



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Influence of the spatial arrangement of catalyst components in the single-stage conversion of synthesis gas to gasoline

Enrico Lorenz, Paul Wehling, Maximilian Schlereth, Bettina Kraushaar-Czarnetzki*

Institute of Chemical Process Engineering CVT, Karlsruhe Institute of Technology (KIT), Kaiserstr. 12, 76131 Karlsruhe, Germany

ARTICLE INFO

Article history:

Received 31 August 2015
Received in revised form 29 February 2016
Accepted 2 March 2016
Available online xxx

Keywords:

Synthesis gas
Gasoline
Single stage
Cu/ZnO
H-ZSM-5
Composite catalyst

ABSTRACT

Aiming at the synthesis of gasoline in a single reaction stage, the conversion of synthesis gas was studied over several spatial arrangements of the catalyst components required for the synthesis of dimethyl ether and for the subsequent formation of hydrocarbons. At pressures of 40 bar and temperatures between 270 °C and 350 °C, extruded catalyst bodies of Cu/ZnO/ γ -alumina and of H-ZSM-5/ γ -alumina were employed as well as trifunctional composite extrudates of Cu/ZnO/ γ -alumina/H-ZSM-5. Using physical mixtures or trifunctional composite catalyst, carbon monoxide conversions can be achieved far above thermodynamic equilibrium levels because dimethyl ether is continuously withdrawn upon conversion to hydrocarbons. However, light hydrocarbon products are prevailing, and gasoline selectivities are very low. In sequential arrangements of copper- (up-flow) and zeolite-based (down-flow) catalysts, boosting of the CO conversion is not possible, but the product distribution is shifted to higher hydrocarbons. The highest gasoline yields were obtained when the copper and zeolite containing catalyst layers were divided in two different temperature zones operating at 270 °C up-flow and at 350 °C down-flow.

© 2016 Published by Elsevier B.V.

1. Introduction

A simplified single-stage process for the production of gasoline from synthesis gas could be an interesting option for the chemical storage of hydrogen, for instance, produced by water electrolysis with excess electrical power from wind or solar power plants offshore or in remote areas. At present, the manufacturing of synthetic gasoline via the so-called methanol route proceeds in multiple stages. Reactions involved are the synthesis of methanol (Eq. (1)) and its etherification (Eq. (2)), the water gas shift reaction (Eq. (3)), and the formation of hydrocarbons.



Copper-based catalysts like Cu/ZnO are active in both, methanol synthesis and shift reaction. In this study, we used extruded catalyst bodies of Cu/ZnO/ γ -Al₂O₃, in which γ -Al₂O₃ has the dual function of a weak acid that catalyzes the dehydration of methanol, and of a ceramic binder providing mechanical strength to the extrudate. The

exothermic reactions (1)–(3) are prone to thermodynamic equilibrium constraints. When bifunctional catalysts like Cu/ZnO/ γ -Al₂O₃ are employed, these reactions are coupled, and the sum Eq. (4) can be used to calculate equilibrium conversion levels as a function of reaction temperature and pressure.



As was discovered by Chang in 1976, the conversion of methanol and DME over zeolite ZSM-5 yields water and a mixture of paraffinic, olefinic and aromatic products; by choice of reaction conditions and Si/Al ratio of the zeolite, the hydrocarbon composition can be shifted to the gasoline range [1]. The underlying mechanisms are complex and have been elucidated in impressive studies by Dahl, Kolboe, Olsbye and co-workers [2–6]. Equation (5) may be used to simplify and summarize the reactions of the hydrocarbon synthesis stage.



A few research groups have investigated the direct synthesis of gasoline from carbon monoxide and hydrogen [7–13]. In most of the studies, catalysts containing chromium oxide (Cr₂O₃/ZnO) [7–10] or palladium (Pd/ZnO) [11,12] were used for methanol synthesis, and these components were combined with amorphous silica-alumina or with H-ZSM-5 either in physical mixtures [7,9,12] or in composite catalysts [8,10]. The only study addressing the issue of spatial catalyst arrangement has been published recently

* Corresponding author.

