Evidence for a high oxygen mobility in Li/MgO

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The oxidative properties of Li/MgO in the absence of O_2 were studied at 730°C using C_2H_4 as a reducing agent and a multisectional flow stainless steel tubular reactor. Large amounts of CO and H_2 were determined. It was demonstrated that Li/MgO exhibited a high oxygen mobility. The exchange capacity was (2.4–4.0) $\times 10^{20}$ oxygen atoms per 1 g of the catalyst and the period of oxygen donation was 150 h or more. After the catalyst reduction, its oxygen transfer ability was fully restored by re-oxidation in the stream of air. Oxidation of C_2H_4 to CO and H_2 was accompanied by its decomposition to C and H_2. The ratio $\Delta H_2/\Delta C_2H_4$ was found to be 1.91 ± 0.13 independently of the oxidation state of the catalyst, the location of the sampling point along the catalyst bed (and the post-catalytic zone) and the duration of the experiment. The mechanism was discussed.

Keywords: lithium; magnesia; oxide reduction; oxygen mobility; ethylene oxidation

1. Introduction

Some uncertainty still exists concerning the extent of mobility and exchangeability of oxygen (adsorbed, surface lattice, bulk lattice) in the catalysts applied for CH_4 oxidative coupling (hereafter referred to as COC), even in the case of Li/MgO, the most studied catalyst system. This catalyst, which belongs to the nonreducible oxides, obviously owes its catalytic activity in COC to some forms of oxygen exchange. It may be attributed, e.g., to the formation of O^- species (Li^+O^- centers being regarded by Lunsford and co-workers [1–3] as responsible for CH_4 activation through H abstraction) and oxygen vacant holes [ ] or oxygen anionic vacancies with a trapped electron [e^-] (resulting from dehydration of surface OH groups), capable of trapping an oxygen atom (formed by O_2 chemisorption) from the surface. Under the usual cofeed mode of operation ($CH_4 + O_2$), the working catalyst is simultaneously in contact with reducing agents (CH_4, C_{2+}, H_2) and with oxidizing (re-oxidizing) agents (O_2, H_2O, etc.). Under steady-state conditions

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occur in parallel oxidative activation of CH_4 and incorporation of oxygen into the catalyst, i.e. re-oxidation (oxidative regeneration) of the active oxygen species on the surface. According to the widely accepted scheme put forward by Lunsford and co-workers [1–3], the primary surface reactions are:

CH_4 activation

$$O^- + CH_4 \rightarrow OH^- + CH_3\cdot ; \tag{1}$$

active sites regeneration (re-oxidation)

$$2OH^- \rightarrow O^{2-} + [\ ] + H_2O \tag{2}$$

$$O^{2-} + [\ ] + \tfrac{1}{2}O_2 \rightarrow 2O^- \tag{3}$$

or

$$2OH^- \rightarrow O^- + [e^-] + H_2O \tag{2'}$$

$$[e^-] + \tfrac{1}{2}O_2 \rightarrow O^- . \tag{3'}$$

The authors do not consider a reaction as (3) to be a single elementary step, but rather a representation of several reactions, such as dissociative chemisorption of O_2, electron transfer, ionic mobility, etc.

Similar schemes were proposed also by other authors. Obviously those workers who suggested a heterolytic rather than homolytic mode of CH_4 activation, proposed alternative schemes.

Detailed schemes of the mechanism usually do not contain any direct indication concerning the contribution of a bulk oxygen. Such suggestions are sometimes included into the more general schemes, as e.g. presented by Dahl et al. [4] who discussed all oxygen exchange possibilities:

$$\begin{array}{ccccc} O_{2(gas)} & \rightleftharpoons & O_{(ads.)} & \rightleftharpoons & O^- \\ & & \uparrow\downarrow & \swarrow\!\!\!\!\!\!\nearrow & \\ & & O_{(bulk^*)} & & \end{array} \tag{4}$$

(*from the lattice or from Li_2CO_3 melt).

