Highly active meso–microporous TaON photocatalyst driven by visible light

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TaON was found to be *ca.* 20 times more active as a visible light activated photocatalyst for the oxidation of methanol, when compared to the well studied UV-visible activated TiO_2 (P25) catalyst.

Photocatalysis using semiconductors is an actively studied current topic, because of its scope for industrial and scientific applications.[1,2] One such application is the total or partial mineralization of contaminants in air and water. Most of the studies have used TiO_2 (band gap = 3.2 eV for anatase and 3.0 eV for rutile) as the photocatalyst, due to its stability and the relatively high activity compared to other photocatalysts. Yet, the potential of photocatalysis in practical applications has not been fully realized due to the inactivity of TiO_2 under visible light irradiation and other system constraints or inefficiencies. The efficiency of TiO_2 photocatalytic systems is rather dismal (often less than 2%). Therefore, it is important to discover a new visible-light-driven photocatalyst,[3–6] which is much more active than the UV-only active TiO_2. So far, in our knowledge, the best visible-light-driven photocatalyst has been carbonate-doped TiO_2, whose activity was four times higher than pure TiO_2 (ST-01 grade, Ishihara Sangyo), when illuminated under a xenon lamp using wavelengths longer than 350 nm.[4]

In this work, we have fabricated a strikingly active visible-light-driven TaON photocatalyst, for oxidation of an organic molecule in water and its activity was found to be *ca.* 20 times better than that of UV-only active TiO_2 (Degussa P25). P25 is, in fact, reported to be more active than ST-01,[7] and over the years has become a benchmark photocatalyst for comparison of catalytic activity.[1] TaON photocatalyst was earlier reported for photocatalytic hydrogen generation from water and methanol.[5,6] In this report, we show that the meso–microporous structure of TaON could significantly aid the photoactivity of the material to obtain superior catalytic activity.

The nitriding of Ta_2O_5 (Fluka) to TaON was performed at 850 °C for 15 h under a flow (0.3 L min^{-1}) of nitrogen gas bubbled through 500 mL of NH_4OH aq (28%), which was replaced with a new solution after half the synthesis time (7.5 h). 3 wt% Pt was loaded on TaON (100 mg) by the photocatalytic reduction of H_2PtCl_4 in Ar purged 20% aqueous ethanol solution (10 mL) under visible light irradiation, for 2 h. The resulting photocatalysts were dried in a rotary evaporator until they became powdered and kept in vacuum at 60 °C for a further period of 2 h. Methanol was selected for the photocatalytic reaction studies, because it is a simple toxic molecule to be removed from certain industrial waters. Photocatalytic experiments were carried out under simulated sunlight (Atlas Suntest CPS+ model lamp), using a batch reactor (volume 60 ml) containing 100 mg of photocatalyst and 10 ml of a 20% aqueous methanol solution purged with O_2. The intensity of the simulated sunlight was equivalent to 1 sun as determined by a calibration cell. A UV cut-off film (<400 nm, University Products) was used, when required, to wrap the batch reactors to admit only the visible light fraction into the reactor. The solution was stirred with a magnetic bar during the photoreaction. The amount of CO_2 produced by the reaction was measured by gas chromatography.

Fig. 1 shows the photocatalytic oxidation of 20% (v/v) methanol in water, under simulated sunlight. TiO_2 showed considerable activity under full sunlight exposure, but did not exhibit any significant activity with only visible light irradiation (only a trace of CO_2 was observed, resulting from the light absorption up to 410 nm by the rutile component). TaON showed very high activity under visible light, when compared to TiO_2 (P25) exposed to

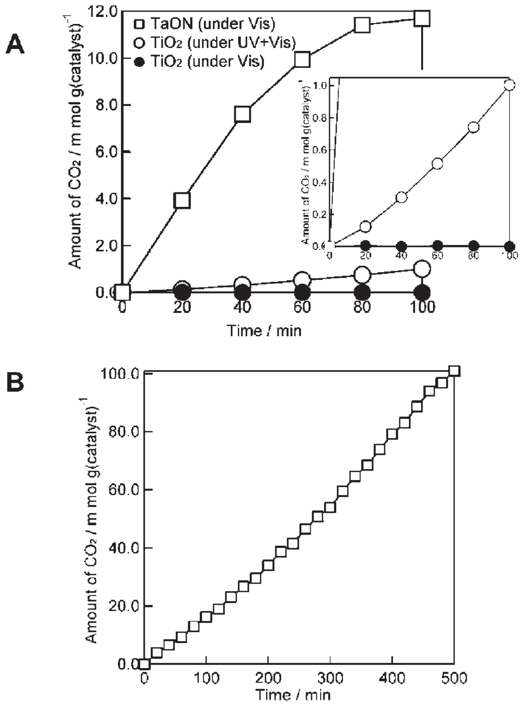

Fig. 1 Photocatalytic oxidation of methanol (20% in H_2O) to CO_2 under simulated sunlight; (A) batch tests of TaON/Pt (3 wt%) (with an UV cut-off filter; Vis (>400 nm)), TiO_2 (P25) under UV + Vis and TiO_2 (P25) under Visible, and (B) the amount of CO_2 produced by TaON/Pt (Vis) during 500 min with O_2 addition after every 60 min. Inset in (A) is a magnified image of (A) at the low end of Y-scale.

