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ELECTRON TRANSFER DURING DECOMPOSITION OF METHANOL ON ZINC OXIDE

By

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Abstract

The form of adsorbed methanol molecule, its mechanism of reaction on the surface and the nature of active sites involved in the process have been discussed from the electrical conductivity measurement. The adsorption of methanol on zinc oxide can be either acceptor or donor type which is governed by the state of surface. During decomposition on reduced zinc oxide the methanol molecule rapidly dissociates in H atom adsorbed on O⁻² sites and CH₃O (or CH₂O) radical adsorbed on Zn⁺ sites. The conductivity of zinc oxide is increased and decreased by the adsorption of H atom and CH₃O (or CH₂O) radical respectively and the overall change in conductivity depends upon the reaction temperature. The radical CH₂O further breaks up slowly into carbon monoxide molecule adsorbed on Zn⁺ sites (causing slow increase in conductivity) and gas phase hydrogen.

Introduction

Catalytic Dehydrogenation of methyl alcohol by zinc oxide has been studied by several workers¹⁻⁶⁾ and it has been suggested that the overall decomposition is a two stage process, the rate determining step depending upon the temperature of reaction. But the nature of adsorption of methanol and of all primary alcohols in general on zinc oxide is not very clearly understood. In case of ethanol chemisorption BHATTACHARYYA et al.⁷⁾ have found decrease in conductivity at temperature up to 180°C. On the other hand BIELANSKI and co-workers⁸⁾ have studied adsorption of ethanol-water mixtures under reaction condition and reported donor type adsorption. A similar mechanism has been suggested by Mc ARTHUR and BLISS⁹⁾ on the basis of conductivity and field effect measurements. Since the sample of zinc oxide used by different workers have different history of preparation it seems that the donor or acceptor type adsorption of alcohols

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will depend upon the nature of the surface. For methanol decomposition on zinc oxide BORESKOV⁵⁾ observed that during reaction the conductivity of zinc oxide and its activity increases rapidly until the oxide attains a metallic behaviour. This indicates that the surface of zinc oxide during reaction is in highly reduced state and any mechanism of adsorption and reaction must take this into account. The present investigation has been taken up with a view to better understanding of the nature of adsorbed methanol and its mode of reaction on the surface of activated zinc oxide from electrical conductivity measurements.

Material

Zinc oxide used was prepared by the oxidation of zinc metal in air and was cured at 500°C for 10 hrs. Methanol (BDH 'Analar' grade) was refluxed with 5% of solid caustic potash on a water bath, distilled, allowed to stand for 24 hrs over 40% freshly burnt quicklime, redistilled from water bath and the distillate was collected at 66~67°C. Final purification was carried out by repeated freezing at -190°C and thawing in vacuum. Hydrogen was purified by passing through Deoxo tube and dried over silica gel. Oxygen and nitrogen were dried over silica gel.

Apparatus

The conductivity cell was of the type shown in Fig. 1. The conductivity measurements were carried out with an A. C. bridge at a frequency of 3 Kc/s. The conductivity cell was attached to an all glass adsorption apparatus and could be evacuated to 10^{-5} torr by a three stage oil diffusion pump. The sample could be heated by a small tube furnace put around the cell and the temperature was measured to $\pm 1^\circ\text{C}$ by means of a Fisher potentiometer.

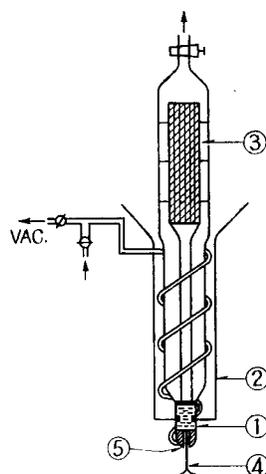


Fig. 1. *Conductivity Cell.*

- (1) Catalyst sample
- (2) Pt disc electrode with lead wires
- (3) Iron weight scaled in glass
- (4) Chromel Alumel thermocouple
- (5) Glass wool

Experimental

Before every experiment the sample was subjected to the treatments indicated below :

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- (1) Evacuation for 1 hour at 450°C
- (2) Treatment with oxygen at 450°C for 4 hrs.
- (3) Evacuation at 450°C for 1.5 hrs.

