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Chemical Engineering Science 63 (2008) 4910–4916

Chemical Engineering Science

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Dynamics of $Mn/Na_2WO_4/SiO_2$ catalyst in oxidative coupling of methane

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Received 26 April 2007; received in revised form 8 August 2007; accepted 13 August 2007
Available online 19 August 2007

Abstract

The dynamics of Mn–Na_2WO_4/SiO_2 catalyst in oxidative coupling of methane (OCM) was investigated by transient experiments at a temperature range of 700–850 °C. Both the on-line analyses by GC–MS and off-line analyses by multi-port sampling valve were employed. The fully oxidized catalyst was exposed to concentration step-change of CH_4 from 0.0% to 10% in Ar and the rate of consumption of CH_4 and the rate of formation of OCM products were monitored. The results reveal that the catalyst has stable redox properties and provides its lattice oxygen for the reaction. Both hydrocarbon products and carbon oxides are formed in the absence of gas-phase oxygen. The reduced catalyst gets fully oxidized when exposed to gas-phase oxygen and recovers its activity to initial activity quite fast. The catalyst does not deactivate during consecutive reduction–oxidation cycles and can be used for cyclic mode of operation to obtain high C_2 yield.

Keywords: OCM; Mn–Na_2WO_4/SiO_2; Transient response; Catalyst selectivity; Catalyst activity; Stability

1. Introduction

The surface processes in the oxidative coupling of methane (OCM) including methane activation and the role of lattice versus adsorbed oxygen in the products formation are not yet fully understood. C–H bond breaking has been reported to be involved in the formation of C_2 products since kinetic isotopic effects (k_H/k_D) have been observed over several catalysts (Kondratenko et al., 1999; Nibbelke et al., 1995). However, there is no consensus on the details of methyl radical formation and the nature of active sites in that regard. Mainly two general attitudes can be found in the literature with regard to the first step of the reaction, i.e. methane activation:

1. Methyl radicals are formed as a result of the interaction of gas-phase methane with active oxygen surface species according to Eley–Rideal mechanism (Driscoll et al., 1985; Dubois and Cameron, 1990; Feng et al., 1991; Tung and Lobban, 1992).
2. Dissociative adsorption of methane is basically responsible for the formation of methyl radicals (Mirodatos et al., 1990; Bytyn and Baerns, 1986; Sokolovskii et al., 1989; Hatano and Otsuka, 1989; Choudhary and Rane, 1991; Lapszewicz and Jiang, 1992).

On the other hand, understanding the role of adsorbed oxygen and lattice oxygen in both the activity and C_2 selectivity is necessary in order to have a clear picture from what is happening on the surface. Some research groups have employed transient techniques to elucidate the role of different types of oxygen in the OCM reaction (Asami et al., 1986; Hatano and Otsuka, 1988; Otsuka and Said, 1987). However, the transient results are mainly catalyst dependent and may not be generalized to all of the OCM catalysts.

Since the introduction of Mn–Na_2WO_4/SiO_2 catalyst by Li et al. (Fang et al., 1992; Wu et al., 1995; Wu and Li, 1995; Jiang et al., 1993), extensive investigation has been performed on this system and found it to be one of the best catalysts for OCM. In the present study, by performing transient experiments and conductivity measurements, the role of lattice oxygen of Mn–Na_2WO_4/SiO_2 catalyst on activity and products formation in OCM is discussed.

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doi:10.1016/j.ces.2007.08.013

2. Experimental

2.1. Catalyst preparation

A $4\%Mn/5\%Na_2WO_4/SiO_2$ catalyst was prepared by dry impregnation of amorphous silica gel Davisil grade 645 (Aldrich) with addition of dropwise of aqueous solution of $Mn(NO_3)_2 \cdot 4H_2O$ (Merck). This step was followed by drying at 403 K overnight. Afterward the catalyst was impregnated with aqueous solution of $Na_2WO_4 \cdot 2H_2O$ (Merck), dried again at 403 K overnight and calcined at 1073 K for 8 h.

2.2. Setup

A transient system was designed and used to study the redox properties of the catalyst. A quartz tube with 7 mm ID and 2.5 cm length was used as the reactor. The tubing used from mass flow controllers to the reactor and from the reactor to GC–MS had a $\frac{1}{16}$ in ID. The system was made as such to have the smallest possible amount of dead volume. The system made use of a Thermo Finnigan GC–MS (Tracer 2340 MS). The system has the ability of on-line analysis of the products for both steady-state and step-change experiments. A schematic of microreactor used in the system and the schematic of the setup are shown in Figs. 1 and 2, respectively.

