The Effect of Alkali Metal Cation Addition on the Photocatalytic Reaction of Methanol with Water over Pt-, Rh-, or Pd-Loaded TiO_2 Catalysts

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Addition of alkali metal cations to Pt-, Rh-, or Pd-loaded TiO_2 catalysts can change the product selectivity of the photoreaction of methanol with water from hydrogen and dimethoxymethane in the case of TiO_2 catalysts free of alkali metal cations to hydrogen, methyl formate, and carbon dioxide in the case of catalysts with added alkali metal cations.

Metal ion loaded-titanium dioxide has been reported to catalyse many photoreactions including decomposition of water[1] or alcohol,[2] reduction of nitrogen,[1,3] and even the synthesis of amino acids from water, methane, and ammonia.[4] In these reactions, the role of platinum is considered to be to receive electrons from the conduction band of TiO_2 in order to reduce the reactants. In heterogeneous catalysis, modification of these electron transfer sites could control the reaction selectivity. This communication reports the effects of added alkali metal cations (Li^+, Na^+, and Rb^+) on Pt-, Rh-, or Pd-loaded TiO_2 catalysts with respect to changes in selectivity of the photoreaction of methanol with water.

The catalysts were prepared by the conventional impregnation method of precursor salts (5 wt% of M_2PtCl_6, M_3RhCl_6, or M_2PdCl_4, M = NH_4, Li, Na, Rb) onto TiO_2 powder (Aerosil P-25). They were placed in a flat bottomed quartz reaction cell, which was connected to a closed gas circulation system. After the reduction by H_2 at 773 K for 20 h, they were oxidized by O_2 at 573 K for 2 h prior to the reaction. A mixture of methanol and water vapour was introduced into the system and the catalyst was irradiated using a 500 W Xe lamp from underneath. The products were analysed by gas chromatography at intervals (for H_2, molecular sieve 13X and for other products, a Porapak Q column was used). Product identification was by mass spectrometry as well as i.r. spectroscopy after the separation of each component by gas chromatography.

The initial rates of the product formation over various catalysts are summarized in Table 1. In the case of Rh/TiO_2 catalysts, without any added alkali metal ions, a 1:1 ratio of hydrogen and dimethoxymethane was produced, with a small amount of methyl formate. However, with lithium ions added to the system, the selectivity changed drastically, and the main products were hydrogen, methyl formate, and CO_2 instead of dimethoxymethane. When the alkali metal cation present was changed from Li^+ to Na^+ or Rb^+, the initial rate of methyl formate formation was increased with a simultaneous decrease in the rate of CO_2 formation. Similar results were obtained using sodium ions with Pd/TiO_2 catalysts. Different results were obtained using platinum catalysts, where a considerable amount of methyl formate was formed even in the absence of alkali metal ions.

These reactions did not proceed without irradiation of the

Table 1. Initial rates of the photodecomposition of methanol over various TiO_2-based catalysts at room temperature.

	Initial rates of the product formation (mmol h^{-1} g-catalyst^{-1})[a]			
Catalyst	H_2	HCO_2Me	CO_2	$CH_2(OMe)_2$
Pt/TiO_2	0.080	0.026	0	0.015
$Pt\text{-}Na/TiO_2$	0.122	0.024	0.020	0
Rh/TiO_2	0.074	0.002	0	0.082
$Rh\text{-}Li/TiO_2$	0.046	0.004	0.010	0
$Rh\text{-}Na/TiO_2$	0.082	0.016	0.008	0
$Rh\text{-}Rb/TiO_2$	0.069	0.018	0.006	0
Pd/TiO_2	0.007	0.000	0	0.006
$Pd\text{-}Na/TiO_2$	0.011	0.003	0.001	0

[a] $P(H_2O) = 5$ Torr, $P(MeOH) = 65$ Torr, $T = 298$ K. The reaction rates were followed for several hours at intervals of 15 or 30 min and the initial rate was determined from the tangent at zero time.

TiO_2-supported catalysts or even on irradiation using SiO_2 supported catalysts, which indicates an important role for TiO_2 and its photoexcitation. The rate of hydrogen formation was proportional to the light intensity, and first order with respect to the partial pressure of water and 0.5 order with respect to methanol at relatively low pressures (<10 Torr). Over the catalysts without added alkali metal ions the rates were independent of the reaction temperature between 297—365 K, but the reaction showed a dependence on the alkali metal cation when present. From these experimental results, we postulate the reaction scheme shown in equations (1)—(4), where equation (2) is the reaction that occurs in the absence of added alkali metal cations and equations (3) and (4) represent the reactions that occur in the presence of alkali metal cations.

$$H_2O \xrightarrow{h\nu} \tfrac{1}{2} H_2 + [OH] \qquad (1)$$

$$3MeOH + [OH] \rightarrow [HCHO] \rightarrow CH_2(OMe)_2 + \tfrac{1}{2}H_2 + 2H_2O \qquad (2)$$

$$2MeOH + 2[OH] \rightarrow [HCO_2H] \rightarrow HCO_2Me + H_2 + 2H_2O \qquad (3)$$

$$MeOH + 3[OH] \rightarrow [HCO_2H] \rightarrow CO_2 + \tfrac{3}{2}H_2 + 2H_2O \qquad (4)$$

The reaction is initiated by the photodecomposition of water to form the OH radical. Over the alkali metal ion-free catalysts, methanol is oxidized to formaldehyde by this OH radical, which reacts rapidly with an excess of methanol to form dimethoxymethane. This latter process was confirmed by the fact that dimethoxymethane was formed rapidly when methanol and formaldehyde vapour were introduced onto these catalysts in the dark. In contrast, over catalysts with added alkali metal cations, formaldehyde may be further oxidized to formate, which reacts with methanol to form methyl formate. This process was also confirmed by the introduction of methanol and formic acid vapour onto these catalysts. Moreover, when methanol and formaldehyde vapour were introduced onto the alkali metal cation-added catalysts. Moreover, when methanol and formaldehyde vapour were introduced onto the alkali metal cation-added water. These results suggest that formate is formed directly from the reaction of methanol and the OH radical without going *via* formaldehyde, with alkali metal cations assisting this process.

A similar effect of the addition of alkali metal cations on the selective formation of methanol from CO and H_2 using similar catalysts, has been reported previously.[5] When formaldehyde, methanol, or $CO\text{–}H_2$ mixture was introduced onto sodium-added Pd/SiO_2 catalyst, the formation of formate on the surface was observed by i.r. spectroscopy, but no i.r. band was observed in the case of the Pd/SiO_2 catalyst in the absence of alkali metal. Although such evidence has not been obtained in this photocatalytic system, the formation of such surface structures on the addition of alkali metal cations can be postulated, which could be responsible for the change in selectivity of this photoreaction.

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