Cant et al. [5,6] and Shi et al. [7,3], in their efforts to correlate H/D kinetic isotope effects during COC over Li/MgO at 700°C with the kinetic models, have replaced, for computational purposes, reaction (3) by the reaction

$$O_2 \rightleftharpoons 2O^- . \tag{5}$$

Under certain conditions (a high CH_4/O_2 ratio, N_2O used as an oxidant etc.) reaction (5) could become a rate-limiting step. According to Cant et al. [6], the quantity of O^- predicted to be removed from the catalyst surface by step (–5) is always significantly greater than the quantity removed by reaction (1). Peil et al. [8], using steady-state isotopic transient kinetics, reported that Li/MgO exhibited rapid exchange of lattice oxygen, both in the presence and absence of CH_4, extending up

to 12 monolayers into the subsurface (at 635°C). The measured bulk oxygen diffusion was rapid enough to conclude that a significant amount of subsurface oxygen can readily participate in CH_4 coupling. Mirodatos and Martin [9] observed in a transient experiment that formation of C_2 over Li/MgO continued after the supply O_2 was cut off. Also Sinev et al. [10] and Dahl et al. [11] observed in a pulse reactor that C_2 hydrocarbons were formed from CH_4 over Li/MgO, even in the absence of O_2 (no formation of CO_x was observed by Sinev et al. [10]). On the other hand, Hutchings et al. [12,13] found Li/MgO to be inactive for CH_4 oxidation in the absence of gas-phase O_2 and concluded that lattice O^{2-} may not be involved in CH_4 activation. Ekstrom [14], reviewing the results of isotopic exchange studies which confirmed an exchange between the gas-phase and lattice oxygen atoms and regarding this exchange as a necessary regeneration step of O^- species, has explained on this basis the observation that C_2 formation ceased immediately after termination of the oxygen flow.

Some observations and opinions presented above differ substantially. As a rule, they were based on isotopic exchange or CH_4 coupling studies performed in transient experiments. Additional studies are therefore needed to clarify the issue of the oxidative properties of Li/MgO (exhibited not only with respect to CH_4), of the extent of potential oxygen mobility and of the contribution of a bulk oxygen (from the lattice or from Li_2CO_3 decomposition).

We have decided to study the oxidative properties of Li/MgO in the absence of O_2 by flow experiments, using C_2H_4 and a reducing agent. The choice of this reagent was based on previous observations showing that oxidation of C_2H_4 by O_2 over Li/MgO to CO_x proceeds much faster than oxidative coupling or oxidation of CH_4. The other reason for the choice of C_2H_4 was our special interest in its behaviour and secondary transformations over a catalyst in the course of COC and in the post-catalytic zone (PCZ) [15,16]. Possible detection of the products of C_2H_4 oxidation in the absence of O_2 would provide evidence in support of the view about oxidative ability of Li/MgO, whereas their yields might reflect the extent of oxygen mobility with respect to C_2H_4.

2. Experimental

The experiments were carried out using a flow method in a scaled-up laboratory unit, which contained a tubular multisectional stainless steel (1H18N9T) reactor (32.2 nm i.d., 650 mm long) with 5 stub pipes (3 mm i.d.) welded into its wall at different levels (fig. 1). This way, the products were sampled for analyses from different points along the reactor length, i.e. along the catalyst bed and PCZ. The reactor was electrically heated by five independent coils. It was designed to study either typical COC or a one-step process of CH_4 catalytic conversion to C_2 hydrocarbons with immediate non-catalytic thermal decomposition of the formed C_2H_6 to C_2H_4 in the heated PCZ.

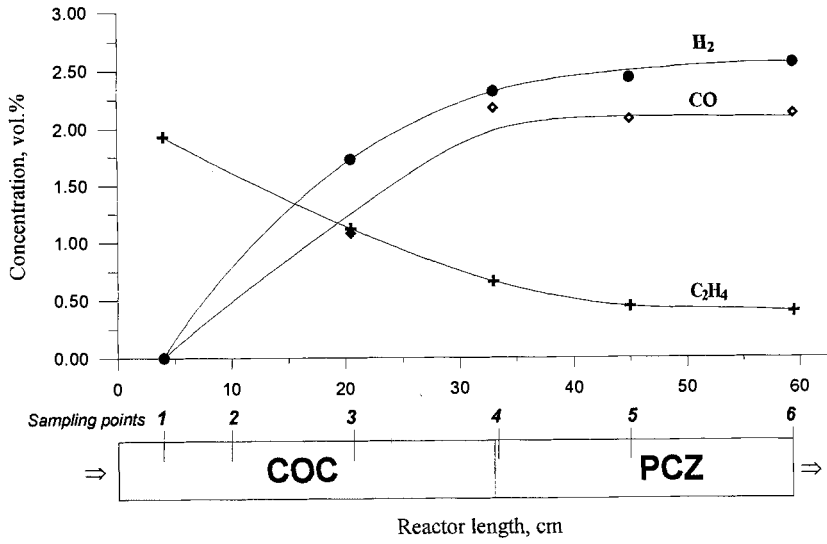

Fig. 1. Variation of the concentrations of C_2H_4 and the major products of its transformation along the reactor length (catalyst: sample after the experiments on CH_4 oxidative coupling; operating conditions: see text).