The sample after these treatments was taken to be in the "oxidised" state. Reduction of the "oxidised" sample for 12 hours in a flow of hydrogen at 350°C followed by evacuation for 1.5 hour at 450°C was carried out to "reduced" the sample.

The following measurements were performed on the sample after necessary treatment.

Run (I)

Adsorption of methanol: Methanol vapour was adsorbed on both "reduced" and "oxidised" sample at 90°C and the change of conductivity with time was followed. After equilibrium has been attained the vapour was condensed in an U-tube cooled in liquid nitrogen and the desorption from the surface was observed for about 30 min. No non-condensable products could be detected indicating that at this temperature no decomposition takes place during adsorption.

Run (II)

Effect of temperature: After equilibration of the "reduced" sample with methanol vapour at 90°C, the liquid nitrogen trap was put in line with the conductivity cell to remove both the unadsorbed and weakly adsorbed methanol. The sample was then heated from 90° to 450°C at the rate of 5°C/min. with the liquid nitrogen trap in position. The changes in pressure (as measured with a Penning and Pirani gauge) and conductivity with temperature was noted. The same experiment was repeated (after regeneration and "reduction") with the sample being continuously evacuated to remove all the gaseous products formed. The temperature dependence of the conductivity of a regenerated and reduced sample was also investigated.

Run (III)

Decomposition of methanol: Methanol vapour (75 torr) was brought in contact with "reduced" and evacuated sample at 350°C and the decomposition process was followed by observing the change in conductivity and pressure with time. The reaction was allowed to continue for 0.5 hour and then the sample was evacuated for 10 minutes. Second and third dose of methanol was added and evacuation was started after 3 hours and 12 hours respectively.

After regeneration and "reduction" of the sample, the decomposition

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was carried out at 300°C and 265°C. The product gases were analysed Gas chromatographically using a column of active carbon at room temperature.

Run (IV)

After regeneration and reduction of the catalyst, evacuation was carried out at 350°C for a few minutes to remove ambient hydrogen only and to retain as much adsorbed hydrogen as possible. Decomposition was carried out with about 80 torr methanol vapour at 350°C and change in conductivity with time was noted.

Results and Discussion

From Fig. 2 it can be seen that at 90°C in presence of methanol vapour the conductivity of "oxidised" zinc oxide shows an increase after an initial drop whereas that of "reduced" oxide decreases very sharply. This indicated both donor and acceptor nature of adsorbed methanol and the surface concentration of the latter form increase with increasing

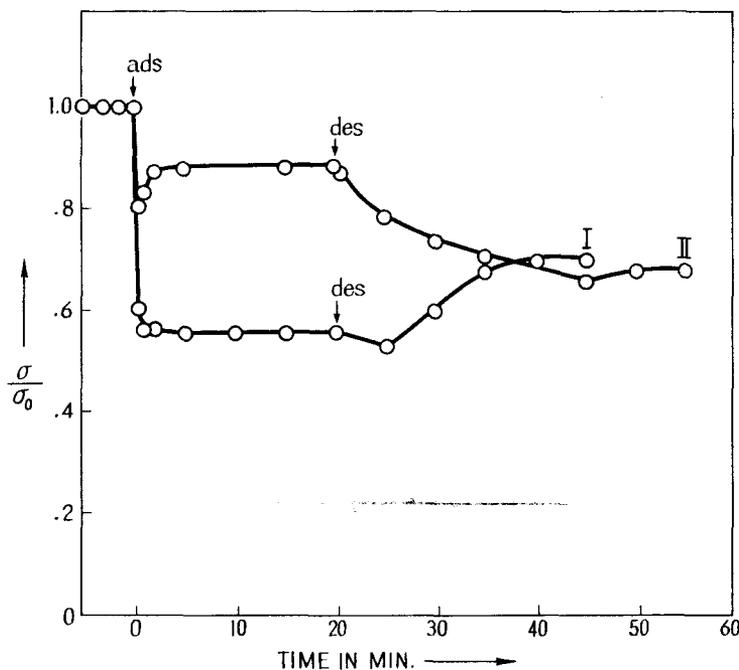


Fig. 2. Conductivity change due to dissociative adsorption of methanol at 90°C on (I) reduced and (II) oxidised zinc oxide.

nonstoichiometry of the surface. That the donor type of adsorption is weaker is evident from the fact that upon desorption in presence of liquid nitrogen the conductivity always shows a decrease initially. The occurrence of two types of chemisorbed methanol can be explained on the basis of the following mechanism.

