Catalytic and electrocatalytic oxidation of propane on V–Mg–O and V–Mg–O (Ag) catalysts

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Vanadium magnesium oxide catalysts prepared in this work were found active in selective oxidation of propane to propene. A selectivity as high as 79% was obtained at 10% conversion (813 K). No oxygenated or C_2 products were detected and the catalysts were found to undergo no change in activity over many weeks of operation. Under electrochemical pumping of oxygen (EOP) towards the catalyst (with oxygen present in the feed gas), both conversion and selectivity were found to increase slightly as external current increased, indicating the effect of electrical current can be exhibited by an oxide catalyst. However, in the absence of oxygen in the feed gas, EOP could lead to an even higher selectivity: 84 and 86.9% respectively for a 24 V–Mg–O and a 24 V–Mg–O (Ag) (1/2) catalyst. The overall results obtained suggest that electrochemically supplied oxygen is more selective towards C_3H_6. Mechanisms of both catalytic and electrocatalytic oxidation of propane were tentatively suggested, with surface oxygen ion vacancy identified as active surface species and the rate determining step involving heterolytic splitting of the C_3H_8 molecule to form a surface bonded $C_3H_7^-$ ion and a surface hydroxyl ion. The higher selectivity towards C_3H_6 in case of EOP was explained on this basis. While mixing with Ag powder was found to improve significantly the electrocatalytic performance of vanadium magnesium oxide, its role appears to be non-chemical: it simply gives rise to a larger area of the gas/catalyst/Ag electrode interface.

Keywords: Electrocatalysis; propane oxidation; V–Mg–O catalysts

1. Introduction

Alkanes are abundant by-products of the oil refining process. Most of them are currently used as fuel. Selective conversion of alkanes to unsaturated hydrocarbons

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will, therefore, be a potentially important process for their utilization. Propane dehydrogenation has been studied over a wide range of oxides in the presence or absence of oxygenated species. It was claimed as far back as 1979 that lithium doped Ti–Zn–O catalyst could dehydrogenate propane almost exclusively to propene in the absence of oxygen. However, the catalyst would lose activity in a matter of minutes and therefore regeneration by oxygen or steam had to be carried out along with the dehydrogenation phase in a cyclic manner [1]. To date, most of the industrial processes are still cyclic processes. New catalysts are still being searched.

Charr and Kungs carried out studies of oxidative dehydrogenation of butane and propane over V–Mg–O catalysts [2,3]. They reported that a selectivity of up to 65% was obtained at 10% conversion (813 K) with no oxygenated products detected. To date, works on V–Mg–O catalysts are still scarce. It appears therefore warranted to carry out further study on this system. Moreover, as part of our efforts of studying electrochemical modification of catalyst performance, it will be interesting to see whether or not the performance of V–Mg–O, an oxide catalyst, can be modified, as in the case of metals so far reported, by electrically pumping oxygen towards or from the catalyst surface. The results of such investigation are also expected to shed some light on the nature of the surface active species as well as reaction mechanism.

2. Experimental

2.1. REACTOR CELL AND ANALYTICAL CONDITION

The reactor cell and analysis system are shown in fig. 1. The catalytic flow reactor (CR) was a flat bottom yttria-stabilized zirconia tube, the inside bottom of the tube was painted with a thin film of Ag on top of which the catalyst was deposited, constituting the catalyst electrode (C); the outside bottom of the tube was painted with two patches of Ag film which acted respectively as counter electrode (CE) and reference electrode (RE). The reactor tube was encased in a "double" copper jacket allowing the outside bottom of the tube to exposed to air (i.e. constant oxygen concentration of 21%). The whole reactor assembly was placed in a tubular furnace (not shown in fig. 1). Thus, depending on the direction of the switch on the galvanostat/potentiostat (DHXII, Xiamen), current could flow from catalyst to CE (i.e. oxygen ion was pumped from CE towards catalyst) and vice versa. Alternatively, the reactor cell could also function as a fuel cell (described by the inner circuit) and current–voltage relationship could be established by varying the resistance afforded by a rheostat (R).

