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A study of the methanation of carbon dioxide on Ni/Al₂O₃ catalysts at atmospheric pressure

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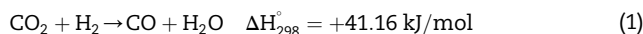
ABSTRACT

The hydrogenation of carbon dioxide producing methane and CO has been investigated over Ni/Al₂O₃ catalysts. The as prepared catalysts have been characterized by XRD and Temperature Programmed Reduction. Spent catalysts have been characterized by XRD and Field Emission SEM. Catalytic activity needs the presence of Ni metal particles which may form in situ if the Ni loading is higher than that needed to cover the alumina surface with a complete monolayer. If Ni content is lower, pre-reduction is needed. Catalysts containing very small Ni particles obtained by reducing moderate loading materials are very selective to methane without CO formation. The larger the Ni particles, due to higher Ni loadings, the higher the CO production. Cubic Ni metal particles are found in the spent catalysts mostly without carbon whiskers. The data suggest that fast methanation occurs at the expense of CO intermediate on the corners of nanoparticles interacting with alumina, likely with a “via oxyginate” mechanism.

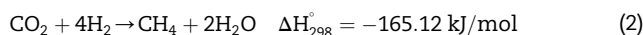
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Introduction

In present years, a number of different technological options are being considered to reduce the amount of carbon dioxide released in the atmosphere by combustion of fossil fuels. In case hydrogen is available or can be produced by renewables [1], the hydrogenation of captured CO₂ is an interesting option as a CO₂ Capture and Storage technology (CCS). Depending on catalysts and reaction conditions, hydrogenation of CO₂ can produce CO via the reverse water gas shift reaction,



methane through methanation



and/or higher hydrocarbons, methanol and/or higher alcohols, formic acid and other oxygenates [2,3].

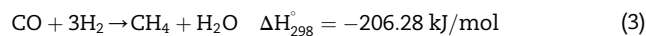
In principle the reverse water gas shift reaction could be an intermediate step in the methanation of CO₂, as suggested previously [2], being possibly followed by the methanation of CO:

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In this case CO would be an intermediate gaseous product, methane being the final reaction product in the reaction (1) + reaction (3) sequence. Alternatively, CO and CH₄ could be assumed as products of two parallel reactions, (1) and (2).

The methanation of carbon oxides is applied industrially since decades mostly to reduce residual carbon oxides present in hydrogen for ammonia synthesis: in this case the reaction is usually carried out at ca 623 K at 30–50 bar in large hydrogen excess with both CO and CO₂ present [4,5]. CO_x methanation can also be performed to produce substitute natural gas (SNG): in this case the catalyst bed temperature is actually varying in larger ranges (up to 973 K) with varying CO/CO₂ ratios and sometimes with defect hydrogen [6,7]. In spite of the large number of supported metal catalysts reported to be active for CO_x methanation, Ni/Al₂O₃ based catalysts seem to be mostly offered by catalyst producers e.g. by Johnson Matthey [8], Topsøe [9] and Clariant-Süd Chemie [10], Ru/Al₂O₃ catalysts being additionally offered for low temperature application by Clariant-Süd Chemie [10]. Recent studies in fact showed high activity of Ru/Al₂O₃ catalysts for CO₂ methanation [11,12]. It has been communicated recently [13] that Clariant, a world leader in specialty chemicals, has supplied a proprietary developed CO₂-SNG catalyst for the methanation unit of Audi's new power-to-gas facility in Werlte, Germany.

The methanation of CO₂-rich gases or of pure CO₂ in the presence of excess hydrogen can also be of interest for the production of methane–hydrogen blends. These blends with H₂ from 5% to 30% vol/vol, sometimes denoted as “hydro-methane”, represent very interesting fuel gases that can be used in current natural gas vehicles and be distributed by present NG refueling infrastructures with advantages such as a more complete combustion, increasing efficiency and reducing hydrocarbon and CO₂ emissions [14–16]. The same catalytic systems used for syngases and CO methanation are considered for CO₂ methanation [17]. In a recent paper concerning low Ni coverage catalysts, Ni/SiO₂ was reported to be more active than Ni/Al₂O₃ in CO₂ methanation [18], but other papers report very high activity of highly loaded Ni/Al₂O₃ catalysts [19] which can be increased by Fe-doping [20]. The aim of the present paper is to study the effect of Ni loading and the nature of the active species on Ni/Al₂O₃ in CO₂ methanation.

