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Formaldehyde as an Intermediate in the Steam Reforming of Methane

In steam reforming of methane to produce synthesis gas on supported Ni catalysts, the possibility of formate species as intermediates has been discussed by Lavrov and Petrenkov (*1*) and Ross (*2*). Thermodynamic calculations by De Deken (*3*) indicated that formaldehyde could be one of the intermediates in methane–steam reforming, but it could not be detected in the usual on-line gas chromatographic analysis of the products formed in an integral reactor at 15 bar pressure. The decomposition or combustion of formaldehyde on the catalyst would of course be very easy under such extreme conditions. Hence the temperature-programmed reaction of methane and water vapor, with continuous scanning of the reaction products, was carried out in an attempt to detect formaldehyde in the reaction product. The results obtained are reported in this paper.

A commercial steam-reforming catalyst (12% Ni/α-Al_2O_3), crushed to a particle size of <0.5 mm was used in the present study. About 150 mg of the catalyst was taken in a 3-mm-i.d. quartz reactor, which was kept in an oven with a Stanton Redcroft temperature programmer. At the exit of the reactor a quartz capillary orifice leak, of the type described by Kasemo (*4*), was connected for local fast-response gas sampling to a quadrupole mass spectrometer (MS) (Balzers, QMG 112). Using Balzers Quadrupole Data Processor (QDP 101), the MS signal for seven components could be preselected and continuously scanned, and recorded on a multipen recorder. With the direct connection of the reactor effluent at 1 bar pressure to the MS operating at 10^{-6} mbar, and with the quartz capillary leak being the only constriction in between, the time lag between the reactor and the MS could be reduced to a few seconds.

The catalyst was initially reduced *in situ* by heating in H_2 at 20 K/min up to 1023 K, keeping at that temperature for 1 hr, and then cooling to ambient temperature in the H_2 stream. Maintaining this H_2 stream, another stream of CH_4, saturated with water in a bubbler at 293 K, was passed over the catalyst (molar ratio $CH_4/H_2 = 2.05$, $H_2O/CH_4 = 0.024$). The temperature of the reactor was then raised at the rate of 5 K/min and the product analysis was monitored continuously by the MS.

Figure 1 shows a typical MS analysis of the product stream with progressively increasing temperature up to 973 K. The thermodynamically favored temperature ranges for the formation of CO_2 and CO,

$$CH_4 + 2\ H_2O \rightleftharpoons CO_2 + 4\ H_2 \quad (1)$$

$$CH_4 + H_2O \rightleftharpoons CO + 3\ H_2, \quad (2)$$

are reflected in the TPR curves. The conversion being low, the H_2 formed in the reaction and the CH_4 and H_2O reacted were not sufficient to indicate changes in the concentrations of these species in the total gas stream, and hence they are not shown in the figure. Formaldehyde at mass 30 is easily detected above 673 K. This signal was not due to ethane, since ethane would have given a prominent secondary signal at mass 29, which was not seen in the present work.

In another series of experiments, a fresh sample of the catalyst was reduced as above, the stream of H_2 was stopped after

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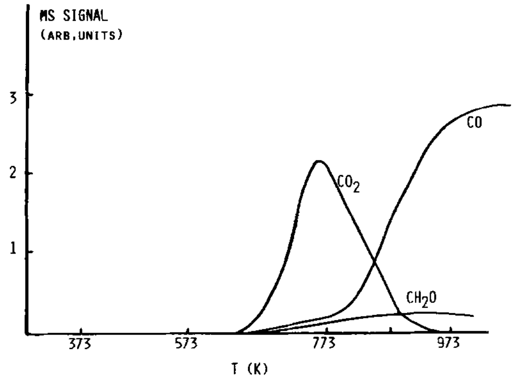


FIG. 1. Temperature-programmed reaction of methane saturated with water vapor over Ni/α-Al_2O_3 steam-reforming catalyst in the presence of hydrogen added to the feed.

cooling the catalyst to 298 K, and a stream of CH_4 saturated with water (molar ratio $H_2O/CH_4 = 0.024$) was passed over the catalyst. The temperature was then raised at the rate of 5 K/min. In the absence of H_2, the reduced Ni in the catalyst is easily reoxidized by steam. With increasing temperature, at a certain stage the methane–steam-reforming reactions start:

$$CH_4 \rightleftharpoons C_{ads} + 2\ H_2 \quad (3)$$

$$C_{ads} + 2\ H_2O \rightleftharpoons CO_2 + 2\ H_2 \quad (4)$$

$$C_{ads} + H_2O \rightleftharpoons CO + H_2 \quad (5)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \text{(water-gas shift)} \quad (6)$$

The hydrogen generated *in situ* reduces the catalyst to its active form. The TPR curves of Fig. 2 show that this reduction and activation of the catalyst occurs rather sharply at 683 K. The sudden burst of catalytic activity at this temperature, producing H_2, CO, and CH_2O, is remarkable.

Under the conditions of steam reforming, it is essential to add some H_2 to the methane–steam feed to ensure that the whole catalyst bed remains in a sufficiently reduced condition. (In commercial practice, some hydrogen is recycled for this purpose.) If this H_2 addition to the feed is stopped at steady-state conditions, the catalyst becomes rapidly deactivated. A postmortem examination of the catalyst in such a case has been reported by us earlier (*5*). Temperature-programmed combustion of the carbon in such a catalyst showed a very slow combustion above 873–973 K over a few hours, suggesting that the carbon from the bulk of the catalyst had to diffuse slowly to the surface to undergo combustion. This was confirmed by XPS studies, which showed that this carbon could be present both as carbidic and graphitic carbon. Furthermore, determination of the depth-composition profile of the Ni particles on the catalyst by sputter-etching during the XPS studies showed that the carbon could diffuse or dissolve into Ni crystallites even up to a depth of 60 nm in such a deactivated catalyst.

