

Nickel catalysts obtained from hydrotalcites by coprecipitation and urea hydrolysis for hydrogen production



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ABSTRACT

Nickel hydrotalcites were subjected to synthesis using two methods: coprecipitation and urea hydrolysis. The thermal decomposition of the hydrotalcite precursors produced mixed oxides corresponding to the active phases or final catalysts.

The precursors and the mixed oxides were characterized using atomic absorption spectroscopy (AA), X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), CO₂ temperature-programmed desorption (TPD-CO₂), textural properties, and temperature-programmed reduction with hydrogen (TPR-H₂).

The catalysts were evaluated under conditions which simulate the autothermal reforming of ethanol toward the selective production of H₂. The solids synthesized via urea hydrolysis revealed the best reduction activity (higher hydrogen consumption at lower temperature) and larger average pore sizes, leading to better catalytic performance (higher H₂ selectivity). Superior catalytic performance is attributed to the production of smaller active phase particles, which are generated during the synthesis based on urea hydrolysis. Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

Using ethanol to produce H_2 has grown more attractive in recent years because it is a renewable resource, highly available, easy to store and possesses a relatively high hydrogen content.

The catalytic reforming of alcohol under autothermal conditions [1] may be chosen from many available processes

to obtain H_2 . The general transformation of an alcohol to hydrogen occurs in the presence of water and oxygen, as illustrated in Eq. (1).

Where the goal is to reach the complete conversion of ethanol and selectively produce hydrogen, minimizing the formation of possible byproducts. However, because this complex reaction involves the cleavage of the ethanolic C–C bond, different reaction pathways may favor or decrease the production of hydrogen [2].

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(1)

Eq. (1) represents the general autothermal reforming of ethanol reaction and with Eqs. (2)-(19) the different reaction routes which are involved and can be carried out during the autothermal reforming of alcohol are summarized [3].

Dehydration $C_2H_5OH \rightarrow C_2H_4 + H_2O$ (2)

Complete oxidation $C_2H_5OH + 3O_2 \rightarrow 3H_2O + 2CO_2$ (3)

Partial oxidation

 $C_2H_5OH + 2O_2 \rightarrow 3H_2O + 2CO$ (4)

 $2C_2H_5OH + O_2 \rightarrow 6H_2 + 4CO \tag{5}$

 $C_2H_5OH + 1.5O_2 \rightarrow 3H_2 + 2CO_2$ (6)

Water gas shift (WGS)

 $H_2O + CO \rightarrow H_2 + CO_2 \tag{7}$

Dehydrogenation

 $C_2H_5OH \rightarrow CH_3CHO + H_2$ (8)

Decomposition

 $C_2H_5OH \rightarrow H_2 + CH_4 + CO \tag{9}$

 $2C_2H_5OH \rightarrow CO_2 + 3CH_4 \tag{10}$

$$2C_2H_5OH \rightarrow CH_3COCH_3 + CO + 3H_2$$
(11)

Acetaldehyde steam reforming

 $CH_3CHO + H_2O \rightarrow 3H_2 + 2CO$ (12)

Acetaldehyde decomposition

 $CH_3CHO \rightarrow CH_4 + CO$ (13)

Methane steam reforming

 $CH_4 + H_2O \rightarrow 3H_2 + CO \tag{14}$

Reaction of decomposition products

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{15}$$

$$CO_2 + 3H_2 \rightarrow CH_4 + 2H_2O \tag{16}$$

Coke formation and gasification

$$2CO \rightarrow CO_2 + C_s$$
 (17)

$$C_2H_4 \rightarrow C_s$$
 (18)

$$H_2O + C_s \rightarrow 2H_2 + CO \tag{19}$$

Mixed oxides obtained from hydrotalcite-type precursors are used to catalyze the conversion of ethanol [4].

Hydrotalcites are layered double hydroxides structurally similar to brucite $Mg(OH)_2$. Brucite layers consist of octahedra that share their borders and contain an octahedrally coordinated Mg^{2+} cation attached to 6 OH⁻ groups. The partial replacement of the Mg^{2+} with Al^{3+} cations leads to the formation of hydrotalcites and generates a partial positive charge ($[Mg_3Al(OH)_8]^+$) compensated for by carbonate anions [(CO₃)_{1/2}·2H₂O]⁻, which are located in the material interlayer region [5,6].

The general formula for the other members of this family is $[M^{II}_{1-x}M^{III}_x(OH)_2]^x + (An^{-})^{x/n} \cdot mH_2O$, where M^{II} represents the divalent metal cation, M^{III} the trivalent metal cation, and An^{-} the interlayer anion [7].

When hydrotalcite-type layered solids are calcined, mixed oxides are generated with high surface areas, good dispersion of the metallic phase, basic properties, thermal stability and the capacity to rebuild the layered structure [6,8,9]. Due to these characteristics, the mixed oxides derived from layered solids are highly promising catalysts for the hydrogen production [7,10,11]. Hydrotalcites (mixed oxide precursors) may be synthesized using different methodologies, such as coprecipitation and urea hydrolysis.

Coprecipitation is the most popular method used to prepare mixed oxides from hydrotalcites; usually, potassium carbonate is used as the precipitation agent [6].

Using the urea hydrolysis methodology also obtains hydrotalcites, but the resultant materials have a higher degree of crystallinity and a narrower particle size distribution [12].

The following reactions are observed during this methodology [13] Eqs. (20)-(22):

$$(\mathrm{NH}_2)_2\mathrm{CO} \rightarrow \mathrm{NH}_4^+ + \mathrm{NCO}^- \tag{20}$$

 $NCO^{-} + 2H_2O \rightarrow NH_4^{+} + CO_3^{2-}$ (21)

$$CO_3^{2-} + H_2O \rightarrow HCO_3^{-} + OH^{-}$$
 (22)

The formation of ammonium cyanate is the rate limiting step Eq. (20), and a rapid hydrolysis of the cyanate to generate ammonium carbonate Eq. (21) occurs. Urea is the precipitation agent, generating carbonate and hydroxyl ions through in situ thermal decomposition.

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