Supporting Information

Durability and activity of Co_2YZ (Y = Mn or Fe, Z = Ga or Ge) Heusler alloy catalysts for dehydrogenation of 2-propanol

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† An-Pang Tsai passed away on May 25, 2019.

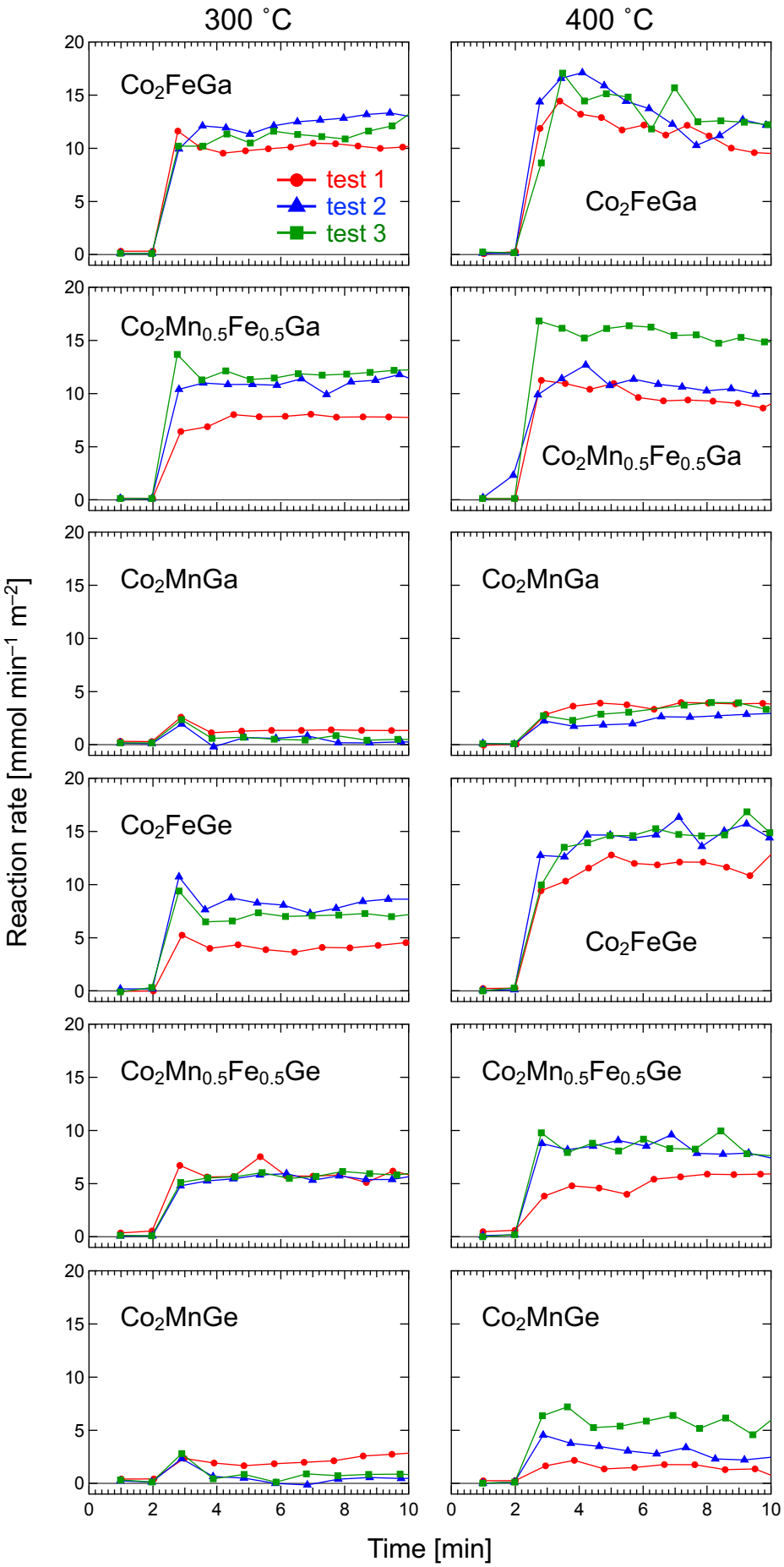

Figure S1. Reaction rate with time on stream measured three times at 300 ˚C (left column) and 400 ˚C (right column).