Kinetic results reported in this paper were all obtained at 813 K with a total flow rate of 80 cm^3/min. Reactants, propane and air, or simply propane diluted in high purity nitrogen were passed through, (after mixing by mixer M) the catalyst

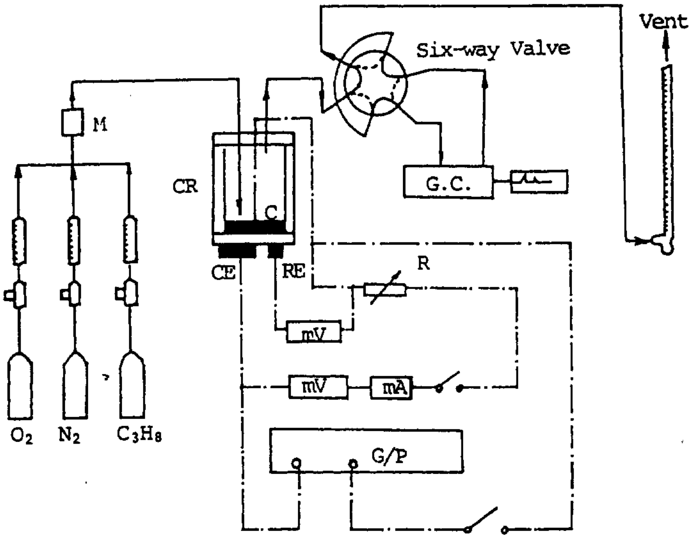

Fig. 1. Reactor–analysis assembly. M, gas mixer; CR, catalytic reactor; C, catalyst electrode; CE, counter electrode; RE, reference electrode; R, variable resistance; G/P, galvanostate/potentiostat.

electrode and the products (as well as reactants) were analysed with on-line gas chromatography. A GDX-501 column was used to separate air, carbon dioxide, propane and propene. A 5A molecular sieve was used to separate nitrogen, oxygen and carbon monoxide.

2.2. PREPARATION OF CATALYST ELECTRODE

A silver paste was coated on the surface of a zirconia flat-bottom tube, followed by calcination at 823 K in a furnace. The silver film was exposed to air and serviced as cathode. V–Mg–O catalyst was prepared by adding an appropriate amount of MgO (see below for preparation) to a NH_4VO_3 solution to form a suspension which was then dried at 353 K overnight, followed by heating at 823 K for 6 h. To prepare the V–Mg–O catalyst electrode, V–Mg–O powder was mixed with *n*-butyl acetate to form a suspension which was then painted on the inside surface of the zirconia tube (that was previously coated with a Ag film as described above for cathode) and subsequently calcined at 723 K for 40 min. The catalyst so obtained is designated as N V–Mg–O with N the weight fraction of V_2O_5 in the solid. Another type of catalyst used was V–Mg–O (Ag) which was prepared by mixing a given V–Mg–O catalyst with an appropriate amount of fine silver powder. The resulting powder was then subject to the same treatment as described above to form an anode. Such anodic catalyst was designated as N V–Mg–O (Ag) (a/b) with a/b representing the weight ratio of N V–Mg–O to Ag.

2.3. CATALYST CHARACTERIZATION

BET surface areas of the catalyst samples, i.e. powder sintered onto the zirconia tube (prior to catalytic runs) were measured by nitrogen adsorption in a flow apparatus. X-ray diffraction data were obtained with a Rigaku Powder diffractometer (RU-200B D/MAX-rC) using Cu K_α target. Scanning micrographs were obtained with a JEOL SEM (JEOL JSM-T330A).

2.4. MATERIALS

MgO was precipitated from a solution of ammonium carbonate and magnesium nitrate. The precipitate so obtained was filtered and dried at 353 K for 24 h, then heated at 973 K for 4 h to form MgO.

NH_4VO_3: Beijing Chemicals, A.R. 99.9%;
$Mg(NO_3)_2 \cdot 6H_2O$: Aldrich A.R.;
C_3H_8: H.K. Oxygen, 100%;
C_3H_6: A.C.S. Calibration Standard;
N_2: H.K. Oxygen, 99.995%.

