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Research paper

Cobalt-boron loaded thermal activated Turkish sepiolite composites (Co-B@tSe) as a catalyst for hydrogen delivery

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ABSTRACT

Cobalt-boron loaded thermal activated sepiolite composites (Co-B@tSe) are prepared with an impregnation-chemical reduction method and calcination step for use as a catalyst for sodium borohydride ($NaBH_4$) hydrolysis, solvolysis, and methanolysis. The catalytic activity of Co-B@tSe can be improved by using a thermal-treated raw sepiolite as a catalyst support (Eskişehir, Turkey). The catalysts are analyzed using XRD, XRF, FT-IR, BET, DTA/TG, SEM/EDS and, TEM measurements. The catalytic performance for hydrogen generation is evaluated at room temperature. Research shows that cobalt-impregnated, heat treated, raw sepiolite at 500 °C (Sample B-2) exhibits a high boron loading ability. These conditions, in conjunction with an appropriate calcination treatment, can improve catalytic activity. When the Co-B@tSe, in the form of Co_3BO_5 sized 6 ± 1.8 nm, is dispersed on sepiolite channels, the catalyzed hydrogen generation rate (HGR) shows a trend of more methanolysis than hydrolysis at room temperature.

1. Introduction

Sepiolite is a fibrous mineral widely used in many industries as an absorbent, deodorant, catalyst support, polyester, asphalt coating, paints, drug development, cosmetics, and animal nutrition (Xie et al., 2010; Ueda and Makiyo, 1992; Shimizu et al., 2004; Duquesne et al., 2007; Yao et al., 2011; Wang et al., 2009; Viseras and Lopez-Galindo, 1999; López-Galindo et al., 2007; Angulo et al., 1995; Alvarez et al., 2011; Mccabe and Adams, 2013). Because of its unique structure, composition, high surface area (͂ 300 $m^2 g^{-1}$), and porosity, it can be utilized in various catalytic reactions due to the silanol groups on the surface of sepiolite. This can contribute to its catalytic activity (Galan, 1996; Suarez et al., 2016; Tabak et al., 2009).

Several deposits of sepiolite in Turkey have been reported and the most commercially used sepiolite is excavated in the region of Eskisehir. Sepiolite may have been used as early as the ancient Roman times to make pipe bowls and cigarette holders in the 1600s (Isık et al., 2010). The mechanical and chemical properties of Eskisehir sepiolite was investigated by Ece and Coban (1994). Recently, sepiolite has been examined by researchers for use as a catalyst support. Research by Güngör et al. (2006) used sepiolite as a silver support in soot combustion. Study by Liu et al. (2013) produced a Ni—Mo supported modified sepiolite catalyst for steam reforming reactions. The synthesis of Co, Ba, and K supported sepiolite catalysts for the abatement of diesel exhaust pollutants was conducted by Milt et al., 2010. Study by Watanabe et al. (2000) used supported Pt/Fe thermal activated sepiolite for the oxidation of hydrocarbons. Research by Bautista et al. (2007), investigated sepiolite and TiO_2 supported vanadium oxide catalysts in the oxidation of toluene.

Due to the consumption of fossil fuels such as coal, natural gas, and oil, greenhouse gases and global warming are increasing rapidly. Hydrogen (H_2) is one of the most important topics of research for renewable and clean energy as a carrier with zero emissions. H_2 is considered the fuel of the future. Sodium borohydride ($NaBH_4$) is a metal hydride with high H_2 storage capacity (10.8% in mass, theoretically). H_2 can be release from $NaBH_4$ by hydrolysis and alcoholysis Reaction (1) mole of $NaBH_4$ can produce 4 mol of H_2 and sodium metaborate/sodium methoxyborate in the presence of a suitable catalyst, according to the following equations (Liu and Li, 2009; Lo et al., 2009):

$$NaBH_{4(s)} + 4H_2O_{(l)} \rightarrow NaB(OH)_{4(aq)} + 4H_{2(g)} \quad (1)$$

$$NaBH_{4(s)} + 4CH_3OH_{(l)} \rightarrow NaB(OCH_3)_{4(aq)} + 4H_{2(g)} \quad (2)$$

H_2 generation from various alcohols can be performed. Primer alcohols such as methanol and ethanol are more active than other bulky alcohols (Arzac and Fernandez, 2015; Chang et al., 2014; Zhuang et al., 2013; Kara and Erdem, 2011). Methanol is more reactive than most alcohols because of the alkyl groups that induce a strong R-OH bonding. The theoretical H_2 density of methanolysis is 4.9%, which is lower than a hydrolysis system. Alcoholysis reactions have some advantages;

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spontaneous alcoholysis is faster than hydrolysis, the reaction rate constant is greater than hydrolysis, alcoholysis and by-products do not tend to plug into a reactor. Alcohols can generate at subzero temperatures because of their low freezing points (Fernandes et al., 2009; Zhang et al., 2006).

Study by Fernandes et al. (2010) generated H_2 with a methanol-water mixture. The study shows that increasing the water ratio decreased the H_2 generation rate (HGR). Research investigating Mg, Ca, Cs, and Co chlorides as catalysts was conducted by Lo et al., 2009. The study shows that cobalt chlorides exhibited the greatest activity. Study by Hannauer et al. (2010) found that a Co-TiO_2 catalyst was more active than a Ru-TiO_2 catalyst. Research by Grosjean et al. (2006) produced ball-milled Mg based catalysts to generate H_2 using various alcohols. The synthesis of an effective Co/Al_2O_3 catalyst for the methanolysis of $NaBH_4$ was developed by Xu et al., 2012. The research of Sahiner and Yasar (2016), Sahiner et al. (2016) used a non-metal polymeric ionic liquid catalyst for hydrolysis and alcoholysis. Another study by Xu et al. (2014) used phosphorus modified boehmite. The synthesis of halloysite clay nanotubes as a catalyst to generate H_2 by methanolysis of $NaBH_4$ was conducted by Sahiner and Sengel (2017a, 2017b).

