

## Durable Ethane Oxidation to Ethanol: Insights into SMSI Effects on TiO<sub>2</sub>-Supported Pt Catalysts

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### Significance and Relevance

The direct oxidation of ethane to ethanol using a durable and selective catalyst represents a promising avenue for sustainable chemical synthesis, with significant implications for the energy and chemical industries. Here, we present an anatase-TiO<sub>2</sub>-supported PtTi alloy catalyst, which achieves over 50% ethanol selectivity while maintaining stable catalytic performance for over 48 hours at 125 °C. Strong metal-support interactions (SMSI) between Pt and TiO<sub>2</sub> were induced to create PtTi alloy sites, endow resistance to CO-induced deactivation, enabling continuous ethanol production.

### Introduction and Motivations

Ethanol, a versatile fuel and feedstock, is conventionally derived through multi-step and energy-intensive processes, primarily from ethane. A direct, single-step catalytic oxidation approach promises a more sustainable and energy-efficient alternative, yet achieving high activity, selectivity, and durability remains challenging. Inspired by natural enzymatic oxidation pathways, our group recently developed a CO-assisted conversion of ethane to ethanol using a Pt-based catalyst, breaking the activity-selectivity tradeoff established so far.<sup>1</sup> However, CO-induced aggregation and deactivation of supported Pt limit prolonged application. This study explores the potential of SMSI to develop sinter-resistant Pt-based catalysts. SMSI frequently induces modification of the surface structure of the supported Pt via interaction with support elements, weakening the interaction with CO and preventing the aggregation of supported Pt nanoparticles.<sup>2</sup>

### Materials and Methods

The catalyst was prepared by impregnating a Pt(II) nitrate solution onto anatase-TiO<sub>2</sub>, followed by hydrogen reduction at 300 or 700 °C, tuning the degree of MSI. These catalysts are denoted as H300, and H700, respectively. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM), X-ray absorption fine structure (XAFS), and diffuse reflectance infrared Fourier transform spectroscopy using CO as a probe molecule (CO-DRIFTS) were applied to examine the structure and electronic states of supported Pt species. Activity test was conducted in a high-pressure batch reactor at 125 °C under 1 MPa ethane, 0.24 MPa CO, and 0.08 MPa O<sub>2</sub>.<sup>1</sup>

