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Studies of the Partial Oxidation of Methane Over Heterogeneous Catalysts

C. F. CULLIS AND D. E. KEENE,*

Department of Chemistry, The City University, London, E.C.1.

AND

D. L. TRIMM

Department of Chemical Engineering and Chemical Technology, Imperial College, London, S.W.7., England

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Studies have been made of the effects of certain gaseous additives on the oxidation of methane over palladium catalysts. It has been shown that, whereas higher alkanes and partial oxidation products of methane simply retard overall oxidation of the hydrocarbon, certain organic halogen compounds not only reduce the rate of oxidation of methane but also result in the production of isolatable quantities of formaldehyde in high selectivity. In the light of a proposed mechanism for the oxidation of methane in the absence of additives, the action of the halogen compounds is interpreted in terms of the ability of such additives to modify the catalyst surface and to inhibit the further oxidation of the initial products of methane oxidation.

INTRODUCTION

Although in certain circumstances it is desirable to effect partial oxidation of methane, the heterogeneous oxidation of this hydrocarbon usually results in its complete conversion to carbon dioxide and water. Indeed the present incomplete understanding of the mechanism of such oxidation is largely attributable to the apparent absence of partial products which could throw some light on the routes followed by the overall reaction. In some cases, traces of methanol, formaldehyde, and formic acid have been identified (*1*), but over palladium catalysts, for example, formaldehyde yields are only of the order of 0.01% even under conditions specifically designed to facilitate the formation of partial oxidation products (*2*).

Conversion of methane to final oxidation products may, in principle, take place either directly or via the formation of molecular intermediates such as formaldehyde (*3*). In order to determine the nature and role of these intermediates and to enable appreciable quantities of such compounds to be isolated, either the direct route for the complete oxidation of methane or the further oxidation of the intermediate products may be inhibited. Since the chemisorption of methane involves dissociation to labile adsorbed methyl or methylene groups (*4*, *5*), which may carry a slight positive charge (*1*), one method of improving the yields of partial products is to control appropriately the further reactions of these adsorbed species.

In the present work, an attempt has been made to investigate the role of intermediates in the catalytic oxidation of methane. In order to facilitate the detection of rather short-lived species, most of the experimental measurements have been made using a

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* Present address: Gas Council, London Research Station, London, S.W.6.

pulsed flow microreactor technique. Particular attention has been paid to the influence of gaseous additives and in the first instance compounds have been introduced which might be expected to compete for adsorption sites and to react with adsorbed intermediates to produce more stable products. Studies have also been made of the effects of added halogen compounds which would be expected to increase the selectivity of conversion of the initial hydrocarbon to partial oxidation products (*1*, *6*, *7*).

EXPERIMENTAL METHODS

Apparatus and Procedure

Comparison of the efficiencies of various halogen-containing inhibitors was carried out by use of a microcalorimeter bead reactor. This reactor, which was essentially the same as that described by Firth (*8*), contained two beads suspended in an atmosphere of methane and oxygen. Since only one bead is coated with catalyst, the temperature difference between the beads gives a measure of the rate of oxidation (*8*, *9*). In order to minimize discrepancies resulting from the use of several beads, each with slightly different electrical characteristics, the effect, I, produced by a given concentration of inhibitor, was expressed as:

$$I = \frac{\text{Inhibited initial reaction rate}}{\text{Uninhibited initial reaction rate}}.$$

More detailed studies of the reaction taking place in the presence of halomethanes (and some nonhalogenated additives) were carried out in a pulsed flow microreactor. This reactor, which was developed from the techniques first outlined by Kokes *et al.* (*10*) allowed premixed pulses of methane and oxygen to be carried over the catalyst in a stream of helium carrier gas. The dead space immediately downstream of the catalyst bed was kept to a minimum and the products were cooled as rapidly as possible. In normal circumstances, the temperature of the gas stream could be lowered by 400° within 3 cm of the exit of the catalyst bed. No chromatographic separation of products and reactants took place during passage of the gases over the catalyst (*11*) and the kinetics of the reactions in the pulsed flow reactor were not controlled by rates of mass transfer (*12*). A fine thermocouple probe, which was placed either directly in the catalyst bed or in a thin glass pocket, was used to show that the bed was essentially isothermal ($\pm 0.5°C$) under all reaction conditions.

