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COMMUNICATION

Photocatalytic homolysis of methyl formate to dry formaldehyde on PdO/TiO₂: Photocatalytic reverse Tishchenko reaction of methyl formate

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Photocatalytic homolysis of dry methyl formate (MF) to dry formaldehyde readily takes place in high selectivity ($\geq 80\%$) upon irradiation of MF vapour on PdO/TiO₂ in the 385-1050 nm region. The Pd(I)Pd(0) nanoparticles supported on Ti(III)-bearing TiO₂ produced during the reaction are proposed to be the active form of the catalyst for this novel reaction.

Methyl formate (MF) has been used as a reagent for the production of perfumes and food flavouring agents and as a solvent. During these applications and through vegetation it is often released to the atmosphere.^{1,2} Dimethyl ether and dimethoxy methane have been used as diesel substituents or as diesel additives as a means to reduce the emission of carbon particulates from automobiles.³⁻⁵ MF is also a key intermediate during their combustion. In this respect, thermolysis,⁵⁻⁹ base-catalyzed thermolysis,^{10,11} photolysis with ultraviolet light,^{1,12,13} and catalytic photolysis of MF on various metal supported TiO₂¹⁴⁻¹⁶ have received great attention.

The theoretical studies on the unimolecular decomposition of MF have shown that there are four sets of decomposition products, (1) CH₃OH + CO, (2) two CH₂O, (3) CH₄ + CO₂, and (4) HCOH + CH₂O, with the activation energy increasing in the order of (1) < (2) < (3) < (4) (Figure 1).⁹ Consistent with this, various experiments have demonstrated that the formation of CH₃OH and CO (CO elimination from MF) is the major reaction during MF thermolysis.⁵⁻⁹ Even during the related base-catalyzed thermolysis, the CO elimination occurs exclusively.^{10,11} In this respect, MF has also been regarded as a CO carrier or a CO storage compound.⁸

In the case of unimolecular photolysis of MF with UV lights (193.3 and 234 nm), the CO elimination has been shown to be the major reaction.^{1,12} In the case of photocatalytic decomposition of MF on M/TiO₂ (M = Pt, Pd, Rh, Ir, and Ru) with UV, the products were CO, CO₂, and H₂, indicating that the formation of CO and CH₃OH takes place first and the dehydrogenation of CH₃OH to HCOOH and the decomposition of HCOOH to H₂ and CO₂ take place subsequently.^{15,16} With bare TiO₂ as the catalyst the photolysis of MF does not take place, unless O₂ is present.¹⁴

Thus, the heterolysis of MF to CO and CH₃OH (CO elimination) has been the exclusive or primary reaction.^{1,5-13,15,16} In this respect, finding a novel reaction that leads to homolysis of MF to two CH₂O molecules or the unprecedented reverse Tishchenko reaction of MF would be a highly valuable addition to the chemistry of MF.

Formaldehyde should be highly pure and anhydrous to be used for the preparation of commercially valuable high polymeric polyoxymethylene¹⁷ and various aminoplast adhesives.¹⁸ Aqueous CH₂O solution can be dehydrated to produce anhydrous CH₂O. However, the drying and concentrating processes are not only highly cumbersome but during these processes formic acid, low molecular weight polymers, and other by-products are also formed, which must be removed.¹⁹ Accordingly, the highly pure anhydrous CH₂O obtained by this method becomes very expensive. Instead of this, anhydrous CH₂O has been prepared by dehydrogenation of methanol on Ag,²⁰ Ag supported on SiO₂/MgO/Al₂O₃,¹⁷ and Fe₂O₃/MoO₃.^{21,22} However, the catalysts are not stable and the reactions are carried out at high temperatures (350-700 °C).²³ In this respect, the novel catalysts that are highly stable and can be used unlimitedly under

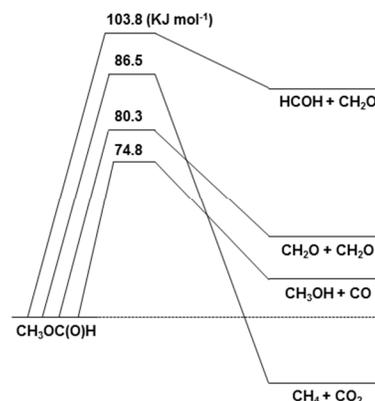


Fig. 1 The potential surfaces for four different types of unimolecular decomposition of MF proposed by Francisco and the coworkers.⁹

mild conditions should be developed.

We now report that MF vapour undergoes homolysis to two anhydrous CH_2O in high selectivity (>80%) upon passing it over PdO-supported TiO_2 (PdO/TiO_2) under a solar simulated light and the catalyst is stable for an unlimited period of time.