### Results and Discussion

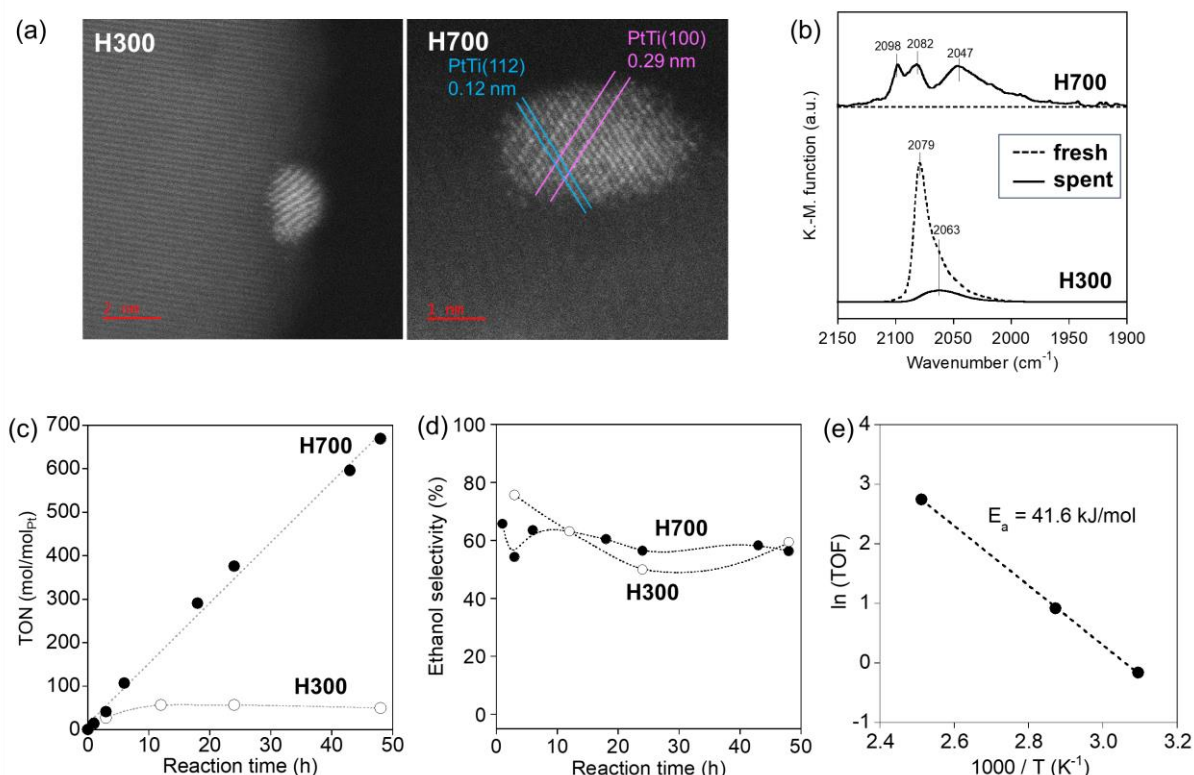
HAADF-STEM images of H300 and H700 are shown in **Figure 1a**. Based on the analyzed lattice spacing and lattice orientations, it was confirmed that Pt and PtTi nanoparticles are formed in H300 and H700, respectively, indicating that high-temperature reduction leads to alloying Pt nanoparticles with reduced TiO<sub>2</sub> surface; that is, SMSI occurred. Wavelet transform of extended XAFS demonstrated that the (k, R) coordinate for Pt–O and Pt–Pt backscattering shifted in response to the SMSI effect, and Pt–Ti backscattering was detected, supporting the formation of PtTi alloy nanoparticles. **Figure 1b** shows CO-DRIFT spectra of H300 and H700 before the reaction (dash lines, denoted as “fresh”). H300 gave a dominant ν<sub>CO</sub> band at 2079 cm<sup>-1</sup> attributed to CO adsorption via atop mode. On the other hand, H700 gave no band except for the gas-phase CO signals, which is the typical signature of SMSI.

**Figure 1c,d** shows the time course of turnover number (mole of liquid-phase product normalized with mole of Pt) and selectivity in ethane oxidation by H300 and H700. For H300, TON increased only up to 12 hours. On the other hand, H700 catalyzed continuous ethanol production with selectivity exceeding

50% over a 48-hour period. These results indicate that the SMSI-assisted surface modification of Pt nanoparticles contributes to the suppression of deactivation. Arrhenius plot was obtained in the 24h reactions using H700 (**Figure 1e**), demonstrating the durable catalysis in ethane oxidation. The apparent activation energy was determined to be 41.6 kJ/mol. The low  $E_a$  value indicates that the PtTi alloy can sustain efficient catalytic activity at low temperatures.

HAADF-STEM images after 48 hours showed that H700 retained a distribution of particle size similar to its initial state, while H300 showed extensive particle growth. CO-DRIFT spectra for spent H700 catalyst provided  $\nu_{\text{CO}}$  bands appeared at 2098, 2082, and 2047  $\text{cm}^{-1}$  which are assignable to CO adsorbed on  $\text{Pt}^{\delta+}$ ,  $\text{Pt}^0$ , and PtTi alloy sites, respectively (**Figure 1b**, solid line). These are indicative that surface modifications further occur during the reaction with the evolution of  $\text{Pt}^{\delta+}$ - $\text{Pt}^0$  dual-site. In our previous, the  $\text{Pt}^{\delta+}$ - $\text{Pt}^0$  dual-site was proposed as the active site in facilitating the oxidation of ethane to ethanol.<sup>1</sup> On the other hand, H300 provided only  $\nu_{\text{CO}}$  band attributed to CO adsorbed on Pt nanoparticles via atop mode; no spectroscopic evidence for  $\text{Pt}^{\delta+}$ - $\text{Pt}^0$  dual-site was obtained.

In summary, SMSI-induced PtTi alloys created CO-resistant surfaces with  $\text{Pt}^{\delta+}$ - $\text{Pt}^0$  dual sites, enabling prolonged catalytic oxidation of ethane to ethanol.



**Figure 1** (a) HAADF-STEM images. (b) CO-DRIFT spectra. Time course of (c) TON and (d) ethanol selectivity. (e) Arrhenius plot.

## References

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