HYDROGEN PRODUCTION FROM METHANOL USING POTASSIUM HEXATITANATE PROMOTED RUTHENIUM OXIDE CATALYSTS

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ABSTRACT

Photocatalysts containing 0.3% wt. of ruthenium oxides on hydrothermally synthesized potassium hexatitanate were investigated for hydrogen production from the decomposition of aqueous methanol. XRD and SEM results show that the hexatitanates synthesized by the hydrothermal conditions formed long, felted–like fibers with smaller crystallite size while those by solid state formed short fibers with larger crystallite size. The activities for the hydrogen production were found to be higher with the catalysts having hexatitanates synthesized under hydrothermal conditions than with those synthesized under solid state conditions.

Key words: Potassium hexatitanate, Ruthenium oxide, Hydrothermal, Photocatalysts, Hydrogen production.

INTRODUCTION

Much work has been focused recently on producing hydrogen as an alternative energy to the fossil fuel due to it being environmentally friendly. The production of hydrogen in providing clean energy has attracted much interest in the development of effective photocatalyst. The design of a photocatalyst requires conditions that allow or promote for formation of photoexcited electrons and holes and also the transfer of the charges to the adsorbed reactants at the surface. Thus, semiconducting metal oxides such as titanium oxides are often used in many photocatalytic applications. However, studies have also been carried out to develop new photocatalytic titanate–based "host–guest type" materials. Among those studied, potassium hexatitanates having noble metal oxides incorporated have been shown to be photocatalytically quite active[1,2]. It has the structure of one of the Wadsley–Anderson type oxide in which the TiO_2 octahedra share an edge at one level in linear groups of three and corner–sharing in another level, giving a tunnel structure characterized by a wide spacing corresponding to three octahedral–2.3[3]. Catalytic active phases, i.e. the noble metal oxides, which promote the photoexcited charges and their transfer to the adsorbed reactants can thus occupy in these tunnels.

In this work, hydrogen production from aqueous methanol solution decomposition is being investigated using ruthenium oxide on potassium hexatitanates. Potassium hexatitanate used were hydrothermally synthesized because of its lower temperature conditions and large surface area.[4-6] products and ruthenium oxides was used as the catalytic active phase due to its excellent reductive properties with the titanates[7].

EXPERIMENTAL

Synthesis – Potassium hexatitanates, $K_xTi_yO_z$ were synthesized by hydrothermal reactions at a pressure of 44 Mpa as described earlier[8]. using potassium hydroxide solution and titanium tetraisopropoxide in K:Ti molar ratio of 1:2. Samples were coded ht–KTO. Heating temperature of 723 K and heating durations of 2 h, 5 h and 25 h were employed. For synthesis by solid state reaction, potassium carbonate and titanium oxide (anatase) in K:Ti molar ratio of 1:6 were used and sample was coded as ss–KTO. The solid reactants were heated at 1403 K at atmospheric pressure for 5 h. Loadings of Ru on KTO were carried out by ion–exchange reaction as described earlier[8].

Characterisation – X–ray diffraction patterns of potassium hexatitanates were recorded on a Rigaku RAD–X system with nickel filtered Cu α radiation. Scanning electron microscopy was performed on a Hitachi S–800 scanning electron microscope to investigate the surface structure and morphology of the photocatalysts. Nitrogen adsorption measurements were carried out at 77 K with a Micromeritics ASAP 2000 instrument. The samples were degassed at 473 K for about 5 h until the pressure reached < 20 mTorr. The volume of adsorbed nitrogen was normalized to standard temperature and pressure. The BET surface area was calculated using the BET equation and the pore size distribution was calculated using the desorption isotherm and the Barret–Joyner–Halenda (BJH) formula.

Photocatalytic activity – Photocatalytic reaction was carried out in a closed gas–circulation system at 303 K. The catalyst (ca. 0.30 g) placed in the pyrex glass reactor containing 500 cm^3 aqueous methanol solution was kept in suspension by stirring continuously with a magnetic stirrer. Before starting the reaction, nitrogen gas was bubbled through the solution to flush off dissolved gas residues for ca. 30 min – 1 h. A UV source with a high pressure Hg lamp (400 W) was used for the reaction. Products formed were automatically monitored by gas GC with an autosampler (1 cm^3).

