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Ethene production by oxidative dehydrogenation of ethane at short contact times over Pt-Sn coated monoliths

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ABSTRACT

The oxidative dehydrogenation of ethane to ethene was studied in a monolithic reactor at short contact times using a Pt-Sn/Al_2O_3 catalyst. The catalyst was characterised by Temperature Programmed Reduction (TPR), Scanning Transmission Electron Microscopy as well as H_2 and CO chemisorption. Three different preparation methods were used for the Pt-Sn catalyst; two-step impregnation where Pt was impregnated first, two-step impregnation where Sn was impregnated first and co-impregnation. The results from the oxidative dehydrogenation of ethane show that the two-step impregnated catalyst with Sn first gave lower ethene selectivity compared to the other impregnation procedures. TPR results indicate that this could be due to a weaker interaction between Pt and Sn in the catalyst. The Pt-Sn catalyst was also compared to $LaMnO_3$, another catalyst which has been reported to be active for oxidative dehydrogenation of ethane. In these experiments Pt-Sn was found to give superior performance when H_2 was added to the feed. Pt-Sn was clearly more active towards the oxidation of hydrogen compared to $LaMnO_3$ which was active towards total combustion of hydrocarbons, even when relatively large amounts of hydrogen were present. It seems that ethene is produced mainly in the gas-phase and that the catalyst is important for the oxidation of hydrogen on the surface thus providing heat to the dehydrogenation reactions. However, the results also indicate that there is some ethene production on the Pt-Sn catalyst, either directly or indirectly.

1. Introduction

Ethene is an important intermediate in many chemical processes. Ethene is mainly utilised in the production of bulk polymers (polyethylenes, vinyl chloride), but also a whole range of other chemicals such as ethene oxide and ethylbenzene use ethene as a reactant [1]. The conventional method for the production of ethene is steam cracking and in Western Europe more than 95% of the total ethene production comes from steam crackers [2]. Steam cracking is carried out in large units where the hydrocarbon feed (usually ethane or naphtha), mixed with steam, passes through tubular reactors at high temperatures in a furnace. Heat is supplied by burners on the outside of the tubes. When exposing hydrocarbons to high temperatures there is always a risk of carbon formation and the use of steam as a diluent is necessary.

In 1993, Huff and Schmidt [3] showed that high yields of ethene could be produced from a mixture of ethane and air over a Pt-coated monolith at very short contact times. Later it was discovered that by promoting the Pt-catalyst with Sn [4], and by adding hydrogen to the feed gas [5], the selectivity towards ethene increased significantly, producing ethene yields above 60%. Other catalysts active for oxidative dehydrogenation of ethane (ODE) at short contact times are $LaMnO_3$ [6,7] and Pt-$LaMnO_3$ [8,9]. However, when oxidative dehydrogenation is investigated, some problems need to be considered. The gas mixtures used for oxidative dehydrogenation are highly flammable and the products from total combustion are thermodynamically favoured [10].

The experiments on oxidative dehydrogenation of ethane reported in the present communication are performed at high temperatures, ranging from 550 °C to 980 °C. At these elevated temperatures, some contribution from gas-phase chemistry is expected to occur. Morales and Lunsford [11] and Burch and Crabb [12] found that gas-phase reactions play a major role in the oxidative dehydrogenation of ethane when the temperatures get sufficiently high. Burch and Crabb [12] showed that the non-catalyzed reaction of ODE could be both efficient and selective under optimum conditions, even being able to outperform several ODE catalysts. Using an undiluted mixture of ethane/air with a mole ratio 1:2, ethane conversion of 45% and ethene selectivity of 73.7% were obtained without a catalyst at 600 °C. Later, several groups [5,13–19] have also reported on the large contribution from

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homogeneous reactions in these systems at high temperatures. In fact, some even propose that ethene could be produced entirely by gas-phase dehydrogenation in the presence of Pt/Al_2O_3 [14,16,18,20–23] or $Pt\text{-}Sn/Al_2O_3$ [5,17]. Silberova et al. [24] could find no evidence for ethene formation on the Pt/Al_2O_3 surface below 600 °C, when experiments were compared under steady-state conditions in a conventional microreactor and under transient conditions using a Temporal Analysis of Products (TAP) reactor. There seems to be a general agreement that the main purpose of the catalyst is to increase the rate of the oxidizing reactions and thereby providing heat for the endothermic dehydrogenation. Some of the ethane is therefore used in exothermic reactions, producing CO, CO_2 and H_2O. The main reason for the high ethene selectivities observed in systems where H_2 is introduced into the feed [5,17,25–27] is that H_2 is oxidized at the reactor inlet instead of the hydrocarbons.

In this contribution, the oxidative dehydrogenation of ethane is studied at short contact times over Pt-Sn monoliths. The effect of the gas-phase chemistry, which is already known to be of great importance, is investigated. Catalyst samples are prepared using different impregnation procedures and subsequently tested for ODE. These catalysts are also characterised using Temperature Programmed Reduction (TPR) as well as CO and H_2 volumetric chemisorption. The stability of the $Pt\text{-}Sn/Al_2O_3$ has been tested at different reaction conditions and the catalysts have been compared to another catalyst known to be active for ODE at short contact times, i.e. $LaMnO_3$.

