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A kinetics study for the oxidative coupling of methane on a $Mn/Na_2WO_4/SiO_2$ catalyst

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ABSTRACT

This paper presents an experimental kinetic study for the oxidative coupling of methane (OCM) over a $Mn/Na_2WO_4/SiO_2$ catalyst prepared by incipient wetness impregnation. Because the catalyst is a reducible metal oxide, the stability of the catalyst has been assessed by Thermo Gravimetric Analysis (TGA). These experiments show that the catalyst has to be pre-treated with oxygen in order to obtain high C_2 selectivity (around 85%) and that a low oxygen partial pressure during the OCM reactions is already sufficient to maintain the catalyst stable in the oxidized state.

The catalyst has subsequently been tested in a micro-catalytic fixed bed reactor. The overall reaction orders and rate constants of the primary reactions were determined by measuring the intrinsic reaction rates at different methane and oxygen inlet concentrations. It was found that the reaction order in oxygen for the coupling reaction is 0.38, while the reaction order in oxygen for ethylene oxidation approaches unity, indicating that low oxygen concentration levels are beneficial for obtaining a high C_2 selectivity (up to 80–90%). Such a low oxygen concentration can be obtained with distributive feeding in a membrane reactor.

Based on the experiments and least-squares minimization, a simplified reaction mechanism is proposed, where the dependency of the ethane (coupling) and carbon dioxide (oxidation) production rates and the secondary ethylene production and C_2 oxidation rates can be described with power-law type reaction rate expressions.

1. Introduction

The oxidative coupling of methane (OCM) is a widely investigated direct route for ethylene production through methane partial oxidation. The reaction involved in OCM carried out at temperatures higher than 750 °C are the following:

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \quad \Delta H^\circ_{298} = -141\ \mathrm{kJ/mol_{CH_4}} \qquad \text{(i)}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad \Delta H^\circ_{298} = -803\ \mathrm{kJ/mol_{CH_4}} \qquad \text{(ii)}$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta H^\circ_{298} = -1323\ \mathrm{kJ/mol_{C_2H_4}} \qquad \text{(iii)}$$

The industrial exploitation of such a reaction system is hindered by the low yield typical of this conversion-selectivity problem: high CH_4 conversions (i.e. feeding a relatively large amount of O_2) are associated with relatively poor product selectivity with a large yield of undesired combustion products like CO_x. In addition, the highly reactive intermediate C_2H_4 may easily react to the unwanted and thermodynamically favored oxidation products at too high O_2 concentrations.

Despite the difficulties in achieving higher yields, this reaction system has always been considered very promising by both industries and research institutions. A total yield higher than 35–40% would already make this system economically feasible. For this reason, since 1980's, many groups investigated the OCM [1,2], mainly focusing on different catalytic materials.

The actual trend in chemical reaction engineering on OCM reaction is towards the development of novel reactor concepts with distributed feeding of oxygen (e.g. with membrane reactors) in order to keep a low concentration of oxygen along the reactor and thus improving the product yield. The design and optimization of such reactors require the development of adequate kinetic models for catalysts operated at high temperatures and low oxygen concentrations.

A widely investigated catalyst for OCM is Li/MgO [3], which is already active and selective at reaction temperatures of 750 °C but is inherently unstable because of the loss of active components.

Usually the research is limited to study the catalyst performance and the determination of a reaction mechanism, however, for reactor modeling and design of a new process involving oxidative coupling of methane, possibly combined with steam reforming, and carried out in membrane reactors an accurate description of the most important reaction rates is required. A quantitative

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