Oxidative coupling of methane over NbO (p-type) and Nb_2O_5 (n-type) semiconductor materials

Yesim Erarslanoglu, Isik Onal [1], Timur Dogu
Department of Chemical Engineering, Middle East Technical University, Ankara, Turkey

and

Selim Senkan
Department of Chemical Engineering, University of California, Los Angeles, CA 90095, USA

Received 13 August 1995; accepted 13 January 1996

Oxidative coupling of methane to higher hydrocarbons was investigated using two types of semiconductor catalysts, NbO (p-type) and Nb_2O_5 (n-type) at 1 atm pressure. The ratio of methane partial pressure to oxygen partial pressure was changed from 2 to 112 and the temperature was kept at 1023 K in the experiments conducted in a cofeed mode. The results indicated a strong correlation between C_{2+} selectivity performance and the electronic properties of the catalyst in terms of p- vs. n-type conductivity. The p-type semiconductor catalyst, NbO, had a larger selectivity (e.g. 95.92%) over the n-type Nb_2O_5 catalyst (23.08%) both at the same methane conversion of 0.64%. Catalyst characterization via X-ray diffraction, TGA and reaction studies indicated that NbO was transformed to Nb_2O_5 during the course of the reaction which limits catalyst life.

Keywords: methane oxidative coupling; semiconductor-type catalysts; n-type and p-type semiconductors; Nb_2O_5; NbO

1. Introduction

Methane is the most abundant component of natural gas, usually containing over 90 mol% of the hydrocarbon fraction, and represents a possible raw material for the synthesis of more valuable products such as ethylene. However, the high molecular stability of methane compared to other aliphatics makes its use difficult, and no significant amount of ethylene is produced commercially from methane today.

Extensive studies have been conducted on the oxidative coupling of methane (OCM) since the works of Keller and Bhasin [1] and of Hinsen and Baerns [2,3]. Work by Ito et al. [4] showed that lithium-doped magnesium oxide has high activity for converting methane to C_{2+} compounds in the presence of O_2. Sofranko et al. [5] reported the use of reducible metal oxides as catalysts for the oxidative conversion of methane to heavier hydrocarbons. Recently, several authors such as Lee and Oyama [6], Dubois and Cameron [7], Amenomiya et al. [8] and Hutchings et al. [9] published review articles on oxidative coupling of methane.

Correlations between n- and p-type conductivity, on one hand, and selectivity and activity of oxidation reactions, on the other hand, have been extensively investigated and discussed by Gamer [10] and Morooka and Ozaki [11]. For the OCM reaction, however, the importance of p-type conductivity of a catalyst has been emphasized only by few researchers. Dubois and Cameron [7] showed that the most selective OCM catalysts are p-type semiconductors under OCM reaction conditions. Norby and Anderson [12] and Anderson and Norby [13] studied the electrical conductivity of a sintered sample of Li/MgO which is a highly active and selective OCM catalyst. Their studies at various temperatures (< 1500 K) and oxygen partial pressures led to the conclusion that electrical conductivity of the Li/MgO catalyst at near-atmospheric oxygen pressures and at high temperatures is mainly of the p-type electronic bulk conductivity. The p-type conductivity was ascribed to the replacement of Mg^{2+} ions by Li^{+} ions to form negative defects [12,13].

In the light of these studies, the aim of the present study was to investigate the correlation between C_{2+} selectivity performance and the electronic properties of two catalyst types, NbO and Nb_2O_5, in the OCM reaction. These two oxides behave as p-type and n-type semiconductors, respectively, under the temperature and oxygen partial pressure range of OCM reaction [14].