3. Results and discussion

The surface area values of the catalyst samples prepared are summarized in table 1. The surface areas of these V–Mg–O samples are generally considerably higher than those used by Charr et al. [2] (their corresponding values are shown in parentheses) presumably due to the fact that the MgO used as starting material in our case had a surface area almost two and a half times larger than theirs. The powder X-ray diffraction data also show that in all these V–Mg–O samples, the predominant compound was magnesium orthovanadate ($Mg_3V_2O_8$) and MgO with the former being suggested to be the active component for propane oxidation.

Under open circuit condition, the reaction was a conventional heterogeneous catalytic reaction. Typical results for V–Mg–O catalysts of different compositions are shown in fig. 2. These data were obtained by varying the $P_{C_3H_8}/P_{O_2}$ ratio at a fixed total flow rate. The ranges for $P_{C_3H_8}$ and P_{O_2} were respectively 1.82 to 0.5%

Table 1
Surface area of catalyst samples

Catalyst	Surface area ($m^2\ g^{-1}$)
MgO	69.87 (28)
19 V–Mg–O	150.71 (46)
24 V–Mg–O	115.58 (74)
40 V–Mg–O	54.83 (31)
V_2O_5	4.36 (35)

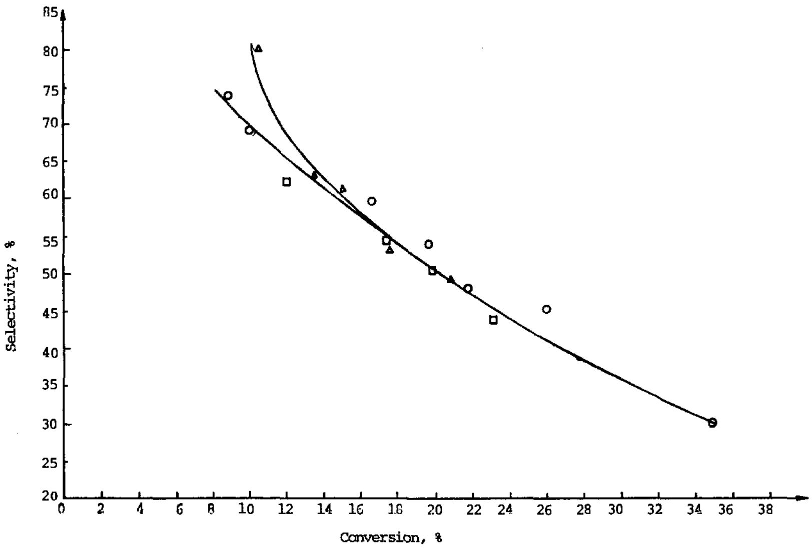

Fig. 2. Performance of V–Mg–O catalysts of different composition under open circuit condition. Catalyst weight = 0.105 g. Total flow rate = 80 ml/min, $T = 813$ K. (○) 19 V–Mg–O, (△) 24 V–Mg–O, (□) 40 V–Mg–O.

and 1.82 to 0.44%. Generally speaking, an increase in conversion was accompanied by a decrease in selectivity. At conversion greater than 13%, the performances of the 19, 24, 40 V–Mg–O catalysts appear to be almost identical. However, below 13% of conversion, the 24 V–Mg–O appears to render the best performance. In fact, for this catalyst the selectivity was found to reach 80% at 10.5% conversion.

Moreover, apart from the absence of oxygenate products like acrolein or acid anhydride, no C_2 products were detected. In the case of 24 V–Mg–O, hardly any CO was present in the product stream either. In other words, our catalysts produce either C_3H_6 or CO_2 with quite high selectivity towards the former product.

3.1. REACTIONS UNDER ELECTROCHEMICAL PUMPING OF OXYGEN (EOP) TOWARDS THE CATALYST

There are several ways of electrical pumping of oxygen. Oxygen can be pumped towards or from the catalyst by an externally supplied current; in the former case, the gas phase in contact with the catalyst can contain oxygen or otherwise. Alternatively, oxygen can be pumped towards the catalyst by a self-generated current, with the presence or absence of oxygen in the gas feed; when oxygen is absent, the cell actually functions as a genuine fuel cell. In addition to V–Mg–O catalysts, attempts were also made to spread very fine Ag powder in the V–Mg–O catalyst in the hope to improve three-phase interfacial area (gas/V–Mg–O catalyst/Ag electrode). Such catalysts yielded almost identical performance in terms of $P_{C_3H_8}/P_{O_2}$

ratio as those without silver under open circuit condition, as shown in fig. 3. Therefore, it appears likely that V–Mg–O and Ag exist as a mixture and the catalyst will be best designated as V–Mg–O (Ag) (a/b) with a, b being the weight portion of V–Mg–O and Ag respectively.

