

X-ray photoelectron spectra for the oxidation state of $\text{TeO}_2\text{--MoO}_3$ catalyst in the vapor-phase selective oxidation of ethyl lactate to pyruvate

H. Hayashi¹, N. Shigemoto, S. Sugiyama, N. Masaoka and K. Saitoh^a

*Department of Chemical Science and Technology, University of Tokushima,
Minamijosanjima, Tokushima 770, Japan*

^a *Shikoku Research Institute Inc., Yashima-nishi, Takamatsu 761-01, Japan*

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X-ray photoelectron spectra of Te $3d_{5/2}$ and Mo $3d_{5/2}$ core electrons of $\text{TeO}_2\text{--MoO}_3$ provided an evidence for reduction of Te to the metallic state even in the presence of oxygen in the feed, while the component Mo was rather stable under reductive environment, in the vapor-phase oxidation of ethyl lactate at 300°C. Lattice oxygen was supplied to make up for the oxygen-deficit at the surface, and the catalyst should be used under oxidative, oxygen-rich conditions.

Keywords: XPS; $\text{TeO}_2\text{--MoO}_3$; redox behavior; ethyl lactate; vapor-phase oxidation

1. Introduction

Comparative reaction studies for catalyst screening in the vapor-phase oxidation of ethyl lactate suggested a binary oxide, $\text{TeO}_2\text{--MoO}_3$, as a promising candidate catalyst to afford pyruvate with a high selectivity over 90% at 250–330°C as reported in the previous paper [1]. However, an abrupt increase in the unfavorable yield of acetaldehyde was observed at high temperatures of 350–400°C due to skeletal decomposition of the product pyruvate. After the reaction at 450°C, a grayish sublimate was found on the wall of the reactor-exit, which dissolved in concentrated H_2SO_4 showing the red color characteristic of metallic Te [2]. Thus tellurium in $\text{TeO}_2\text{--MoO}_3$ was reduced by the organic substrate at high temperatures, even in the presence of molecular oxygen.

X-ray photoelectron spectra (XPS) for used $\text{TeO}_2\text{--MoO}_3$ catalysts were measured in the present work to elucidate the oxidation state of the metallic components of Te and Mo in reference to the reaction conditions.

¹ To whom correspondence should be addressed.

2. Experimental

The vapor-phase catalytic oxidation of ethyl lactate was carried out by a conventional fixed-bed flow apparatus at 300°C with a space velocity of 1800 h⁻¹. Ethyl lactate was supplied as 10 mol% solution in toluene by a Micro-Feeder (type JP-S, Furue Science Co., Tokyo) into the reactor and diluted with O₂/N₂ to result in the gas-phase composition of 5% ethyl lactate with 0–30% O₂. The reactor effluent was scrubbed by ice-cooled *n*-propanol, and analyzed for organic species by gas chromatography (15% PEG 4000/Uniort B; Hitachi 163-FID).

The catalyst, TeO₂-MoO₃, was prepared by kneading the component oxides in a molar ratio of TeO₂/MoO₃ = 1/2 with a small amount of water in an automatic kneading porcelain mortar (type 101, Ishikawa, Tokyo) for 2 h. The resultant paste was spread over a glass plate, dried overnight at 80°C, crushed, and calcined at 500°C in air for 5 h.

Ethyl lactate was purchased from Wako Pure Chemicals, Osaka, and used as supplied. Ethyl pyruvate for the calibration of GC analysis was obtained from Aldrich Chemical Co., Milwaukee. TeO₂ and MoO₃ were obtained from Wako, Osaka, and Merck, Darmstadt, respectively.

X-ray photoelectron spectra of the Te 3d_{5/2} and Mo 3d_{5/2} core electrons were measured by a Perkin Elmer-Phi 5500 (Ulvac-Phi, Inc., Chigasaki), irradiated with Mg K α , and the observed binding energies were calibrated with 285.0 eV for C 1s electron.

3. Results and discussion

Illustrative results for oxidation of ethyl lactate at 300°C on TeO₂-MoO₃ (2 cm³, 3.21 g) are compared in fig. 1. Ethyl pyruvate was obtained even in the absence of oxygen in the feed (a) with a low selectivity of 40–50% at the initial 1 h on-stream followed by a rapid degeneration. In the presence of oxygen, a steady-

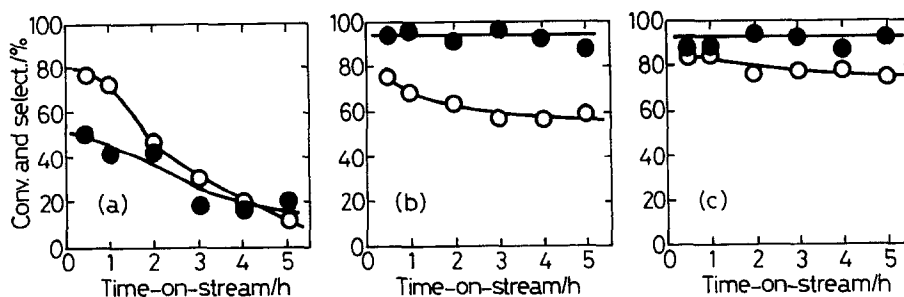


Fig. 1. Vapor-phase oxidation of ethyl lactate on TeO₂-MoO₃. Temperature 300°C; SV 1800 h⁻¹; 5% ethyl lactate; (a) in the absence of O₂, (b) 10% O₂, (c) 30% O₂. (○) Conversion of ethyl lactate; (●) selectivity to ethyl pyruvate.

state activity with a high selectivity to pyruvate of over 90% was observed both for 10% O_2 (b) and 30% O_2 (c).

