



Ni–Ta–O mixed oxide catalysts for the low temperature oxidative dehydrogenation of ethane to ethylene



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ABSTRACT

The “wet” sol–gel and “dry” solid-state methods were used to prepare Ni–Ta–O mixed oxide catalysts. The resulting Ni–Ta oxides exhibit high activity and selectivity for the low temperature oxidative dehydrogenation of ethane to ethylene. The Ta/(Ni + Ta) atomic ratios (varying from 0 to 0.11 in “wet” sol–gel method, and from 0 to 0.20 in “dry” solid-state method) as well as the preparation methods used in the synthesis, play important roles in controlling catalyst structure, activity, selectivity and stability in the oxidative dehydrogenation of ethane. Electron microscopy characterizations (TEM, EELS mapping, and HAADF-STEM) clearly demonstrate that the Ta atoms are inserted into NiO crystal lattice, resulting in the formation of a new Ni–Ta oxide solid solution. More Ta atoms are found to be located at the lattice sites of crystal surface in sol–gel catalyst. While, a small amount of thin layer of Ta₂O₅ clusters are detected in solid-state catalyst. Further characterization by XRD, N₂ adsorption, SEM, H₂-TPR, XPS, and Raman techniques reveal different properties of these two Ni–Ta oxides. Due to the different properties of the Ni–Ta oxide catalysts prepared by two distinct approaches, they exhibit different catalytic behaviors in the ethane oxidative dehydrogenation reaction at low temperature. Thus, the catalytic performance of Ni–Ta–O mixed oxide catalysts can be systematically modified and tuned by selecting a suitable synthesis method, and then varying the Ta content.

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1. Introduction

Ethylene is the most important petrochemical building block and is a major feedstock for polymers. Global ethylene demand is expected to increase significantly in the near future. Currently, the bulk of the global ethylene demand is supplied via steam cracking of a hydrocarbon feedstock [1]. Shortcomings of steam cracking are obvious, including large energy demand from the high endothermicity of the reaction, long residence times, and the loss of valuable feedstock from coke formation on the reactor walls requiring periodic maintenance. The development of selective, energy efficient direct alkane oxidation chemistry could lead to environmentally and economically superior chemical processes for the manufacture of high value chemical building blocks, such as olefins and oxygenates from natural gas and petroleum [2]. The oxidative dehydrogenation (ODH) of ethane, in particular, is considered a more economical route to ethylene, as compared with

the thermal pyrolysis process [3,4]. Therefore, the utilization of ODH of ethane to ethylene is a potentially competitive process.

A number of catalysts have proven active for oxidative dehydrogenation of ethane to ethylene [5]. Overall, the catalysts can be divided into two groups according to their range of operational temperature. The ethane ODH reaction catalyzed by alkali and alkaline earth-based materials (e.g., Li₂CO₃/MgO) is conducted at temperatures above 600 °C [6,7]. Perovskite-type and perovskite-like oxides, such as SrFeO_{3-δ}Cl_δ [8], La_{1-x}Sr_xFeO_{3-δ}X_δ (X = F, Cl) [9], YBa₂Cu₃O_{7-δ}X_δ (X = F, Cl) [10], La_{1.85}Sr_{0.15}CuO_{4-δ}X_δ (X = F, Cl) and Nd_{1.85}Ce_{0.15}CuO_{4-δ}X_δ catalyst [11], show good activity and durability for the ODH reaction above 550 °C. Also, rare-earth metal oxides are highly active catalysts for converting ethane to ethylene at temperatures higher than 600 °C [12]. However, the viability of ethane ODH would be substantially improved if the catalysts operated at low temperature, especially below 450 °C, because the energy consumption will be significantly reduced. NiO is known to be very reactive and capable of activating ethane at moderate temperature (below 400 °C) [13,14]. Furthermore, the physical and chemical properties of

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NiO can be modified and improved by doping with transition metals, such as Nb [15–20], Zr [21,22], W [23], the main group element Sn [24] or by supporting it on SiO₂, Al₂O₃, ZrO₂, and MgO [25–29]. The resulting NiO based materials deliver increased ethylene yield.

Lemonidou et al. systematically investigated the effect of a series of metals (Me = main group elements or transition metals), including Li, Mg, Al, Ga, Ti, Nb, and Ta, on the properties and catalytic behaviors of Ni–Me–O mixed metal oxides in the ethane ODH reaction [30]. These authors found that the Ni–Nb-oxide with a Nb/Ni ratio of 0.176 exhibits the highest activity in the ethane ODH reaction. The reactivity of the catalysts roughly follows the following order of Ni–Nb \gg Ni–Mg > Ni–Li > Ni–Ga = NiO \gg Ni–Al \gg Ni–Ti \gg Ni–Ta. Surprisingly, the Ni–Ta–O catalysts showed the lowest activity, delivering ethane conversion that did not exceed 10% even at a high temperature of 450 °C. The authors prepared the Ni–Ta oxide catalysts by an evaporation method and did not vary the preparation despite the poor performance of this group of catalysts. Our recent study showed that the method of preparation of niobium doped nickel oxides as well as their Nb content had a critical impact on the resulting ethane ODH catalytic properties [15,16]. With this key information on the impact of catalyst preparation on performance, we decided to investigate the impact of various modes of preparation of Ni–Ta–O mixed metal oxides on ethane ODH performance.

To examine the generalizability of our newly developed preparation methods, we prepared Ni–Ta oxide materials by our “wet” sol–gel method and our newly developed “dry” solid-state preparation method and examined the performance of the Ni–Ta oxide in ethane ODH. The obtained Ni–Ta oxide catalysts showed excellent reactivity in the low temperature ethane ODH. The combined effect of the Ta/Ni ratio and preparation method used, on structural properties and resulting activity, selectivity, as well as stability of the Ni–Ta materials are described.

