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# NOTE

# Oxidation of Hydrocarbons in an *in Situ* Redox Fluidized Bed Reactor

Mode of contact is an issue of the utmost importance in selective oxidation of hydrocarbons. In particular, when oxygen supplied from the gas phase is used as an oxidant, the reactor design should be aimed to maximize the presence of the type of oxygen which is active and selective for the reaction. A rational approach to this problem entails a previous identification stage, in order to establish whether the presence of gas phase oxygen, oxygen adsorbed on the catalytic surface, or lattice oxygen is to be favored. This often requires the use of transient experiments with isotopic tracing (e.g., (1)).

Once the preferred type of oxygen has been established, the reactor design can be tailored to minimize interference from other types of oxygen. It is often found that the presence of gas phase oxygen in high concentrations favors the formation of deep oxidation products and therefore leads to a decrease in the selectivity to the desired product. There are so far few examples of reactor design that avoid the presence of gas phase oxygen, a necessary reactant that must be transferred to the reaction environment. Among these there are several examples of the use of dense ceramic or metallic membranes (2–4), which gave a good selectivity at the expense of reduced conversions due to the low permeation fluxes involved. If a less strict requirement is used (low concentration of gas phase oxygen instead of absence of gas phase oxygen), then porous membranes can be employed to distribute the oxygen feed to the reactor. These are capable of much higher permeation fluxes and have been used successfully in several oxidation reactions (5–10).

Another possibility to operate with little or no oxygen in the gas phase is to use redox reactors in cyclic operation. In this case, during the reduction stage a reducible metal oxide is contacted with an oxygen-free hydrocarbon stream, yielding oxidation products from reaction with lattice oxygen. The oxide is regenerated with gas phase oxygen after a purge step to remove hydrocarbon species (reactants and products) from the reactor (11–13). The obvious disadvantage with this approach lies in the unsteady catalytic behaviour obtained in this type of redox system, where the catalyst itself is a reactant. To overcome this problem, circulating fluidized bed reactors with continuous catalyst regeneration have been proposed (e.g., (14, 15)). This system also has significant disadvantages related to the need for catalyst recirculation: Large amounts of catalyst must be transferred to and from the regenerator and the slip of oxygen into the reactor and of hydrocarbons into the regenerator cannot be completely avoided.

In this work, a different system has been selected: Instead of circulating the catalyst between reactor and regenerator, two different zones have been created within the same fluidized bed reactor. Such a system was proposed by Hupp and Swift (16) for the oxidative coupling of toluene to stilbene, but the system was not studied. Also, in a previous work, Montgomery *et al.* (17) used a fluidized bed reactor with separate inlets for hydrocarbon and oxygen. Again, only reaction results were provided, and the separation of the oxidation and reduction zones was not studied. An *in situ* redox fluidized bed reactor has the very strong advantage of avoiding catalyst transfer. However, it also presents the problem of attaining a sufficient separation of the oxidation and reduction zones within the same vessel. We present here some results that show that this separation can be effectively achieved, provided that adequate operating conditions are selected. To our knowledge, this is the first work in which the feasibility of separating oxidation and reduction zones in the same reactor under steady-state conditions has been experimentally demonstrated.

The reaction experiments were carried out in a 30-mm-i.d., 25-cm-long quartz fluidized bed reactor, equipped with a quartz distributor plate. A schematic diagram is shown in Fig. 1. Two axial quartz probes were used respectively to introduce the hydrocarbon feed and to take samples at different reactor heights. A He/$O_2$ mixture was fed through the quartz distributor, while the hydrocarbon (methane in this case) entered through one of the quartz probes at a specified height. Both streams were mass flow controlled. The reaction products were analized by on-line mass spectrometry (HIDEN HAL 2/201). On-line gas chromatograpy was sometimes used to check the concentration profiles of the different species obtained by mass spectrometry, and good agreement was found between both methods.