The reactor was arranged so that the gas chromatographic columns were in series with and received the total product sample from the exit of the reactor. All runs were performed with a carrier gas flow rate of 25 ml min^{-1} (at STP) and at a total pressure of 35 psi, a 2-ml plus of (methane + oxygen + any additives) being injected into the stream of pure helium.

Surface areas of the catalyst sponge were measured *in situ* by the chemisorption (at 30°C) and desorption (at 480°C) of carbon monoxide, using a technique based on the pulsed flow method described by Gruber (*13*).

Analytical Methods

Analysis of gaseous reactants and products was carried out with a 5-ft silica gel column (maintained at 0°C), a 6-ft Porapak T column and a 6-ft Polypak 2 column (both maintained at temperatures between 100 and 170°C). Confirmation of product identity was obtained by sampling the eluted fractions and either recycling these through separate columns or applying appropriate chemical tests. Mass spectrometric analysis was used to check the identity of inert gases.

Materials

Catalysts were prepared from "spectrographic purity" materials supplied by Johnson Matthey Limited. The microcalorimeter catalytic beads were formed by coating alumina with a mixture of 10 mole % palladium + 90 mole % thoria as described by Firth (*8*); the thoria, which improves the physical strength and adhesion of the catalyst, has been shown not to affect the catalytic properties of the palladium (*9*). The catalyst beds for the pulsed flow reactor was prepared from 100–

120 mesh palladium sponge which had been annealed at 500°C *in vacuo* in order to yield a material of constant surface area.

Oxygen, nitrogen, and helium were obtained from cylinders, oxygen being purified by fractional distillation of a liquid sample collected at —195°C. Nitrogen and helium were purified by passage first through a bed of copper turnings at 500°C and then through a cold trap (—78°C for N_2, —195°C for He) packed with glass wool, followed by a bed of Linde 3A molecular sieve at room temperature. Mass spectrometric analysis of the purified gases showed that, with the exception of other inert gases, no impurity was present in a concentration exceeding 10^{-3} ppm. Methane, supplied by Air Liquide, was of 99.98% purity and propane, supplied by the Matheson Company, had a quoted minimum purity of 99.5%; both these gases were further purified by fractional distillation. Formaldehyde was generated by controlled heating of paraformaldehyde and stored at 125°C. Methanol and the halomethanes were of Analytical Reagent quality and were carefully fractionated before use.

RESULTS

The Catalyst

Characterisation of the palladium sponges used in the pulsed flow reactor involved carbon monoxide and oxygen adsorption experiments and X-ray examination of the solid.

On the assumption that carbon monoxide is adsorbed with 50% in the linear and 50% in the bridged form (*14*), samples of used palladium sponge (after reduction to the metallic state) were found to have a surface area of ca. 0.16 $m^2\ g^{-1}$. The apparent surface area could be altered by the deposition of carbon on the surface. Carbon was deposited by passage of pulses of pure methane over the catalyst at 480°C, as a result of which the amounts of carbon monoxide adsorbed were found to decrease by a fixed amount (Table 1). The surface area of the catalyst could be restored to its original value by oxidation (carbon dioxide and water being the only detectable products) followed by reduction with hydrogen. As a result of the deposition of carbon, the shape of the carbon monoxide vs time desorption curve was altered (Fig. 1), the total area under the curve being reduced and one lobe removed.

TABLE 1

EFFECT OF METHANE PYROLYSIS ON THE ACTIVE SURFACE AREA OF A PALLADIUM CATALYST

Weight of catalyst, 2.077 g of Pd; volume of carbon monoxide pulse, 0.3 ml (at STP).

Run no.	Area of "clean" catalyst ($m^2\ g^{-1}$)	Run no.	Vol of methane pulse (ml STP)	Area of "contaminated" catalyst ($m^2\ g^{-1}$)
1	0.147	3	6.4	0.113
2	0.156	4	12.8	0.116
5	0.158	7	2.0	0.116
6	0.151	8	4.0	0.117
9	0.149			
10	0.144			
Mean	0.151 (± 6.5%)			0.116 (± 2.5%)

There is evidence that, during methane oxidation experiments, oxygen adsorbed on the catalyst surface may react further with the catalyst to produce bulk palladium oxide. At 450°C, the extent of such oxidation was found to be a function of the methane:oxygen ratio, oxidation of the catalyst being rapid when this ratio was less than unity (Fig. 2). Repeated passage of pulses containing the same amounts of methane and oxygen caused decreasing amounts of catalyst oxidation, until the catalyst approached a constant level of activity. Unless otherwise stated, all catalysts used in the present work were conditioned to constant activity with a $CH_4 + 2O_2$ mixture and should therefore be considered to consist largely of palladium oxide. X-ray examination of the catalysts showed that this was indeed the case.