RESULTS AND DISCUSSION

X–ray Diffraction (XRD)

Figure 1a shows the XRD patterns of the ht–KTO samples and the ss–KTO sample. Diffraction peaks observed with d_{200} ca. 7.69 (2 theta of 11.5° for the 100% intensity) are in good agreement with those reported[4] for KTO. The XRD patterns for all the ht–KTO samples appeared similar though peaks for ss–KTO sample are sharper than the ht–KTO samples. This
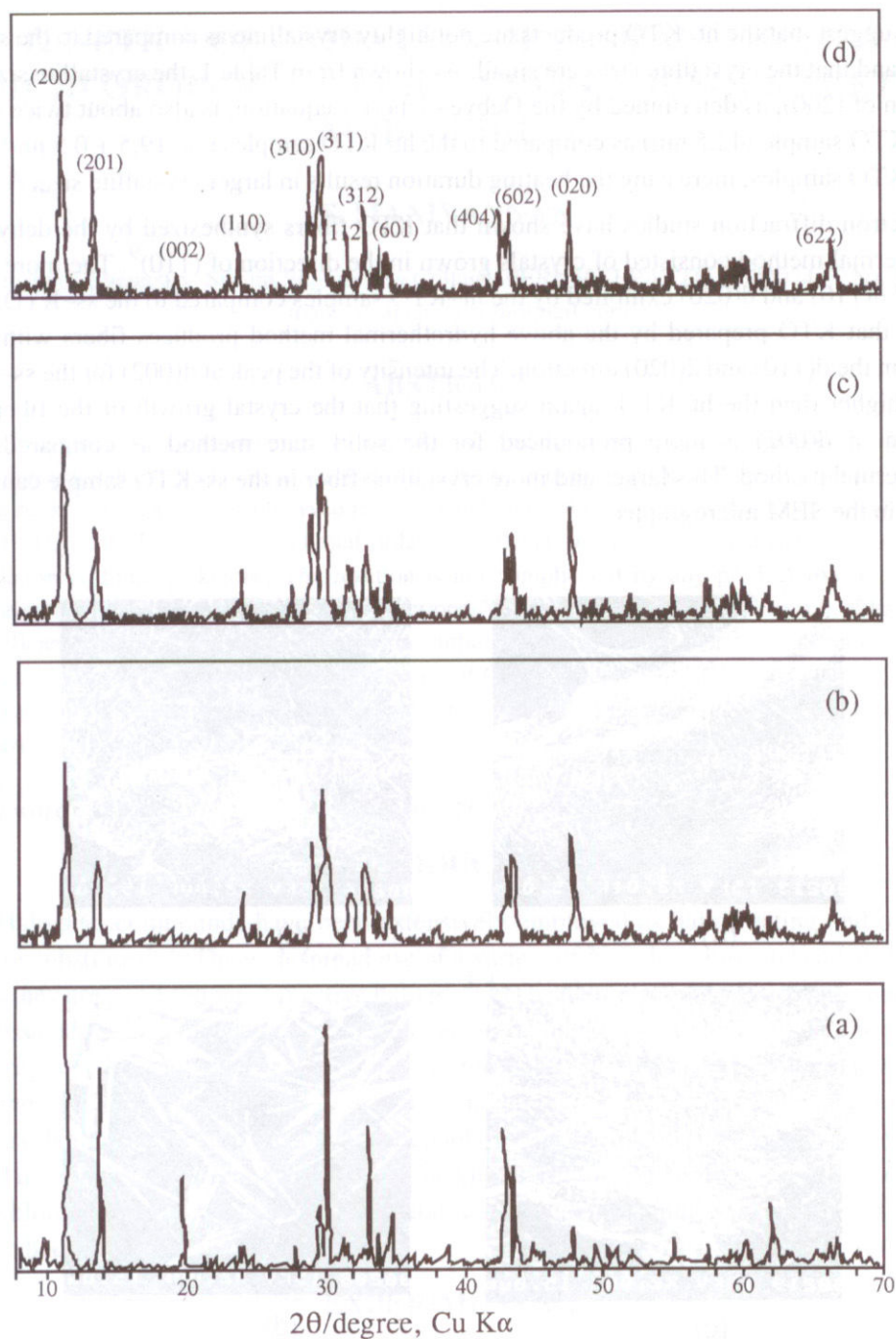
Figure 1. X–ray diffraction pattern of potassium hexatitanates synthesized by the solid state reaction method (a) and by the hydrothermal method at various heathing conditions of (b) 2 h, (c) 5 h and (d) 25 h

results suggest that the ht–KTO products are not highly crystalline as compared to the ss–KTO sample and that the crystallite sizes are small. As shown from Table 1, the crystallite size in the direction of (200), as determined by the Debye–Scherrer equation, is also about twice as large for ss–KTO sample (42.5 nm) as compared to the ht–KTO samples (ca. 19.5 ± 0.5 nm). As for the ht–KTO samples, increasing the heating duration results in larger crystallite size.