The catalysts to be used in a redox fluidized bed unit would have to be fluidizable, present sufficient attrition resistance, and, most importantly, have enough oxygen carrying capability. The latter was measured in a separate unit, consisting of a 6-mm-i.d. quartz fixed bed reactor, equipped with a set of 4-way and 6-way valves which allowed for pulse

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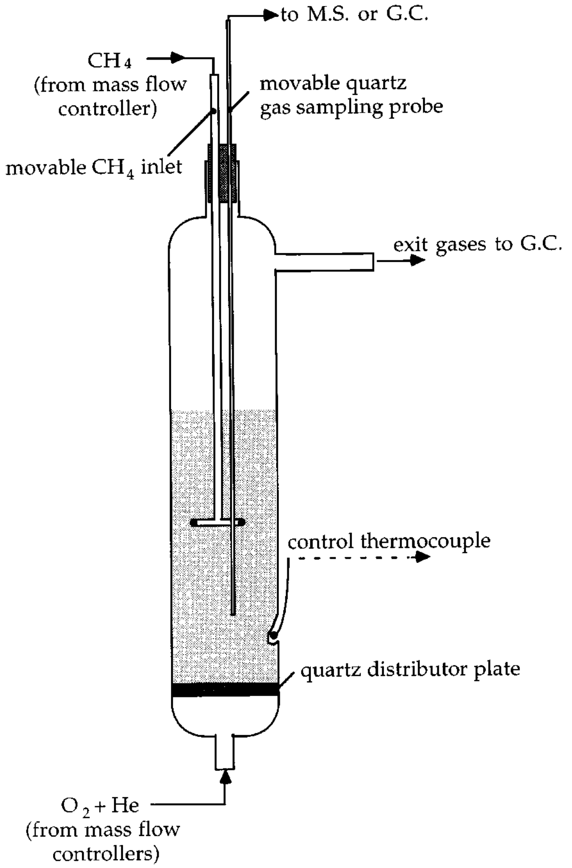

**FIG. 1.** Schematic diagram of the reactor used.

and step experiments to be carried out. Although several catalysts were subjected to preliminary testing, a Mn/P/Si catalyst was selected for the study in view of the characteristics discussed. It was prepared by wet impregnation of 80 g of fluidizable silica with 48.8 g of $Mn(NO_3)_2$ and 5 g of $Na_2P_2O_7$. The catalyst was dried and calcined at 850°C for 10 h, then sieved to a particle size between 100 and 250 $\mu$m. The BET area of the catalyst was between 0.2 and 0.3 $m^2/g$. A catalyst loading of 50–60 g was typically used in the fluidized bed reactor.

The minimum fluidization velocity, $U_{mf}$ (measured in He at 800°C), was 0.9 cm/s. The relative velocity, $U_r$, defined as $U/U_{mf}$, varied between 1.05 and 2.0. In this work, $U$ is defined as the ratio of the actual flows of He plus $O_2$ at the distributor plate (measured at 800°C), to the cross sectional area of the reactor. The proposed reactor concept is based on the solids recirculation that takes place in the bubbling fluidization regime. In the upper part of the bed above the hydrocarbon entrance, the reaction takes place with the lattice oxygen of the catalyst, which becomes reduced. In the region near the distributor plate, the catalyst is reoxidized with the $O_2$/He mixture fed through the distributor plate. Catalyst recirculation times under the conditions used in this work were estimated to be between 0.5 min (for a relative velocity of 2) and 2.5 min (for a relative velocity of 1.2). It should be noticed that the values of the relative velocity reported in this work are nominal values; i.e., they are accurate at the distributor plate, although they change significantly along the bed. In the lower part of the reactor (catalyst reoxidation zone), the gas velocity decreases as oxygen is consumed. Then, at the hydrocarbon inlet, a sudden increase in gas velocity takes place.