In this work, EOP effects of all types were investigated. However, here we shall highlight the comparison between the V–Mg–O and V–Mg–O (Ag) catalysts in terms of the effects of EOP towards catalyst by external current.

3.1.1. Presence of oxygen in the feed gas

Fig. 4 shows the effect of current on the conversion and selectivity of a 24 V–Mg–O and a 24 V–Mg–O (Ag) (1/2) catalyst at a $P_{C_3H_8}/P_{O_2}$ ratio of 1.77. For both catalysts, EOP causes a rise in conversion as well as selectivity. While the effect on selectivity is very comparable for both catalysts, the effect on conversion is obviously greater for the 24 V–Mg–O (Ag) (1/2) catalyst (at 40.5 mA, a 29.4% increase versus 20.5% increase for 24 V–Mg–O from open circuit conversion for the two catalysts). But the most interesting feature is an increase in conversion that is not at the expense of selectivity and vice versa.

Vayenas and his colleagues suggested the name NEMCA effect (non-Faradaic electrochemical modification of catalytic activity) for such phenomenon when they studied a number of reactions using metal catalysts under EOP conditions (see e.g. ref. [4]). They also suggested the NEMCA effect owes its origin to the overpotential developed at the interface of the gas–metal catalyst electrode–solid electrolyte and thereby lowering or raising the work function of the metal catalyst which in turn affects the reaction rate one way or another. The value of the so-called NEMCA factor for the rate of O^{2-} ion consumption, Λ, defined as the ratio of the change in catalytic rate, Δr, due to the application of an electric current i, to the number of carrier ions with charge n being transported towards or away from the catalyst viz. i/nF, with F being the Faraday constant (in this case $\Lambda = \Delta r_{O^{2-}}/(i/2F)$), could

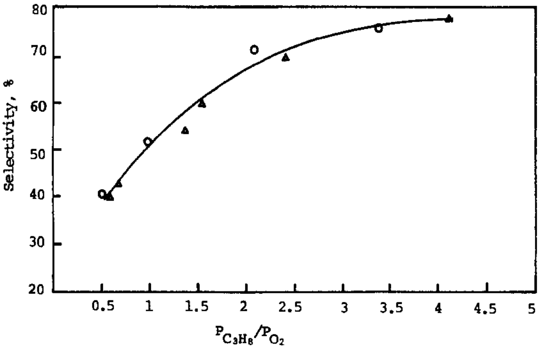

Fig. 3. Comparison of effect of Ag on selectivity performance (in terms of $P_{C_3H_8}/P_{O_2}$) under open circuit condition. $T = 813$ K, total flow rate = 80 ml/min. (○) 24 V–Mg–O (Ag) (1/2) [0.301 g], (△) 24 V–Mg–O [0.105 g].

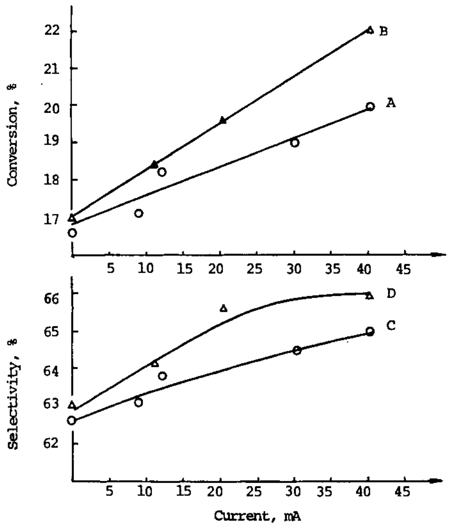

Fig. 4. Effects of external current on conversion and selectivity in the presence of oxygen in the gas feed. (A, C) 24 V–Mg–O [0.105 g] (O: A, C). (B, D) 24 V–Mg–O (Ag) (1/2) [0.105 g : 0.205 g] (Δ: B, D). $P_{C_3H_8} = 0.011$ atm, $P_{O_2} = 0.0062$ atm, $T = 813$ K, total flow rate = 80 ml/min. $P_{C_3H_8}/P_{O_2} = 1.77$.

be calculated from our results as 0.28 and 0.5 respectively for the 24 V–Mg–O and 24 V–Mg–O (Ag) (1/2) catalysts. Thus, the observed modified behaviour of the V–Mg–O catalysts under EOP condition strictly speaking is not a NEMCA effect in that the change in conversion and selectivity may not be due to the facilitating of the original catalytic mechanism but rather to a new mechanistic path.

