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NOTES

Methane Synthesis over Transition Metal Electrodes in a Solid State Ionic Cell

INTRODUCTION

Predominantly oxide ion conduction in heavily doped ZrO_2 at elevated temperatures has enabled its wide use as a solid electrolyte in passive devices such as oxygen sensors.

The "active," as distinct from passive, use of such a solid state electrochemical cell involves controlling and/or changing the oxygen activity on one side of the electrolyte with respect to a fixed reference oxygen activity on the other side via an externally applied voltage drop across the cell. Earlier work in this laboratory has shown that this technique can increase the rate of NO decomposition by orders of magnitude (*1*). A similar approach has been applied to the oxidation of NH_3 (*2*) and ethylene (*3*). More recently, it has been shown in this laboratory that both the CO_2 and CO methanation rates on Ni electrodes can be enhanced significantly (*4*).

The present Note provides a brief report of some experiments that demonstrate the use of this solid state ionic technique for the synthesis of methane from H_2 and CO over Fe, Ni, and CO electrodes. The methane synthesis reaction has been extensively studied (*5, 6*) and most of the reported rate expressions are of the general form

$$r_{CH_4} = A \exp(-E/RT)(P_{H_2})^x (P_{CO})^{-y}. \quad (1)$$

The commonly observed inverse dependence of the methanation rate on the partial pressure of CO implies that the reaction is inhibited by this species when using transition metals as catalysts under normal conditions. However, recent work (*7*) has shown that by applying a voltage drop across an underlying solid electrolyte, one should be able to "actively" alter the oxygen activity on the catalyst surface to sufficiently low values that the adsorbed CO becomes thermodynamically unstable and readily dissociates.

EXPERIMENTAL ASPECTS

Research purity CO and H_2 gasses were used for preparing synthesis gas mixtures with H_2/CO ratios of 2 and 3 by pressure mixing. This synthesis gas was diluted with He such that the partial pressure range for H_2 and CO was 0.02–0.15 and 0.01–0.05 atm, respectively. Gas analyses of the reactants and products were carried out using a Varian Aerograph Model 142010 gas chromatograph featuring a Chromosorb-106 column.

The schematic design and description of the electrochemical reactor have been given elsewhere (*7*). It consisted of a one-end-closed yttria-stabilized zirconia (YSZ) tube enclosed in a quartz jacket in a furnace such that the open end of the tube is exposed to ambient air. The electrodes were deposited on the inside and the outside of the closed end of the zirconia tube. The inner, i.e., reference air, electrode was made from Pt paste (Hanovia, No. 6926). The outer, i.e., synthesis gas side, electrodes were made of Ni, Co, and Fe deposited from a paste of the individual powders in a viscous organic vehicle. The geometric areas of the outer electrodes were about 10 cm^2.

RESULTS

The effect of controlling the oxygen activity on the rate of CO hydrogenation on

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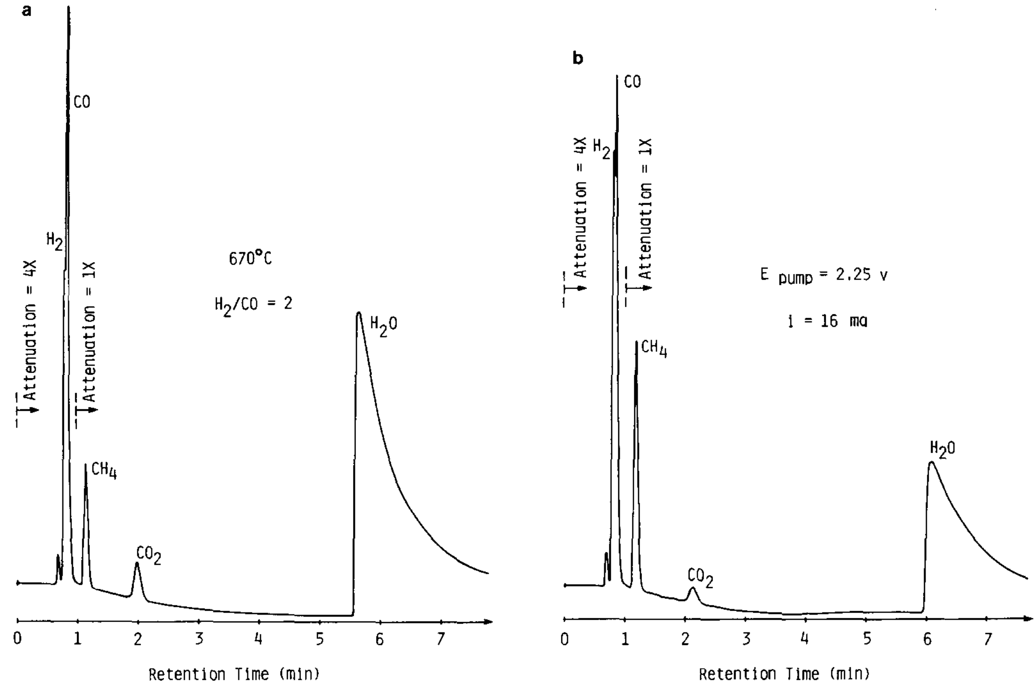

FIG. 1. Gas chromatograms of the product gases under (a) open circuit and (b) dc biased conditions on Ni electrodes.