Figure 2 shows an example of the experiments carried out to evaluate the oxygen carrying capacity of the Mn/P/Si catalyst. It corresponds to an experiment in which a step change from $N_2$ to He/$O_2$ was effected in the reactor feed over a previously reduced catalyst. The amount of oxygen replenished by the catalyst during the oxidation can be calculated from the area between the curves corresponding to the He and $O_2$ signals. The measured oxygen uptake from the Mn/P/Si catalyst was 0.13 and 0.22 mmol/g of catalyst at 800 and 900°C, respectively. By comparison, a 3%Li/0.3%Sn/MgO catalyst showed a negligible oxygen uptake in the same type of experiment due to the low load of reducible metal. A sufficiently high oxygen exchange capability is desirable since the reaction rate and therefore the conversion are directly related to it. In the reaction experiments reported below using the Mn/P/Si catalyst at 800°C, the measured specific reaction rates were between $3 \times 10^{-5}$ and $10^{-4}$ moles of $CH_4$/(min)($m^2$ of catalyst area).

Figure 3 shows the relative variation along the bed of the mass spectrometer signals corresponding to methane and oxygen. All the experiments were carried out with the methane inlet (indicated by the dotted line in the figure), located 9 cm above the distributor plate. In Fig. 3a it is interesting to note that methane practically dissappears 7 cm above the distributor plate. By the time this takes place, the oxygen signal has dropped to about 80% of its original value. Since under the conditions used in this work, the relative variations of the MS signals were very approximately equivalent to the relative variations of the concentration of the

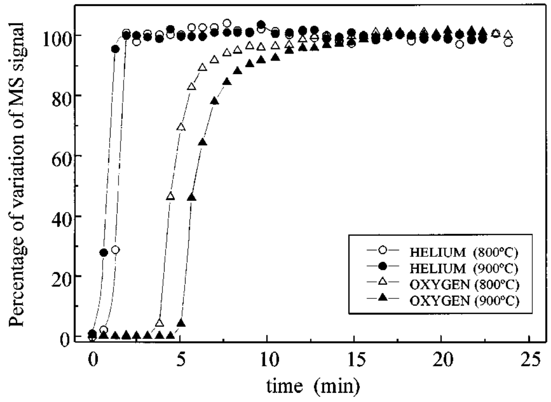

**FIG. 2.** Step experiments ($N_2$ to He/$O_2$) over a reduced Mn/P/Si catalyst at 800 and 900°C, respectively.

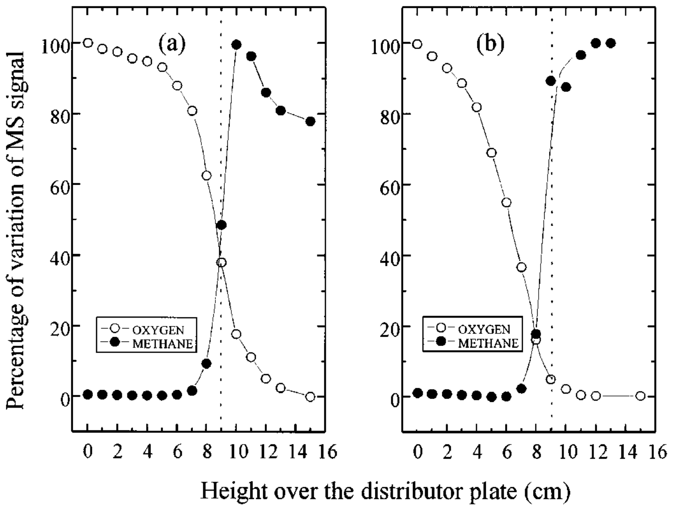

**FIG. 3.** Variation of the relative concentrations of methane and oxygen along the bed at relative velocities of 2.0 (a) and 1.05 (b). Total bed height: 14 cm. Height of $CH_4$ inlet: 9 cm. $T = 800°C$, $CH_4/O_2 = 2$.

different species, this means that a 20% decrease in the oxygen partial pressure has taken place in the absence of gas phase methane. This is due to the oxygen uptake of the reduced catalyst when recirculated to the oxygen-rich reactor entrance. In spite of this, a considerable amount of oxygen still remains in the gas phase, and it can be seen that methane and oxygen coexist in a wide region of the fluidized bed (from about 7 to 14 cm above the distributor plate). One of the reasons for this behaviour is that the bed was operated at a relative velocity of 2, with approximately half of the gas going initially into the bubble phase, which favours the bypass of oxygen. When the same experiment was carried out at a reduced velocity of 1.05 (Fig. 3b), the concentration patterns changed radically: Over 60% of the oxygen feed dissappeared from the gas phase before methane was detected in significant quantities.