PdO/TiO_2 was prepared by impregnation of $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ onto TiO_2 powder (Degussa P25), followed by calcination at 400°C for 4 h. The amount of Pd loading was 1%. Similarly, Pt-loaded TiO_2 (PtO/TiO_2), Au_2O_3 -loaded TiO_2 , (AuO/TiO_2) and CuO-loaded TiO_2 (CuO/TiO_2) were prepared. A metal oxide (MO)-loaded TiO_2 (MO/TiO_2) powder (300 mg) was placed on a Petri dish and the MO/TiO_2 -containing Petri dish was placed at the bottom of a stainless steel reactor having a quartz window at the top. The temperature of the reactor was maintained at 30°C . The MF vapor was introduced into the reactor in the vapor phase by passing a carrier gas (Ar, H_2 , or O_2) through a glass bubbler filled with MF. The MF used in this study was carefully dried in a glove box charged with dry Ar by storing it in a bottle charged with dried Na-zeolite A pellets for 1 day. The small amount of methanol that exists in MF as the stabilizer was not completely removed. So the MF used in this work contained 0.4% of methanol (Supporting Information).

The flow rate of the carrier gas was 6 mL min^{-1} . The temperature of the MF-containing bubbler was maintained between -40 and -1°C . The rate of MF input into the reactor was between 5.5 and $680\ \mu\text{mol h}^{-1}\text{ cm}^{-2}$. The MF conversions varied between 33 and 0.1% depending on the rate of MF input, the nature of catalyst, and the reaction condition. In many cases, the rate of MF input was maintained to be very high ($>450\ \mu\text{mol h}^{-1}\text{ cm}^{-2}$) to minimize the secondary reaction of the primary product by rapidly sweeping the primary products away from the catalyst. To see the effect of the moisture on the reaction rate and the product selectivity, the gas stream of MF and a carrier gas was passed through a water bubbler to simultaneously introduce moisture and MF into the reactor. The

MF-to-moisture ($\text{MF}/\text{H}_2\text{O}$) ratio was 17 ± 3 . Four different types of lights were used for photocatalytic reactions. The AM-1.5 solar simulated light but with the spectral width between 320 and 1050 nm (light A) was used as the primary irradiation source (Figure 2). The power of the solar simulated light used in our work was 72 mW cm^{-2} due to the absence of the infrared lights in the $1150\text{--}3200\text{ nm}$ region. By using long pass cut off filters the solar simulated lights with the spectral widths between 385 and 1050 nm (light B) and between $515\text{--}1050\text{ nm}$ (light C) were also produced and used. We also used a UV light with the spectral width between 235 and 400 nm (light D). The plots of the power density of the lights with respect to the wavelength are shown in Figure 2. The diffuse-reflectance spectra of PdO/TiO_2 and the PdO/TiO_2 irradiated with light A in the presence of the MF vapour are also shown.

The irradiated area was 6 cm^2 . For dark reactions the quartz window of the reactor was covered with an opaque lid. The stream of vapours from the outlet of the reactor was introduced on-line into one or two gas chromatographs (GCs) equipped with a flame ionization detector (FID) and a pulsed discharge detector (PDD). Several different types of GC columns were used to analyze the products (SI). The amounts of reactants and products are reported in terms of μmol per a unit area (1 cm^2) and per h ($\mu\text{mol cm}^{-2}\text{ h}^{-1}$).

With the dry MF vapour in high input rates ($>450\ \mu\text{mol cm}^{-2}\text{ h}^{-1}$), PdO/TiO_2 as the photocatalyst, light A as the light source, and Ar as the carrier gas, the reacted amount of MF was $16.0\ \mu\text{mol cm}^{-2}\text{ h}^{-1}$ (Figure 3A). With O_2 as the carrier gas the reacted amount increased substantially (to $20.0\ \mu\text{mol cm}^{-2}\text{ h}^{-1}$), indicating that the cheaper anhydrous air can be used as a better carrier gas. However, with H_2 as the carrier gas, the reacted amount decreased sharply ($6.0\ \mu\text{mol cm}^{-2}\text{ h}^{-1}$).

The nature of MO also sensitively affected the reacted amount. Thus, with PdO, PtO, AuO, and CuO as MO, respectively, the reacted amounts were 16.0 to 6.2 , 2.2 , and to $2.0\ \mu\text{mol cm}^{-2}\text{ h}^{-1}$, respectively (Figure 3B). Thus, PdO/TiO_2 is most active. The nature of light also sensitively affected the reacted amount. Thus, while light A gave $16.0\ \mu\text{mol cm}^{-2}\text{ h}^{-1}$, light B, light C, and light D gave 8.0 , 2.6 , $31.0\ \mu\text{mol cm}^{-2}\text{ h}^{-1}$, respectively (Figure 3C).