2. Experimental

The reactor set-up was a conventional gas flowing

---

[1] Present address: Chemical Engineering Department, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, CA 90095, USA.

system where high purity methane and oxygen reactants were cofed with a high purity helium carrier gas over the catalysts. The fixed bed reactor was a 5.08 mm i.d. quartz tube that was bent into a U-shape and was placed inside a temperature controlled furnace. Quartz wool was placed as a preheater material in the inlet section of the reactor. The catalyst was placed in powder form (100 mesh and approximately 0.5 g) very close to the outlet of the reactor in order to rapidly quench the reaction products and to minimize gas phase combustion reactions. Reactor temperature was monitored using a ceramic-lined Ni–Cr–Ni type thermocouple located just outside the catalyst bed. Reactor effluent gases were analyzed using a gas chromatograph equipped with a thermal conductivity detector. A CTR-I column (Alltech) was used to separate the gases. The inner section of the CTR-I column was 6 ft × 1/8 inch with Porapak Q packing. The outer column was 6 ft × 1/4 inch and packed with activated molecular sieve for the separation of O_2, CO and CO_2. In all experiments GHSV, total pressure and the catalyst bed temperature were kept constant at 6115 h^{-1} (inlet conditions), 101.3 kPa and 1023 K, respectively. Oxygen partial pressure was changed as a parameter between 0.66 and 25.3 kPa while methane partial pressure was kept at about 70 kPa in most of the experiments. Helium was used as the inert diluent. He concentration was changed to compensate changes in O_2 levels to establish the desired composition and flow rate of the reactor inlet stream.

3. Results and discussion

First, experiments were made with the Nb_2O_5 catalyst (white crystalline powder) to establish its conversion, selectivity, and activity. Based on the maximum reaction time of about 250 min considered in these experiments the activity of this catalyst did not show any variation (see discussion below). Experiments were then carried out using the NbO catalyst which is a black crystalline powder. Conversion of methane showed an increasing trend from about 3.1 to 7.0% within the time interval of 250 min for the P_{CH_4}/P_{O_2} ratio of 13, as shown in fig. 1. The selectivity for C_2H_4 remained nearly constant at 32% throughout the experiments. On the other hand, C_2H_6 and C_{2+} selectivities showed decreasing trends in the same time interval. The C_{2+} selectivity decreased from 57.6 to about 39.1% and C_2H_6 selectivity decreased from 24.1 to 8.5%.

An important observable associated with the experiments was the color of the NbO catalyst. The color of NbO powder originally was black, but gradually changed during the reaction and became gray with a distribution of color from white to black within the bed in the direction of flow. In the experiments carried out with relatively high P_{CH_4}/P_{O_2} ratios (i.e., 13, 25 and 40), this color change in the bed was more abrupt. The upstream portion (gas inlet) of the bed became white while the downstream section remained black. The X-ray diffraction analysis of the catalyst bed showed that the white portion has the crystal structure of Nb_2O_5, whereas the black portion, which was the downstream part of the bed, did not change its crystal structure and was still mostly NbO. Evidently, NbO became oxidized and changed its crystal structure to Nb_2O_5 during the course of the experiments. During the reaction, a significant amount of oxygen was adsorbed on the catalyst surface and used up in the formation of ethane molecules. Clearly, some fraction of this adsorbed oxygen would be used for the oxidation of NbO to Nb_2O_5. Since oxygen was the limiting reactant, its concentration along the reactor would decrease, and the amount left at the downstream section of the reactor would not be enough for the conversion of all NbO to Nb_2O_5. The color profile along the catalyst bed, as observed at the end of the experiments, supports this argument.

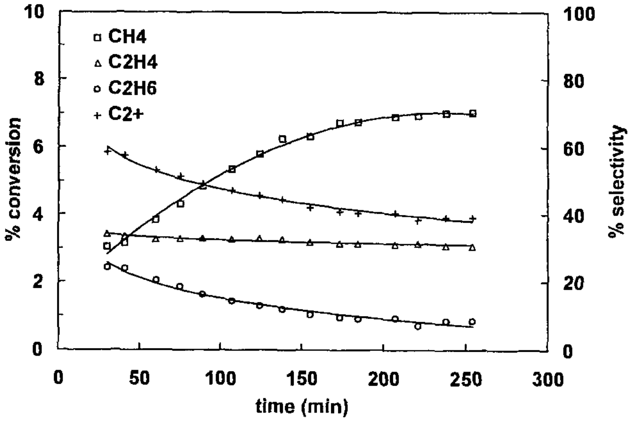

Fig. 1. Change in % CH_4 conversion and % selectivity with respect to reaction time with NbO catalyst. ($P_{CH_4}/P_{O_2} = 13$, $T = 1023$ K, $P_{tot} = 101.3$ kPa, $P_{CH_4} = 67.1$ kPa, GSV = 36.4 $cm^3/(min\ g\text{-}cat)$).