The catalyst (1% Li/MgO; particle size, 1.0–1.5 mm) was prepared as described previously [17]. The catalyst fixed bed (32.5 cm long; amount of catalyst, 274 cm^3, i.e. 360 g) was placed between the reactor inlet and the sampling point 4, whereas an area between the points 4 and 6 was an empty PCZ (fig. 1).

The composition of the gaseous feed and reaction products was determined by GC analyses.

C_2H_4, polymer grade, >99.9%, was supplied by MZRiP Płock. All other gases were pure or technical grade and were carefully dried before use. Absence of O_2 in the feed was constantly checked.

The sample of Li/MgO used in this study was previously applied in our investigations on COC. Before use in the present series of experiments (and between appropriate runs) the catalyst was heated in situ in the flow of nitrogen, under reaction conditions (see below), until full disappearance of loosely adsorbed O_2.

All experiments on C_2H_4 transformations in the absence of free O_2 were carried out under other operating conditions identical with those applied in parallel by us in investigations on a one-step process of catalytic oxidative CH_4 transformation followed by C_2H_6 pyrolysis (temperature in the catalyst area, 730°C; temperature in PCZ, 840°C; feed flow rate, about 2.74 dm^3 (STP) min^{-1}, corresponding to a GHSV of about 600 h^{-1}; residence time in the catalyst area, about 1.6 s; residence time in PCZ, about 1.2 s). By heating PCZ also in the present study, additional information about the secondary transformation of the products was expected.

The feed was a mixture of C_2H_4 (about 2 vol%) and N_2 (about 98 vol%).

3. Results

In the first set of experiments (figs. 1 and 2) we investigated the catalyst possessing the oxidation level of the COC working catalyst (used directly after the experiments on COC).

Typical curves illustrating the variation of concentrations of the main components of the reaction mixture along the reactor length are presented in fig. 1. As shown, C_2H_4 gradually disappears, mainly in the catalyst area, but also in PCZ. CO and H_2 were found to be major products (with minor amounts of CH_4, traces of C_2H_6, etc.). No CO_2 was detected. CO was generated only in the catalyst area. H_2 was formed mostly in the catalyst area, but also in PCZ. All observations confirmed the occurrence of C_2H_4 oxidation over the catalyst and its thermal decomposition in PCZ.

Fig. 2 presents typical results of the prolonged experiment which lasted over 150 min. It shows the variation of the concentrations of the components in the reactor effluent as a function of time-on-stream. Only negligible gas volume changes were noticed. Oxidation of C_2H_4 was observed during a remarkably long period (CO, though declining with time, was detected until 150 min or more). At the same time, the C_2H_4 concentration was growing and that of H_2 decreasing, until they reached the values representing, perhaps, a non-oxidative C_2H_4 decomposition, occurring mostly in PCZ [16]. The total production of CO was about 0.392 mmol per 1 g of the catalyst, corresponding to 0.196 mmol O_2 g^{-1} or 2.4×10^{20} exchanged oxygen atoms g^{-1}.

An attempt to re-oxidize the catalyst was undertaken next. It was carried out at 730°C with the use of a stream of air. Both CO_2 and CO, formed obviously from a deposit, were detected in the effluent gas. After about 2 h, CO_2 disappeared and the flow of air was continued for another 3 h.

The results of the investigation of the oxidative activity of the re-oxidized sample, which was carried out under identical conditions as before, are given in figs. 3 and 4.

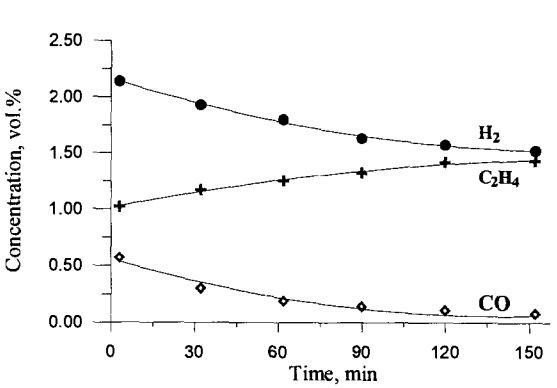

Fig. 2. Variation of the concentrations of C_2H_4 and the major products of its transformation, in the reactor effluent, with time-on-stream (catalyst and operating conditions as in fig. 1).