Interestingly, when moist MF ($\text{MF}/\text{H}_2\text{O}$ ratio = 17) was fed into the reactor under the condition of light A, PdO/TiO_2 , Ar, the reacted amount increased by 2.5 times (to $41.0\ \mu\text{mol cm}^{-2}\text{ h}^{-1}$) with respect to that produced under the dry condition (Figure 3D). Under this moist condition, the use of O_2 or H_2 as the carrier gas gave rise to a decrease in the reacted amount by $\sim 50\%$.

Other products and the overall product selectivities are shown in Figure 4. The minor products are CH_3OH , CO_2 , CO, and H_2 . The CH_2O selectivity remained at $\sim 80\%$ regardless of the carrier gas under the condition of light A, PdO/TiO_2 , and dry MF (Figure 4A). The high selectivity maintained until the conversion reached to 33% by decreasing the input rate of dry MF to $5.5\ \mu\text{mol cm}^{-2}\text{ h}^{-1}$. In contrast, the nature of MO sensitively affected the CH_2O selectivity and the product distribution. Thus, with PdO, PtO, AuO, and CuO, respectively, the CH_2O selectivities were 84, 89, 59, and 34%, respectively (Figure 4B). The nature of the light also affected the product distribution (Figure 4C). Thus, the CH_2O selectivities with lights A, B, C, and D were 84, 97, 86, and 65%, respectively. In the presence of moisture ($\text{MF}/\text{H}_2\text{O} = 17$), the CH_2O selectivity decreased

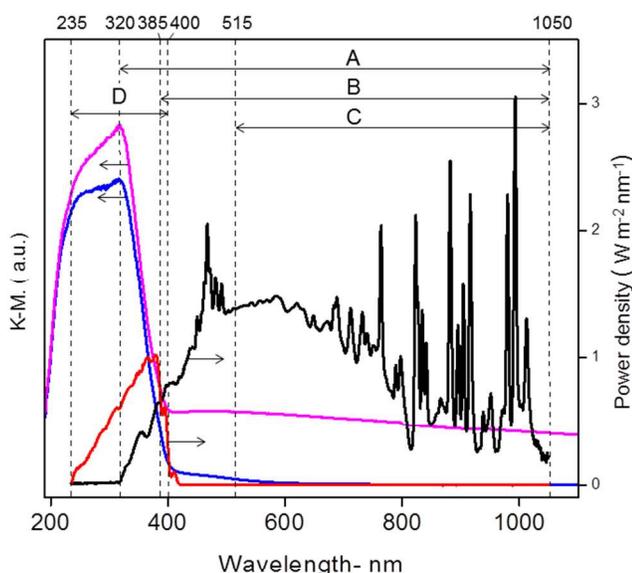


Fig. 2 Plots of power density of the solar simulated light and UV light used in this study and the diffuse reflectance spectra of PdO/TiO_2 (blue) and PdO/TiO_2 irradiated with the solar simulated light in the presence of dry MF vapor (pink).

sharply to below 55% with Ar as the carrier gas and even to below 30% with O₂ and H₂ as the carrier gases. Thus, the elimination of moisture is crucial for higher CH₂O selectivities.

The PdO/TiO₂ powder is nearly white because the loaded amount of PdO (black) is only 1%. Accordingly, the diffuse-reflectance spectrum of (blue spectrum in Figure 2) has only a weak absorption tail between 400 and 700 nm. However, the color of PdO/TiO₂ immediately turned grey and a very broad absorption band appeared over the entire visible region (pink spectrum in Figure 2) upon adsorption of MF either in the dark or under the light. We attribute the broad new absorption band to the absorption by the reduced forms of PdO, such as Pd(I) and Pd(0) species.

The EPR spectra of the related various samples taken at 25 K in the dark and under light B are shown in Fig. 5. TiO₂ alone in the dark gave a very weak signal due to Ti(III) at $g = 1.975$ (Fig. 5A). Upon irradiation with light B, two strong signals due to the hole (h^+ , $g = 2.01$) and Ti(III) ($g = XX, YY, ZZ$) appeared (Fig. 5B). This phenomenon happens because TiO₂ absorbs light in the 385-400 region. Indeed, the two signals became more intense when TiO₂ was irradiated with UV (light D). The MF-adsorbed TiO₂ (TiO₂-MF) does not show any EPR signal in the dark except the original weak Ti(III) signal (Fig. 5C). However, a weak h^+ signal and a strong Ti(III) signal appeared upon irradiation of TiO₂-MF with light B (Fig. 5D), indicating that the electron transfer from MF to h^+ took place. PdO/TiO₂ did not give additional ESR signals due to h^+ and Ti(III) in the dark (Fig. 5E). Upon irradiation with light B, it gave a weak and broad signal at $g = 2.1$ due to Pd(I),²⁴ together with the signals due to h^+ and Ti(III) (Fig. 5F). In the presence of MF, either in the