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simulated full beam sunlight. The activity of TaON (Vis) was found to be 19.3 times higher than that of TiO_2 (P25) (UV + Vis) after 60 min of reaction. The batch mode activity of TaON photocatalyst reached a plateau at 100 min, since most of the available O_2 in the batch reactor was consumed to form CO_2, within this time. Separate experiments were carried out to ascertain the involvement of TaON in the reaction. Fig. 1(B) shows typical data from one such run, where the reaction was allowed to continue for 500 min and the TaON generated 101×10^{-3} mol of CO_2 per gram of catalyst, by the photooxidation of methanol in water. One gram of TaON corresponds to only 4.7×10^{-3} mol. Therefore, the turnover number recorded within 500 min works out to be 21.5 (mol(CO_2) per mol(TaON)). This is an indication that the observed methanol oxidation is indeed catalytic and that TaON is sufficiently stable for photocatalytic applications. Studies to evaluate the long-term stability of TaON as a catalyst and methods to immobilize it on solid transparent substrates[8] are currently progressing.

Fig. 2 shows the pore-size distribution of Ta_2O_5 and TaON. The diameter of channels inside TaON, which were observed as holes on its surface in SEM images (Fig. 3(B)),[6] has in fact a size distribution between 10 and 100 nm (Fig. 2(A)) with a distribution maximum centered at 28.6 nm. As the surface of Ta_2O_5 is smooth without many pores (Fig. 3(A)), NH_3 could only act slowly on the surface and transform the oxide into an oxynitride. The reaction proceeds from Ta_2O_5 to TaON through an intermediate, with an accompanying molecular volume change, causing pore generation. As the porosity becomes very high, the material becomes friable and breaks down to smaller particles (Fig. 3(B)). This mechanism seems credible when the enlarged surface area of the oxynitride is also considered. Ta_2O_5 and TaON showed BET areas of 0.691 and 4.64 $m^2\ g^{-1}$, respectively. The enhanced surface area of TaON comes from the newly formed micropores (<2 nm). These micropores could act as a reservoir for organic molecules, and the pore volume of TaON originates from mesopores, which can efficiently transport the reactant and product molecules between the inside and the outside regions of particles.[9] An efficient transport of this nature should improve the catalytic activity of the material. Often inefficient molecular transport leads to poor catalytic activity.[10]

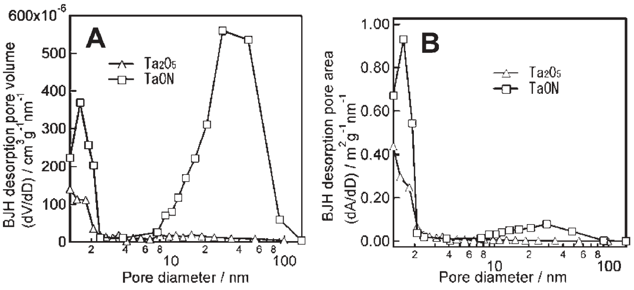

Fig. 2 Pore-size distribution of Ta_2O_5 and TaON: (A) BJH pore volume distribution (dV/dD) and (B) pore area distribution (dA/dD).

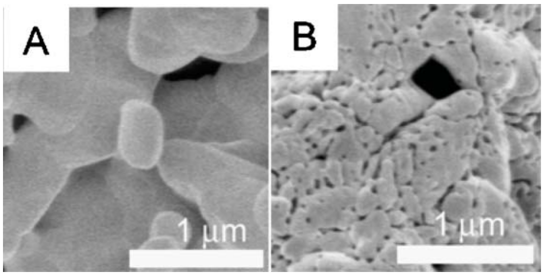

Fig. 3 SEM of Ta_2O_5 (A) and TaON (B).

One of the major factors affecting the activity of a photocatalyst is its BET surface area, because, in general, the surface interactions yield sorption isotherms of a Langmuirian nature.[1] A photocatalyst with large surface area generally shows higher catalytic activity, provided all other reaction conditions are comparable and well controlled. However, since the surface area of TaON was observed to be ten times smaller than that of TiO_2 (P25, *ca.* 55 $m^2\ g^{-1}$), some other factors must be favorably influencing the activity of TaON. The first reason is attributed to the larger number of absorbable photons in the visible light of the simulated sunlight. The second reason could be its meso–microporous structure: the micropores could seize the reactant molecules like a molecular sieve and the mesopores transport them easily to the numerous active sites available on the catalyst surface.[9] Removal of the reaction products from the active sites is also facile, when the catalyst is sufficiently porous. Since it was reported that small pores (10 nm) hindered the transport of molecules (I^-),[11] the smaller micropores are believed to be contributing only very little to the molecular transport. The movement of molecules would be smooth through the mesopores. The third reason for the relatively better activity of TaON photocatalyst may be that the quantum yield of electron–hole recombination is smaller in this new catalyst, when compared to TiO_2. In TiO_2, the quantum yield of electron–hole recombination is substantially larger than that of radical generation.[12] This aspect needs more detailed studies.

In summary, TaON showed superior photocatalytic activity for oxidation of methanol under simulated sunlight. To our knowledge, for this reaction, no other visible-light-driven photocatalyst has surpassed the activity of the benchmark TiO_2 (P25) catalyst under full beam sunlight irradiation. The photocatalytic activity of this meso-microporous TaON was 19.3 times higher than that of TiO_2 (P25) under the simulated sunlight. The reaction over TaON has been shown to be photocatalytic and not stoichiometric. This TaON photocatalyst may become useful in processes related to the purification of contaminated water. In future, other meso–microporous nitride materials may become useful materials in photocatalysis. A reduction in the level of Pt loading or finding an alternative to Pt will be helpful. Future research will focus on this aim.

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