XPS results for Mo 3d and Te 3d core electrons of $\text{TeO}_2\text{-MoO}_3$ calcined at 500°C in air for 5 h are compared with those of the component oxides MoO_3 and TeO_2 in fig. 2. The Mo 3d_{5/2} binding energy for $\text{TeO}_2\text{-MoO}_3$ was observed at 232.9 eV (fig. 2b), characteristic of Mo(VI), without any appreciable chemical shifts from the component MoO_3 (233.2 eV; fig. 2a) in good agreement with literature [3,4]. Te 3d_{5/2} binding energy for $\text{TeO}_2\text{-MoO}_3$ (fig. 2e) was observed at 577.3 eV, showing a higher oxidation state of Te(VI) [5,6], as compared with TeO_2 (576.0 eV; fig. 2d).

Figs. 3a–3c show XPS for Te 3d_{5/2} of $\text{TeO}_2\text{-MoO}_3$ catalyst after 5 h on-stream under different conditions, of which the reaction results are given in figs. 1a–1c, respectively. Solid lines show the spectra for the sample as it is taken from the reactor, and dashed lines for the finely ground catalyst to expose the bulk on the surface. The major Te 3d_{5/2} in fig. 3a was observed at 573 eV, showing Te was reduced to the metallic state by ethyl lactate in the absence of gas-phase oxygen. Essentially no difference in XPS between the ground catalyst and the catalyst as it is, suggests the reduction extended over the bulk phase. The rapid degeneration given in fig. 1a shows that simple dehydrogenation on the metallic Te was minor and the reaction to pyruvate was oxidative, for which oxygen was supplied from the bulk of the oxide catalyst in the absence of oxygen in the feed. The component Mo in $\text{TeO}_2\text{-MoO}_3$ appears more stable in reductive environment. Fig. 2c shows XPS for the Mo 3d region of $\text{TeO}_2\text{-MoO}_3$ after 5 h on-stream without oxygen, where Mo(VI) at 232.9 eV was again predominant with minor Mo(V) at 231.9 eV [3,4] as shoulder.

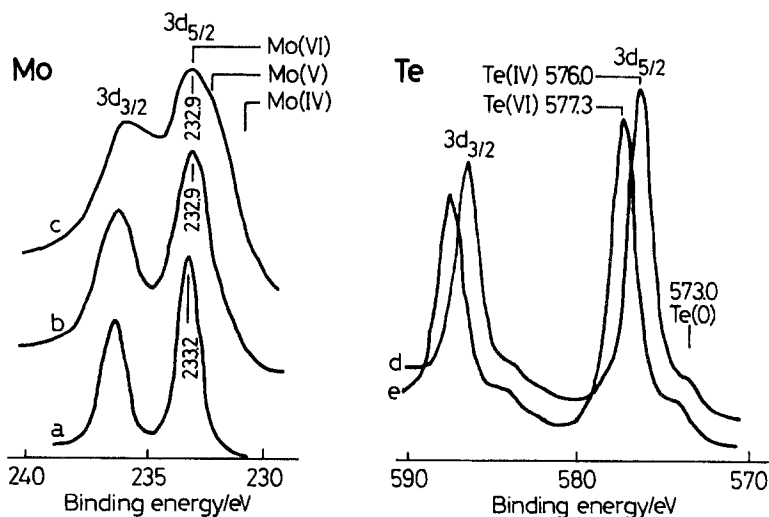


Fig. 2. X-ray photoelectron spectra for $\text{TeO}_2\text{-MoO}_3$. (a) MoO_3 , (b) $\text{TeO}_2\text{-MoO}_3$ calcined at 500°C for 5 h, (c) used $\text{TeO}_2\text{-MoO}_3$ in the same conditions as in fig. 1a, (d) TeO_2 , (e) $\text{TeO}_2\text{-MoO}_3$ calcined at 500°C for 5 h.