The Methane–Oxygen Reaction in the Absence of Gaseous Additives

The kinetics of this reaction have been studied in some detail both over micro-

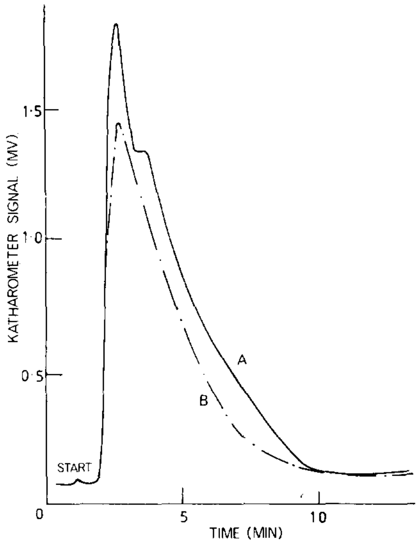


FIG. 1. Desorption vs time curves for carbon monoxide monolayers: Weight of catalyst, 2.077 g (as Pd); carbon monoxide desorbed at 480°C into helium carrier gas at 25 ml min^{-1} and 35 psi. Curve A, "clean" catalyst; curve B, catalyst "contaminated" by methane pyrolysis at 480°C.

catalytic beads (*8*) and in a pulsed flow reactor (*15*) and a tubular reactor (*16*). For purposes of comparison with the measurements obtained in the presence of gaseous additives, it is perhaps useful to summarize previously unpublished results obtained in the pulsed flow reactor.

Over a range of methane:oxygen ratios varying from 0.125 to 1.0, the reaction rate at 300°C was found to be proportional to the square root of initial methane concentration and to be independent of initial oxygen concentration. These measurements, which were carried out at total conversions from 10 to 50%, were extended up to 400°C to give an apparent activation energy of 19 ± 1 kcal $mole^{-1}$ for a $CH_4 + 2O_2$ mixture.

The reaction products were investigated over a range of temperature (280–480°C), methane:oxygen ratio (0.33–4.0) and weight of catalyst (0.09–2.22 g of Pd). In addition, the effect of an inert diluent (up to 90 vol % He) was studied over an "equilibrium" catalyst (i.e., a catalyst conditioned to constant activity as described above), a metallic catalyst (i.e., a catalyst carefully

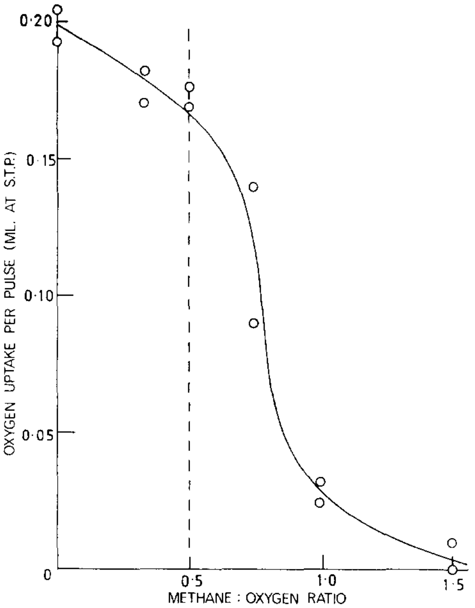


FIG. 2. Extent of oxidation of palladium catalyst by methane + oxygen mixtures at 450°C: Weight of catalyst, 0.77 g (as Pd); each pulse contains 0.663 ml of O_2 (at STP). Flow rate, 25 ml min^{-1}; pressure, 35 psi; contact time, ca. 2 sec.

reduced and used only once) and an oxide catalyst (i.e., a catalyst carefully oxidized and used only once). Over the whole range of experimental conditions, carbon dioxide and water nearly always accounted for over 99% of the methane consumed. Traces of hydrogen (maximum yield, 3%) were observed under conditions favoring the "cracking" of methane but carbon monoxide could not be detected among the products at temperatures below 450°C. Formaldehyde was found to be present at only very low levels (yields varying from 0.005–0.05%); the amounts of this compound were not reproducible but an oxide catalyst tended to give larger quantities than a metal catalyst.

