CO_2 for the Production of Methanol and Dimethylether

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Fossil fuels depletion and environmental protection imply new routes for energy production. Restrictions concerning gas emissions lead towards clean technologies with low carbon dioxide emissions and high-energy efficiency. Electricity generation from renewable sources (wind, solar, geothermal and hydroelectric plants) presents a very satisfactory progress. Yet, electricity demand and supply do not always coincide. On the other hand, progress in alternative fuel production for the transport sector is slow, due to various reasons, among which the availability of raw materials. An interesting idea, which would address the above problems, is to store electric energy in the form of chemical energy. Hydrogen, (coming from water electrolysis during low electricity demand) and CO_2 (from flue gas and any other CO_2-rich stream) can be used for the synthesis of a mixture of methanol and dimethyl ether, alternative fuels for heat engines or Fuel Cells. Many research efforts focus on the development of effective catalysts for CO_2 hydrogenation [1-4].

In the present work CO_2 hydrogenation for the production of methanol/DME has been studied over bifunctional catalytic systems comprising of a methanol synthesis (eq. 1) and a methanol dehydration catalyst (eq. 2).

$$CO_2 + 3H_2 \rightleftarrows CH_3OH + H_2O \qquad \Delta H = -49.2\ \text{kJ mol}^{-1} \qquad (1)$$

$$2CH_3OH \rightleftarrows CH_3OCH_3 + H_2O \qquad \Delta H = -24.0\ \text{kJ mol}^{-1} \qquad (2)$$

A commercial $CuO/ZnO/Al_2O_3$ catalyst has been used for the methanol synthesis reaction. A variety of commercial and home-made catalysts (γ-Al_2O_3, WO_3/Al_2O_3 and various zeolites, Ferrerite(10), Faujasite, HZSM-5(11.5) and HZSM-5(25)) with different acidic properties and physicochemical characteristics have been used for the methanol dehydration reaction. The investigated materials have been characterized with respect to their textural properties (B.E.T. and B.J.H. methods) and crystallinity (XRD). Methanol dehydration catalysts have been also studied regarding their acidity by TPD-NH_3 and FT-IR with in situ pyridine sorption. Furthermore, the adsorption/desorption properties of catalysts toward methanol and water as well as the dehydration reaction mechanism have been investigated with the use of transient-MS and in situ DRIFTS techniques. Catalytic tests were performed over mechanical mixtures of the above materials, at 3.0 MPa and temperatures 180-250 °C and a gas mixture (CO_2/H_2). Prior to testing the catalysts were reduced in situ with pure H_2 under atmospheric pressure at 300 °C (TPR 2 °C/min) for 1 hour.

Regardless of the catalytic configuration used, CO_2 conversion increased with temperature (180-250°C) but it is always lower than that predicted by thermodynamics, indicating that the reaction occurs under the kinetic regime. Although there are no significant differences in the activity, there are noticeable differences regarding the yields of reaction products over the various catalysts investigated. The main product of the catalytic configurations containing alumina (as methanol dehydration component) is methanol, indicating that methanol produced is not consumed for the formation of DME. This behaviour may be due to the poor acidity of these samples, to the nature of acid sites (Lewis and Brönsted) or to the fast deactivation of acid sites by the adsorption of water formed. Catalysts containing zeolitic materials produce mainly DME and lower amounts of methanol, showing that an important amount of the latter is consumed via the dehydration reaction (eq. 2). Differences in DME yields are observed for the various zeolites, depending on parameters such as the zeolite micropore structure and Si/Al ratio, as well as on the number, strength and nature of active acid sites. The performance of these zeolites for methanol dehydration does not follow the same trend when used under 0.1MPa and 3.0 MPa. Catalysts deactivate with time on stream but, in most cases, catalytic activity is almost completely restored after regeneration.

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