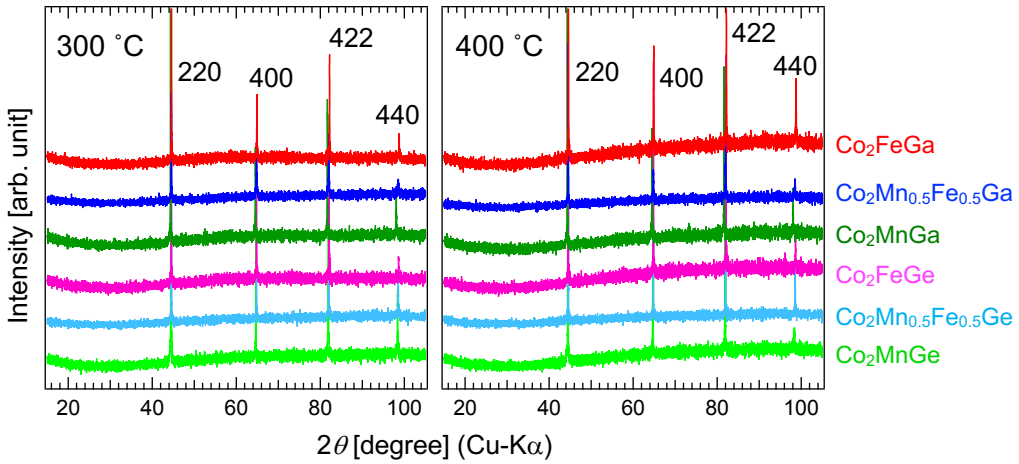

Figure S2. XRD pattern after reaction at 300 ˚C and 400 ˚C for 3 h. Measurement conditions, including a sample amount, a powder size, and an accumulation time were not optimized for observing 110 and 220 superlattice peaks, which also resulted in a fluctuated intensity ratio.

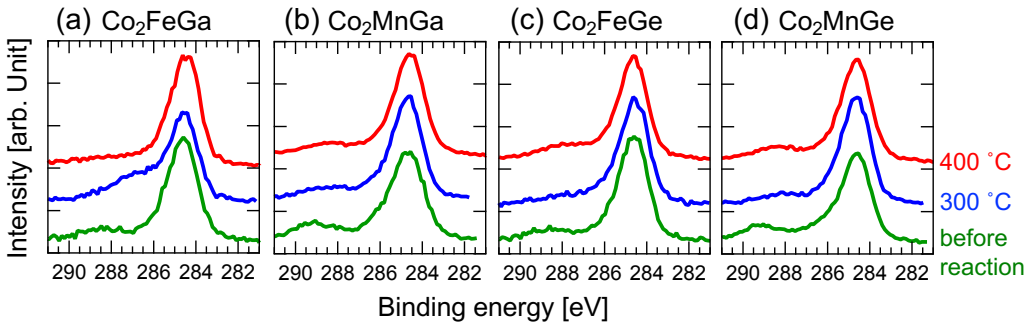

Figure S3. XPS spectra of C 1s core level before and after reaction at 300 ˚C and 400 ˚C for 3 h for (a) Co_2FeGa, (b) Co_2MnGa, (c) Co_2FeGe, and (d) Co_2MnGe. Each peak intensity was normalized by each peak area.