The Methane–Oxygen Reaction in the Presence of Gaseous Additives

Experiments were carried out in the pulsed flow reactor to determine the effect which partial products of methane oxidation and higher alkanes exert on the reaction. Some typical results are shown in Table 2. Added methanol and formaldehyde

TABLE 2

INFLUENCE OF PROPANE AND OF PARTIAL METHANE OXIDATION PRODUCTS ON THE RATE OF OXIDATION OF METHANE OVER AN "EQUILIBRIUM" PALLADIUM CATALYST

Reactant mixture, $CH_4 + 2O_2$ + additive; flow rate, 25 ml min^{-1} (at STP); pressure, 35 psi.

Wt of catalyst (g as Pd)	Reaction temp (°C)	Additive (mole %)	Methane conversion (%)	Additive conversion (%)
0.770	410	7.00 He	11.46	—
			11.46	—
			11.46	—
		7.82 C_3H_8	7.14	10.7
			7.47	10.4
			8.12	9.9
0.770	399	4.50 He	5.90	—
			6.20	—
		4.34 HCHO	4.03	100
			3.75	100
			3.90	100
2.226	254	11.87 He	11.90	—
			12.20	—
			11.70	—
		11.24 CH_3OH	4.21	100
			4.55	100
			4.34	100

both retard the oxidation of methane but are themselves completely oxidized. Propane, which also inhibits methane oxidation, is consumed to a relatively small extent.

Studies were also made of the effects of some halogen-containing additives, since such compounds are known to facilitate the isolation of intermediate products during the heterogeneous catalytic oxidation of other hydrocarbons, e.g., ethylene (*1*). A comparative survey of the effects of a number of halomethanes was first made using the microcatalytic bead reactor. Experiments with the four chloromethanes showed that, although at inhibitor concentrations sufficient to give $I < 0.5$ the inhibiting efficiency of these compounds depended on both the number of chlorine atoms in the molecule and their reactivity, at lower concentrations of inhibitor the effects of the different compounds were not very different (Fig. 3). Comparison of the effect of dichloromethane with some other halomethanes showed that this compound had about the same inhibiting efficiency as difluoromethane but was a considerably less powerful inhibitor than dibromomethane or diiodomethane (Fig. 4). However, owing to the possibility of more marked catalysis by bromine or iodine compounds of the homogeneous oxidation of hydrocarbons, it was decided to make somewhat fuller studies with a chlorine compound.

Studies in the pulsed flow reactor of the influence of small quantities of some chloromethanes showed that these compounds decrease the overall rate of oxidation of methane but increase considerably the yields of formaldehyde. It was considered, however, that the underlying mechanism of oxidation could be better elucidated by the use of an additive which did not cause too complete inhibition; and for this reason dichloromethane, which had the least powerful inhibiting effect of the four chlorine compounds studied (Fig. 3), was selected for more detailed investigation.

Figure 5 shows the effect of 0.1–10 mole

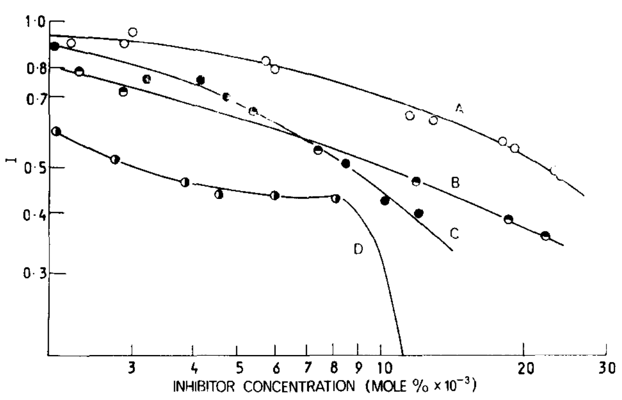


FIG. 3. Influence of chloromethanes on the rate of oxidation of methane over a Pd/ThO_2 catalyst bead at 447°C: I = (inhibited initial reaction rate)/(uninhibited initial reaction rate). Reactant mixture, 4 mole % of CH_4 in O_2; pressure, 5.9 psi. Additive: curve A, CH_2Cl_2; curve B, CH_3Cl; curve C, $CHCl_3$; curve D, CCl_4