Electron diffraction studies have shown that KTO fibers synthesized by the dehydration hydrothermal method consisted of crystals grown in the direction of (110)[9]. The more intense peaks at d(110) and d(020) exhibited by the ht–KTO samples compared to the ss–KTO sample suggest that KTO prepared by the above hydrothermal method produces fibers with crystal growth in the d(110) and d(020) direction. The intensity of the peak at d(002) for the ss–KTO is 6–fold higher than the ht–KTO; again suggesting that the crystal growth of the fiber in the direction of d(002) is more pronounced for the solid state method as compared to the hydrothermal method. This larger and more crystalline fiber in the ss–KTO sample can clearly be seen in the SEM micrographs.
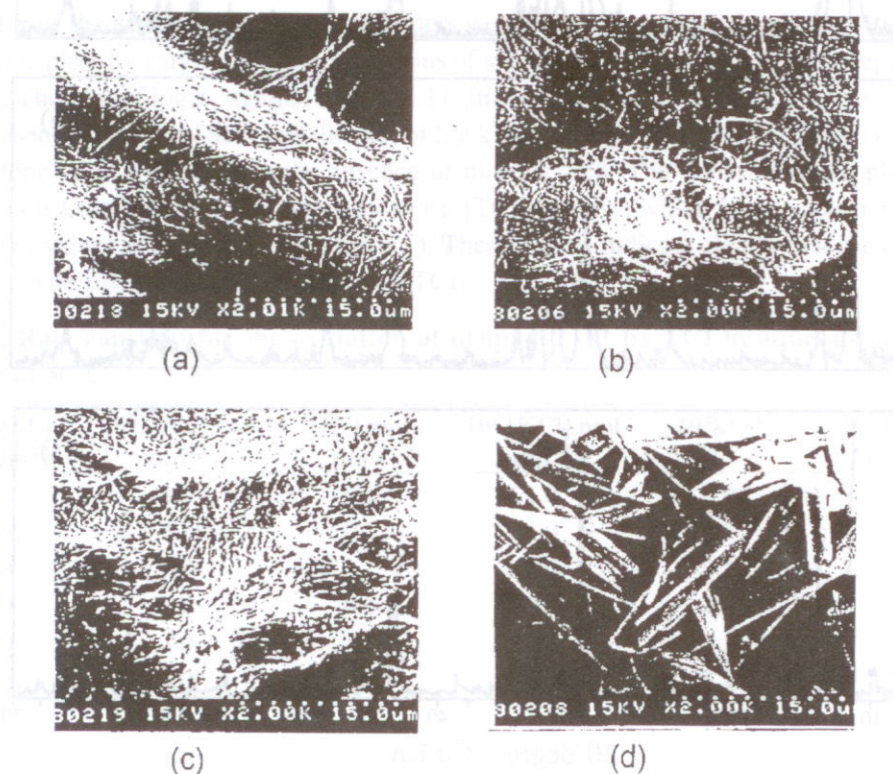

Figure 2. Scanning electron micrographs of potassium hexatitanates synthesized by hydrothermal method at heating duration of (a) 2 h, (b) 5 h, (c) 25 h and by (d) the solid state reaction method

Scanning Electron Microscopy (SEM)

Figure 2 shows the SEM micrographs of the ht–KTO and ss–KTO samples. All the ht–KTO samples generally showed similar morphology of long, felted–like fibrous structures irrespective of the heating temperatures and durations while that of the ss–KTO sample showed short fibers and only few long fibers. The larger crystallite particle size of ss–KTO sample observed compared to ht–KTO samples is in accordance with the results obtained from XRD above.

N_2 adsorption measurement

As shown in Table 1, increasing the heating durations during the synthesis of KTO, does not affect the surface areas of the clacined RuO_2/ht–KTO samples while much lower surface area was obtained with the RuO_2/ss–KTO sample. Surface areas of these ht–KTO samples (ca. 38 ± 1 m^2g) are found to be more than ten times larger when compared to the ss–KTO samples (3.2 m^2/g). The lower surface areas obtained indicate formation of larger crystals as seen in the SEM.

