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High selectivity of oxidative dehydrogenation of ethane to ethylene in an oxygen permeable membrane reactor†

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An oxygen permeable membrane based on $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ is used to supply lattice oxide continuously for oxidative dehydrogenation of ethane to ethylene with selectivity as high as 90% at 650 °C.

Selective oxidation of alkanes to corresponding olefins and oxygenates is an important catalytic process. One of challenges for the process is how to achieve a high selectivity for the aimed products, *i.e.*, olefins and oxygenates, because they are usually more reactive than the raw materials, *i.e.*, alkanes, and are easier to deeply oxidize to CO_x by O_2. One way to overcome these difficulties is to use lattice oxide (O^{2-}) as oxidant, such as in a periodic shift reactor, which has been used in the ammoxidation of propylene to acrylonitrile[1] and of metaxylene to isophthalonitrile.[2] In this way, a high selectivity of the target product was achieved due to the utilization of lattice oxide (O^{2-}). However, these processes can only be operated periodically.

In this paper, we will exploit the possibility to continuously supply lattice oxide (O^{2-}) to control the oxidative dehydrogenation of ethane to ethylene (ODE) by using an oxygen permeable membrane reactor (OPMR).[3–5] The primary idea is shown in Fig. 1 which shows that molecular oxygen accepts electrons on one surface of the membrane to form O^{2-} which is then transported through the bulk of the membrane to another surface and reacts with ethane before recombination to molecular oxygen. Local charge neutrality is maintained by the joint diffusion of oxygen vacancies ($V_O^{\cdot\cdot}$) and electrons (e) or electron holes ($h^{\cdot}$). The fact that no gaseous O_2 is detected in the reaction side with the presence of ethane indicates that the rate of the reaction between the lattice oxide and ethane is much faster than the rate of lattice oxide recombining into O_2. Therefore, the mechanism of reaction on the reaction side is $C_2H_6 + O^{2-} \rightleftharpoons C_2H_4 + H_2O + 2e$. As a result, lattice oxide converted from molecular oxygen by OPMR will be continuously supplied to the reaction system, and the selectivity of the oxidation reaction can be controlled at a very high level.

In this work, we constructed an OPMR reactor as shown in Fig. 2(a). The material of oxygen permeable membrane as well as catalyst used here is $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (here δ is the oxygen non-stoichiometry, $0 < \delta < 1$) with the preparation method newly developed in our laboratory.[6,7,8] As sketched in Fig. 2(a), air was fed to the air side and ethane (diluted with ~90% He) was allowed to flow through the reaction side where ethane reacted with the permeated oxygen through the OPMR at 650 °C to produce ethylene. The products were analyzed for all species by a two-column GC (Agilent 6890). The reaction results are reported in Table 1. These results were repeated several times with reproducibility within a few percent and no significant changes occurred during several hours of operation. It was surprising that more than 90% selectivity to ethylene was obtained at an ethane conversion of 18% in the OPMR reactor. The oxygen permeation flux was 0.36 ml min^{-1} cm^{-2}. As indicated in our mechanism of reaction in the OPMR, we attributed the high selectivity of ethylene to the fast reaction between ethane and O^{2-}. To verify this speculation, we designed a periodic operation mode using the membrane tube as a catalyst, as shown in Fig. 2(b). In this experiment, nitrogen instead of air was fed to the air side. O_2 and ethane diluted with helium were fed to reaction side alternately. When O_2 was fed to reaction side, the lattice oxide (O^{2-}) can be formed in the membrane oxide by the reactions: $O_2(g) \leftrightarrow O_2(ads) \leftrightarrow 2O^{2-}(s)$.[9] In order to sweep out the gaseous oxygen ($O_2(g)$) and adsorbed oxygen ($O_2(ads)$) on the membrane surface the reaction side was purged with helium before the ethane was introduced into the line. When ethane diluted with helium was supplied to the reaction side, ethane directly reacted with the lattice oxide (O^{2-}) of the membrane oxides. Since the reaction

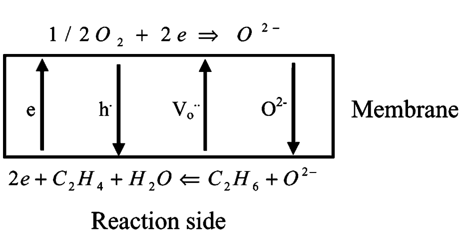

Fig. 1 Mechanism of oxidative dehydrogenation of ethane to ethylene in an oxygen permeable membrane reactor.

