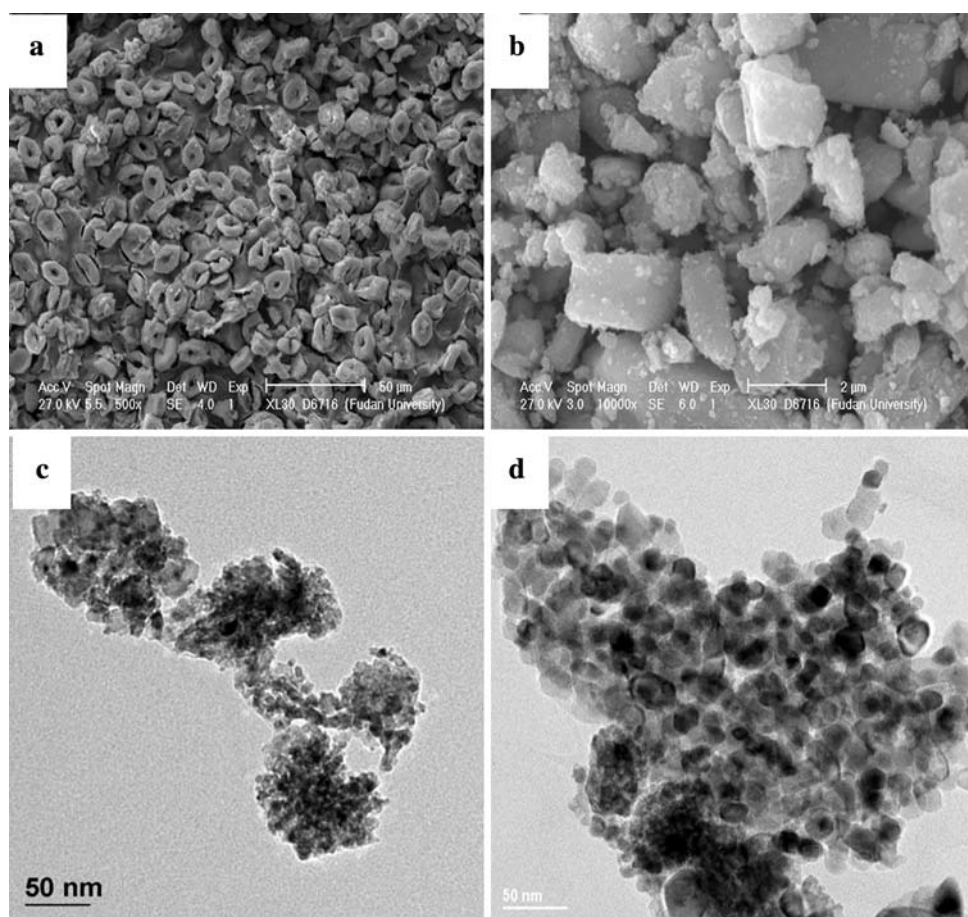
and the surface of an aggregate in CeNi$_2$O-OG (Fig. 3c), but the CeNi$_2$O-OC is constituted of two types of particle: roundish particles of CeO$_2$ with homogeneous size (about 10 nm) and particles of NiO with hexagonal shape, homogeneous in size about 20 nm (EDX results confirmed). The facts reveal that there is strong interaction between the Ni and Ce and NiO is well dispersed in CeNi$_2$O-OG sample, but the CeNi$_2$O-OC catalyst is constituted of isolated CeO$_2$ and NiO particles.

The remarkable low temperature performance of the Ce–Ni–O catalysts prepared by the gel-coprecipitation of oxalate precursor can be seen from Table 1. No reaction occurred without catalyst under the reaction conditions used here. Propane was also converted over pure CeO$_2$ and NiO. The combination of Ce and Ni oxides remarkably increased propane conversion and the selectivity for partial oxidation products. Propene was formed with high selectivity over the Ce$_m$Ni$_n$O-OG catalysts with higher Ni content and the propene yields were comparable with that obtained at 500 °C over V–Mg–O catalysts [14]. As shown in Table 1, the CeNi$_2$O-OG sample exhibited much higher C$_3$H$_6$ formation rate and selectivity to propene than those of CeNi$_2$O catalysts prepared by other techniques. It is remarkable that propene selectivity up to 82.7% at a moderate propane conversion of 12.8% could be achieved over the catalyst of CeNi$_2$O-OG.