Table 1. Analytical data, crystalline size values in the direction of (200) and (020) reflection and rate of hydrogen evolved for the various KTO photocatalysts

Sample code	Heating duration h	Ru wt%	Surface area (m^2/g)	Pore vol. (cm^3/g)	L (200) Å	L (020) / A°	Rate of H_2 evolved (μmol/h)
ht–RK1	2	0.27	40	0.13	190	349	1203
ht–RK2	5	0.27	37	0.11	195	355	892
ht–RK3	25	0.27	39	0.13	201	353	1342
ss–RK	5	0.26	3.2	0.007	425	289	50
ss–BK	5	0	0.9	0.004	–	–	16
ht–BK	5	0	40	0.09	–	–	30

L is the crystallite size as determined from the Scherrer equation and Ru wt.% determined from ICP analysis. ht and ss refers to hydrothermal conditions and solid state conditions, respectively.

As for the pore size distribution, results showed that the average pore size remains unchanged as heating duration increased.

Photocatalytic activity

Figure 3 shows the time–dependence profiles of hydrogen evolution from decomposition of aqueous methanol solution over the RuO_2/ht–KTO and RuO_2/ss–KTO photocatalysts. Generally, for all the photocatalysts, the hydrogen production increased progressively with irradiation time; over prolonged irradiation time (more than 300 min) the production became less. The Ru O_2/ht–KTO samples showed higher activity of more than 18–folds higher (in
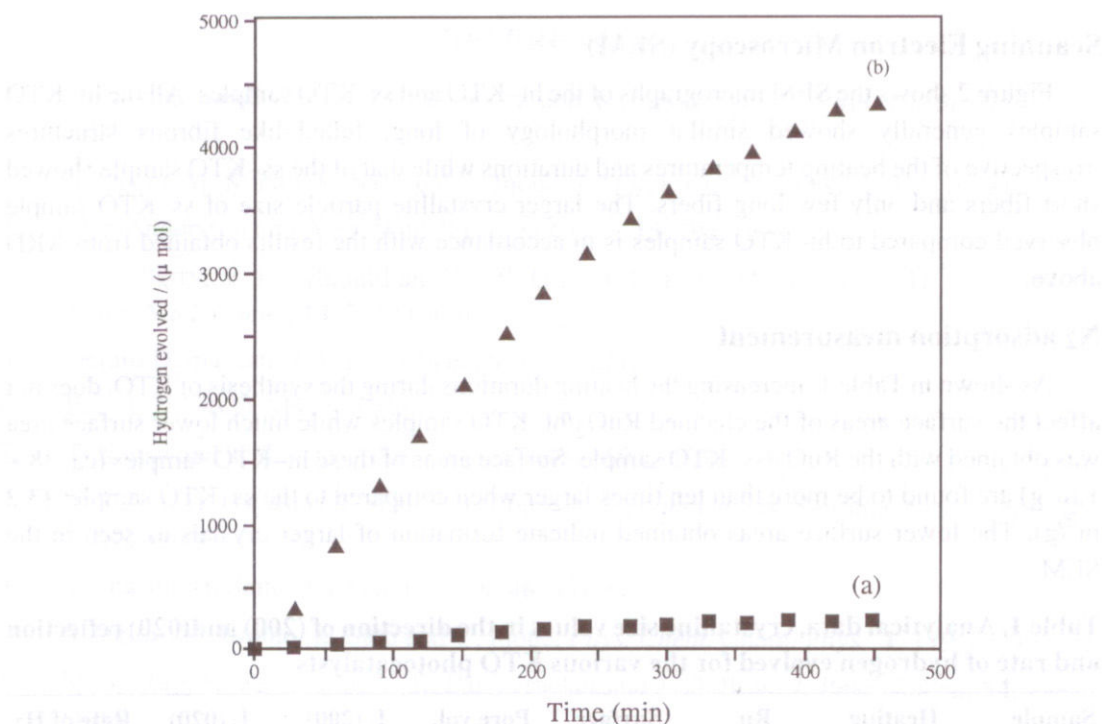
Figure 3. Amount of hydrogen evolved from aqueous methanol solutions over (a) Ru oxide/ss–KTO and (b) Ru oxide/ht–KTO

Table 1) compared to the RuO_2/ss–KTO sample. However, increasing the duration times for ht–KTO synthesis does not seem to change the activity of RuO_2/ht–KTO. Activity somehow seems to relate to the surface area whereby higher surface areas give higher activity (Table 1).