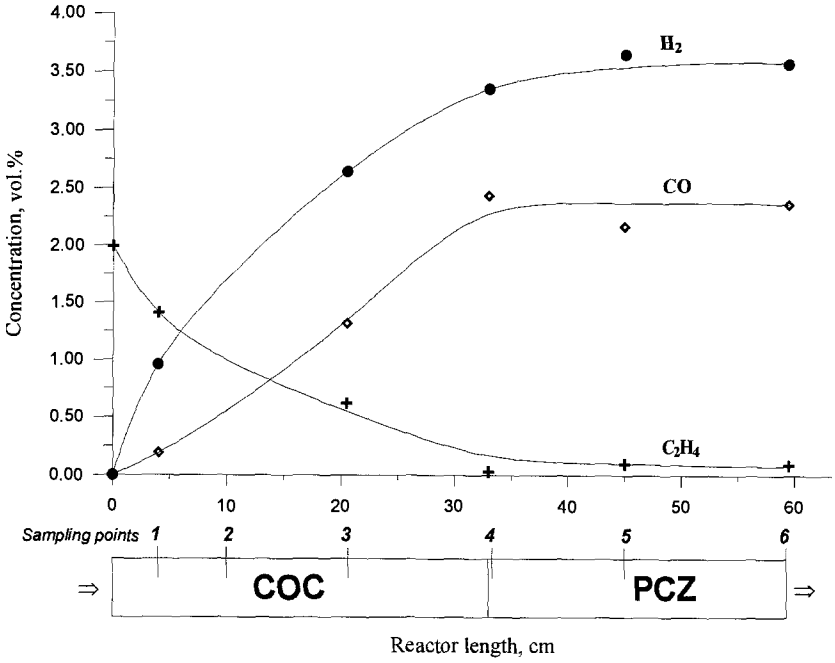

Fig. 3. Variation of the concentrations of C_2H_4 and the major products of its transformation along the reactor length (catalyst: re-oxidized sample; operating conditions: see text).

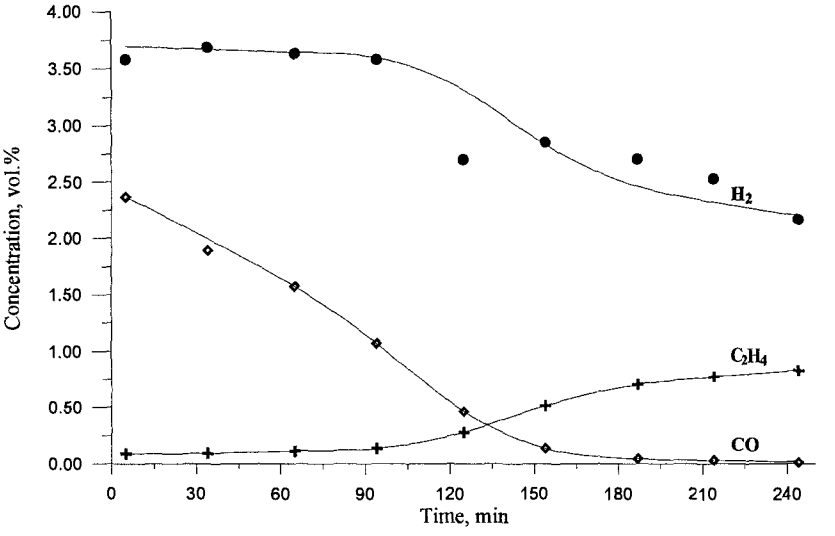

Fig. 4. Variation of the concentrations of C_2H_4 and the major products of its transformation, in the reactor effluent, with time-on-stream (catalyst and operating conditions as in fig. 3).

Fig. 3 shows the concentration changes of C_2H_4, CO and H_2 as observed along the length of the reactor during the first period (1–18 min) after re-oxidation. As demonstrated, the re-oxidation of the catalyst has undoubtedly occurred. The same major products as before (CO and H_2) were formed in the same areas (cf. fig. 1). Concentrations of CO were also similar. This time, almost full conversion of C_2H_4 was observed, perhaps due to a stronger wall effect exerted by metal after a partial removal of a deposit in the course of re-oxidation.