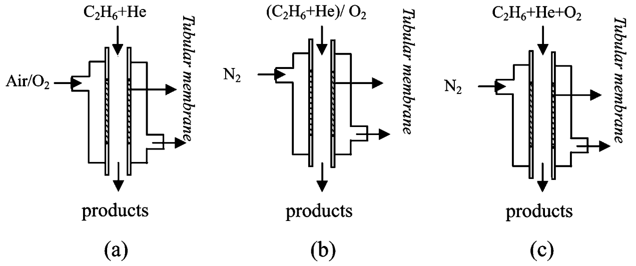

Fig. 2 (a)–(c) Comparative study of oxidative dehydrogenation of ethane in different operation modes. (a) Membrane mode; (b) meriodic mode (O_2 and ethane diluted with helium were fed to reaction side alternately); (c) co-feed mode.

Table 1 Typical results of oxidative dehydrogenation of ethane to ethylene at 650 °C in different operation modes. A feed of 6.1 ml min^{-1} ethane and 53.9 ml min^{-1} helium was applied to the reaction side. In the co-feed mode, 0.91 ml min^{-1} O_2 was also applied to the reaction side.

		Product selectivity (%)			
Operation mode	C_2H_6 conv. (%)	C_2H_4	CH_4	CO	CO_2
Membrane mode (air to air side)	18.0	90.6	3.50	2.20	3.73
Membrane mode (O_2 to air side)	23.0	90.2	3.77	2.10	3.98
Periodic mode	3.40	91.0	4.53	3.32	1.14
Co-feed mode	15.8	57.6	1.55	0.62	40.2

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b2/b203168j/

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between ethane and O^{2-} was transient in this mode the measurements were made before O^{2-} was completely consumed. The ethylene selectivity in this mode was 91.0%, which is very similar to that in the OPMR, as shown in Table 1. The similarity in the selectivity between the two modes strongly suggests that our mechanism of reaction in the OPMR is correct. In order to elucidate the role of gas phase O_2 in the ODE, we also carried out the reaction of ODE in a co-feed operation mode with a catalyst of the membrane tube, as shown in Fig. 2(c). In this experiment, nitrogen was also fed to the air side while the oxygen (0.91 ml min^{-1}) equal to the oxygen permeation flux of the membrane under reaction condition and ethane were co-fed to the reaction side. As shown in Table 1, only 57.6% selectivity of ethylene was obtained in this mode, indicating that molecular oxygen is responsible for the deep oxidation of ethane to CO_x. Based on the comparative results, we can state that the high ethylene selectivity for ODE in the OPMR is due to the lattice oxide supplied by the oxygen permeable membrane.

Ethane conversion should be similar to that in periodic operation mode and decrease gradually with time if the lattice oxide consumed for ODE in the OPMR are only those incorporated in the membrane oxides. However, ethane conversion (18.0%) is much higher than that in periodic operation mode (only 3.40%) as shown in Table 1, and was kept steady level all the time during 2 h experiments. This indicated that the lattice oxide for ODE in the OPMR is supplied continuously through the membrane, rather than those incorporated in the membrane oxides. This speculation can also be indirectly proved by the following experiment. When pure O_2 instead of air was fed to the air side of the OPMR, the ethane conversion increased from 18.0 to 23.0% while the ethylene selectivity was almost the same (90%), as shown in Table 1. The oxygen permeation flux reached 0.52 ml min^{-1} cm^{-2}. This indicates more lattice oxide transport to the reaction side from the air side through the membrane tube when the oxygen partial pressure in the air side increased from 0.21 atm (air) to 1.0 atm (pure oxygen). A blank experiment using a quartz tube instead of the BSCFO tubular membrane showed that the ethane conversion is $< 0.5\%$ at 650 °C.

Based on the above results we can conclude that the higher ethylene selectivity for ODE in the OPMR is due to utilization of lattice oxide, which can be supplied continuously from the air side by the oxygen permeable membrane. The novel approach could be applied to supply lattice oxide for a wider range of selective oxidation reactions.

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