The surface of zinc oxide contains Zn^+ sites whose concentration increases with the degree of reduction of the surface. Methanol molecules can adsorb on these defect sites in two different ways

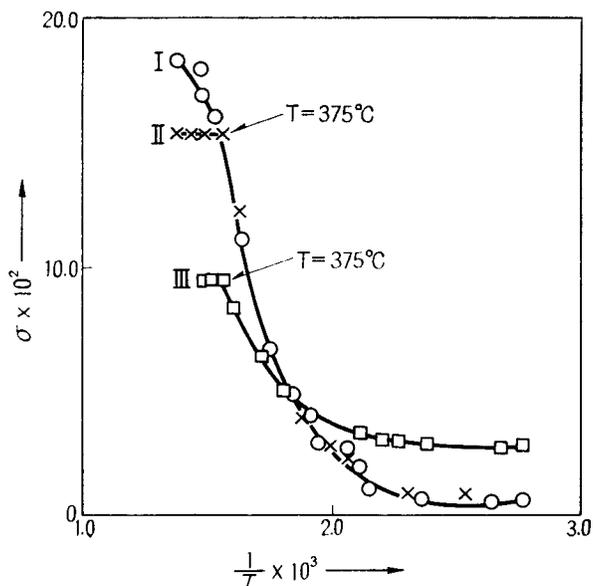
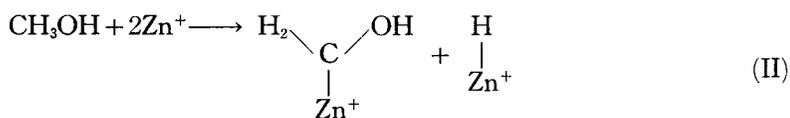
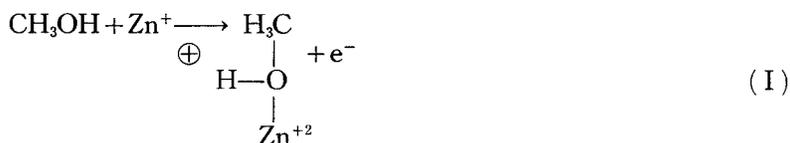


Fig. 3. Effect of temperature upon conductivity of zinc oxide under different surface conditions.

- I. methanol adsorbed and trapped out at $90^\circ C$. Product gases continuously pumped out up to $450^\circ C$.
- II. methanol adsorbed and trapped out at $90^\circ C$. Pumping cut off.
- III. reduced and evacuated.

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Type I adsorption is similar to the one suggested by McARTHUR⁹⁾ for ethanol adsorption and is termed "donor like" because in this case the free electron is generated in the adsorption process rather than supplied by the adsorbate. The valence electron associated with the defect Zn^+ site is transferred to the conduction band and increases the conductivity. Type II adsorption can be termed "acceptor like" because in this case no charge transfer takes place but the valence electron of Zn^+ site is localized by $-CH_2OH$ radical obtained from the dissociative adsorption of methanol and the conductivity decreases. A similar type of mechanism has been suggested by TEICHNER¹⁰⁾ to explain the decrease of conductivity of non-stoichiometric zinc oxide upon adsorption of ethylene. In type II adsorption suggested above, hydrogen is chemisorbed on Zn^+ sites and this type of adsorption which can take place below $100^\circ C$ does not affect the electrical conductivity of zinc oxide¹¹⁾.

