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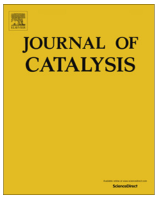

Electrochemical promotion of the hydrogenation of CO_2 on Ru deposited on a BZY proton conductor

I. Kalaitzidou [a], A. Katsaounis [a], T. Norby [b], C.G. Vayenas [a,c,*]

[a] Department of Chemical Engineering, Caratheodory 1, St. University of Patras, GR-26504 Patras, Greece
[b] Department of Chemistry, University of Oslo, FERMiO, Gaustadalléen 21, NO-0349 Oslo, Norway
[c] Academy of Athens, Panepistimiou 28 Ave., GR-10679 Athens, Greece

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ABSTRACT

The kinetics and the electrochemical promotion of the hydrogenation of CO_2 on polycrystalline Ru deposited on BZY ($BaZr_{0.85}Y_{0.15}O_{3-\alpha}$ + 1 wt% NiO), a proton conductor in wet atmospheres, with $\alpha \approx 0.075$, was investigated at temperatures 300–450 °C and atmospheric pressure. Methane and CO were the only detectable products and the selectivity to CH_4 could be reversibly controlled between 15% and 65% by varying the catalyst potential by less than 1.2 V. The rate and the selectivity to CH_4 are very significantly enhanced by proton removal from the catalyst via electrochemically controlled spillover of atomic H from the catalyst surface to the proton-conducting support. The effect is strongly non-Faradaic and the apparent Faradaic efficiency of methanation takes values up to 500 and depends strongly on the porous Ru catalyst film thickness. The observed strong promotional effect, in conjunction with the observed reaction kinetics, is in good agreement with the rules of electrochemical and chemical promotion.

1. Introduction

The hydrogenation of CO_2 to hydrocarbons or alcohols is among the most important chemical conversions of CO_2 not only for the production of renewable fuels but also as a possible means for decreasing the overall CO_2 emissions [1–5]. In addition to Cu, which is the main component of current commercial catalysts for the industrially important CO_2 hydrogenation to CH_3OH [4–7], several other metals (e.g. Pt, Rh, Pd, Ru, Fe, Co, Ni) have been investigated as catalysts on a variety of supports (e.g. Nb_2O_5, ZrO_2, Al_2O_3, SiO_2) with several alkali-based promoters. Work in this area has been reviewed recently [1,3,4]. The hydrogenation of CO_2 on Ru, which is known to give only CH_4 and CO as products, has received considerable attention in recent years [8–10].

When co-feeding CO_2 and H_2 over a hydrogenation catalyst there are two main reactions that can take place (Eqs. (1) and (2)):

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{1}$$

$$xCO_2 + (2x - z + y/2)H_2 \rightarrow C_xH_yO_z + (2x - z)H_2O \tag{2}$$

The former is the reverse water–gas shift reaction (RWGS), which is a redox reaction, while the latter is a synthesis reaction leading to the formation of hydrocarbons and/or alcohols.

The adsorption of H_2 on Ru(001) and other Ru crystallographic planes is dissociative and has been investigated thoroughly in the past [11–16] using a variety of techniques including TPD [11–14], work function measurements [12], low energy electron diffraction (LEED) [13,14], molecular beams [15] and high-resolution electron loss spectroscopy (HREELS) [13,16]. The desorption energy decreases from 110 kJ/mol to 46 kJ/mol as the H coverage increases from 0 to 0.8 [11].

The adsorption of CO_2 on Ru/TiO_2 and its coadsorption with CO and H_2 on the same catalysts have been investigated by Grätzel and coworkers using Fourier transform infrared (FTIR) spectroscopy as well as $^{13}CO_2$ isotopic studies [17]. They reported that even though CO_2 methanation occurs via CO as an intermediate, the nature of the transition species was different in the hydrogenation of CO and CO_2. Thus whereas adsorption/hydrogenation of CO gives rise to multiple CO binding states corresponding to $RuO_x(CO)_n$ where x = 0–2 and n varies from 1 to 3, only monocarbonyl species, a precursor to methanation, is formed during CO_2 hydrogenation [17].

