



Aqueous-phase reforming of Fischer-Tropsch alcohols over nickel-based catalysts to produce hydrogen: Product distribution and reaction pathways

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ABSTRACT

Catalytic aqueous-phase reforming (APR) can be applied to process the organic compounds in the water fractions derived from the Fischer-Tropsch (FT) synthesis. This work aimed at finding an active nickel-based catalyst to convert organic compounds typically found in FT-derived waters, such as alcohols, into hydrogen. In addition, this work aimed at proposing potential reaction pathways that explain the product distribution resulting from the APR of C₁–C₃ alcohols. Solutions with 5% mass fraction of either methanol, ethanol, propan-1-ol or propan-2-ol in water were processed in APR at 230 °C and 3.2 MPa over different nickel-based catalysts in a continuous packed-bed reactor. Methanol was successfully reformed into hydrogen and carbon monoxide with conversions up to 60%. The conversion of C₂–C₃ alcohols achieved values in the range of 12% to 55%. The results obtained in the APR of C₂–C₃ alcohols suggest that in addition to reforming to hydrogen and carbon monoxide, the alcohols underwent dehydrogenation and decarbonylation. The most stable catalyst, nickel-copper supported on ceria-zirconia, reached feedstock conversions between 20% and 60% and high hydrogen selectivity. Monometallic nickel supported on ceria-zirconia catalysts reached higher H₂ yields; however, the yield of side products, such as alkanes, was also higher over the monometallic catalysts. Accordingly, ceria-zirconia nickel-based supported catalysts constitute suitable candidates to process the alcohols in the water fractions derived from the FT synthesis.

1. Introduction

The water fraction derived from the Fischer-Tropsch (FT) process contains organic, water-soluble compounds that are challenging for conventional wastewater treatment processes [1]. These compounds consist of oxygenated hydrocarbons such as alcohols that can be converted into valuable products including hydrogen by aqueous-phase reforming (APR) [2,3]. The conversion of the alcohols in the FT water fraction into hydrogen may enhance the economic efficiency of renewable fuel production through FT-synthesis and reduce the organic content in the water fraction directed to wastewater treatment.

Aqueous-phase reforming takes place at low temperatures, 200 °C to 250 °C, and above the bubble point pressure of the feedstock [4], avoiding an energy demanding evaporation step. APR constitutes a suitable candidate to process wastewater with diluted organic compounds because it is energetically efficient compared to steam and autothermal reforming [5]. The energy efficiency becomes significant

because evaporation of the highly diluted organic solution is avoided in APR. Consequently, a number of research groups have studied the APR of oxygenated hydrocarbons [6–8]. The mass fraction of oxygenated hydrocarbons in the water stream from the FT process is typically below 10%. A mixture of short-chain alcohols (C₁–C₃) is the largest group of organic constituents in the FT water fraction [9,10]. Although polyols such as ethylene glycol and glycerol have been the main model compounds applied in APR, monohydric alcohols have also been considered [3]. Methanol [11–14] and ethanol [15,16] were model compounds in APR for hydrogen production over platinum-based catalyst. Iridium supported on different metal oxides was also utilized as catalyst in the APR of methanol [17], and iridium, rhodium and rhenium supported on TiO₂ in the APR of ethanol [18,19]. The APR of ethanol has been additionally conducted over nickel-based catalyst supported on hydro-talcite-like compounds [20], alumina [21], and ceria [22]. The APR of C₃ alcohols has been investigated over Pt-based catalysts supported on alumina [23,24] and on polymer-derived carbon [25]. Moreover, real

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FT derived water fractions have been processed over Ru supported on active carbon and on metal oxides to produce alkanes via hydrodeoxygenation [26,27].

In a previous work on the APR of methanol, doping of nickel on alumina with copper or cerium enhanced the hydrogen production compared to the monometallic catalyst [28]. Furthermore, nickel on ceria-zirconia catalysts exhibited high performance in terms of methanol conversion and hydrogen production [29]. Several authors have similarly described the positive effect of cerium on the catalyst activity in APR. This effect has been attributed to oxygen vacancies that may promote reforming to hydrogen and carbon monoxide, and the conversion of carbon monoxide through the water-gas shift (WGS) reaction. The addition of cerium may also enhance the stability of the catalyst [22,30–36]. Furthermore, copper has been applied as a catalyst dopant to improve the hydrogen selectivity in APR by limiting the formation of side products such as alkanes [37–39].

This work focuses on comparing the APR of methanol, ethanol, propan-1-ol and propan-2-ol. Water solutions of these alcohols were selected as model feedstock because they are representative of the FT-derived water fraction. Self-prepared nickel catalyst on ceria-zirconia supports with different ceria contents, and nickel doped with cerium on γ -alumina were selected due to their high activity and hydrogen selectivity, reported in previous studies [28,29]. Furthermore, nickel doped with copper or cerium supported on ceria-zirconia were considered as potential catalysts to improve the hydrogen production in APR. The results obtained from the APR of C₁-C₃ alcohols elucidate the effect of alcohol chain-length, the influence of the location of the hydroxyl group in alcohols and the type of catalyst applied on the reaction pathway and the product distribution.