The ht–KTO and the ss–KTO without RuO_2 samples exhibited very low activity (Table 1). This suggests the importance of ruthenium oxide presence in promoting the decomposition of the aqueous methanol solution. Ogura et al.[10] demonstrated that ruthenium oxide promote the efficiency of photoexcited charge transfer to the adsorbed reactant. As absorption of UV light for the separation of these photoexcited charges was not hindered by the presence of the ruthenium oxide[8], the photoexcited electron formed can readily be transferred through the ruthenium oxide for the reduction of the protons occur to form hydrogen. The RuO_2/ht–KTO samples having higher surface area and smaller crystals than the RuO_2/ss–KTO sample is expected to have better dispersion of ruthenium oxide. The higher dispersion of ruthenium oxide will increase the efficiency of photoexcited charge separation and transfer to the surface reactants, thus giving rise to the higher activity as shown in Table 2. As to how these ruthenium oxide is dispersed on the KTO fibers has yet to be studied although it has been reported that the ruthenium oxide loaded on supports with tunnel structure could be dispersed both on the surface and in the tunnels[1,2]. The slight activity shown by the ht–KTO compared to ss–KTO can be

explained along similar lines. The ht–KTO sample, having smaller crystallite size, has larger surface area, thus it is able to undergo the photoexcited charge separation better than ss–KTO but slow charge transfer to the surface in both cases is due to the absence of a promoter.

As compared to that of water decomposition obtained from earlier work[8], the production of hydrogen and activity of the decomposition of aqueous methanol solution are much higher. This can be expected as the decomposition mechanism of the two reactions is different[7,11]. In the aqueous methanol solution decomposition, holes generated by the light would oxidize CH_3OH, HCHO and HCO_2H eventually to produce carbon dioxide while the electrons in the conduction band would simultaneously reduce protons in the solution to produce hydrogen. Thus, hydrogen was produced in three consecutive redox reactions. The decrease in activity observed over prolonged time could be due to the slight acidic environment of CO_2 because as decomposition progresses, CO_2 was evolved. It has been reported that TiO_2 photocatalysts showed ageing effects in acidic environment of H_2SO_4 and also ease of dispersion of photocatalysts decreased with decreasing pH[12].

$$CH_3OH \xrightarrow{\text{h}\nu,\ \text{catalyst}} HCHO + H_2 \quad ...(1)$$

$$HCHO \xrightarrow{\text{h}\nu,\ \text{catalyst}} HCO_2H + H_2 \quad ...(2)$$

$$HCO_2H \xrightarrow{\text{h}\nu,\ \text{catalyst}} CO_2 + H_2 \quad ...(3)$$
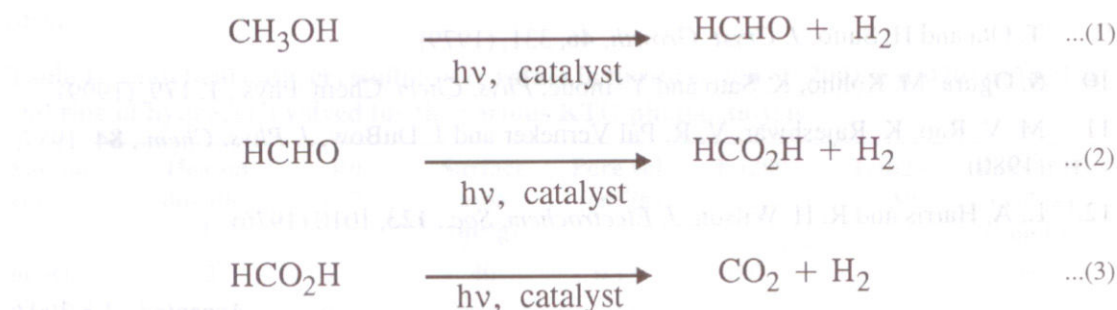
Figure 4. Mechanism of aqueous methanol solution showing methanol undergoes oxidation in 3 steps

CONCLUSION

The photocatalytic activities for the decompositions of aqueous methanol solution over the RuO_2/ht–KTO are remarkably higher than RuO_2/ss–KTO photocatalysts, suggesting that photocatalysts with higher surface area exhibit better activity. These high–activity photocatalysts can be achieved by preparing the KTO under hydrothermal rather than the solid state method.

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