Thermogravimetric analysis (TGA) of oxidation of NbO to Nb_2O_5 conducted in our laboratory indicated a sudden weight increase of about 22% at around 525°C. This weight increase is consistent with the formation of Nb_2O_5 from NbO. The TGA results also suggest that, at the temperature of the OCM reaction, the oxidation of NbO to Nb_2O_5 should be expected in the presence of oxygen, which was supported by the X-ray diffraction studies and oxygen conversion calculations. These results are also consistent with the observed decrease in selectivity in fig. 1 due to lower selectivity of the Nb_2O_5 catalyst as discussed below. The oxidative coupling experiments were also repeated with NbO catalyst at low P_{CH_4}/P_{O_2} ratios, e.g. 2. In these cases ethane conversions were high, but selectivities were small and large amounts of CO were detected in the products. In addition, no significant variations in conversion and selectivity were observed with time.

Percent CH_4 conversion vs. percent C_{2+} selectivity results for the OCM reaction using NbO and Nb_2O_5 catalysts are plotted in fig. 2. The data points in this figure correspond to different P_{CH_4}/P_{O_2} ratios and total reaction times of about 40 min for the case of NbO catalyst. If C_{2+} selectivity values for the two catalysts are compared at a constant methane conversion, the p-type semiconductor catalyst, NbO, clearly has a large selectivity advantage (e.g., 66.27 vs. 27.59% C_{2+} selectivity at 2.26% methane conversion and 95.92 vs. 23.08% C_{2+} selectivity at 0.64% methane conversion) over the n-type catalyst.

If the electronic theory of catalysis in the context of a rigid band model originally proposed by Hauffe [15], and further expanded by Morrison [16] and Volkenstein [17], is considered for the OCM, then the concept of generation of free-radicals in a Rideal-type mechanism is consistent with the donor property of p-type semiconductors with adsorbed oxygen creating anionic vacancies in the lattice. Assuming that the OCM reaction follows in general a Rideal-type mechanism, as suggested by Lunsford [18], in which methane reacts but does not adsorb (or weakly adsorb) onto the metal oxide surface, methyl radicals are released and the resulting hydrogen atom is adsorbed. In the absence of gas phase oxygen (or another oxidizing gas), this process will most readily take place on an n-type semiconducting oxide. However, the presence of gas phase oxygen and a p-type oxide will generate chemisorbed anionic oxygen species. A direct conclusion from this discussion is that, as long as the adsorbed oxygen is not in its fully reduced state (i.e., O^{2-}), it has the potential to accept electrons from the adsorbing hydrogen atom and thus generate methyl radicals [7].

Oxygen in the formal −1 oxidation state is an attractive possibility for an active site in OCM reaction since the unoccupied ionic surface states O^- are essentially radicals, and are expected to react strongly to form covalent bonds with impinging gas molecules. One expects a strong bond to a hydrogen atom, extracted from an incoming hydrocarbon molecule such as methane, to form an OH^- group as postulated in the kinetic mechanism of Lunsford [18]. Depending on whether the solid is p-type or n-type, more or less O^- can be expected at equilibrium. The ionic surface associated with anions will often be in the band gap, so statistics demands that a finite density

$$[O^-] = [O^{2-}]\exp[-(E_F - E_t)/kT] \qquad (1)$$

of O^- be present, where $[O^{2-}]$ is the concentration of lattice oxide ions at the surface (a half monolayer or so), E_F is the Fermi energy level and E_t is the energy level of the ionic state [16]. For a p-type oxide, E_F is near the valence band and hence near E_t. The converse is true for an n-type oxide. Thus, if the −1 oxidation is required to provide the active oxygen species, then a correlation concerning the OCM activity between p-type and n-type semiconductors immediately suggests itself. For to a first approximation, the Fermi energy level will be higher going from p-type to insulating, to n-type oxides. Then, from eq. (1), neglecting surface barrier effects, i.e. the density of the surface states, the concentration of O^- will decrease in that order.