To prevent the separation of the effluent gases and to have on-line analyses, empty column was replaced by the GC–MS column. Also, the reactor effluent was divided into two portions, one of which was introduced to the GC–MS and the other portions vented. To minimize the fluctuation of the feed pressure during the step-change experiments, a mercury column and a purge system were placed in the feeding section of the setup. An oxygen trap was also placed just after the methane feed to adsorb the possible trace of oxygen in it.

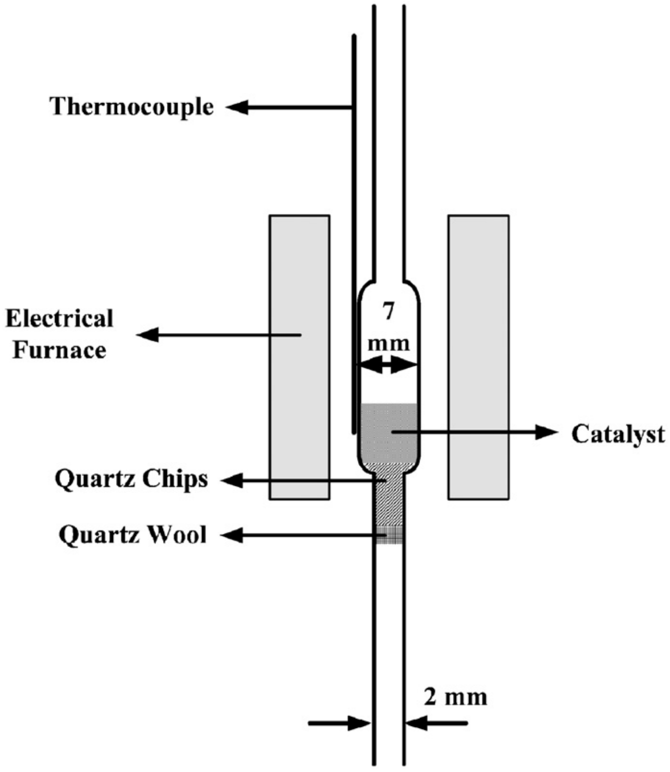

Fig. 1. Microreactor used for transient experiments.

Whenever the oxygen was introduced to the reactor for oxidizing the catalyst, the reactor effluent was totally purged. This was done in order to protect the detector filament from being oxidized.

Although ultrahigh-pure methane and argon along with oxygen trap were used, a blank experiment was done to make sure that there was no oxygen due to the influx of air into the system. Following molecular masses were selected for different compounds: 44 (CO_2), 40 (Ar), 32 (O_2), 30 (C_2H_6), 28 (N_2, CO, C_2H_4, C_2H_6) and 16 (CH_4).

In the first set of step-change experiments, the catalyst bed was first exposed to 20.0 sccm of oxygen for 20 min at the reaction temperature. The bed was then flushed with a flow of argon for 10 min. Afterward the argon flow was switched to the mixture of 10% methane in argon and the reactor outlet was analyzed by GC–MS. The scan rate of the GC–MS was set to be at 6 scans per second. After each step-change in methane the feed was switched to oxygen for the catalyst to be fully oxidized and the experiment was repeated to make sure that the activity of the catalyst does not change after several cycles of reduction and oxidation. It was proved that the catalyst was quite stable and the results of consecutive step-change experiments were almost identical.

In the second setup experiments, 0.4 g of catalyst was exposed to 80.0 sccm of 10% CH_4 in Ar. This way the GHSV for this set of experiments was the same as that of set no. 1 experiments. The analyses of the reactor effluent after each step-change in methane concentration were done off-line by using a 16-port sampling valve. Sampling was done every 10 s at the first minute and every 2 min afterward. After all 16-port sampling loops were filled, the samples were injected into a multi-column Carl 400 A gas chromatograph. The GC could identify CH_4 as well as C_2H_6, C_2H_4, CO and CO_2 in the samples. This way methane conversion and products selectivity could be calculated during each transient experiment.

In the third set of experiments the changes in electrical conductivity of the catalyst during transient experiments were measured. For this set, a system containing a conductivity cell was used in which 0.1 g of the catalyst was placed between two gold electrodes. The catalyst powder was fixed in the reactor from the top and the bottom by quartz wool. The cell was placed in an electrical furnace, the temperature of which was controlled by a PID temperature controller. The two gold electrodes were connected to a data acquisition system by gold wires. A schematic of the system is shown in Fig. 3.

2.3. Catalyst characterization

The crystalline phases of the catalyst were identified using a Philips instrument with Cu-Kα target. A scan rate of $0.02° min^{-1}$ was used.