When the methanol treated zinc oxide is heated from $90^\circ C$ to $450^\circ C$ without evacuation there is a continuous rise of conductivity (Fig. 3 Curve I) as well as increase in the pressure of gaseous products formed, (Fig. 4 Curve II). This is due to the fact that during heating two phenomenon

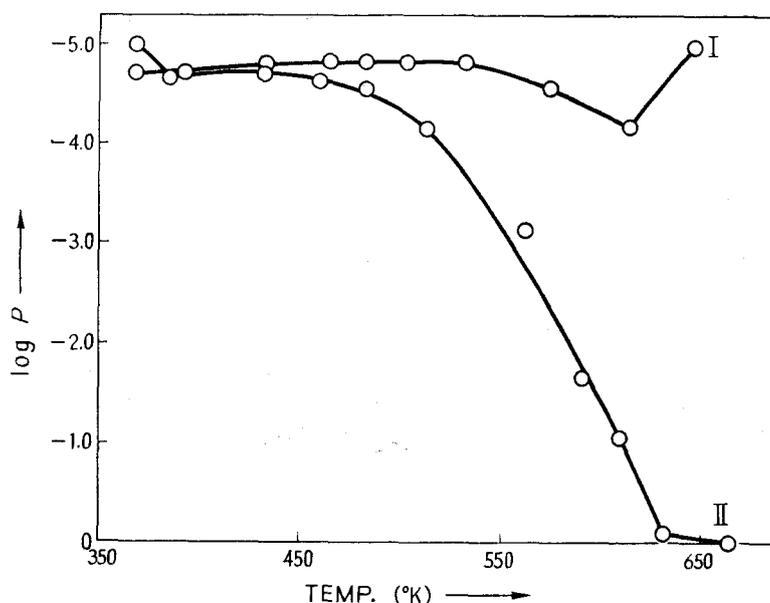


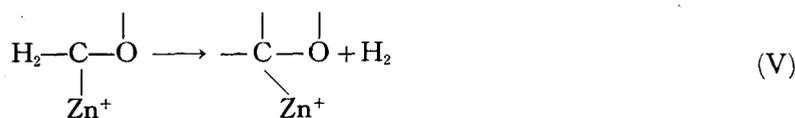
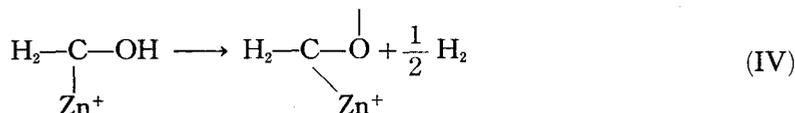
Fig. 4. Variation of pressure with temperature due to thermal decomposition of adsorbed methanol. (I) with and (II) without evacuation.

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can take place. The weakly adsorbed hydrogen is desorbed causing increase in pressure



and also the $-\text{CH}_2\text{OH}$ radical undergoes further breakdown producing gaseous hydrogen



A part of hydrogen formed for step (III) to (V) can be re-adsorbed on O^{2-} sites if the temperature is higher than 100°C . This type of adsorption produces free electrons and increases the conductivity¹¹.

When methanol vapour is contacted with reduced and evacuated zinc oxide at 350°C , an equivalent amount of hydrogen is rapidly formed and there is a sharp increase in conductivity (Fig. 5, Curve I) which is due to re-adsorption of hydrogen. This is followed by a slow increase of pressure and carbon monoxide now appeared one of the products indicating that the decomposition of $-\text{CH}_2\text{O}$ radical according to steps (V) is a slow process. Such an assumption is further supported by the fact that at 300°C there is a sharp drop in conductivity initially whereas at 265°C there is no increase in conductivity at all, because increase of temperature enhances the decomposition of $-\text{CH}_2\text{O}$ radical setting free the trapped valence electron of Zn^+ site.

TABLE I

TREATMENT	CONDUCTIVITY ohms ⁻¹
1. H_2 (flow) 12 hours 350°C	1.54×10^{-1}
2. Evacuation 1.5 hours 450°C	1.66×10^{-1}
3. CH_3OH 80 mm 12 hours 350°C	2.08×10^{-1}
4. Evacuation 1.5 hours 450°C	2.12×10^{-1}