Since it is very difficult to detect oxygen radicals under reaction conditions by conventional techniques such as EPR, it is only possible to make indirect conclusions from the literature as to the nature of oxygen species which depends on the n- or p-type characteristics of the oxide material under reaction conditions.

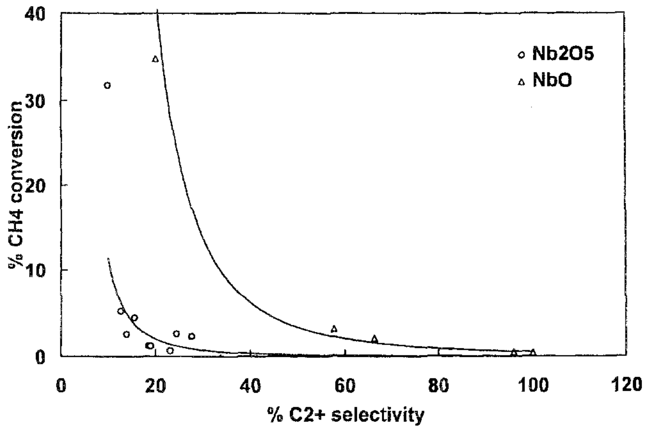

Fig. 2. % CH_4 conversion vs. % C_{2+} selectivity for constant reaction temperature of 1023 K.

Acknowledgement

The authors wish to thank Scientific and Technical Research Council of Turkey (TUBITAK Project No. MAG-965), NATO (Collaborative Research with Professor John B. Butt of Northwestern University, Grant 870762) and the University of California, Los Angeles for financial support.

References

[1] G.E. Keller and M.M. Bhasin, J.Catal. 73 (1982) 9.
[2] W. Hinsen and M. Baerns, Chem. Ztg. 107 (1983) 223.
[3] W. Hinsen, W. Bytyn and M. Baerns, in: *Proc. 8th Int. Congr. on Catalysis*, Berlin 1984, Vol. 3 (Verlag Chemie, Weinheim, 1984) p. 581.
[4] T. Ito, J.X. Wang, C.H. Lin and J.H. Lunsford, J. Am. Chem. Soc. 107 (1985) 5062.
[5] J.A. Sofranko, J.J. Leonard and C.A. Jones, J. Catal. 103 (1987) 302.
[6] J.S. Lee and S.T. Oyama, Catal. Rev. Sci. Eng. 32 (1988) 249.
[7] J.L. Dubois and C.J. Cameron, Appl. Catal. 67 (1990) 49.
[8] Y. Amenomiya, V.I. Birss, M. Goledzinowski, J. Galuszka and A.R. Sanger, Catal. Rev. Sci. Eng. 32 (1990) 163.
[9] G.J. Hutchings, M.S. Scurrel and J.R. Woodhouse, Appl. Catal. 38 (1988) 157.
[10] W.E. Garner, ed., *Chemistry of the Solid State* (Academic Press, New York, 1955).
[11] Y. Moorooka and A. Ozaki, J. Catal. 5 (1966) 116.

[12] T. Norby and A.G. Anderson, Appl. Catal. 71 (1990) 89.
[13] A.G. Anderson and T. Norby, Catal. Today 6 (1990) 575.
[14] P. Kofstad, *Nonstoichiometry, Diffusion and Electrical Conductivity in Binary Metal Oxides* (Wiley–Interscience, New York, 1972).
[15] K. Hauffe, Adv. Catal. 87 (1957) 187.
[16] S.R. Morrison, in: *The Chemical Physics of Surfaces* (Plenum Press, New York, 1977) ch. 7.
[17] T. Volkenstein, *Electronic Processes on Semiconductor Surface During Chemisorption* (Consultants Bureau, 1991).
[18] J.H. Lunsford, in: *Natural Gas Conversion*, eds. A. Holmen, K.J. Jens and S. Kolboe (Elsevier, Amsterdam, 1991).