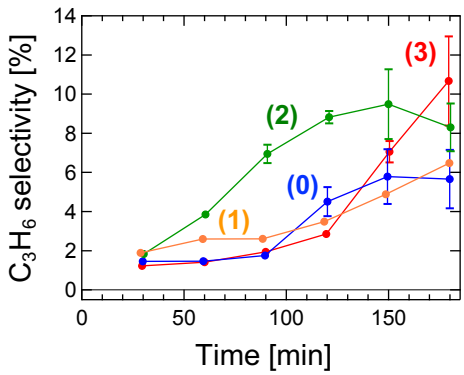

Figure S4. C_3H_6 selectivity with time on stream in reaction at 400˚C for Co_2FeGa using different 2-PrOH reagents: (0) standard grade (redisplay from Fig. 1f), (1) with 1 wt% H_2O added, (2) with ultralow H_2O impurity ($\leq$ 0.001 wt%), (3) with ultralow H_2O with Ar bubbling. Inset of (b) shows magnification within 30 min. Error bars are estimated by the same procedure as Fig. 1(f).

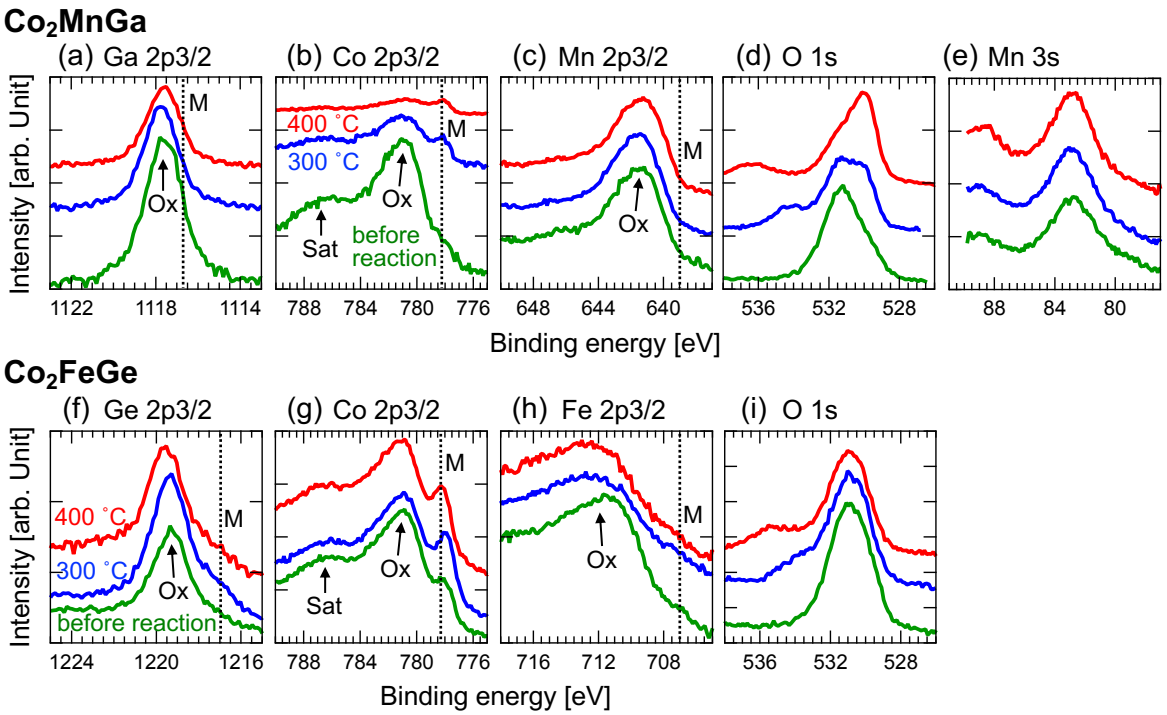

Figure S5. Core level XPS spectra of (a) Ga 2p3/2, (b) Co 2p3/2, (c) Mn 2p3/2, (d) O 1s, and (e) Mn 3s for Co_2MnGa, and of (f) Ge 2p3/2, (g) Co2p3/2, (h) Mn 2p3/2, and (i) O 1s for Co_2FeGe before and after reaction at 300 ˚C and 400 ˚C for 3 h. In (a–c) and (f–h), dashed lines with "M" show the reference positions for pure metal states [S1], and "Ox" indicates peaks from oxides. "Sat" in (b,g) indicates a satellite peak of Co 2p3/2. In (a–c), intensities were normalized by Mn 2p3/2 peak area for each sample, and the same scale is used. The normalization was done by Co 2p3/2 peak for (f–h) that use the same scale interval. In (d,i), each peak intensity was normalized by each peak area. In (e), although an accurate value of energy difference between split peaks cannot be estimated due to a weak intensity of the left peak and an insufficient scan range, it seems to be in 5.6–6.1 eV, indicating the existence of MnO at the surface [S2,S3].

References

[S1] J. F. Moulder, W. F. Stickle, P. E. Sobol and K. D. Bomben, "Handbook of X-ray photoelectron spectroscopy" (ULVAC-PHI, Inc., Chigasaki, Japan, 1995).
[S2] A. J. Nelson, J. G. Reynolds and J. W. Roos, J. Vac. Sci. Technol. A, 2000, 18, 1072–1076.
[S3] E. S. Ilton, J. E. Post, P. J. Heaney, F. T. Ling and S. N. Kerisit, Appl. Surf. Sci., 2016, 366, 475–485.

