

Hydrogen production from dimethyl ether on Rh based catalysts.

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Introduction

It is a common opinion to consider hydrogen as the most accredited clean fuel for the near future. At present, high temperature operating molten carbonate fuel cell (MCFC) seems to be most promising for electrical energy production from H₂, because of its highly advanced technology. Nowadays, H₂ is industrially produced mainly from natural gas (CH₄). Moreover, recently considerable research interest has focused on production of H₂ from (renewable) liquid biofuels rather than from conventional fossil fuels. Some of these can be easily directly be derived from biomass (i.e. bioethanol and biodiesel), while new fuels produced from syngas (e.g., methanol, dimethyl ether, etc...) are the liquid fuels mixture converted again to syngas. In particular, dimethyl ether (DME) can easily be handled and transported, and represents a good liquid storage of syngas. In recent literature a wide variety of catalysts has been studied for DME steam-reforming. Rhodium performs best by far, while its high cost advises against industrial applications in the near future.

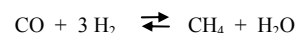
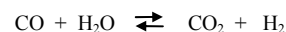
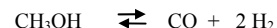
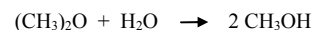
As the acidity of the support can play an important role in the general reaction mechanism, a dual function catalyst is needed. In this study the feasibility of DME steam-reforming over Rh based catalysts has been investigated; a preliminary screening has been made by supporting the noble metal on Al₂O₃.

Materials and Methods

Four Rh based catalysts have been prepared by impregnating the Al₂O₃ support with solutions of Rh nitrate hydrate (Rh(NO₃)₃ · n H₂O). Solutions have been prepared by dissolving about 2.0 g of Rh salt in 100 mL of water and multiple impregnations have been carried out to obtain a better distribution of the metal phase. After each impregnation, the wet catalyst was dried at 650 K. Finally, a prefixed amount of sample positioned in a quartz testing tube was treated "in situ" in a reducing atmosphere before each test. The Rh weight percentage was evaluated "a posteriori" by AAS analysis. Alumina starting material (AKZO 001-3P) was milled and sieved (40-70 mesh), while other reagents were commercial SIGMA-ALDRICH products. Tests have been carried out by a conventional plug-flow microreactor (laboratory scale), equipped with an on-line gas-chromatograph Agilent Technologies 6890 for inlet-outlet analyses.

Results and Discussion

The reaction proceeds according to a consecutive two – step mechanism. In the first stage acidic sites of Al₂O₃ (S_A) catalyze hydrolysis of DME, whereas successively the noble metal (S_{Rh}) catalyzes the decomposition of methanol and governs the distribution of the reaction products (CO, CO₂, CH₄, H₂), as follows:



As the acidic sites - responsible for hydrolysis of DME - also favour coke formation, these sites are poisoned progressively. Figure 1 shows the results of a typical experiment.

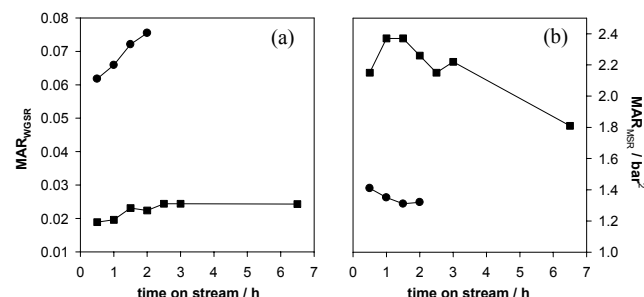


Figure 1. Outlet composition modification during time on stream evaluated by the apparent equilibrium constants (Mass Action Ratios = MAR): (a) MAR for water gas shift reaction and (b) MAR for methane steam reforming reaction, Vs. time on stream at 0.5 wt% Rh charge (●). The alumina support Rh free (■), is reported as base line (only acid function active).

Poisoning of acidic sites leads to a progressive decrease in S_A/S_{Rh} ratio, and consequently, to variation in selectivity of the overall reaction. In other words, within certain limits, after several hours on stream a catalyst of low Rh loading behaves as a fresh catalyst of high loading. Experiments carried out at different GHSV over catalysts containing 1 to 5 wt% Rh have confirmed this approximation.

Significance

In this study, the performance of Rh based catalysts for the steam reforming of DME has been investigated at MCFC operative conditions (T = 923 K). Because of the consecutive acidic-hydrogenating mechanism, a particular Al₂O₃/Rh ratio optimizes the hydrogen yield at each prefixed contact time. From the kinetic point of view, the (fast) hydrogen production rate seems to be almost independent from the initial (slow) DME hydrolysis reaction. On the other hand acid sites also catalyze cracking of the products and the best compromise between hydrolysis and cracking is to be found for each experimental conditions. In any case, a small amount of DME is always detected in the outlet. Among the hydrogen production reactions the water-gas shift is close to equilibrium and no coke formation is detected in the short-time tests (time on stream 5-6 h). Further considerations on process mechanism, that can explain particular reaction pathways, were also reported.