Selective partial oxidation of light alkanes over alkali-ion-modified silica-supported vanadium oxides excited with visible light

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Alkali-ion (Na⁺, K⁺, and Rb⁺)-modified V₂O₅/SiO₂ irradiated with visible light catalyzes the partial oxidation of 2-methylpropane to form mainly propanone and 2-methylpropan-2-ol. The addition of alkali ions to V₂O₅/SiO₂ is essential to generate the active site that can be excited with visible light. It is confirmed that there are two types of reaction paths for the formation of 2-methylpropan-2-ol.

Keywords: partial oxidation of 2-methylpropane, alkali ions, silica-supported vanadium oxide, photocatalyst, active oxygen species

1. Introduction

Various promoters are incorporated into catalysts with a view to control activity and selectivity of the catalytic reaction and to improve thermal stability of catalysts. For example, alkali metal is often used as one of the typical modifiers for metal oxide catalysts [1]. As is well-known, one of their distinct functions is their electron-donating ability leading to the enhancement of the basicity of metal oxides. Rare earth metals are added into supported catalysts to prevent the supports such as alumina from sintering [2].

Vanadium oxide-based catalysts are extensively used for the catalytic oxidation of hydrocarbons. To achieve a good activity and selectivity level, V₂O₅ should be dispersed on a support. The improvement of activity and selectivity of supported vanadium oxide catalysts has been widely attempted by addition of alkali ions. Van Hengstum et al. [3] observed that the influence of potassium additives on V₂O₅/TiO₂ catalysts depended on the type of hydrocarbons oxidized. Potassium changed the nature of the active sites, which was attributed to the possible formation of amorphous bronzes between vanadium oxide and potassium. Rives et al. [4, 5] have reported a larger selectivity for propene oxidation to acrolein on V₂O₅/TiO₂ when these catalysts are doped with alkali ions. The results obtained by XRD, DTA (differential thermal analysis), IR, TPR (temperature-programmed reduction) and XANES (X-ray absorption near-edge structure) indicate that doping V₂O₅/TiO₂ with increasing amounts of sodium ions leads initially to formation of VO₃⁻ excited by light of 310–390 nm. The other (S 400) is that arising from addition of alkali ions, excited by irradiation by light of wavelengths λ > 390 nm. In the photooxidation of propene over alkali-ion-modified V₂O₅/SiO₂ catalysts under the conditions where only S 400 was excited, propene was converted to propanone selectively. We have also observed the formation of 2-methylpropan-2-ol in the photooxidation of 2-methylpropane over Rb⁺-modified V₂O₅/SiO₂ [13]. These results suggest that S 400 is effective for activation of the C−H bond of light alkanes and it is much affected by the presence of alkali ions.

In the present paper, we report the results of photooxidation of 2-methylpropane over alkali-ion-modified V₂O₅/SiO₂ catalysts and describe activity and selectivity...
in these reactions to discuss the promotion effect of alkali ions. We also investigate active oxygen species for the formation of 2-methylpropan-2-ol and the factor for the formation of S 400 in alkali-ion-modified V2O5/SiO2.

2. Experimental

**Materials.** Reactants (2-methylpropane, propane and oxygen), tetraethyl orthosilicate (TEOS), ammonium metavanadate, NaOH, KOH, KNO3, RbOH, Mg(NO3)2, Eu(NO3)3, Pr(NO3)3, and Ce(NO3)3 were commercially supplied. Gaseous reactants were refined by vacuum distillation. C18O2 and H218O were supplied from ICON (purity 99.5%) and CEA-ORIS (purity 98.1%), respectively, and used without further purification. Silica was prepared by the hydrolysis of distilled TEOS and calcination at 773 K for 5 h as described elsewhere [14].

**Catalysts.** V2O5/SiO2 (VS; V2O5 2.5 wt%) was prepared by impregnating SiO2 with an aqueous solution of ammonium metavanadate in the same manner as given in ref. [14]. Modified VS catalysts were prepared by impregnating VS with aqueous solutions of NaOH (Na-VS), KOH (K-VS), KNO3 (K-VS), RbOH (Rb-VS), Mg(NO3)2 (Mg-VS), Eu(NO3)3 (Eu-VS), Pr(NO3)3 (Pr-VS), or Ce(NO3)3 (Ce-VS).

**Pretreatment of the catalysts.** Pretreatment of the catalysts was performed first by evacuation at 673 K for 1 h, then treatment with 60 Torr of oxygen at the same temperature for 2 h and evacuation at the same temperature for 10 min prior to reaction and measurement of each spectrum.

**Reactions.** Reactions were carried out in a conventional closed gas-circulating system (dead space 280 cm3) described elsewhere [14]. The powder catalyst (500 mg) was spread on the flat-bottom of a quartz reactor and irradiated at room temperature by light from a 250 W ultra-high-pressure Hg lamp through glass filters, UV-31 or UV-39, which permit light with wavelength \( \lambda > 310 \) nm or \( \lambda > 390 \) nm, respectively. The experiments were repeated more than twice to examine the reproducibility of data. In the dark, the reactions did not take place. After each run, the catalyst bed was heated to 573 K for collecting products which were tightly adsorbed on the catalyst at room temperature. The desorbed products were frozen out in a trap cooled by liquid nitrogen, and analyzed by GLC and GLC–mass spectrometry. In order to measure quantum yields in reactions of 2-methylpropane, the wavelengths of the irradiating light were selected by a monochromator and the intensity was calibrated by the method of chemical actinometry using potassium ferrioxalate developed by Hatchard and Parker [15].

**Photoluminescence.** Phosphorescent emission spectra of the catalysts were recorded with a Hitachi F-3010 fluorescence spectrometer [16].

3. Results and discussion

3.1. Reactions

Table 1 shows the results of the photooxidation of 2-methylpropane over VS and alkali-ion-modified VS catalysts by irradiation with light of wavelengths \( \lambda > 310 \) nm. Both the active sites (S 310 and S 400) were excited under this condition. Over VS, a variety of products, for example, propanone, ethanal, 2-methylpropanal, 2-methylpropan-2-ol and so on, were detected. In spite of the higher conversion level over alkali-ion-modified catalysts than over VS, the selectivity to propanone increased considerably over alkali-ion-modified VS catalysts. In addition, formation of 2-methylpropan-2-ol was detected.

<table>
<thead>
<tr>
<th>Catalysts b</th>
<th>Conv. c (%)</th>
<th>Selectivity d (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IB</td>
<td>PR</td>
</tr>
<tr>
<td>VS e</td>
<td>58.4</td>
<td>8</td>
</tr>
<tr>
<td>Na-VS</td>
<td>84.6</td>
<td>7</td>
</tr>
<tr>
<td>K-VS</td>
<td>90.7</td>
<td>6</td>
</tr>
<tr>
<td>Rb-VS e</td>
<td>94.3</td>
<td>6</td>
</tr>
</tbody>
</table>

a Catalyst 0.5 g, 2-methylpropane 70 \( \mu \)mol, O2 140 \( \mu \)mol, irradiation time 60 min.
b The contents of alkali-ion are 1, 2, or 4 wt% as Na2O, K2O, or Rb2O, respectively.
c Based on introduced 2-methylpropane.
d Based on converted 2-methylpropane. IB 2-methylpropene, PR propene, AA ethanal, AC propanone, TB 2-methylpropan-2-ol, BA 2-methylpropanol, ML methacrolein, COx CO and CO2. Trace amounts of methanol, ethene, propene oxide, propanal, propan-2-ol, and 2-methylpropanol were formed.
e Taken from ref. [13].