The $CH_4/O_2$ ratio is another important variable in determining the separation of the oxidation and reduction zones, as shown in Fig. 4. When a $CH_4/O_2$ ratio equal to 4 was used (Fig. 4a), the catalyst underwent a considerable degree of reduction in the upper part of the bed, and as a consequence, a rapid oxygen uptake ensued when it was recirculated to the fluidized bed entrance (around 80% of the oxygen feed was consumed in the absence of any gas phase methane). This led to a good separation, with methane and oxygen coexisting in the gas phase only in a narrow zone, from 6 to about 8 cm above the distributor plate. On the other hand, when the $CH_4/O_2$ ratio was decreased to 1 (Fig. 4b), the zone of coexistence of methane and oxygen widened considerably, from 6 to 13 cm above the distributor plate.

The region of coexistence of methane and oxygen can also be narrowed by changing the height of introduction of methane. In a separate experiment (not shown), methane was introduced at a height of 5.5 cm, leaving 6.5 cm for

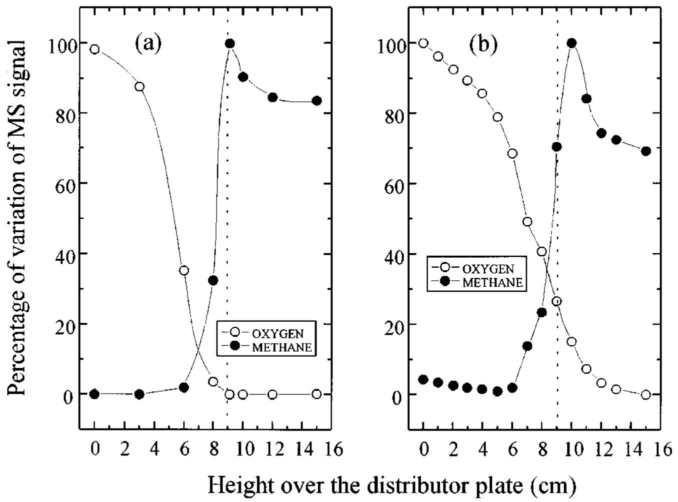

**FIG. 4.** Variation of the relative concentrations of methane and oxygen along the bed at $CH_4/O_2$ ratios of 4.0 (a) and 1.0 (b). Total bed height: 14 cm. Height of $CH_4$ inlet: 9 cm. $T = 800°C$, relative velocity = 1.2. The $CH_4$ flow rate was changed, while the same $O_2$ and He flow rates were kept in both experiments.

catalyst reduction above the inlet point. The result was a less than 3-cm-wide coexistence zone at $U_r = 1.2$ and a $CH_4/O_2$ ratio of 2.

In spite of the good separation obtained between oxidation and reduction zones, the reaction results obtained for the particular process tested in this work (methane oxidative coupling), were poor, as can be observed in Table 1, where the three main operational variables (reactant ratio, relative velocity, and height of methane introduction) have been varied. While almost complete oxygen conversion was achieved except in those experiments where a high relative velocity or a low $CH_4/O_2$ ratio was used, methane conversion and hydrocarbon selectivities remained at modest values. The reason for this behaviour lies in the catalyst used and on the preparation method, which was preferentially aimed at attaining a sufficient oxygen exchange capability rather than a high selectivity in methane oxidative coupling. Figure 5 shows the concentration profiles of the