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* Corresponding author at: Department of Chemical Engineering, Caratheodory 1, St. University of Patras, GR-26504 Patras, Greece.
E-mail address: cgvayenas@upatras.gr (C.G. Vayenas).

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The dissociative adsorption of CO_2 to CO and O has been suggested in the past to be the initial step reaction for CO_2 hydrogenation. According to this mechanism CO is further decomposed to C and O followed by the hydrogenation of C to CH_4.

An alternative mechanism has been also proposed [18,19] introducing the formation of formate at the metal–support interface which acts as intermediate for methane and CO production. Marwood et al. [20] observed these formate species by infrared spectroscopy (IRS). They appeared to be mainly on the support while metal-supported $CO_{(ads)}$ was also detected. Even though the formate adsorption sites were located on the support, the rate of formation of this species was a function of the metal loading, which implied that the formate had to migrate from the metal, or the metal–support interface (three-phase-boundaries (tpb)), to the support. Panagiotopoulou et al. [21,22] suggested that hydrogen adsorbed on Ru migrates to the metal–support–gas three phase boundaries and reacts with CO_2 to yield formate and finally Ru-CO species. Prairie et al. [9] used dispersive in situ infrared spectroscopy and detected formate species which again appeared to be mainly on the support. Based on their results they proposed the following reaction scheme:

$$CO_{2(g)} \leftrightarrow CO_{2i} \quad (3)$$

$$H_{2(g)} \leftrightarrow 2H_m \quad (4)$$

$$CO_{2i} + 2H_m \leftrightarrow HCOOH_{(i)} \quad (5)$$

$$HCOOH_{(i)} \leftrightarrow H^+_{(s)} + HCOO^-_{(s)} \quad (6)$$

$$HCOOH_{(i)} \leftrightarrow CO_{(m)} + H_2O \quad (7)$$

$$CO_{(m)} + 6H_m \rightarrow CH_4 + H_2O \quad (8)$$

where “m”, “s” and “i” denote metal, support and unspecified (possibly interfacial) adsorption sites. In the same study [9] the mobility and accumulation of the formate on the support were also demonstrated by IR spectroscopy. Tada et al. [19] demonstrated via Fourier transform IRS measurements the presence of formate and carbonate species and that the decomposition of formate species was fast over Ru/CeO_2 and $Ru/CeO_2/Al_2O_3$ in contrast to Ru/Al_2O_3, leading to improvement of CO_2 reduction to CO.

It is worth noting that the above mechanism does not involve any electrochemical steps. It nevertheless suggests that by interfacing the metal catalyst with a H^+ conducting support and by controlling, via electrical potential application, of the electrochemical potential of H^+ at the support/catalyst interface one may be able to influence via step (6) the coverages of formic acid and formate ion on the catalyst surface and thus also the catalytic activity and selectivity. This is an idea pursued in the present work.

A parallel approach to classical chemical promotion is the electrochemical promotion of catalysis (EPOC), also known as non-faradaic electrochemical modification of catalytic activity (NEMCA effect) [23–31], which can be used to reversibly promote metal catalyst films deposited on solid electrolyte supports, such as yttria-stabilized-ZrO_2 (YSZ, an O^{2-} conductor) or β''-Al_2O_3 (a Na^+ or K^+ conductor), or mixed ionic–electronic conductors such as TiO_2 or CeO_2 via application of an electric potential (±2 V) between the catalyst film and an auxiliary electrode. Electrochemical promotion allows for continuous in situ control of the coverage of promoting species ($Na^{\delta+}$, $K^{\delta+}$, $O^{\delta-}$) on the catalyst surface. EPOC has been investigated extensively during the last 30 years for more than 100 catalytic reaction systems using a variety of metal catalysts (or conductive metal oxides), solid electrolytes and catalytic reactions. Work in this area has been reviewed several times in recent years [23–28].

