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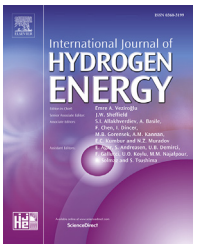

Structural transformations of highly porous nickel catalysts during ethanol conversion towards hydrogen

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ABSTRACT

In this work, we report a liquid-phase reduction method to prepare porous non-supported amorphous nickel catalysts with high surface areas (65–250 m^2/g). A highly crystalline face center cubic Ni (fcc-Ni) catalyst with 110 m^2/g surface area was also prepared by frontal crystallization of the amorphous nickel catalyst. The catalytic activity and stability of these catalysts for ethanol decomposition was investigated at different time on stream (TOS) to understand structural transformations occurring at the early stages of catalyst activation-deactivation. Activity vs. TOS results obtained at 473 K show that on the amorphous catalysts the conversion increases from about 50% to 60–75% reaching a steady value at ~30 h TOS, which remains constant during the observed 96 h of TOS. The fcc-Ni catalyst initially exhibits a higher conversion (~85%), however, it quickly deactivates to a conversion in the similar range as the amorphous catalysts. It is also shown that BET surface areas of amorphous catalysts decreases during hydrogen pretreatment at 473 K due to crystallization, grain growth, and sintering. The structure of amorphous catalysts continuously refines to form a combination of fcc-Ni and hexagonal close-packed nickel (hpc-Ni) phases, as well as nickel carbide (Ni_3C) and carbon layers that stabilize catalytic activity. The structure of the fcc-Ni catalyst remains unchanged during the 96 h TOS experiment indicating that carbon deposition might cause its initial deactivation. At 523 K, the amorphous catalyst shows 100% conversion, which remains constant during 96 h of TOS, while the fcc-Ni crystalline catalyst initially exhibits 95% conversion and then slowly deactivates to ~80% at 96 h TOS. Thus at 523K the stabilized amorphous catalyst does not deactivate under the same TOS compared to the crystalline fcc-Ni catalyst, showing that the active sites on these catalysts are different. The findings of this work suggest that the liquid-phase reduction method can be used to prepare active and stable catalysts for reactions involving decomposition of alcohols and hydrocarbons to produce hydrogen.

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Introduction

Ethanol (C_2H_5OH) is a potential hydrogen carrier for fuel cell applications. It is non-hazardous and can be produced readily from renewable sources, agricultural wastes, and forestry residues [1–6]. The possible routes for hydrogen production from ethanol include *steam reforming* [7–9], *partial oxidation* [4,10,11], and *decomposition* [12–14] reactions. Steam reforming provides a high hydrogen yield, but it is a highly endothermic reaction and requires high operating temperatures. Ethanol partial oxidation is an exothermic reaction and exhibits rapid start-up and response times, but it is difficult to control due to the simultaneous hydrogen combustion, which also reduces the hydrogen yield. Ethanol decomposition is a less common reaction for hydrogen generation due to the formation of small amount of undesirable byproducts such as acetaldehyde and carbon monoxide.

Ethanol activation pathways in all reactions depend on the metallic catalyst nature [5,6]. The less oxophilic metals, such as Pd and Pt, promote C–H bond activation, while on the surface of the more oxophilic metals (Co and Ni) activation takes place via the O–H bond. In the latter case the cleavage of C–C bond produces adsorbed $^*CH_x$ and $^*CO$ surface species, then $^*CH_x$ species decompose to produce surface carbonaceous species.

A large number of studies aimed at improving the understanding of the catalysts' behavior during ethanol conversion reactions have been reported. Cobalt and nickel are considered the most promising active metals for industrial application due to their relatively low cost and high activity [15–22]. Cobalt, however, is highly reactive toward oxygen and oxidizes rapidly under the reaction condition resulting in an unstable $Co–CoO_x$ system [23,24]. Nickel-based catalysts show significantly lower reactivity toward oxygen, but two major factors; *sintering of nickel nanoparticles* and *coke deposition*, have been identified to contribute to their deactivation [6]. Utilization of a support with stronger metal-support interaction could potentially reduce sintering of the active phase [22,25]. Our recent results showed that Ni supported on highly porous silica could readily inhibit coalescence of ultra-small (2–5 nm) nickel nanoparticles during ethanol decomposition [26]. However, the effect of process parameters on the coalescence of active metallic nanoparticles into larger crystallites is not well known.