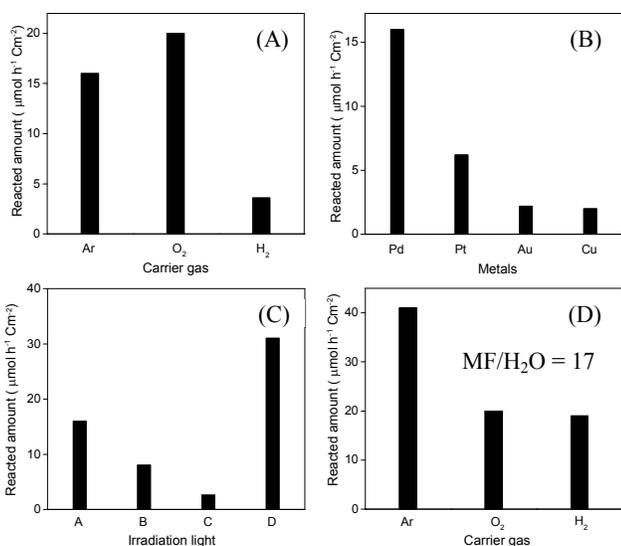


Fig. 3 (A) Effect of the carrier gas on the reacted amount of dry MF during the photocatalytic reaction on PdO/TiO₂ with light A. (B) Effect of the nature of MO (PdO, PtO, AuO, and CuO) on the reacted amount of dry MF during the photocatalytic reaction with the solar simulated light and Ar as the carrier gas. (C) Effect of the irradiation light (A, B, C, and D) on the reacted amount of dry MF during the photocatalytic reaction on PdO/TiO₂ Ar as the carrier gas. (D) Effect of the carrier gas on the reacted amount of moist MF (MF/H₂O = 17) during the photocatalytic reaction on PdO/TiO₂ with light A.

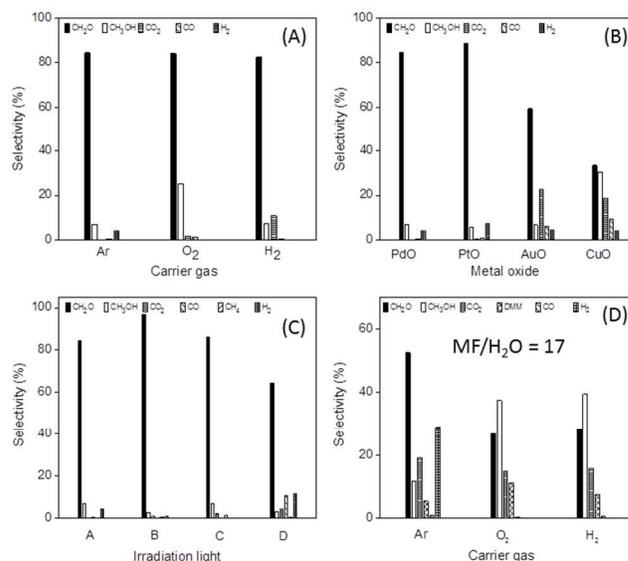


Fig. 4 (A) Effect of the carrier gas on the product distribution during the photocatalytic reaction of dry MF on PdO/TiO₂ with light A. (B) Effect of the nature of MO (PdO, PtO, AuO, and CuO) on the product distribution during the photocatalytic reaction of dry MF with the solar simulated light and Ar as the carrier gas. (C) Effect of the irradiation light (A, B, C, and D) on the product distribution during the photocatalytic reaction of dry MF on PdO/TiO₂ Ar as the carrier gas. (D) Effect of the carrier gas on the product distribution during the photocatalytic reaction of moist MF (MF/H₂O = 17) on PdO/TiO₂ with light A.

dark (Fig. 4G) or under light B (Fig. 4H), PdO/TiO₂ gave a stronger Pd(I) signal and no h^+ signal, indicating that the h^+ scavenging by MF took place, giving rise to the formation of Pd(I) species and Ti(III). Coupled with the broad UV-vis spectrum due to Pd nanoparticles, we conclude that MF converts PdO into Pd(I)/Pd(0) nanoparticles and TiO₂ into the electron rich Ti(III)-trapping TiO₂.