Ni electrodes is illustrated in Fig. 1, where gas chromatograms of the product gases are given for two cases. Figure 1a is indicative of the intrinsic catalytic rate observed under open circuit conditions. Figure 1b illustrates the situation when an external voltage drop of 2.25 V was imposed across the cell such that the air side electrode was positive. Similar behavior was also observed for Co and Fe electrodes. The concentration of methane in the product gases was always higher for the dc biased cases than for the open circuit experiments.

Due to the severe tailing of the H_2O peak and the poor resolution of the CO peak, quantitative evaluation of the kinetic rate expression parameters for the synthesis reaction was not possible in this brief study. For the same reasons, an oxygen mass balance could not be made on the system. The rate of hydrogenation was obtained from the rate of formation of methane, as analyzed by gas chromatography. The specific surface areas of the transition metal electrodes were difficult to measure accurately. The methanation rates under otherwise identical open circuit (i.e., intrinsic) and dc biased conditions are presented in Table 1 in terms of moles of CH_4 formed per second. The rates under dc bias conditions were calculated from the methane concentrations at the highest applied voltage. It is recognized that the temperature under which these experiments were performed was far from ideal for the methanation reaction. The range of accessible temperature was limited in these experiments, due to the fact that the resistance of zirconia decreases to sufficiently low values only at elevated temperatures.

The enhancement factor, EF, is a measure of the influence of the solid state ionic technique upon the methanation rate and is the ratio of the rate under dc bias to that under open circuit conditions. Significant enhancement, up to fivefold, was observed in the methanation rates over these transition metal electrodes by the use of this

TABLE 1

Comparison of Methanation Rates on Transition Metal Electrodes under Intrinsic and dc biased Conditions

Electrode material	T (°C)	H_2/CO ratio	Rate (moles CH_4/sec)		EF
			r_{in}	r_{DC}	
Co	535	2	2.72×10^{-9}	8.38×10^{-9}	3.1
	610	2	8.68×10^{-10}	4.13×10^{-9}	4.8
Ni	670	2	2.28×10^{-8}	4.69×10^{-8}	2.0
	700	2	2.71×10^{-8}	5.01×10^{-8}	1.8
Fe	538	3	3.19×10^{-8}	4.57×10^{-8}	1.4
	590	3	1.94×10^{-8}	2.82×10^{-8}	1.4
	700	3	5.76×10^{-9}	2.82×10^{-8}	4.9

Note. r_{in}, intrinsic rate under open circuit conditions; r_{DC}, rate under dc biased conditions.'

method. Co seems to possess lower intrinsic catalyticity than either Ni or Fe at these temperatures (*5*).

DISCUSSION

The rate of hydrogenation of CO has been found to be strongly dependent on the voltage imposed across a doped zirconia solid electrolyte cell underlying Fe, Ni, and Co transition metal catalysts. A similar dependence was reported earlier for the hydrogenation of CO_2 on Ni electrodes (*4*). A substantial increase in the methane concentration in the effluent gas is found only when E_{pump} exceeds 1.5 V. This finding agrees well with observations reported in an earlier study of the electrochemical decomposition of NO on stabilized zirconia (*1*). At these high voltages the surface region of zirconia at the cathode side becomes partially reduced, creating a large concentration of electrons, as well as oxygen vacancies. It thus acts as an in situ mixed-conducting electrode with superior catalytic properties. The oxygen activity for $E_{pump} > 1.5$ V is equivalent to a pressure of less than 10^{-30} atm, which is well into the predominantly electronic transport regime of zirconia at these temperatures (*8*). Both electrons and oxygen vacancies are readily accessible to the chemisorbed CO at the surface of the zirconia. This accessibility enhances the C—O bond scission rate as well as the rate of oxygen incorporation and transport through the zirconia electrolyte.

Some carbon deposition was observed with these transition metal electrodes, in accordance with the thermodynamics of the C—H—O equilibria (*9*). All synthesis gas mixtures with H_2/CO ratios less than 3 lie within the carbon deposition boundary under these experimental conditions. Carbon deposition was observed to be most severe for Fe and least for Ni, in accordance with the tendency of these metals to form carbides. Interestingly, Raupp and Delgass (*10*) observed that alloying equimolar amounts of Fe and Ni completely prevents bulk carbide formation. Although the formation of a surface carbide seems to be a precursor for the hydrogenation reaction scheme (*11*), excessive carbide formation and carbon deposition can cause rapid deactivation of the catalyst. In fact, Takeuchi and Wise (*12*) showed that at low coverages the chemical potential of surface carbon on Ni is considerably higher than that of graphite. With increasing overlayer coverage and temperature, the formation of C—C bonds leads to graphite formation.

CONCLUSIONS

This work demonstrates that the use of the solid state electrochemical technique can significantly enhance the rate of hydrogenation of CO over Fe, Ni, and Co catalysts. In situ control of the oxygen activity at the gas/catalyst interface can cause an enhancement of up to fivefold in the reaction rates at temperatures in the range 535 to 700°C.

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