Figure 4 shows the Raman spectra of Ce–Ni–O samples prepared by various methods and pure compounds of CeO$_2$ and NiO. In pure CeO$_2$ (*Fm3m* space group), the intense band assigned to *F*2g mode is observed at 460 cm^{-1} [15]. For pure NiO, only one weak broad band associated with NiO phase at ca. 530 cm^{-1} is identified. Remarkable spectral changes are observed in the mixed oxide catalysts, suggesting significant modification of M–O bonding symmetry in the CeNiO catalysts. For the CeNi$_2$O-imp, CeNi$_2$O-KC and CeNi$_2$O-OC catalysts, the spectra are dominated by a single strong band associated with the *F*2g mode, which shifts to lower frequencies with respect to that of pure CeO$_2$. In addition, two weak bands at ca. 223 and 580 cm^{-1} are identified over the two samples of CeNi$_2$O-KC and CeNi$_2$O-OC, suggesting a substantial modification of the M–O bonding symmetry. Note that four bands at ca. 223, 547, 460, and 632 cm^{-1} are observed in the CeNi$_2$O-OG catalyst. Such spectral features were suggested to be due to a further modification of the oxygen sublattice in the CeNi$_2$O-OG sample [15].

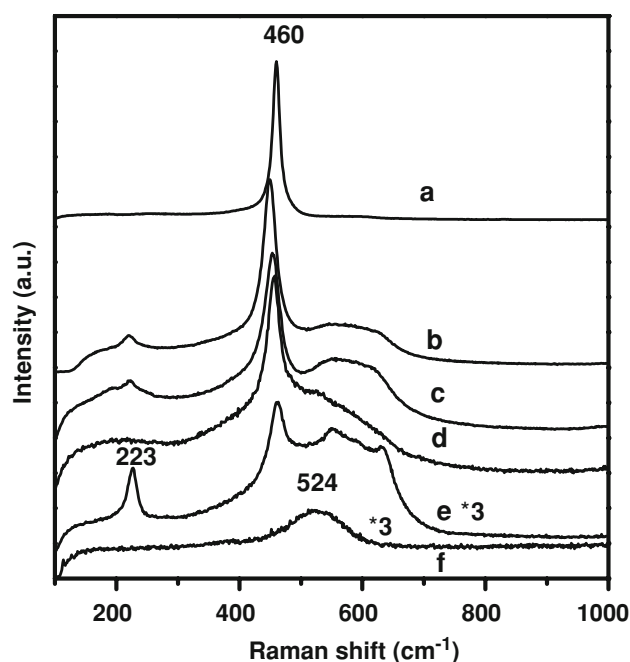Previous investigations concerning the use of NiO-based catalysts for the ODH of propane have shown that a

Fig. 4 Laser-Raman spectra of different catalysts: *a* CeO$_2$, *b* CeNi$_2$O-OC, *c* CeNi$_2$O-KC, *d* CeNi$_2$O-imp, *e* CeNi$_2$O-OG, *f* NiO

4 Conclusion

In conclusion, we have successfully demonstrated that Ce–Ni–O mixed oxide catalysts prepared by oxalate gel-coprecipitation exhibit superior catalytic performance for the highly selective propene production in the low-temperature ODH of propane. The enhanced propene selectivities at higher propane conversions achievable over the present Ce–Ni–O catalysts has been attributed to the favorable creation of higher concentration of active surface oxygen species and higher dispersion of NiO species over the oxalate gel-coprecipitated samples, which allow the highly selective conversion of propane to the target product of propene.

number of parameters such as the nature of support, coordination state and reducibility of nickle species as well as the nickle content of the catalysts have to be considered in order to account for the observed catalytic behavior for the oxidative dehydrogenation of light alkanes [11, 12, 16]. Generally, catalyst with high redox properties shows better performance in the catalytic oxidative dehydrogenation of propane. At this juncture, it is interesting to point out that the present doughnut-like structured CeNi$_2$O-OG sample exhibit superior catalytic performance (see Table 1) for the highly selective propene production in the low-temperature ODH of propane, in contrast to the much lower selectivites previously reported for the conventional coprecipitation-derived Ni–Ce–O catalysts [12]. In terms of the low temperature activity, the present CeNi$_2$O-OG material is also far more active than the Ni–V–O catalysts recently reported by Zhaorigetu et al. [16]. The fact that significantly higher activity and selectivity could be achieved for the present oxalate gel-coprecipitation-derived CeNi$_2$O-OG system can be understood by taking into account the favorable creation of more reducible and dispersed NiO species and a higher concentration of surface reactive oxygen species as a conseqence of high component dispersion of the CeNi$_2$O-OG system. In this respect, it appears that in order to obtain more active and selective Ce–Ni–O catalysts for ODH of propane one should achieve a high dispersion of the nickle oxide species as high as possible.

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