Experimental

Materials preparation

The preparation and characterization of the fresh catalysts has already been reported [21]. The catalyst denoted as Ni α is obtained by calcination at 973 K of Ni(NO₃)₂·6H₂O, the same precursor used for the preparation of the supported catalysts, and is constituted by NiO (bunsenite), with a BET surface area of 4 m²/g. The support material used to prepare the Ni/Al₂O₃ catalysts is Siralox 5/170 from Sasol, 170 m²/g. The virtual composition of this support is 95% Al₂O₃, 5% SiO₂ wt/wt. Ni16 and Ni39 catalysts have been prepared by wet impregnation using Ni(NO₃)₂·6H₂O water solution (1 ml/g_{Al₂O₃}), followed by a

drying step at 363 K for 5 h. Due to the definitely bigger amount of salt to be used, the preparation of Ni125 was slightly different: 3 ml/g_{Al₂O₃} and 24 h drying. Finally calcination at 973 K for 5 h was performed in all cases. Ni16 (137 m²/g), Ni39 (107 m²/g) and Ni125 (76 m²/g) are Ni/Al₂O₃ samples with 16%, 39% and 125% Ni calculated as 100 wt_{Ni}/wt_{support}.

Materials characterization

Microscopic analyses on all the samples were performed by the SEM ZEISS SUPRA 40 VP, with a field emission gun. This instrument is equipped with a high sensitivity “InLense” secondary electrons detector, together with a solid state backscattered electrons detector and with a EDX microanalysis OXFORD “INCA Energie 450 × 3”. Samples for SEM analysis were suspended in ethanol and exposed to ultrasonic vibrations to decrease the aggregation. A drop of the resultant mixture was finally deposited on a Lacey Carbon copper grid.

X-ray diffraction patterns of samples were obtained using a vertical powder diffractometer X'Pert with Cu K α radiation ($\lambda = 0.15406$ nm). The patterns were collected in the 2 θ –100° range with a step of 0.02° and a counting time for each step of 12 s. Powder patterns were indexed by comparing experimental results to the data reported in the Pearson's Crystal Data database [22].

Temperature programmed reduction tests (TPR) are used to identify and evaluate the reducibility of the various nickel species present on the alumina-supported catalysts. In a typical H₂-TPR test the as-calcined catalyst is reduced by a 10% H₂/Ar gas mixture, while the temperature is ramping up from to 1173 K at a rate of 15 K/min.

Catalytic experiments

All the catalytic experiments were carried out in a fixed-bed tubular silica glass flow reactor, operating isothermally, loaded with 44 mg of catalyst mixed with 500 mg of silica glass particles (60–70 mesh sieved). A gaseous mixture of CO₂ and H₂ in the molar ratio 1– : 5 without any dilution in a carrier gas was fed, with GHSV equal to 52,300 h⁻¹. Temperature was varied step by step in-between 523 K and 773 K and back down to 523 K. Experiments have been performed for all catalysts without any pretreatment (“as prepared samples”). In some cases prerduction of the catalyst was performed flowing a 20% H₂/He mixture (vol/vol) at 973 K for 1 h and then keeping in He until room temperature was reached (“prereduced samples”). Both families of catalysts have also been characterized after reaction (“spent samples” and “prereduced spent samples”).

Products analysis was performed with a gas-chromatograph Agilent 4890 equipped with a Varian capillary column “Molsieve 5A/Porabond Q Tandem” and TCD and FID detectors in series. Between them a Nickel Catalyst Tube was employed to reduce CO and CO₂ to CH₄.

CO₂ conversion (X_{CO_2}), selectivities and yields to products, S_i and Y_i , are defined as:

$$X_{\text{CO}_2} = \frac{n_{\text{CO}_2\text{in}} - n_{\text{CO}_2\text{out}}}{n_{\text{CO}_2\text{in}}}; \quad S_i = \frac{n_i}{n_{\text{CO}_2\text{in}} - n_{\text{CO}_2\text{out}}}; \quad Y_i = \frac{n_i}{n_{\text{CO}_2\text{in}}}$$

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