Sepiolite is a fibrous material that can be used in many industries as a catalyst support. In the present study, sepiolite composites are used as catalyst for $NaBH_4$ hydrolysis, solvolysis, and methanolysis for H_2 generation at ambient temperatures. The non-noble metal cobalt-boron nanoparticles are loaded on thermal treated sepiolite channels to obtain a Co-B@tSe catalyst. The catalyst is prepared by an impregnation-chemical reduction method followed by a calcination step. The effects of the thermal treatment temperature, boron loadings, and calcination temperature on the catalytic activity are analyzed.

2. Experimental

2.1. Materials

Naturally occurring sepiolite with a chemical composition of 31% SiO_2, 4% Al_2O_3, 1% Fe_2O_3, 18% CaO, 18% MgO, 28% L.O·I was found in sample A based on the X-ray fluorescence (XRF) measurement. The sample had a 275 $m^2\,g^{-1}$ specific surface area with a 21.863 nm average pore size. The sepiolite was purchased from Eskişehir, a town in Central Anatolia, Turkey, and was used as a support for a cobalt-boron catalyst. Chemically pure grades of sodium borohydride ($NaBH_4$, Fluka, 96%), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, Merck, > 98%), methanol (CH_3OH, MeOH, Merck, ≥ 99.9 %) were used, and a technical grade of sodium hydroxide (NaOH, Labor Teknik) was used. All solutions were prepared with deionized water (H_2O).

2.2. Characterization

The characterization techniques applied in this study are shown below:

- Powder X-ray diffraction (XRD) patterns were obtained using a Philips PANalytical X'Pert Pro X-ray Powder Diffractometer with Cu Kα radiation (λ = 1.5406 Å) at 40 mA and 45 kV. A scanning speed of 1°/min from 2θ = 10°–80° was used. To test for the existence of sepiolite in the sample, XRD analysis below 2°Theta < 10 was also performed (2θ = 3°–10°, with a scanning speed of 0.0061°/sec). The consequent pattern is shown in the inset of Fig. 1.
- Samples were analyzed quantitatively using an X-ray fluorescence technique. The “STANDARDLESS” analysis software on the Minipal4-Panalytical XRF spectrometer was used to determine the major constituents and trace elements. Samples were analyzed three

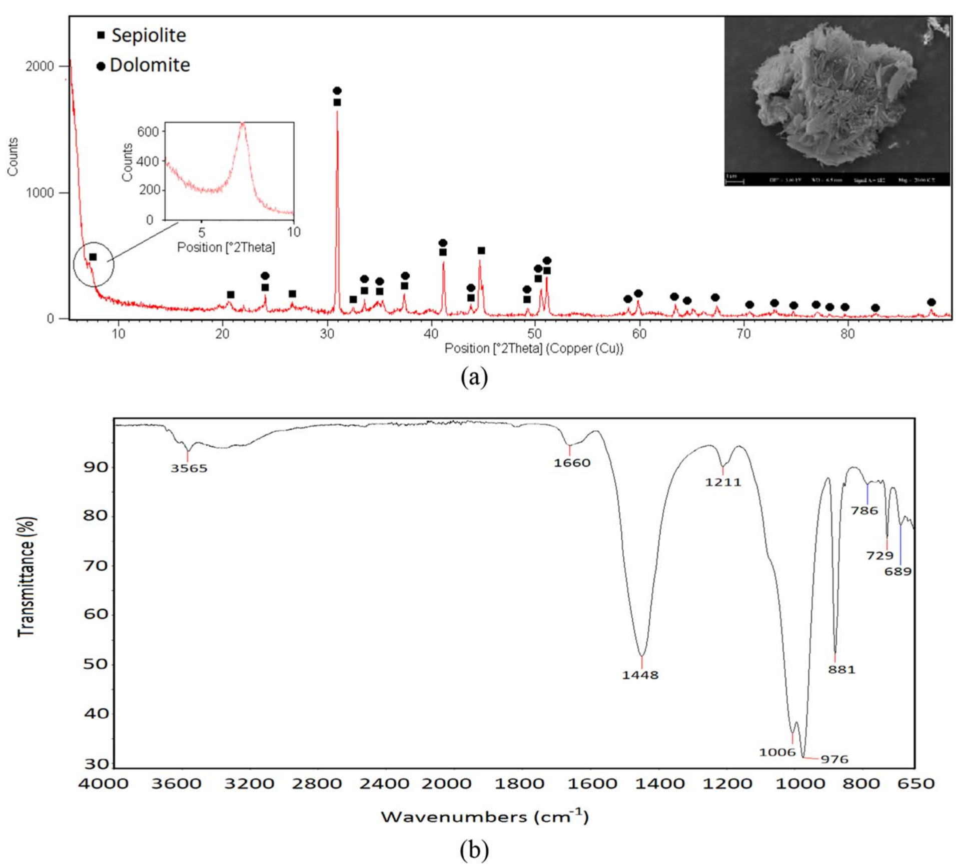

Fig. 1. Characterization results of raw sepiolite (Sample A), (a) XRD pattern, inset shows the SEM images at 1000 × magnification, (b) FT-IR spectrum.