% of dichloromethane which strongly inhibits the overall oxidation of methane. At the same time, however, this compound promotes the formation of formaldehyde (Fig. 6) and it will be seen that one characteristic feature of these experiments is that the production of formaldehyde continues for a time after the direct addition of the additive has been stopped. After use of mixtures containing dichloromethane, the accumulated residues on the catalyst surface may be removed by repeated pulses of pure methane + oxygen, the activity and selectivity of the catalyst gradually reverting to the values attained before halogen-containing mixtures were used. The introduction of dichloromethane did not produce detectable amounts of any other partial oxidation products of methane and the consumption of the inhibitor was always complete with pulses containing less than 0.005 ml of halogen compound. The results in Fig. 6 show that the amounts of formaldehyde produced are much greater

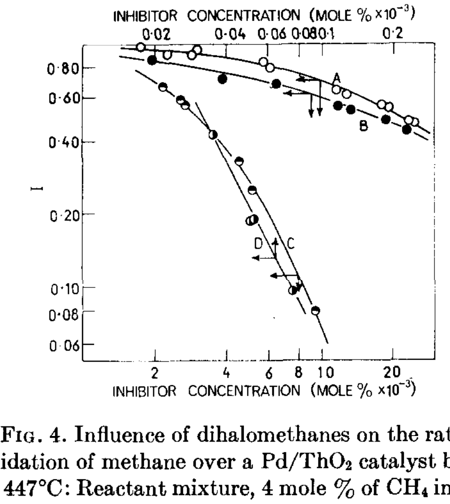


FIG. 4. Influence of dihalomethanes on the rate of oxidation of methane over a Pd/ThO_2 catalyst bead at 447°C: Reactant mixture, 4 mole % of CH_4 in O_2; pressure, 5.9 psi. Additive: curve A, CH_2Cl_2; curve B, CCl_2F_2; curve C, CH_2Br_2; curve D, CH_2I_2. Lower horizontal scale: conc of dichloromethane, difluorodichloromethane, and dibromomethane; upper horizontal scale: conc of diiodomethane.

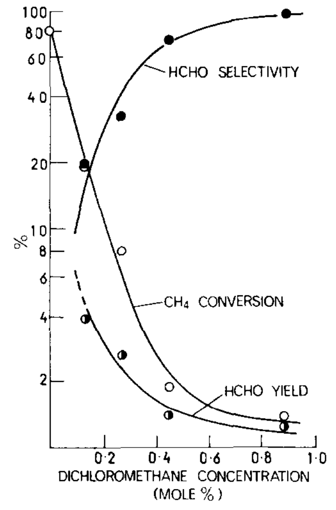


FIG. 5. Influence of dichloromethane on the oxidation of methane over an "equilibrium" palladium catalyst at 375°C: Weight of catalyst, 2.077 g (as Pd); reactant mixture, $CH_4 + 2O_2$ + additive; flow rate, 25 ml min^{-1}; pressure, 35 psi; pulse volume, 2.1 ml (at STP).

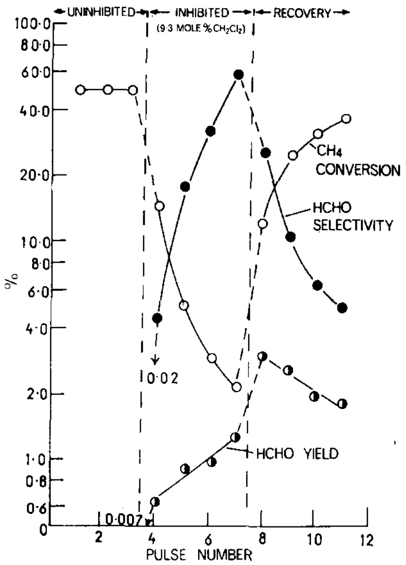


FIG. 6. Cumulative influence of dichloromethane on the oxidation of methane over an "equilibrium" palladium catalyst at 375°C: Weight of catalyst, 2.077 g (as Pd); reactant mixture, $CH_4 + 2O_2 +$ 9.3% additive (or helium); flow rate, 25 ml min^{-1}; pressure, 35 psi; pulse volume, 2.1 ml (at STP).

than can be accounted for by oxidation of the dichloromethane itself.