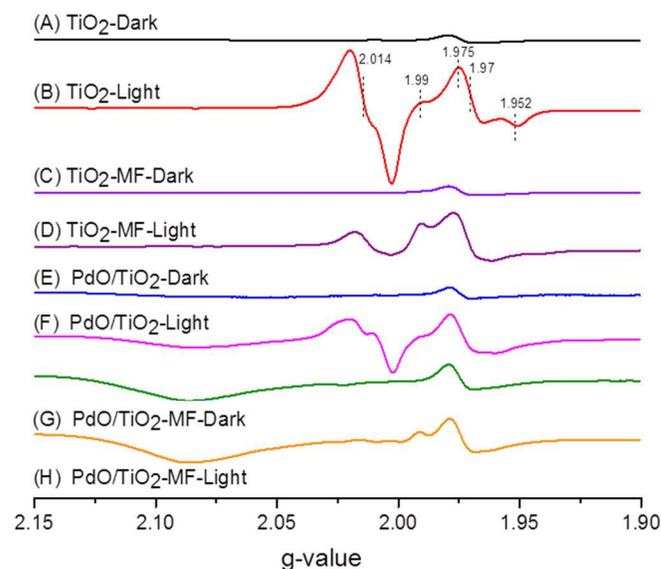


Fig. 5 EPR spectra of various samples (as indicated) taken at 25 K in the dark and under the light (light B) in the presence and absence of MF.

We conclude that this is the active catalyst which carries out the photocatalytic conversion of MF to two CH_2O .

Although a detailed study is necessary to elucidate the precise mechanism, we tentatively propose the reaction mechanism as follows. Thus, MF undergoes an oxidative addition by cleaving the C-O bond to the electron rich Pd(I)Pd(0) nanoparticles which are also supported on electron rich TiO_2 (Fig. 6, step A). The hydrogen atom transfer from the Pd-bound methoxy group to the Pd-bound formyl group and the reductive elimination of two CH_2O takes place to give two CH_2O molecules (Fig. 6, step B). For this reaction we propose that the formation of electron rich Pd nanoparticles and TiO_2 is the key to this photocatalytic reaction. The activation of the surface plasmon of the Pd nanoparticles by photons as well as the maintenance of the electron rich Pd and TiO_2 seems to be essential for the oxidative addition and reductive elimination reactions.

In the presence of H_2O , significant amounts of CH_3OH , CO_2 , and H_2 were formed while the produced amount of CO is very small. In

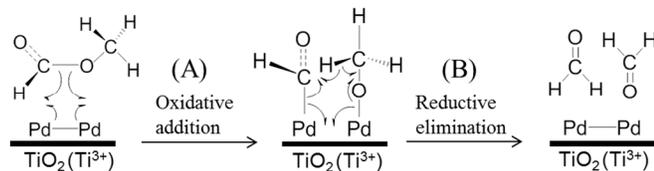


Fig. 6 Schematic illustration of the proposed mechanism.

this case, we conclude that CH_3OH was not produced from the heterolysis of MF (CO elimination process) but from the photocatalytic hydrolysis of MF yielding CH_3OH and HCO_2H , which decomposes into CO_2 and H_2 according to the recent report.²⁵

Solymosi and the coworkers recently reported that CO_2 , CO and H_2 are the major products during the photocatalytic decomposition of MF on M/TiO_2 ($\text{M} = \text{Pt}, \text{Pd}, \text{Rh}, \text{Ir},$ and Ru) by irradiating the catalyst with a UV light with the spectral width between 250-440 nm with the maximum intensity at 254 nm.¹⁵ As noted, this result is quite different from ours. We think the difference arises from the fact that Solymosi's group adopted the circulation system in which the primary products undergo secondary reactions while we used on-line reaction system with high input rates of reactants to minimize the secondary reactions of the primary products by rapidly sweeping the primary products away from the catalyst. The production of H_2 and CO_2 without CH_4 indicates that the reaction system of Solymosi's group contains a significant amount of moisture. In such a case MF will primarily undergo hydrolysis to CH_3OH and HCO_2H , which subsequently undergo photocatalytic decomposition into CO_2 and H_2 . The presence of CO also indicates that CO elimination to CH_3OH and CO also took place.

In summary, we have demonstrated the photocatalytic homolysis of dry MF vapour into dry CH_2O vapour in high selectivity (>80%). PdO/TiO_2 is the best catalyst to produce dry CH_2O in high selectivity with an inert gas or more preferentially with dry air as the carrier gas. The UV-free solar simulated light is best to produce dry CH_2O in high selectivity and in high yield.

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Notes and references

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