2. Experimental

2.1. Catalyst preparation

Ni(NO₃)₂·6H₂O (98.5%, Aldrich), citric acid (99.5%, Aldrich), tantalum tetraethoxyacetylacetonate (99.9%, Strem), tantalum tetraethoxide (99.9%, Aldrich), oxalic acid (99.0%, Aldrich), as well as tantalum oxide (99.0, Aldrich) were obtained from commercial sources, and used without further purification.

2.1.1. Preparation of tantalum doped nickel oxides

Protocol 1: preparation of Ta-doped NiO by “wet” sol–gel (SG) method. A series of Ni_{1–x}Ta_xO ($x = 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.09, 0.11$) were prepared according to the description in our previous publication for the SG preparation of Nb-doped NiO [15]. The typical synthesis, in this case of the Ni–Ta–O catalyst with Ta/(Ni + Ta) atomic ratio of 0.05 was performed as follows: 6 g of Ni(NO₃)₂·6H₂O and 0.51 g of tantalum tetraethoxyacetylacetonate were dissolved in 100 mL of water. Then, 12 g of citric acid was added into this mixture. The resulting blue solution was stirred at 80 °C for 24 h in a closed glass vessel. Then the system was opened and the resulting sol was stirred for another 12 h to remove the water, giving a blue gel. The gel was dried in 3 steps. First, it was heated at 120 °C for 2 h. Then it was heated to 140 °C and kept at this temperature for 2 h. Lastly, the gel was dried at 160 °C for 12 h in open air. The obtained black xerogel was calcined at 450 °C (ramp rate of 1 °C/min from room temperature to 450 °C) for 4 h in static air.

Protocol 2: preparation of Ta-doped NiO by dry, solid-state (SS) method. The dry, solid state procedure was used to synthesize materials with compositions of Ni_{1–x}Ta_xO ($x = 0, 0.01, 0.03, 0.05,$

0.07, 0.10, 0.15, 0.20) and at constant molar ratio of H₂C₂O₄/(Ni + Ta) of 0.75 [16]. The following preparation is for the synthesis of Ni_{0.95}Ta_{0.05}O catalyst: 4.74 g of Ni(NO₃)₂·6H₂O, 1.13 g of H₂C₂O₄, and 0.35 g of tantalum tetraethoxide were mixed in a mortar bowl and ground together using a mortar and pestle at room temperature for 10 min to get a uniform paste. This mixture was dried at 90 °C for 4 h and then calcined under static air at 300 °C (ramp rate of 1 °C/min from room temperature to 300 °C) for 4 h, giving a black solid.

Protocol 3: preparation of Ni_{0.95}Ta_{0.05}O with different oxalic acid concentration. The synthesis is the same as the procedure in protocol 2, however different amounts of oxalic acid corresponding to H₂C₂O₄/(Ni + Ta) mole ratio of 0.25, 0.50, 0.75 and 1 were used in the preparation.

For clarity purposes, the catalysts are labeled as W-Ni_xTa_{1–x} or D-Ni_xTa_{1–x}, where W identifies the catalysts prepared using the wet, sol–gel method, D identifies the catalysts prepared by the dry, solid-state method, and x indicates the metal atomic percentage of Ni in the oxide composites.

2.1.2. Preparation of pure NiO

The pure NiO materials synthesized by the SG and SS methods and used as reference catalysts were prepared using the methods described in protocols 1 and 2. The NiO from SG method were obtained by calcination of the synthesized nickel-citrate gel at 450 °C for 4 h, and the NiO from SS method was obtained by calcination of the nickel-oxalate mixture at 300 °C for 4 h.

2.1.3. Preparation of Ta₂O₅

The amorphous Ta₂O₅ used as the reference was obtained by calcination of tantalum tetraethoxyacetylacetonate at 300 °C (ramp rate of 1 °C/min from room temperature to 300 °C) for 4 h in static air.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns of all samples were recorded on a Bruker D8 Advanced A25 diffractometer, operated at 40 kV and 40 mA and using Cu K radiation ($\lambda = 1.5406 \text{ \AA}$). The datasets were acquired in step-scan mode over the 2θ range 10–90°, using a step interval of 0.05° and a counting time of 1s per step.

N₂ adsorption/desorption isotherms at 77 K were measured on a Micromeritics ASAP2420. Before the test, the samples were degassed at 300 °C under vacuum for 2 h. The specific surface areas were calculated based on the multipoint BET analysis method with the pressure range of $P/P_0 = 0.05–0.30$.

Temperature-programmed reduction (TPR) was performed using an Altamira Instrument equipped with a thermal conductivity detector (TCD); data were analyzed using the AMI software provided by the instrument company. The sample (30 mg) was placed in a U-shaped quartz tube for analysis. Pretreatment was carried out under Ar flow (30 mL/min) for 0.5 h at 350 °C to remove water and gas adsorbed by the sample, followed by cooling to room temperature. TPR analysis was performed from room temperature to 800 °C under 5% H₂/Ar at a flow of 30 mL min^{–1} at a ramp rate of 20 °C min^{–1}. The uptake of the H₂ was estimated from 5 blank pulse calibrations.

Raman spectroscopy was performed on a Horiba Yvon LabRAM Aramis with a CCD-camera as a detector using a 100× objective, a 600 gr mm^{–1} grating, a 100 μm hole, a 100 μm slit, a D1 filter and a 473 nm cobalt laser.

X-ray photoelectron spectroscopy (XPS) was taken from a Kratos AMICUS/ESCA 3400 spectrometer, using a monochromatic Mg K α X-ray source operating at 120 W and a pass energy of 20 eV under an operating pressure of 10^{–6} mbar. The binding

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