E-mail address: kraushaar@kit.edu (B. Kraushaar-Czarnetzki).

by Wang et al. [13]. This group used Cu/ZnO/ γ -Al₂O₃ and PdZSM-5 and compared the performances of physical mixtures of these catalysts with those of sequential (layered) arrangements in the syngas conversion. Surprisingly, the effects of catalyst arrangement on the thermodynamic equilibria of reactions (1)–(3) have not been taken into consideration. This issue will be addressed in detail in the study, where we employ extruded catalyst bodies of Cu/ZnO/ γ -Al₂O₃ and of H-ZSM-5/ γ -Al₂O₃ arranged either as a physical mixture or in sequential beds as well as trifunctional composite extrudates of Cu/ZnO/ γ -Al₂O₃/H-ZSM-5 with different zeolite contents. On purpose, ZSM-5 was not loaded with metals (like Pd) in order to prevent hydrogenation of intermediates, olefins and/or aromatics which are required to obtain high octane numbers of the gasoline fraction.

2. Experimental

2.1. Preparation of catalysts

Three types of catalysts were used in this study: (i) bifunctional Cu/ZnO/ γ -Al₂O₃ for the conversion of synthesis gas to methanol and dimethyl ether, (ii) H-ZSM-5/ γ -Al₂O₃ for hydrocarbon synthesis, and (iii) three trifunctional Cu/ZnO/ γ -Al₂O₃/H-ZSM-5 composite catalysts containing different portions of zeolite ZSM-5. In contrast to many other authors, catalyst was not employed as a powder but rather shaped catalyst bodies with sizes and porosities typical for industrial application were applied. Therefore, in all cases, the final stage in the preparation comprised an extrusion to form cylindrical bodies with diameters of 2 mm and lengths of 5 mm, followed by drying and a subsequent calcination in air at 550 °C (heating rate: 2 °C/min) for 3 h. Comparative tests with crushed extrudates indicated that external and internal mass transfer limitations over full extrudates can be excluded.

2.1.1. Cu/ZnO/ γ -Al₂O₃

This catalyst was produced in the (molar) composition 2Cu/1ZnO/1.5 γ -Al₂O₃ following a procedure evaluated in earlier works [14]. In a first step, a mixed carbonate (molar ratio CuCO₃:ZnCO₃=2:1) was precipitated by feeding simultaneously and under vigorous stirring 1 M solutions of Cu(NO₃)₂·3H₂O (Merck, purity \geq 99.5% m/m), Zn(NO₃)₂·6H₂O (Merck, purity \geq 99% m/m) and Na₂CO₃ (Merck, purity \geq 99.5% m/m) at 86 °C. Feed rates were adjusted such that pH 7 was maintained. When all solutions were combined, stirring without heating was continued for one hour; during this time, the suspension cooled down from 86 °C to room temperature. The precipitate was filtered, washed with demineralized water and dried for 12 h at 120 °C. The second step comprised preparation of a paste for extrusion by mixing the dry carbonate powder with pseudoboehmite (Pural SB-1, Sasol) and an aqueous solution of hydroxyethyl cellulose (HEC 8% m/m, Sigma). The extruded greenbodies were dried and subsequently calcined. During calcination, the plasticizer HEC is burnt off, the metal carbonates decompose into the respective oxides and CO₂, and pseudoboehmite transforms into γ -Al₂O₃. Reduction of CuO to metallic copper was performed *in situ* (*vide infra*).

2.1.2. H-ZSM-5/ γ -Al₂O₃

This catalyst was composed (on dry basis) of 50% m/m zeolite and 50% m/m alumina. The ZSM-5 (ExxonMobil) exhibited an atomic ratio Si:Al=32 and was employed in the alkaline-free TPA⁺ form such that no ion exchange was necessary to obtain the H⁺ form. The catalyst was produced by mixing the appropriate amounts of zeolite and pseudoboehmite with an aqueous HEC solution, followed by extrusion, drying and calcination.