Above 820 K in Fig. 2, there is a loss of methane from the gas phase without any corresponding increase in the concentration of the monitored reaction products (concentration of H_2 was already beyond the measuring range). This may be due to the onset of cracking of methane.

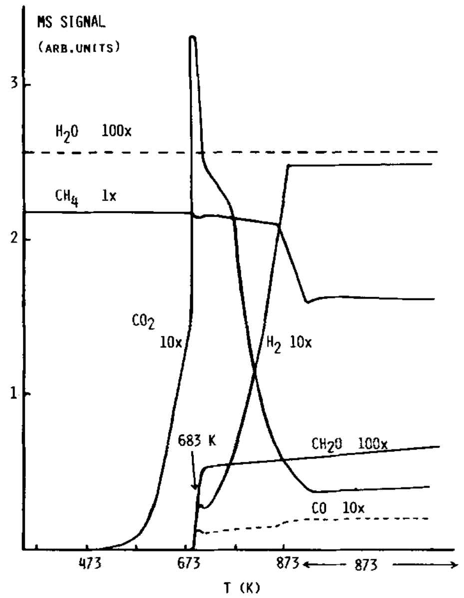
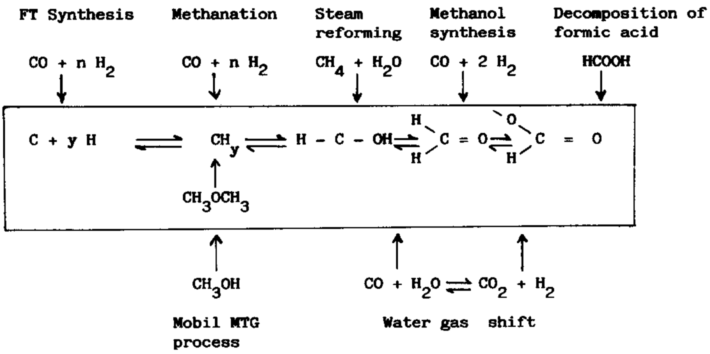


FIG. 2. Temperature-programmed reaction of methane saturated with water vapor over the steam-reforming catalyst in the absence of hydrogen in the feed.



SCHEME 1. Surface species possibly common to several catalytic reactions.

The detection of formaldehyde in the product stream in the stream reforming of methane conforms to the general pattern of carbonaceous species (oxygenated or not) as intermediates on the catalyst surface in different types of reactions on a variety of metal and oxide catalysts:

$$CH_x + H_2O \rightleftharpoons CH_yO_{ads} \rightleftharpoons CO + yH_{ads}. \quad (7)$$

Whether the CH_yO intermediate is in an enolic or ketonic form, whether y in it has the values 1, 2, or 3, whether the C–O bond rupture occurs before or after the attachment of hydrogen to the carbon in the case of ($CO + nH_2$)-type reactions, etc., may depend very much on the specificity of the catalyst used, the composition of the reaction mixture, and the severity of the prevailing experimental conditions. For instance, the present general consensus (*6*) on Fischer–Tropsch synthesis is that carbidic carbon is the reaction intermediate whereas graphitic carbon can deactivate the catalyst. The role of oxygenated intermediates as precursors of the carbidic species has also been proposed by several investigators in the past:

$$CO + yH_{ads} \rightleftharpoons CH_yO_{ads} \rightleftharpoons CH_{x\,ads} + H_2O \quad (8)$$

which is the reverse of the steam-reforming reaction [Eq. (7)]. From a kinetic study of methanation over supported Fe, Co, Ni, Pt, Pd, Ir, Rh, and Ru catalysts, Vannice (*7*) proposes that $CHOH_{ads}$ is the most abundant surface intermediate on the catalyst. Earlier studies on the decomposition of formic acid into $CO + H_2O$ or $CO_2 + H_2$ on metal catalysts (*8*) and oxide catalysts (*9*) have shown that in most cases the formate ion $(HCOO)^-$ is the intermediate on the catalyst surface. From kinetic and infrared spectroscopic studies, Scholten *et al.* (*10*) propose the formate ion as a common intermediate for both formic acid decomposition and the water-gas shift reaction (Eq. 6) on alumina and magnesia catalysts. From temperature-programmed reaction studies, Bowker *et al.* (*11*) conclude that the formate appears to be the pivotal intermediate in reactions of synthesis gas on zinc oxide catalysts, decomposing into CO and H_2 or, depending on the hydrogen coverage, becoming hydrogenated into methanol. In reactions of $CO + H_2$ on $LaRhO_3$ catalysts, the presence of CH_x and CH_xO precursors and the changes in their relative concentrations with temperature leading to different selectivities have been reported by Watson and Somorjai (*12*). Also in the formation of C_2-oxygenated species from $CO + H_2$ over Rh/SiO_2 catalysts, an insertion of CO into adsorbed C_1 species and subsequent formation of acetate ions have been established by Orita *et al.* (*13*) very recently.

In view of the above broad consensus on the nature of carbonaceous and/or oxygenated species on catalyst surfaces, Scheme 1 may be proposed as a general chemical framework for all these reactions. Even the conversion of methanol to gasoline (MTG) on ZSM-5-type catalysts by the Mobil process may be included here, since it is believed to proceed in the sequence

$$\text{methanol} \rightarrow \text{dimethyl ether} \rightarrow \text{olefin} \rightarrow (CH_2)_n.$$

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