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Oxidative dehydrogenation of ethane over Ni–W–O mixed metal oxide catalysts

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ABSTRACT

Ni–W–O mixed oxides were prepared through the evaporation of aqueous solutions of nickel nitrate and ammonium tungstate and calcined in air at 500 °C for 2 h. The catalysts were characterized by several techniques (N_2 adsorption, X-ray diffraction, temperature-programmed reduction, X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy of adsorbed CO, and $^{18}O/^{16}O$ isotope exchange) and tested in the oxidative dehydrogenation of ethane. The catalytic activity and catalyst reducibility decrease when the W content increases. Thus, nickel sites seem to be the active centers for ethane activation in these catalysts. However, the selectivity to ethylene strongly changes depending on the Ni/W ratio. In W-rich catalysts, in which $NiWO_4$ and WO_3 are mainly observed, a strong influence of ethane conversion on the selectivity to ethylene is observed. However, in Ni-rich catalysts, in which NiO crystallites and WO_x nanoparticles are mainly observed, ethane conversion hardly influences the selectivity to ethylene. It has been demonstrated that the nature of the Ni sites and the characteristics and number of the acid sites determine the catalytic behavior of these catalysts. The presence of Lewis acid sites with high acid strength in W-rich catalysts facilitates the decomposition of ethylene during ethane oxidation.

1. Introduction

Ethylene is the principal petrochemical building block and is a major feedstock for polymers. Global ethylene production capacity as of January 2009 was 126.7 million tons per year [1], and it is expected to increase significantly in the near future. However, ethylene is currently produced in addition to propylene by steam cracking of hydrocarbons, the most energy-consuming process in the chemical industry [2]. Oxidative dehydrogenation of lower alkanes is an interesting alternative to the current industrial processes (steam cracking or catalytic dehydrogenation) for the production of olefins [3–6]. In fact, ethylene could be produced by the oxidative dehydrogenation of ethane (ODHE), an exothermic process operating at about 400 °C in which catalyst deactivation by coke can be minimized because of the presence of molecular oxygen as an oxidant in the reactor feed. However, the development of both active and selective catalytic materials proves to be a very hard task, since the desired products, olefins, are usually more reactive than the corresponding alkanes, so that the formation of carbon oxides is the thermodynamically favored route [3–6].

From an industrial point of view, it has been proposed that ethylene yields between 65% and 70% are required to compete with the steam-cracking process [3,6]. Several catalytic systems have been proposed in the past two decades, and it is known that the reaction conditions and the mechanism involved strongly depend on the catalytic system [2–7]. At the moment, the limiting factor in the development of most of the proposed catalytic systems is the high formation of carbon oxides, especially by the consecutive deep oxidation of ethylene [2–7]. This has been improved by using MoVTeNbO catalysts, which seems to be the most competitive alternative nowadays to the current industrial process in ethylene production [8,9]. However, the ethylene productivity achieved with these catalysts is probably still low for their industrial implementation.

NiO-based mixed oxides are also potential catalysts for ODHE [18–21], especially Ni–Nb–O materials [11–14]. Nickel is a low-cost metal capable of activating ethane at very low temperatures. The incorporation of niobium makes this catalyst more selective. A drastic decrease in surface area has been observed after catalytic tests, but it only causes a small decrease in catalytic performance. After 100 h on line, the surface area of a Ni–Nb–O catalyst decreased 40%, while the ethane conversion only dropped from 42% to 38%, with the selectivity to ethylene remaining constant [18].

Recently, it has been reported that alumina-supported Ni–W–O mixed oxides are also active and relatively selective in ODHE [21]. As with Ni–Nb–O catalysts, one interesting feature of this catalytic system is that ethylene deep oxidation during the oxidative dehydrogenation of ethane can be minimized by controlling the catalyst composition.

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The goal of this work is the synthesis, characterization, and investigation of the catalytic behavior of bulk Ni–W–O mixed oxides in the ODHE. It will be shown that the variation of the selectivity to ethylene with ethane conversion and the physicochemical properties (using appropriate characterization techniques) depend strongly on the catalyst composition. In addition, it will be shown that both primary and consecutive nonselective steps in this reaction can be tuned by changing the Ni/W ratio in the catalysts.

2. Experimental

2.1. Catalyst preparation

Ni–W–O mixed metal oxide catalysts were prepared through the evaporation at 90 °C of aqueous solutions of nickel nitrate and ammonium tungstate. NiO and WO_3 were obtained by evaporation of the corresponding aqueous solutions at 90 °C. The solids were dried overnight in a furnace at 120 °C and finally calcined in static air for 2 h at 500 °C. The catalysts will be named NiW*n*, in which *n* corresponds to the atomic ratio W/(Ni + W).

The $NiWO_4$ single phase was prepared similarly to the other Ni–W–O catalysts by calcining the samples twice, first at 500 °C and later at 600 °C. The composition observed was that corresponding to $NiWO_4$, i.e., presenting a Ni/W atomic ratio of 1.

2.2. Catalyst characterization

Catalyst surface areas were determined by multipoint N_2 adsorption at −196 °C using the BET method.

Powder X-ray diffraction (XRD) was used to identify the crystalline phases present in the catalysts. An Enraf Nonius FR590 sealed tube diffractometer with a monochromatic Cu Kα_1 source operating at 40 kV and 30 mA was used.

Temperature-programmed reduction (TPR) was carried out in a Micromeritics Autochem 2910 equipped with a TCD detector, in which the reducing gas was 10% H_2 in Ar (total flow rate 50 ml min^{-1}). The temperature range explored was from room temperature to 800 °C. The heating rate was maintained at 10 °C min^{-1}.