3.1.2. Absence of oxygen in feed gas

When the gas phase does not contain oxygen, the propane oxidation process must involve electrochemically transported oxygen.

As shown in fig. 5, the selectivity observed is in the range 79–82.1% for 24 V–Mg–O and 82–86.9% for 24 V–Mg–O (Ag) (1/2) respectively (as opposed to 79%, the highest selectivity obtained at $P_{C_3H_8}/P_{O_2}$ value of 4.0 under open circuit condition for both catalysts). For the former, the selectivity appears to reach a saturation value at about 10 mA whereas for the latter, there seems to be a shallow maximum at 13 mA. Regarding conversion, the 24 V–Mg–O (Ag) (1/2) catalyst was superior especially at higher current range.

Curves E and F in fig. 5 show the total amount of oxygen ions consumed to produce propene and carbon dioxide (and water) for the 24 V–Mg–O and 24 V–Mg–O (Ag) (1/2) catalyst respectively, while curve G represents the calculated amount of O^{2-} ions transported to the catalyst ($i/2F$) (an oxygen analysis of the product stream was occasionally performed to check oxygen balance). As can be seen, curve F coincides with G up to about 9 mA, then the two curves depart with the differ-

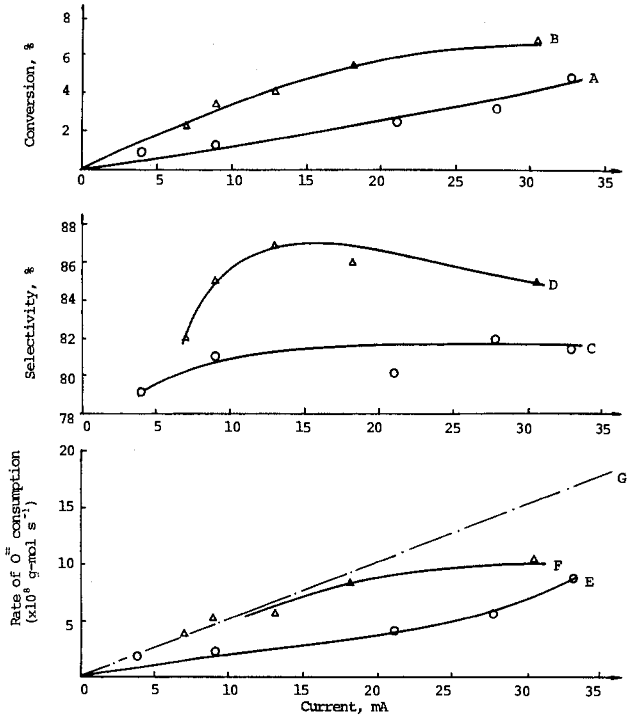

Fig. 5. Effects of external current on conversion, selectivity and rate of O^{2-} ion consumption in the absence of O_2 in the gas feed. 24 V–Mg–O [0.105 g] (○: A, C, E), 24 V–Mg–O (Ag) (1/2) [0.105 g : 0.205 g] (△: B, D, F). Dotted line: calculated O^{2-} ion supply rate ($i/2F$). Conditions: $T = 813$ K, total flow rate = 80 ml/min, $P_{C_3H_8} = 1.1\%$.

ence accentuated as the current increases. Similar behaviour is exhibited by curve E except it is further apart from G than that of F. This means that as the current becomes larger, though the conversion of propane increases concomitantly, more and more oxygen ions transported electrochemically do not participate in the reaction(s) but evolved as molecular oxygen which may subsequently oxidize propane through normal catalytic mechanism. If one looks at the case of 24 V–Mg–O (Ag) (1/2) more closely (curves B, D, F), it seems there exists a current beyond which selectivity will level or drop off[#1] as well as evolution of molecular oxygen to the gas phase will become significant.

