

Conversion of Ethanol into Acetone catalysed by Iron Oxide treated with Tellurate Ion¹

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A catalyst for conversion of ethanol into acetone was obtained by exposing $\text{Fe}(\text{OH})_3$ to 0.05 M H_2TeO_4 followed by calcination in air at 600 °C; this catalyst showed a selectivity of up to 75% for 94% conversion.

We have previously reported that ZrO_2 catalysts treated with selenate and tellurate ions showed selective dehydrogenation activity for alcohols; this catalyst converted propan-2-ol into acetone with 100% selectivity.² In continuation of our studies on the catalytic ability of these selenate- and tellurate-treated materials, we have now found that Fe_2O_3 catalysts treated with tellurate ion are active for the conversion of ethanol into acetone.

The synthesis of acetone from ethanol ($2\text{EtOH} + \text{H}_2\text{O} \rightarrow \text{Me}_2\text{CO} + \text{CO}_2 + 4\text{H}_2$) is of importance from the point of view of using 'biomass' as a chemical resource. This reaction is known to proceed through intermediate formation of acetaldehyde catalysed by $\text{Fe}_2\text{O}_3\text{-CaO}$, $\text{Cr}_2\text{O}_3\text{-ZnO}$, and Cu ;³ CaO-ZnO was recently also found to be active.⁴

Iron hydroxide was obtained by hydrolysing $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ with aqueous ammonia, washing, drying at 100 °C, and powdering the precipitate (32–60 mesh). The hydroxide (2 g) was exposed to 0.05 M aqueous telluric acid (H_6TeO_6) (30 ml) for 30 min followed by filtering, drying, and calcining in air at 600 °C for 3 h. Reactions were carried out by a conventional flow method using nitrogen as carrier gas;

ethanol and nitrogen were passed through the fixed-bed catalyst (1 g) at flow rates of 1.22 ml/h (liquid) and 40 ml/min, respectively. Effluent products were directly introduced into a gas chromatographic column for analysis [Gaskuropack 54, 2 m, 80–160 °C (10 °C/min)]. Conversions were obtained from the product yields 4 h after the start of the reactions.

The reaction of ethanol was performed at 350 °C over iron oxide treated with tellurate ion, together with other similarly treated metal oxides for comparison; the results are shown in Table 1. Larger molecules, methyl isopropyl ketone (MIK) and pent-3-en-2-one (PO), were observed as products in addition to ethylene (C_2'), ethane (C_2), acetaldehyde (AA), acetone (A), and ethyl acetate (EA). The selectivity of product is calculated with respect to all the organic materials produced; the mass balance was conserved in the products taking into account the carbon oxides which were produced in equimolar amounts with respect to acetone. Iron oxide prepared by calcining $\text{Fe}(\text{OH})_3$ gave comparatively uniform yields of C_2' , C_2 , AA, and EA. However, the Fe_2O_3 catalyst treated with telluric acid produced acetone, and the longer the contact time, resulting from an increase in amount of catalyst,

Table 1. Reaction of ethanol at 350 °C.

| Catalyst | Conversion (%) | Selectivity of product (%) | | | | |
|---|-----------------|-----------------------------------|----|----|----|-----|
| | | C ₂ ' + C ₂ | AA | A | EA | MIK |
| Fe ₂ O ₃ ^a | 7 | 40 | 30 | 0 | 30 | 0 |
| Fe ₃ O ₄ ^b | 20 | 44 | 37 | 0 | 19 | 0 |
| Te/Fe ₂ O ₃ | 25 ^c | 24 | 10 | 24 | 37 | 5 |
| | 42 ^d | 29 | 6 | 34 | 18 | 8 |
| | 98 ^e | 31 | 0 | 40 | 0 | 21 |
| Te/SiO ₂ ^f | 9 | 67 | 0 | 0 | 0 | 0 |
| Te/ZnO ^g | 21 | 24 | 48 | 0 | 28 | 0 |
| Te/SnO ₂ ^h | 22 | 0 | 87 | 0 | 13 | 0 |
| Te/ZrO ₂ ⁱ | 33 | 92 | 0 | 0 | 0 | 0 |
| Te/TiO ₂ ^j | 48 | 41 | 4 | 0 | 0 | 0 |

^a Support only. ^b Commercial Fe₃O₄, supplied by Wako Pure Chem. Ind., Ltd. Catalyst amount: ^c 0.5 g, ^d 1.0 g, ^e 8.0 g. ^{f,i,j} Ethyl ether and butanol were also observed as products. Selectivity for PO: ^d 5, ^e 2%. Selectivity for C₂: ^a 26, ^b 34, ^d 23, ^e 24%. Surface area: ^f 333, ^g 10, ^h 29, ⁱ 59, ^j 44.

the greater the yield of acetone. Table 1 also suggests that longer contact times led to lower selectivities for AA and EA and higher selectivities for MIK and acetone.

Other metal oxides were examined; the catalytic activity was found to be highly dependent on the metal oxides used as supports. The catalysts were prepared from Si(OEt)₄, Zn(NO₃)₂, SnCl₄, ZrOCl₂, and TiCl₄ as starting materials in the same manner as the Fe₂O₃ catalyst; all the materials were calcined at 600 °C. It is seen from Table 1 that only Fe₂O₃ gave acetone. The specific surface area and amount of Te in the Fe₂O₃ catalyst treated with 0.05 M H₂TeO₄ followed by calcination at 600 °C were 27 m²/g and 2.00 wt%, respectively. With regard to the supported quantity of tellurium, catalysts were prepared by evaporation to dryness with 0.6, 5.6, and 11.2 wt% Te; total conversions were 27.7, 57.9, and 62.1% with 22.6, 36.6, and 38.4% selectivity for acetone (catalyst amount, 1.0 g; reaction temp., 350 °C). The differences in the selectivities were small compared with the large difference in the activities.

The reaction was also performed with aqueous ethanol (40% v/v), the results being shown in Table 2. Conversions were lower than those in reactions without water (Table 1), but high selectivities for acetone were observed. It is considered that the surface acidity was weakened by the

Table 2. Reaction with aqueous ethanol (40% v/v) over Te/Fe₂O₃ (600 °C).^a

| Reaction temp./°C | Conversion (%) | Selectivity of product (%) | | | | |
|-------------------|----------------|-----------------------------------|----|----|-----|----|
| | | C ₂ ' + C ₂ | AA | A | MIK | PO |
| 350 | 29 | 20 | 9 | 70 | 0 | 0 |
| 370 | 51 | 23 | 4 | 70 | 3 | 0 |
| 420 | 94 | 14 | 3 | 75 | 4 | 1 |
| 450 | 97 | 12 | 4 | 70 | 7 | 4 |

^a Catalyst amount: 2 g.

addition of water as a result of the suppression of dehydration, no EA being formed. Moreover, high conversions were obtained by reactions at higher temperatures, the high selectivity being maintained; up to 75% selectivity was observed for 94% conversion. The yield of acetone at 420 °C was almost constant up to 8 h (93, 94, 92, and 90% conversion for 1, 4, 6, and 8 h, respectively), with 76–70% selectivity.

With regard to the crystalline structure of the catalyst, the tellurate-treated material calcined at 600 °C showed the presence of crystallized α-Fe₂O₃, which was completely converted into the X-ray pattern of Fe₃O₄ after reaction. However, no acetone was formed over the Fe₃O₄ catalyst (Table 1). As for the carbon oxides produced, much more monoxide was formed than dioxide over the present catalyst. The reaction mechanism and the role of Te on the catalytic action are under investigation.

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