X-ray photoelectron spectroscopy (XPS) measurements were taken on a SPECS spectrometer with an MCD-9 detector and using a nonmonochromatic Al Kα (1486.6 eV) X-ray source. Spectra were recorded using analyzer pass energy of 50 V and an X-ray power of 200 W and under an operating pressure of 10^{-9} mbar. Spectra treatment was performed using the CASA software. Binding energies (BE) were referenced to O1*s* at 361.5 eV.

FTIR spectra were collected with a FTS-40A BioRad spectrometer equipped with a DTGS detector (4 cm^{-1} resolution, 32 scans). An IR cell allowing in situ treatment under controlled atmospheres and temperatures from −176 to 500 °C was connected to a vacuum system with a gas dosing facility. Self-supporting pellets (ca. 10 mg cm^{-2}) were prepared from the sample powders and treated at 250 °C in oxygen flow of 20 ml min^{-1} for 1.5 h, followed by evacuation at 10^{-4} mbar at the same temperature for 1 h. After activation, the samples were cooled to −176 °C under dynamic vacuum conditions, followed by CO dosing at increasing pressure (0.4–8.5 mbar). IR spectra were recorded after each dosing.

Oxygen isotopic-exchange experiments were conducted using a quartz microreactor coupled to a quadrupole mass spectrometer (Omnistar QMG 220 M1). Before each experiment, the catalyst was pretreated in 50% $^{16}O_2$/Ar flow (36 ml/min) at 450 °C for 2.5 h, followed by cooling to 150 °C in the same 10% $^{16}O_2$/Ar flow. Once 150 °C was attained, oxygen was replaced by argon (20 ml min^{-1}) and keep at that temperature for 1.5 h before being cooled to 25 °C. For the temperature-programmed isotopic-exchange experiments (TPIE), the catalyst (0.162 g) was subjected to a 10% $^{18}O_2$/Ar flow (22 ml min^{-1}), and the temperature was raised from 25 to 650 °C at a heating rate of 10 °C/min. The concentration profiles of the exit gas composition were obtained by acquiring the mass spectra signals relative to $^{16}O_2$ (m/e = 32), $^{16}O^{18}O$ (m/e = 34) and $^{18}O_2$ (m/e = 36). Blank run experiments were carried out using an empty reactor in order to check contributions of the gas-phase reactions and stability of the mass spectrometer.

2.3. Catalytic tests

The catalytic experiments were carried out at atmospheric pressure, in the temperature range 200–475 °C, mainly at 400–450 °C, using a fixed-bed quartz tubular reactor (i.d. 20 mm, length 400 mm). The feed consisted of a mixture of C_2H_6/O_2/He with molar ratio of 30/30/40. Several catalyst weights (from 0.05 to 5 g) and total flows (from 20 to 150 ml min^{-1}) were studied. Catalyst samples were introduced into the reactor diluted with silicon carbide in order to keep constant volume in the catalytic bed. Reactants and products were analyzed by gas chromatography using two packed columns: (i) molecular sieve 5 Å (2.5 m) and (ii) Porapak Q (3 m). Blank runs showed no conversion at a reaction temperature of 475 °C.

3. Results and discussion

3.1. Catalyst characterization

Table 1 lists the characteristics of catalysts. Chemical analysis of W and Ni is in good agreement with the nominal composition. On the other hand, it can be seen that both pure NiO and WO_3 present low surface areas (4 and 9 m^2 g^{-1}, respectively). However, mixed oxides show higher surface areas even in the case of the lowest W loadings. The sample with a W/(Ni + W) atomic ratio of 0.26 presents the highest surface area, ca. 57 m^2 g^{-1}. This enhanced surface area of mixed Ni–W–O catalysts is likely due to the presence of a W heteroatom that hinders the crystallization of NiO, preventing the formation of large particles.

XRD patterns of calcined samples are shown in Fig. 1, while the description of crystalline phases is summarized in Table 1. For comparison, the XRD patterns of pure $NiWO_4$, with the main diffraction peaks at 2θ = 31.0°, 54.7°, 65.9°, 36.6°, 41.8°, 19.4°, 24.0°, and 25.0° [JCPDS: 15-0755] (Fig. 1, pattern h) have also been included. A W-free sample presents diffraction peaks at 2θ = 37.3°, 43.3°, and 62.9°, characteristic of cubic NiO [JCPDS: 78-0643] (Fig. 1, pattern a), while an Ni-free sample (i.e., NiW1) presents main diffraction peaks at 2θ = 23.19°, 23.59°, 24.38°, and 34.14°, which correspond to the (0 0 2), (0 2 0), (2 0 0), and (2 2 0) crystallographic planes, respectively, of monoclinic WO_3 [JCPDS: 43-1035] (Fig. 1, pattern g). For mixed metal oxides, the XRD patterns suggest an important decrease in the crystal sizes of both NiO and WO_3 and the appearance of new crystalline phases.

In the Ni-rich region (i.e., W/(Ni + W) ratio lower than 0.4), NiO is formed over almost all the catalysts, although the appearance of new diffraction peaks can also be seen at 2θ = 14.4°, 25.1°, 28.9°, 32.7°, 47.1°, 53.6°, 56.0°, 57.7°, and 61.7°, whose intensities increase with the W content up to W/(Ni + W) ratios of 0.36. Similar diffraction peaks have also been observed when a stoichiometric mixture of $H_{26}N_6O_{41}W_{12}{\cdot}18H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ (Ni/W molar ratio of 1) at 400 °C was treated in air, and it has been related to tungsten trioxide of low crystallinity [22].

On the other hand, no changes in the NiO lattice constants have been observed (Table 1), suggesting that W^{6+} ions are not incorporated into the lattice of the NiO crystals. However, a broadening of the diffraction peaks related to NiO is clearly observed in the XRD