3.2. MECHANISMS OF CATALYTIC AND ELECTROCATALYTIC OXIDATION OF PROPANE

Judging by the fact that the selectivity mildly increases in the order open circuit

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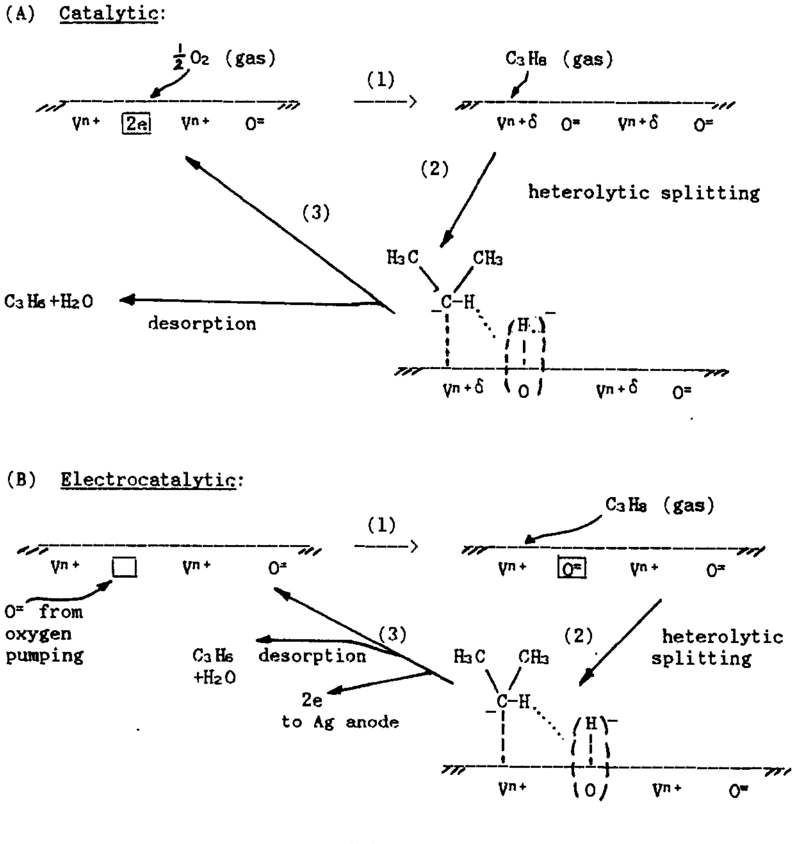
[#1] In another run, selectivity was found to reach a saturation value at about 13 mA rather than a shallow maximum – in other words, very similar to curve C for the 24 V–Mg–O catalyst.

< EOP with oxygen in the gas feed < EOP without oxygen in the gas feed, it appears to indicate that electrochemically supplied oxygen is more selective towards propene than oxygen supplied from the gas phase. Charr and Kungs [3] suggested that propane oxidation on V–Mg–O catalysts is initiated by a highly reactive surface oxygen species without identifying the nature of this species. Taking together the catalytic and electrocatalytic results obtained in this work, it may be speculated that the active species is a lattice surface oxygen ion vacancy in the neighbourhood of a surface vanadium ion. The surface oxygen ion vacancy will be filled either from oxygen in the gas feed or electrically supplied oxygen. A surface vanadium and an oxygen ion together split a methylenic C–H bond[#2] heterolytically, followed by the extraction of a methyl hydrogen by the nearly formed surface hydroxyl ion to form a water molecule. A mechanism scheme may be described by the sketch in scheme 1.

[#2] Incorporating the idea of Charr et al. that a methylenic C–H bond is broken first.



Scheme 1.

The catalytic mechanism (A) operates under open circuit condition as well as EOP in the presence of oxygen in the gas feed. The electrocatalytic mechanism (B) operates under EOP in the presence as well as absence of oxygen in the gas feed. In other words, (A) operates exclusively under open circuit condition whereas (B) operates exclusively under EOP in the absence of oxygen in the gas feed.