2.1.3. Cu/ZnO/ γ -Al₂O₃/H-ZSM-5

The trifunctional composite catalysts combine all catalytic functions and were produced by extrusion of pasty mixtures consisting of CuO/ZnO, pseudoboehmite, zeolite and aqueous HEC solution. Here, Cu and Zn were not added as a mixed carbonate but rather as a mixed oxide (molar ratio CuO:ZnO=2:1; obtained by calcination of the carbonates at 550 °C prior to mixing with the other ingredients) in order to prevent ion exchange of metal ions with the acid sites of the H-ZSM-5. After extrusion, the greenbodies were dried and calcined as described above. In all trifunctional catalysts, the molar ratio of Cu:ZnO: γ -Al₂O₃ was fixed to 2:1:1.5 as in the catalyst for the synthesis of methanol and DME. However the mass ratio of (Cu + ZnO + γ -Al₂O₃):H-ZSM-5 was varied such that three samples were obtained, containing (on dry and reduced basis) 10, 50, and 90% m/m of zeolite H-ZSM-5, respectively.

2.2. Catalyst characterization

All characterization methods except for the determination of the copper surface were applied to the calcined extrudates; hence, in Cu-containing catalysts, the copper was present in the oxidized form as CuO.

Total surface areas were determined by means of nitrogen physisorption at 77 K,

according to the BET method using an ASAP 2020 (Micromeritics) after *in situ* outgassing at 350 °C for 9 h. Analyses of porosities and pore size distributions were performed by mercury porosimetry (Autopore III, Micromeritics) at pressures up to 4135 bar.

Scanning electron microscopy was used to examine particle sizes and morphologies of the solid catalyst ingredients. Furthermore, micrographs were taken of the trifunctional catalysts in order to examine the morphology. Although sputtered with a 3 nm layer of Pt, the massive electric charging of the samples disturbed the measurements in a conventional SEM device. Hence, environmental scanning electron microscopy (ESEM) was carried out in the presence of water vapor on a Quanta FEG 650 (FEI).

The copper surface areas in Cu-containing catalysts were measured by selective surface oxidation with N₂O according to a method described by Chinchén et al. [15]. Typically, 1 g of catalyst was placed in a tubular quartz reactor and heated up to 140 °C in a helium flow of 225 cm³/min (STP). Further heating up to 240 °C was performed in the presence of 7% v/v of hydrogen. The reduction of Cu was completed by increasing the portion of H₂ in the gas flow to 55% v/v and holding for 1 h at 240 °C. After cooling down to 60 °C, the surface oxidation was started by switching the gas stream from He + H₂ to a mixture of He with 800 ppm of N₂O. Copper surfaces were calculated from the amount of N₂O consumed [15].

2.3. Catalytic experiments

A continuously operated reaction unit with on-line GC analysis and a catalytic afterburner for continuous monitoring of the carbon balance was used which could be operated either with one single tubular fixed-bed reactor, or with two equal reactors in series. The reactors (stainless steel, d_i = 13 mm, L = 35 mm) were equipped with three heating zones. In all cases, the reactor inlet zone up-flow to the catalyst bed was filled with coarse SiC particles (diameter 1 mm), and the voids in-between the extruded catalyst granules were filled with fine SiC particles (diameter 0.2 mm). This measure ensures plug flow conditions in the reactor. Furthermore, the non-reactive silicon carbide exhibits a high thermal conductivity and improves the heat transfer. In spite of the pronounced heat release upon processing, isothermal conditions ($\Delta T_{\text{max}} = 2$ °C) could be realized at all conditions.

Download English Version:

<https://daneshyari.com/en/article/4757336>

Download Persian Version:

<https://daneshyari.com/article/4757336>

[Daneshyari.com](https://daneshyari.com)