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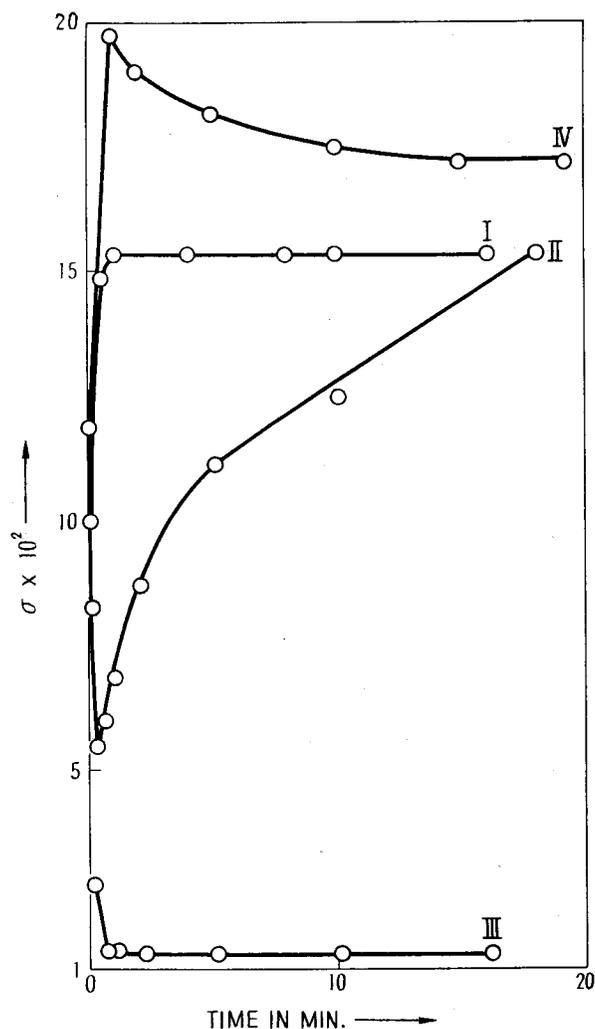
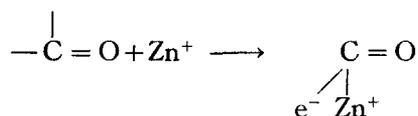


Fig. 5. Change in conductivity during decomposition of methanol on zinc oxide (I) at 350°C (II) 300°C (III) 265°C and (IV) at 350°C in presence of presorbed H_2 .

It can be seen from Table I given above that the conductivity of zinc oxide is higher in presence of methanol than in presence of hydrogen for identical conditions of time and temperature. This is possible if a part of carbon monoxide produced during decomposition of methanol is adsorbed as donors. Since no carbon dioxide but a trace of methane could be detected in the product gases, the adsorption centres for carbon monoxide

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cannot be O^{-2} but Zn^{+} sites. The donor type adsorption of carbon monoxide involving Zn^{+} site have been postulated by AMBERG¹²⁾ and TEICHNER¹³⁾. During adsorption out of the two free valence electrons of carbon monoxide or monoxide molecule one can pair with that of Zn^{+} site as in (II) and the other can be donated to the solid raising the conductivity.



The adsorbed $Zn^{+}-C=O$ species can react with hydrogen to form methane because as shown by EISHENS¹⁴⁾ for methanation reaction on transition metals carbon monoxide should be adsorbed as $M=C=O$ (M =metal atom).

From Fig. 4 (Curve I) it can be seen that when the adsorbed methanol decomposes during heating to 450°C, the reaction becomes very fast between 250 to 350°C so that there is an increase of pressure in spite of continuous evacuation. Above 350°C no further evolution of gases take place and the pressure falls again (the pressure becomes constant in absence of evacuation). But comparison of curves II and III of Fig. 3, shows that even when there is no further reaction, evacuation does not restore the original conductivity *i.e.* that of the reduced oxide. It can be due to strong adsorption of carbon monoxide. From Table I also it can be seen that the conductivity of the oxide evacuated at 450°C after methanol treatment at 350°C for 12 hours is higher than that of the reduced oxide. These observations lead to the conclusion that carbon monoxide is strongly adsorbed on Zn^{+} sites.