2. Experimental

2.1. Catalyst preparation

Cordierite monoliths with 400 cells/in^2 (Corning) were used as support for the catalysts. The monoliths were cut into cylindrical pieces, 10 mm high and 15 mm in diameter. A 3 mm hole was drilled in axial direction in the middle of each piece to make space for a thermocouple. The monoliths were first impregnated with a washcoat of γ-alumina by dip-coating them in a mixture of water and Disperal P2 (Sasol) and dried at 100 °C for 4 h. This procedure was repeated until the desired weight gain was obtained. Thereafter the monoliths were calcined for 4.5 h at 550 °C. The amount of γ-alumina was typically 15 wt% after calcination.

Pt and Sn were added to the monoliths using wet impregnation. Most samples were made with 1 wt% Pt and 2 wt% Sn, but 0.1 wt% Pt and 0.2 wt% Sn were also used on some samples. The weight percent is given with regard to the whole monolith, which means that the loading with regard to the alumina washcoat is higher (1 wt% Pt on the monolith corresponds to approximately 6.7 wt% Pt on the alumina washcoat). As a first step, Pt was impregnated by using an aqueous solution of $Pt(NH_3)_4(NO_3)_2$. It was subsequently dried for 4 h before it was calcined in a flow of air for 4.5 h at 550 °C. After calcination, Sn was impregnated with an aqueous solution of $SnCl_2$. The impregnated monoliths were then dried overnight at room temperature and calcined in two steps; first at 100 °C for 30 min and then at 700 °C for 90 min. Some Pt-Sn catalysts were also made by changing the order of the impregnation steps (Sn first) and by co-impregnation. The Pt-Sn catalysts were reduced *in situ* prior to experiments in a flow of hydrogen at 600 °C for 30 min.

The γ-alumina washcoated monoliths were also used as support for the $LaMnO_3$-catalysts. The monoliths were first stabilised by 5 wt% La_2O_3 by impregnating them with an aqueous solution of $La(NO_3)_3\cdot 6H_2O$. Then the pieces were impregnated with an equimolar aqueous solution of $La(NO_3)_3\cdot 6H_2O$ and $Mn(CH_3COO)_2\cdot 4H_2O$. Subsequently the monoliths were dried and calcined at 800 °C for 3 h. The latter impregnation was repeated until 30 wt% perovskite relative to the washcoat was obtained.

2.2. Catalyst characterisation

2.2.1. Temperature Programmed Reduction (TPR)

The TPR experiments were performed in a Quantachrome Chembet 3000 set-up. 1 wt% Pt and 2 wt% Sn monoliths were crushed and sieved before 0.3 g of sample was placed in a U-shaped quartz reactor. Prior to reduction, the catalyst was dried for 1 h at 300 °C in a flow of Ar. The calcined sample was then exposed to 7% H_2 in Ar while the temperature was increased by 10 °C/min from room temperature to 900 °C.

2.2.2. Chemisorption and Electron Microscopy

The reduced catalysts were carefully crushed into smaller pieces and studied by volumetric H_2 adsorption at 40 °C and CO adsorption at 35 °C in a standard volumetric glass apparatus (Micromeritics ASAP 2020C). The calcination was performed according to the procedure described under catalyst preparation and the monoliths were thereafter reduced in a flow of hydrogen at 600 °C for 30 min.

Scanning Transmission Electron Microscopy (STEM) and Energy Dispersive Spectroscopy (EDS) were performed using a JEOL 2010F instrument equipped with an Oxford INCA system for EDS. The instrument was operated in dark field scanning mode, using an annular dark field (ADF) detector to acquire images. In this imaging mode, the image intensity increases with both sample thickness and atomic number. This means that particles of Sn and Pt give strong contrast relative to the Al_2O_3 washcoat. EDS analysis was performed with the electron beam dwelling at fixed positions on the sample that were selected from the image. An automatic routine in the acquisition system was used to correct for sample position drift during analysis.

2.3. Apparatus for activity/selectivity measurements

The oxidative dehydrogenation of ethane was studied at atmospheric pressure in the temperature range of 550–980 °C. The ethane flow was kept constant at 308 Nml/min in all experiments. Nitrogen was used as a diluent, and when either the air or the hydrogen flow was varied, this was compensated for by increasing or decreasing the volume of the nitrogen flow. In this way the total flow rate was always kept constant at 2000 Nml/min giving a contact time of 37 ms at ambient conditions (20 °C, 1 atm).

A continuous flow apparatus consisting of a monolithic reactor made of quartz with an inner diameter of 15 mm was used. The experimental set-up has been described previously [22]. The monolith was placed between two cordierite pieces of the same sizes as the catalyst, acting as radiation shields in the axial direction. A movable thermocouple was placed in a quartz tube inside the holes that are drilled through the monoliths making it possible to measure the temperature profiles through the catalyst bed and in the front and back zones of the catalyst. The temperature measured at the outlet of the middle monolith is referred to as the reactor temperature and the furnace temperature was measured between the quartz reactor and the inside of the furnace at the same axial position as the reactor temperature. The furnace temperature was used to control the furnace that heated the reactor. Downstream of the reactor, water was removed by two water-cooled condensers and the dry product gas was analysed by two on-line gas chromatographs (Agilent 6890N and HP 5890).

3. Results and discussion

3.1. Characterisation of the Pt-Sn catalysts

The $Pt\text{-}Sn/Al_2O_3$ catalysts were characterised using Temperature Programmed Reduction (TPR). Fig. 1 shows the TPR results with a heating rate of 10 °C/min. Results from samples