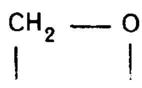
DISCUSSION

Studies of the desorption of carbon monoxide from a palladium catalyst (Fig. 1) suggest that the molecules of this gas can be adsorbed in two distinct ways. The more firmly bound molecules, which account for ca. 20% of the total gas adsorbed, are believed to be bridge-bonded while the remainder are presumably linearly-bonded (*17*). Deposition of carbon on the surface has the effect of blocking selectively those sites which favor bridge-bonding. Chemisorption of methane is known to be dissociative, the production of either methyl or methylene radicals involving an activation energy of ca. 100 kcal mole^{-1} (*18*). It seems likely, however, that methane is most strongly chemisorbed on the "bridge sites" as bridge-bonded methylene radicals (*4*) and that oxidation involves primarily the reaction of less stable linearly-bonded radicals with surface lattice oxygen (*1*).

The results in the presence of nonhalogenated additives suggest that these compounds inhibit reaction simply by competing successfully with methane for surface sites (*19*). In no case was the product spectrum significantly different from that observed during the oxidation of methane alone.

The addition of halomethanes also strongly inhibits the oxidation of methane and the effectiveness of inhibition increases with the lability of the carbon–halogen bond (Fig. 4). Adsorption of haloalkanes on metals is believed to be dissociative (*20*) and, as a result, the palladium catalyst will tend to become covered by negatively charged halogen species. However one striking effect of the halomethanes is to increase dramatically the yields of formaldehyde (Figs. 5 and 6). Most, if not all, of this partial oxidation product must be derived from methane rather than from dichloromethane, since the quantity of formaldehyde is considerably greater than the amount of additive introduced. Furthermore the enhanced production of formaldehyde continues for some time after the introduction of the additive has ceased (Fig. 6).

The finding that formaldehyde can be formed in quite high yields indicates that this compound is an important intermediate in certain circumstances. The observed dependence of rate on reactant concentrations in the uninhibited oxidation (see Results) suggests that the rate-determining step is a surface reaction between adsorbed methane fragments and adsorbed oxygen, the latter being present in excess. By analogy, however, with other catalytic insertion reactions (*21*), it seems likely that the immediate precursor of formaldehyde is a complex:

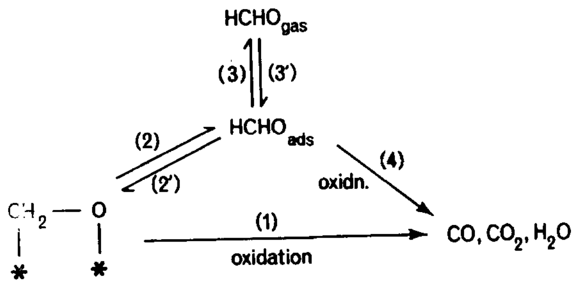


$$\begin{array}{ccc} CH_2 & — & O \\ | & & | \end{array}$$

formed by the interaction of linearly-bonded methylene radicals with some oxygen-containing species.

The observation that the addition of dichloromethane has an effect which is initially cumulative and that the catalyst only slowly returns to its original state when the halogen compound is no longer introduced (Fig. 6) suggests that the additive acts primarily by modifying the electronic properties of the catalyst surface. The introduction of halo-compounds would be expected to lead to the formation of dipoles with the negative charge facing outwards, and the presence of these will tend to decrease the coverage by oxygen ions.

Since the direct conversion of the methylene–oxygen complex to final products [reaction (1)]:



probably involves interaction with adsorbed oxygen, the extent of this reaction relative to reaction (2) would be expected to be decreased by halogen-containing additives. Furthermore, if formaldehyde, like other oxygenated intermediates, acts as an electron-acceptor, the presence of negative dipoles should enhance desorption [reaction (3)] rather than further oxidation [reaction (4)] of this partial oxidation product.

If this explanation of increased formaldehyde yields is correct, it might be expected that other gaseous additives giving rise to negative dipoles on the surface would have similar effects. Experiments are at present in progress to ascertain whether this is the case.

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