**TABLE 1**

**Performance of the Redox Fluidized Bed Reactor in Methane Oxidative Coupling**

| $CH_4/O_2$ ratio | $U_r$ | Height of $CH_4$ inlet (cm) | Methane conversion (%) | Oxygen conversion (%) | Hydrocarbon selectivity (%) |
|---|---|---|---|---|---|
| 2.0 | 1.05 | 9 | 35.4 | 99.8 | 27.5 |
| 2.0 | 1.2 | 9 | 32.0 | 99.2 | 29.6 |
| 2.0 | 2.0 | 9 | 40.0 | 93.5 | 29.3 |
| 1.0 | 1.2 | 9 | 72.3 | 89.3 | 12.5 |
| 4.0 | 1.2 | 9 | 14.1 | 99.9 | 27.7 |
| 2.0 | 1.2 | 5.5 | 31.5 | 99.8 | 28.7 |
| 2.0 | 1.2 | 9.5 | 26.9 | 99.8 | 25.1 |

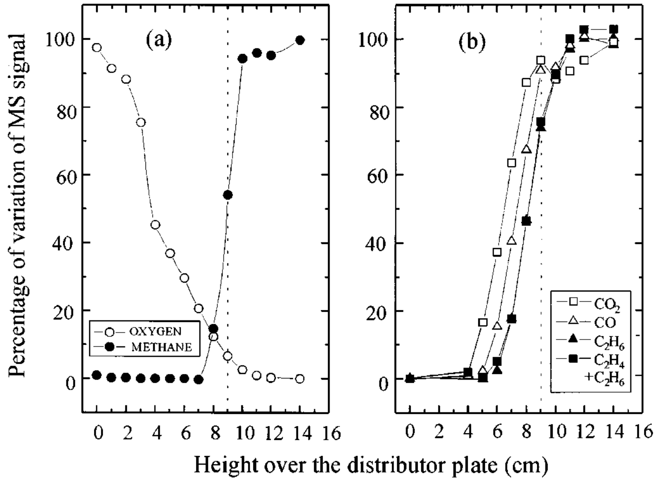

**FIG. 5.** Variation of the relative concentrations of methane and oxygen (a) and of the main reaction products (b) along the bed. $CH_4/O_2 = 2.0$. Total bed height: 14 cm. Height of $CH_4$ inlet: 9 cm. $T = 800^\circ C$, relative velocity = 1.2.

main species along the reactor. It can be observed that, while around 60% of the oxygen is consumed, no reaction products are evolved in the first 4 cm of the reactor. Only after lattice oxygen has been replenished (at least partially) carbon oxides start to appear in the gas phase. Since no methane is present in the gas phase at 4–6 cm height, the initial production of carbon oxides is probably related to hydrocarbon species adsorbed on the catalyst. An alternative explanation would be the formation of coke over the reduced catalyst. However, in separate experiments (not shown), it was observed that coke formation on the catalyst was rather small, even after 5 min under a pure $CH_4$ atmosphere.

The product concentration profiles in Fig. 5 also show that the first evolved product is $CO_2$, followed by CO, and finally by the selective oxidation products ($C_2$ hydrocarbons). This indicates that the fully oxidized catalyst behaves nonselectively and that a certain degree of reduction is needed to increase hydrocarbon selectivity. Given a suitable catalyst, the desired degree of reduction can be achieved by adjusting operating parameters such as the relative gas velocity, the feed rates of hydrocarbon and oxygen, and the height of the hydrocarbon inlet.

The results discussed above show that, by an appropriate choice of operating conditions, redox operation can be attained in a single fluidized bed reactor. The extent to which oxidation and reduction zones are separated is strongly affected by operating conditions such as the relative fluidization velocity, the hydrocarbon to oxygen ratio, the total bed height, and the location of the hydrocarbon inlet. Other important variables such as the redox capacity and the mobility of lattice oxygen, although also affected by the operating conditions, are mainly related to the nature of the catalyst used.

Due to the low selectivity of the catalyts employed the yields obtained in this work for the methane oxidative coupling reaction were relatively modest (the maximum yield was around 13%). However, the results obtained are sufficient to prove the feasibility of the *in situ* redox operation. Current work in our laboratory is aimed to the development and optimization of other catalyst/reaction systems which are suitable for fluidized bed redox operation.

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