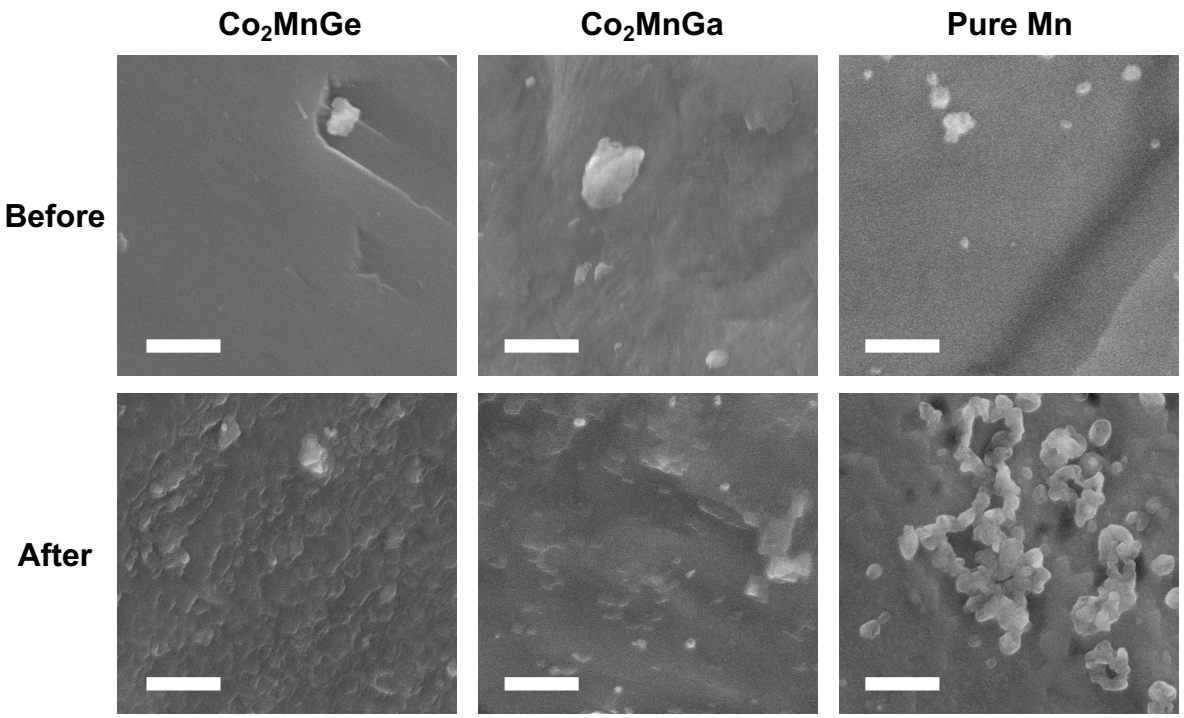

Figure S6. SEM images for Co_2MnGe (left), Co_2MnGa (center), and pure Mn (right) before (upper) and after (lower) reaction at 400 ˚C for 3 h. All scale bars indicate 500 nm.

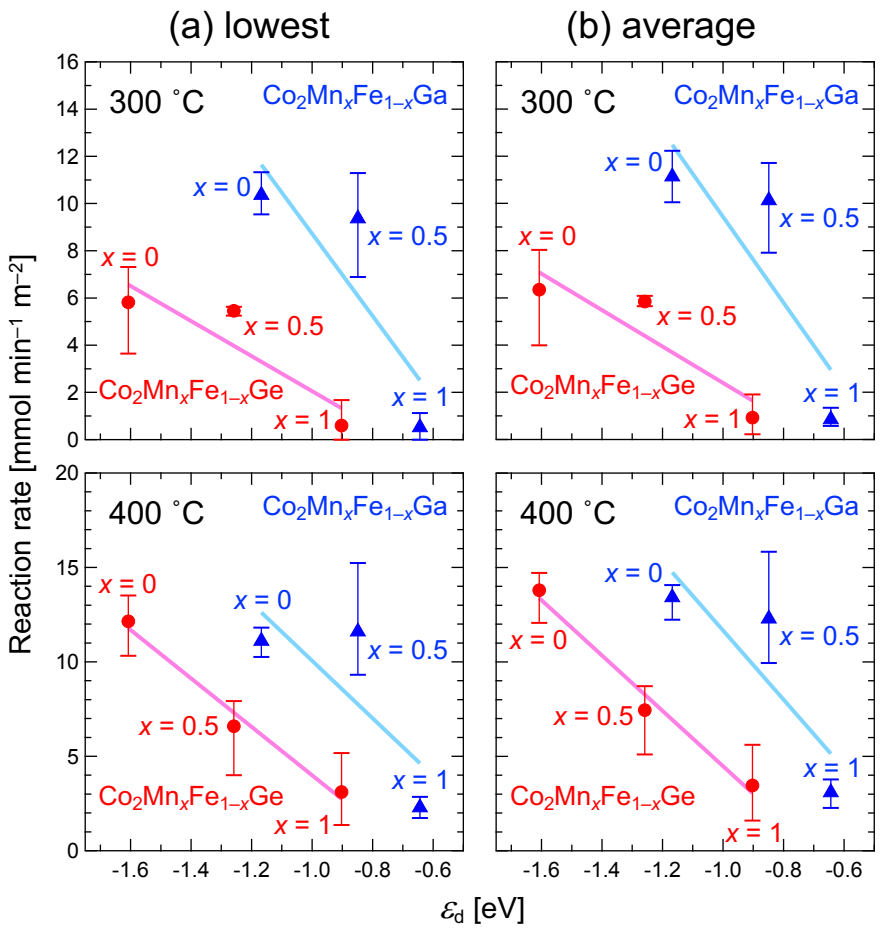

Figure S7. Initial reaction rate of 2-PrOH at 300 ˚C and 400 ˚C vs. ε_d for $Co_2Mn_xFe_{1-x}Ga$ (blue triangles) and $Co_2Mn_xFe_{1-x}Ge$ (red circles) with x = 0, 0.5, and 1, where (a) the lowest rate in the reaction time of 3.0–8.0 min and (b) the average rate in 4.0–8.0 min were used. The data averaging, the determining error bar, and the least-squared fit were done as well as Fig. 6.