2. Experimental

2.1. Materials

Ceria-zirconia supports with mass percentage of ceria in zirconia equal to 17% or 25% were supplied by MEL Chemicals in powder form. Engelhard supplied the γ -Al₂O₃ support. The metal precursors used in impregnation were nickel (Ni(NO₃)₂·6H₂O, ≥97.0%), copper (Cu(NO₃)₂·3H₂O, 99–104%) and cerium (Ce(NO₃)₃·6H₂O, ≥99.0%) nitrates. These chemicals were supplied by Sigma-Aldrich. The feedstock were aqueous solutions with 5% mass fraction of either methanol (MeOH), ethanol (EtOH), propan-1-ol (1-PrOH) or propan-2-ol (2-PrOH). The chemicals were supplied by VWR Chemicals (assay on anhydrous substance is 100%), Altia Industrial (Etax Aa, assay of 99.5%), VWR Chemicals (assay of 100%) and Fluka (assay of > 99.9%) respectively.

2.2. Preparation and characterization of catalysts

The catalysts listed in Table 1 were prepared through incipient wetness impregnation, similarly as in [29]. The ceria-zirconia supports

Table 1

List of catalysts and target contents of impregnated metals.

Catalyst	ID	Ni target (mass fraction)	Cu or Ce impregnated target (mass fraction)
Ni/17 % CeO ₂ -ZrO ₂	Ni/17CeZr	10%	n.a.
Ni/25 % CeO ₂ -ZrO ₂	Ni/25CeZr	10%	n.a.
Ni-Cu/25 % CeO ₂ -ZrO ₂	NiCu/25CeZr	10%	5.0%
Ni-Ce/25 % CeO ₂ -ZrO ₂	NiCe/25CeZr	10%	5.0%
Ni-Ce/ γ -Al ₂ O ₃	NiCe/Al	13%	1.3%

n.a.: not applicable.

were calcined at 450 °C for 10 h in flowing synthetic air, pelletized, crushed and sieved to 200–300 μ m prior to metal impregnations. The bimetallic catalysts supported on 25% ceria-zirconia were prepared through co-impregnation of nickel and copper or cerium precursors in water solutions. After impregnating the metal precursors on 17% and 25% ceria-zirconia supports, the impregnated materials were kept for 24 h at room temperature, followed by drying at 110 °C and calcination in flowing air at 500 °C for 4 h. The bimetallic catalyst supported on γ -Al₂O₃ was prepared through sequential impregnation of first cerium precursor followed by nickel precursor. The catalyst was dried at 80 °C under vacuum and calcined at 500 °C for 2 h in flowing air after impregnation. Prior to the APR experiments, the catalysts were reduced in situ at 450 °C and 2.5 MPa for 2 h with a H₂:N₂ = 1 gas flow of 10 dm³ h⁻¹. The values of target mass percentage included in Table 1 were calculated as the mass of metal in zero oxidation state per total mass of catalyst.

The equipment and methods utilized for the characterization of catalysts were detailed in [29] and briefly described here. The supports, after calcination in the case of mixed-oxide materials, calcined catalysts and spent catalysts were characterized using atomic absorption spectroscopy (AAS) and inductively coupled plasma - optical emission spectroscopy (ICP-OES) to analyse metal loadings. For the AAS, 200 mg of catalyst was dissolved in aqua regia at 120 °C and subsequently diluted with Milli-Q water. Ni and Cu loadings were determined with a Varian AA240 AAS equipment applying air-acetylene flame, and Ce loading with a Perkin Elmer 7100 ICP-OES. Nitrogen physisorption was applied to determine BET surface areas and BJH method to determine pore volumes and pore sizes distribution. Nitrogen physisorption was conducted in an Thermo Fisher Ultra Surfer after degassing the calcined catalyst samples at 200 °C for 3 h in vacuum, and the samples of spent catalysts at 120 °C for 5 h. X-ray diffraction (XRD) was conducted to identify crystalline phases and to determine the crystallite sizes of nickel species. A PANalytical X-pert PRO MPD Alpha-1 diffractometer with Cu K α 1 radiation (45 kV and 40 mA) was utilized to obtain the XRD data. The scanning was continuous and ranged from 10° to 90° (2 θ) with step size of 0.0131°. Based on peak broadening, Scherrer equation [40] was applied to estimate the particle size of nickel species. The X-Ray wavelength of Cu K-alpha was assumed to be 0.154 nm, and a crystallite shape-factor of 0.94 was applied, considering sphere-like catalyst particles. Attempts to identify nickel species and determine their particle size with a scanning transmission electron microscope (STEM) were made with no success. In the results from STEM, Ni species were not detected, most likely because the atomic weight of nickel is considerably lower than the atomic weight of the metals in the support, cerium and zirconium [29].

2.3. Aqueous-phase reforming of alcohols

Aqueous solutions prepared with Milli-Q water and 5% mass fraction of either MeOH, EtOH, 1-PrOH or 2-PrOH were processed in APR over the catalysts listed in Table 1. The experiments were conducted over 1.5 g of catalyst in a continuous fixed-bed reactor described in detail elsewhere [29]. The gaseous products were analysed with an online Agilent 490 Micro GC Biogas Analyzer with two thermal conductivity detectors (TCD), and the liquid products were analysed offline with an Agilent GC 6890 series with a flame ionization detector (FID) according to the detailed methods described in [29]. The operating conditions were set to be 230 °C, 3.2 MPa of inlet pressure, and 2.0 cm³ min⁻¹ of aqueous solution flow.

Ideally, the reforming of MeOH, EtOH, 1-PrOH or 2-PrOH results in the formation of H₂ and CO (Eqs. 1–4). At low temperatures, the WGS reaction (Eq. 5) is favoured to convert CO with H₂O into CO₂ and H₂. The Gibbs free energy changes presented in this work were calculated at 503 K with HSC Chemistry 8, software from Outotec. In addition to the APR operating conditions, potentially spontaneous reactions (Eqs. 2–4) due to slightly positive Gibbs free energy changes [41], and the type of

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