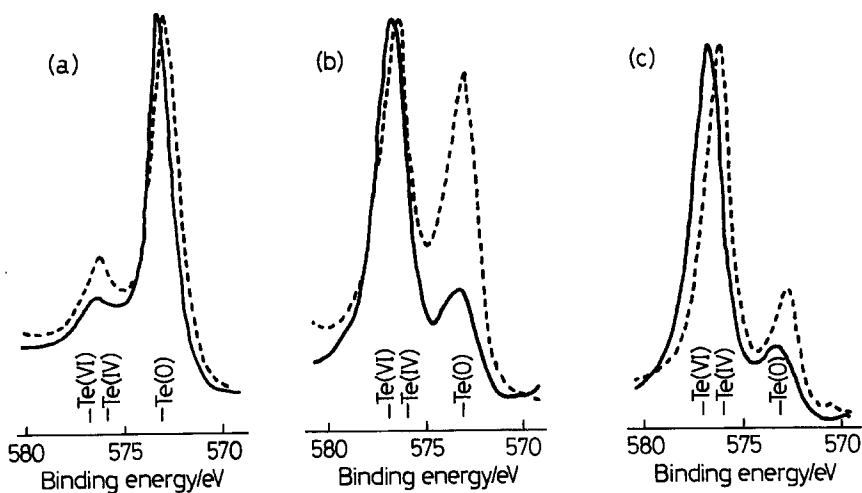


Fig. 3. X-ray photoelectron spectra for Te $3d_{5/2}$ of used $\text{TeO}_2\text{-MoO}_3$ corresponding to figs. 1a, 1b, and 1c, respectively. Solid lines: measured as is. Dashed lines: after being ground into powder.

In the presence of oxygen, ethyl lactate was oxidized selectively to pyruvate on $\text{TeO}_2\text{-MoO}_3$ without degeneration as in figs. 1b and 1c, and the surface Te $3d_{5/2}$ electron was observed at 577 eV, showing a higher oxidation state, both for 10% O_2 and 30% O_2 , as given in figs. 3b and 3c (solid lines). On exposure of bulk Te to the surface by grinding the catalyst (fig. 3, dashed lines), the ratio of $\text{Te(0)}/\text{TeO}_x$ substantially increased at 10% O_2 (fig. 3b), while it remained unchanged at 30% O_2 (fig. 3c). Thus lattice oxygen was employed to make up for the oxygen requirement at the reacting surface under the conditions of low oxygen-pressure.

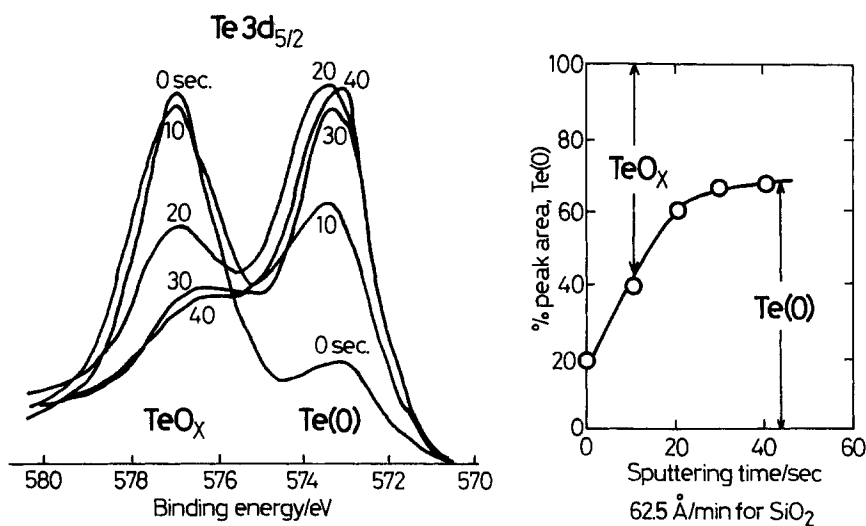


Fig. 4. Depth profile of the oxidation state of Te. Catalyst: $\text{TeO}_2\text{-MoO}_3$ used in fig. 1b.

Fig. 4 shows spectral change due to argon sputtering and the depth profile for Te $3d_{5/2}$ of $\text{TeO}_2\text{-MoO}_3$ catalyst after 5 h on-stream in the ethyl lactate oxidation with 10% O_2 . The relative intensity of $\text{Te}(0)/\text{TeO}_x$ increased with increasing sputtering time, where the rate of sputtering was calibrated as $62.5 \text{ \AA}/\text{min}$ for authentic SiO_2 . The profile suggests that 80% of the surface Te was in the oxidized state in contact with molecular oxygen, but 70% of Te under the surface skin ($\sim 20 \text{ \AA}$) was reduced to the metallic state. The pseudo-steady-state activity at 10% O_2 (fig. 1b) would be observed on a temporary oxygen-balance at the surface with pumping out the oxygen deficit from the bulk oxide.

4. Conclusion

A binary oxide, $\text{TeO}_2\text{-MoO}_3$, showed an excellent activity for vapor-phase oxidation of ethyl lactate to pyruvate with over 90% selectivity without any appreciable degeneration at 300°C . XPS of Te $3d_{5/2}$ and Mo $3d_{5/2}$ core electrons provided an evidence for reduction of Te to the metallic state even in the presence of oxygen in the feed, while the other component, Mo, was more stable in reductive environment. $\text{TeO}_2\text{-MoO}_3$ should be used under oxygen-rich conditions.

References

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