In the mechanism suggested above the $-CH_2O-$ radical is supposed to have a finite lifetime on the surface of the catalyst. If after 0.5 hour reaction (Fig. 6, Curve I) the products are removed by evacuation the conductivity increases and it falls again when a second dose is added. The phenomenon can be due to the desorption of adsorbed species $-CH_2O-$ and delocalisation of valence electrons of surface Zn^{+} atoms. However if the reaction is allowed to continue for 3 and 12 hours there is a decrease and increase in conductivity upon evacuation and addition of second dose of methanol respectively (Fig. 6, Curve II and III). This indicates that when $-CH_2O-$ radical is left in contact with the catalyst for a longer period it is transformed into carbon monoxide and hydrogen both of which are electron donors. The free electron concentration of catalyst is thereby increased and desorption of hydrogen in this case becomes easier than when the surface is covered with $-CH_2O-$ radical. Addition of second

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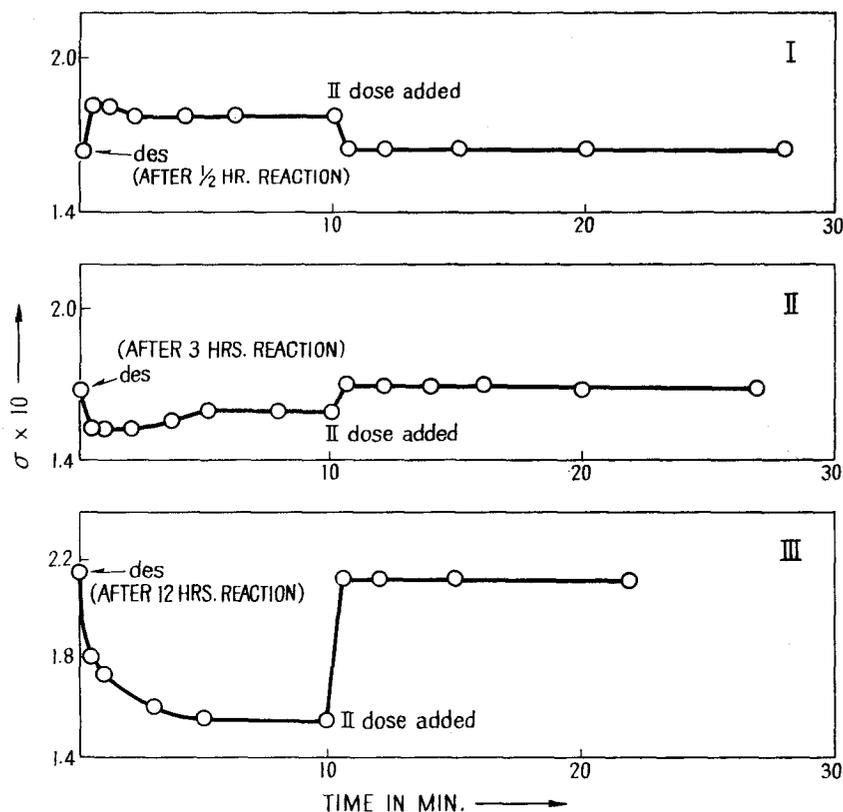


Fig. 6. Effect of desorption and adsorption at 350°C on conductivity of zinc oxide after methanol decomposition for (I) 0.5 hour (II) 3 hours and (III) 12 hours.

dose of methanol produces hydrogen which is re-adsorbed on vacant sites and the conductivity increases again.

The decomposition of $-\text{CH}_2\text{O}-$ radical is also inhibited if the catalyst surface is covered with pre-adsorbed hydrogen. In that case presence of large concentration of free electron will retard the delocalisation of valence electron of Zn^+ site. Consequently the conductivity of the catalyst will tend to decrease due to increasing concentration of $-\text{CH}_2\text{O}-$ radical on the surface as is evident from Fig. 5 (Curve IV).

Conclusion

From electrical conductivity measurements during adsorption and decomposition of methanol on zinc oxide it has been suggested that the

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breakdown of the $-\text{CH}_2\text{O}-$ radical into carbon monoxide and hydrogen is one of the rate determining steps and the surface Zn^+ sites act as active centres for the reaction. DANDY¹⁾ has suggested a similar mechanism from kinetic measurements in a static system. Further investigations using labelled methanol is in progress for a thorough understanding of the different steps involved in the overall process.

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