While (A) and (B) appear to be similar, a subtle difference lies in the fact that the surface oxygen ion replenishment invokes electron depletion of the solid surface only for the former. Consequently, the charge of the surface vanadium ion involved in the activation complex is somewhat increased, which should hold the nucleophilic C_3H_7 tighter making it more vulnerable for deep oxidation, in agreement with the experimental results. The observed insensitivity in conversion towards EOP appears to suggest that step (1) of (A) is unlikely to be rate determining, because the oxygen adsorption should be disfavoured by a higher work function of the catalyst surface due to oxygen being pumped towards it. On the other hand, step (2) is possibly rate determining since the formation of the surface hydroxyl ion is electrophilic (by a proton) while the formation of C_3H_7–$V^{(n+\delta)+}$ is nucleophilic, leading to some kind of compensation effect, rendering the insensitivity in rate of this step towards the change of work function resulting from EOP. Thus the observed modification of catalytic performance in this case could not be explained by simply considering a change of work function due to EOP; but rather it must invoke the consideration of a detailed mechanism.

Before we leave the mechanism, it should be noted that step (3) of the electrocatalytic mechanism must take place at the gas/V–Mg–O/Ag electrode interface because electrons need to be given off to the electrode.

3.3. THE ROLE OF Ag IN A V–Mg–O (Ag) CATALYST

The experimental results obtained appear to bear out our idea: to raise the efficiency of the catalyst through an increase in the gas/catalyst/electrode interface area by allowing additional Ag in close contact with V–Mg–O. Fig. 5 shows very clearly that a 24 V–Mg–O (Ag) (1/2) catalyst yielded a considerably higher conversion rate than a 24 V–Mg–O catalyst. A comparison of curves E, F and G indicates that the smaller propane conversion (for a given current) in the case of 24 V–Mg–O is due to a much larger portion of O^{2-} ions transported electrically discharging at the Ag electrode to form molecular oxygen. Presumably the three-phase interfacial area in a V–Mg–O catalyst is very limited and the O^{2-} ions cannot find the way to react this propane; some of the oxygen molecules so evolved may actually return to the catalyst surface to convert propane according to mechanism (A) resulting in a smaller selectivity as compared to the case of V–Mg–O (Ag) catalyst. On the other hand, the nature of the observed saturation current effect on selectivity in all cases of EOP (with or without oxygen in the gas feed) (curves C, D in fig. 4 and C, D in fig. 5) is intriguing. It is not clear whether this is an indication that the physical characteristic of the V–Mg–O/electrode interface could be improved further or a current dependent "electronic" effect due to EOP that affects primarily selectivity and not rate. In any event, mixing an electrode material with the active catalyst appears to be a generally applicable method in improving electrocatalytic efficiency.

4. Conclusion

The V–Mg–O catalyst obtained in this work was found to have comparable activity, but higher selectivity (at low conversion end) than those reported by Charr et al. The highest selectivity is 79% for a 24 V–Mg–O catalyst at 10% conversion. Under the condition of EOP, whether or not the gas feed contains oxygen, these catalysts exhibit concomitant increase of conversion and selectivity. Such increase is more pronounced if a V–Mg–O catalyst is mixed with some Ag powder to form a V–Mg–O (Ag) catalyst. The role of Ag was found to be "non-chemical"; it simply increases the three-phase (gas/catalyst/Ag electrode) interfacial area. The highest selectivity exhibited by a 24 V–Mg–O (Ag) (1/2) catalyst is 86.9–85% under EOP (current 13–30 mA) in the conversion range 4–7%. Thus the approach of mixing an electrode material with the active catalyst could well be a general method for the preparation of oxide electrodes and on this count alone, there is still scope to improve the electrocatalytic performance of the V–Mg–O (Ag) catalyst.

For both the catalytic and the electrocatalytic process, a surface oxygen ion (or vacancy) was suggested to be involved whereas the rate determining step involves heterolytic splitting of the C_3H_8 molecule leading to the formation of a surface bonded C_3H_7 ion and a surface hydroxyl ion. The higher selectivity towards C_3H_6 in the case of EOP is attributed to the relatively weaker surface bond between C_3H_7 and the vanadium ion and thereby less vulnerable towards deep oxidation.

Acknowledgement

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