The second factor involved in deactivation of the nickel-based catalysts, is carbon formation and deposition on the active sites that catalyzes the formation of CH_4 at low temperatures [12]. CH_4 dissociates on the nickel surface and produces additional reactive carbon species, a fraction of which may react with water and is removed from the surface [27,28]. The low methanation rates could lead to polymerization of reactive carbon species into a passive carbon phase, which accumulates on the surface. A commonly accepted deactivation mechanism assumes that carbon dissolves in the nickel lattice and form nickel carbide (Ni_3C). Dissolved carbon and the presence of Ni_3C phase promote the nucleation and growth of carbon filaments [5]. Specific supports, such as CeO_2, and some noble metals (e.g., Pt) could slow carbide formation [22,25]. However, the initial stages carbon formation and its relation to catalyst structure are not well understood.

In this work, we prepared novel non-supported amorphous and crystalline nickel catalysts with high surface areas (65–250 m^2/g) and investigated the early stages of phase and carbide layer formation and sintering of Ni active phase. We selected ethanol decomposition as a model reaction to probe structural and morphological transformations that occurs during early stages of catalysts deactivation. To this end, we investigated the reaction at relatively low temperatures (473–523 K) to identify structural refinements of catalysts and to avoid decomposition of thermally unstable nickel carbide phases. To study crystallization, sintering, and phase transformation processes that occur on the catalyst during reduction pretreatment and during the reaction at different times on stream (TOS), we utilized, *dynamic* TEM heating experiments, BET surface area measurements, and *ex-situ* XRD and XPS analysis. The novelty of the work is the use of liquid phase reduction that resulted in an amorphous Ni unsupported catalysts with relative high surface area that were very active and stable for 96 h TOS.

Material and methods

Catalyst preparation

We have prepared four nickel catalysts with different structure and textural characteristics (Table 1). Three catalysts were prepared by a modified liquid-phase synthesis of nickel nitrate using $NaBH_4$ as reducing agent [29], referred hereafter as liquid-phase synthesis, to distinguish it from the gas phase reduction in H_2 before reaction. In this work, to control the BET surface area of the resulting amorphous metallic catalysts we carefully controlled the synthesis temperature. The first catalyst was prepared without controlling the reaction temperature by mixing nickel nitrate (2.5 g) solution in ethyl alcohol (50 ml) and $NaBH_4$ (2.5 g) solution in water (75 ml) at room temperature under vigorous stirring and nitrogen flow. This liquid-phase reduction reaction is exothermic, and the maximum temperature increased to ~350 K. Two other catalysts were prepared under controlled cooling conditions. Before the reaction, the nickel nitrate solution was cooled to 275 K and 250 K using either ice or a dry ice bath, respectively. Then, a cold solution (275 K) of $NaBH_4$ was added. The maximum temperatures observed during the reactions in these cases were 300 K and 270 K, respectively. These three amorphous catalyst are designated below as Ni-350, Ni-300 and Ni-270.

The fourth catalyst was prepared by frontal crystallization of amorphous nickel. Previously, we showed that local heating

Table 1 – BET surface areas of the catalyst prepared at different liquid phase reduction as freshly prepared, reduced in hydrogen and after reaction.

Catalysts Designations	Synthesis temperature, K	BET surface area, m^2/g		
		As-prepared	Reduced	Spent (96 h TOS)
Ni-350	350	65	65	63
Ni-300	300	210	132	125
Ni-270	270	250	146	138
fcc-Ni-600	600	110	86	88

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