Fig. 4, analogous with fig. 2, presents the variation of the concentrations of the components in the effluent gas as a function of time-on-stream. The CO concentration, at first very high, slowly decreased, until it disappeared after 180 min or more. The amount of C_2H_4, fully converted at the initial period, was slowly rising with CO disappearance (and, perhaps, with a coverage of a deposit on the walls). Simultaneously, the H_2 concentration was slightly decreasing. The total production of CO was about 0.655 mmol per 1 g of the catalyst, corresponding to 0.328 mmol O_2 g^{-1} or 4.0×10^{20} exchanged oxygen atoms g^{-1}.

The results presented in figs. 1–4 revealed that the ratio $\Delta H_2/\Delta C_2H_4$ was always close to 2, independent of the duration of the experiment, the location of the sampling point (catalyst area or PCZ) or the oxidation state of the catalyst (before or after re-oxidation). The average value of this ratio, as calculated from all experimental points given in figs. 1–4, was 1.91 with only negligible scattering (average standard deviation 0.13).

4. Discussion and conclusions

All the results presented above clearly indicate that Li/MgO is potentially capable to exhibit a high oxygen mobility. It may serve, even in the absence of gas-phase O_2, as the supplier of oxygen to strongly reducing agents (such as C_2H_4), showing remarkable exchange capacity and period of donation. After a certain time, the oxygen transfer ability gradually disappears, but it may be fully restored by re-oxidation with the use of air (and, perhaps, of other oxidants as well).

Taking into account our observations showing that (1) CO and H_2 were the only major gaseous products, (2) the ratio $\Delta H_2/\Delta CO$ was always >1, (3) the ratio $\Delta H_2/\Delta C_2H_4$ was always close to 2, (4) the carbon balance always showed a deficit, whereas the hydrogen balance was close to 100%, a general scheme can be presented with two parallel pathways of C_2H_4 transformation, its oxidation and decomposition:

$$C_2H_4 + \text{catalyst (oxidized)} \rightarrow 2CO + 2H_2 + \text{catalyst (reduced)} \quad (6)$$

$$C_2H_4 \rightarrow 2C + 2H_2 . \quad (7)$$

Reaction (6) dominates over (7) on the oxidized form of Li/MgO. Reaction (7) increasingly contributes in the course of catalyst reduction and, of course, dominates in PCZ (especially in heated PCZ).

Based on good hydrogen balances and on the observation that $\Delta H_2/\Delta C_2H_4$ is close to 2, one can deduce that H_2O, if formed, is next transformed (by reactions with a coke, hydrocarbon, etc.), becoming only a minor component of the final product (cf. an absence of H_2O observed by Sinev et al. [10] in their study with CH_4). Absence of CO_2 would indicate that under oxygen-free conditions, no oxidation of CO to CO_2 occurs on the catalyst.

Re-oxidation of the catalyst by O_2 could be represented as

$$\text{catalyst (reduced)} + O_2 \rightarrow \text{catalyst (oxidized)}. \tag{8}$$

The mechanisms of the catalyst reduction (reaction (6)) and re-oxidation (reaction (8)) could only be speculated. During the catalyst reduction, under the applied conditions, the partial pressure of O_2 should be close to zero and the equilibrium of such reactions as (5), (3) and (3′) should be shifted to the left. Oxidation of C_2H_4 may, therefore, proceed either directly by O^- on the surface via O (or O_2) on the surface or in a gas phase:

$$O^- \begin{cases} \rightarrow O(\tfrac{1}{2}O_2) + [e^-] \\ \xrightarrow{C_2H_4} CO \text{ etc.} \\ \xrightarrow{C_2H_4} CO, \text{etc.} + [e^+] \end{cases} \tag{9}$$

The relatively high magnitude and long duration of the oxidative effect may imply that also O^{2-} ions contribute to C_2H_4 oxidation e.g. by the following reaction:

$$O^{2-} \rightarrow O^- + [e^-] \tag{10}$$

followed by reactions (9).

The effective diffusion of a bulk oxygen to the surface appears to be plausible and the contribution of some special forms of a bulk oxygen, e.g. connected with the presence of Li_2CO_3, etc. cannot be excluded from consideration.

The mechanism of the re-oxidation operation (8) may be identical with the re-oxidation component of the cofeed COC process, i.e. involving such reactions as (3), (3′), globally (5), or similar.

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