Numerous surface science and electrochemical techniques have shown that EPOC is due to an electrochemically controlled migration (spillover or more commonly reverse-spillover or backspillover) of promoting ionic species (e.g. O^{2-} in the case of YSZ, Na^+ or K^+ in the case of β''-Al_2O_3), from the ionic or mixed ionic–electronic conductor-support and the gas exposed catalyst surface, through the catalyst–gas–electrolyte three phase boundaries (tpb) [23–28]. Thus, both catalytic activity and selectivity are affected in a pronounced, reversible, and, to some extent, predictable manner [23,26]. The close connection between EPOC, classical chemical promotion and metal–support interaction (MSI) with ionically conducting supports has been established by a variety of techniques [23,24,28,32,33].

Two parameters that are commonly used to quantify the magnitude of EPOC [23] are as follows:

1. The rate enhancement ratio, ρ, defined by Eq. (9) is

$$\rho = r/r_o \quad (9)$$

in which r is the electropromoted catalytic rate and r_o is the unpromoted rate (i.e. the open-circuit catalytic rate), and

2. The apparent Faradaic efficiency, Λ, defined by Eq. (10) is

$$\Lambda_i = \Delta r_{\text{catalytic}}/(I/F) \quad (10)$$

where $\Delta r_{\text{catalytic}}$ is the current- or potential-induced observed change in catalytic rate (in g-eq/s), and I is the applied current. In the present case this implies

$$\Lambda_{CH_4} = 8\Delta r_{CH_4}/(I/F) \quad (11)$$

$$\Lambda_{CO} = 2\Delta r_{CO}/(I/F) \quad (12)$$

where r_{CH_4} is in mol CH_4/s and r_{CO} is in mol CO/s.

A reaction is termed electrophobic (or nucleophilic) when the rate increases with increasing catalyst potential ($\partial r/\partial U_{WR} > 0$), electrophilic when the rate decreases with increasing catalyst potential ($\partial r/\partial U_{WR} < 0$), volcano-type when the reaction rate exhibits a maximum with varying potential, and inverted volcano when the rate goes through a minimum with varying potential [23]. The catalyst potential U_{WR} is an increasing function of the work function, Φ, of the catalyst surface and over wide temperature ranges the two are related via $\Delta\Phi = e\Delta U_{WR}$ [23,28].

The range of validity of this equation, which has been extracted both from Kelvin probe measurements [34] and from the cutoff electron energy of UPS spectra [35], has been investigated both experimentally, using Pt, Au, Ag [36,37], Ir–IrO_2 [38,39] and Ru–RuO_2 electrodes [40] and theoretically [41,42]. It has been found that the equation is valid as long as a sufficiently dense adsorption layer, formed by adsorbed species and spillover ions and their compensating charge in the metal, is present at the metal–gas interface. When the temperature is too low, e.g. below 300 °C for Pt, the ion mobility is too low and thus this effective double layer cannot form [36,41] and significant deviations from equality are observed [34–37]. When the temperature is too high, e.g. above 450 °C for Pt, this effective double layer desorbs and thus again significant deviations from the above equality are observed.

It has been found that simple rules exist, valid both for classical promotion and for electrochemical promotion [43–45], which allow for the prediction of the promotional behavior on the basis of the open-circuit reaction kinetics with respect to the electron donor (D) and electron acceptor (A) reactant species.

The electrochemical promotion of CO_2 hydrogenation has been studied in the past over Cu [46,47], Rh [46,48], Pt [46,49–51], Pd [52] and Ni [53] catalyst film electrodes deposited on YSZ [46,48,49,52,53], and K-β''-Al_2O_3 [47,50,51] ceramic supports. In general, methanation was found to exhibit electrophobic behavior, whereas the RWGS follows electrophilic behavior. The same type