

EELS Study of Co-Based Fischer-Tropsch Catalysts on TiO₂ and SiO₂ Supports

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As a potential way to ease the energy crises, Co-based Fischer-Tropsch (FT) heterogeneous catalysts have been extensively studied. Mn is found to be an effective promoter which could increase the selectivity of the catalysts. The enhanced catalytic performance is due to the generation of Co-Mn mixed oxide species that could potentially create active sites of more selectivity. That means the location of the Mn-promoter on the catalyst surface is a very important factor for the FT catalysis studying. TiO₂ and SiO₂ are two commonly used supports. For TiO₂ support, strong metal support interaction (SMSI) has been reported. On the contrary, SiO₂ is considered an inert support without any SMSI. In this presentation, by using the Z-contrast imaging and EELS, we will show the Mn distribution and migration in Co/TiO₂ and Co/SiO₂ catalysts. The different morphologies of the two catalysts will demonstrate that the Oxygen vacancies are the key factors controlling the Mn promotion effect in FT catalysis. [1, 2]

Strong electrostatic adsorption (SEA) and dry impregnation (DI) are used to deposit Mn onto the Co/TiO₂ catalyst. SEA deposits Mn selectively onto the Co particle that Mn forms a shell covering the Co particle surface after calcination (Figure 1(a)). After reduction in H₂, the Mn shell ruptures and Mn moves to the Co/TiO₂ interface, as in Figure 1(b). On the contrary, DI results in a random Mn distribution over the Co/TiO₂ surface. As seen in Figure 1(c), Mn is separated from Co. However, Figure 1(d) shows that Mn moves to the Co/TiO₂ interface after reduction in H₂. In order to understand the mechanism of Mn migration, we characterize the Co catalyst on SiO₂ support. Figure 2 shows the elemental distribution of Co/SiO₂ sample with Mn deposited by SEA. Before and after reduction, the Mn distribution does not change. The Mn still selectively covers the Co particle surface. No Mn moves to the Co/SiO₂ interface after reduction.

As the Oxygen vacancy on the TiO₂ surface could act as the anchoring sites for the metal particles, we use Ti *L*-edge spectrum to examine the presence of interfacial Oxygen vacancies. Figure 3 shows a spectrum image of the reduced Mn/Co/TiO₂ sample. The negative chemical shift of Ti *L*-edge onset from the TiO₂ support bulk to Co/TiO₂ interface indicates the lower Ti valence at the interface, which means that Oxygen vacancies exist at the interface. Figure 4 shows the Si *L*-edge extracted from the Co/SiO₂ interfaces in Figure 2. The Si *L*-edge onset at 105.5 eV indicates only SiO₂ exist at the Co/SiO₂ interfaces, and no interfacial Oxygen vacancies are found. The comparison shows the Co/TiO₂ interfacial Oxygen vacancies generated by the sample's reduction might be the factor controlling the Mn migration to the Co/TiO₂ interface. In summary, we will give a detailed theoretical explanation and experimental evidence for the mechanism of Mn migration in Co/TiO₂ and Co/SiO₂ catalysts after calcination and reduction treatment. [3, 4]

References

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- [3] H. Iddir, V. Skavysh, S. Ogut, *et al.*, Physical Review B 73, 041403 (2006).
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Figure. 1

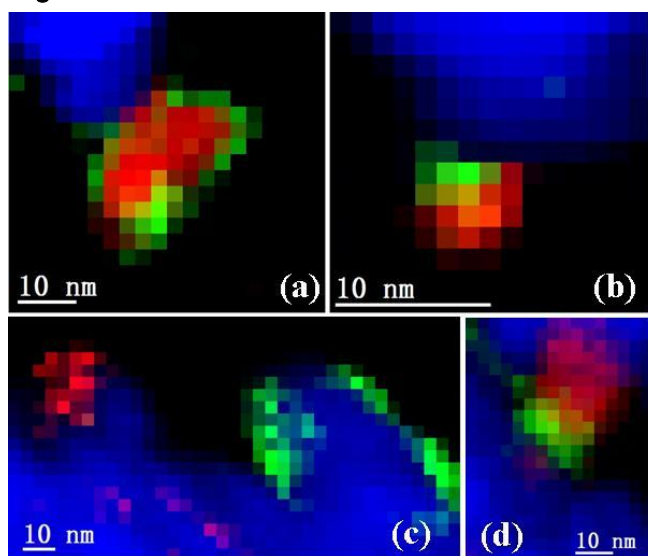


Figure. 1 (Color). EELS spectrum image (Blue–Ti, Red–Co, Green–Mn) for the Mn^{SEA}/Co/TiO₂ catalyst (a) calcined and (b) reduced and the Mn^{DI}/Co/TiO₂ catalyst (c) calcined and (d) reduced.

Figure. 2

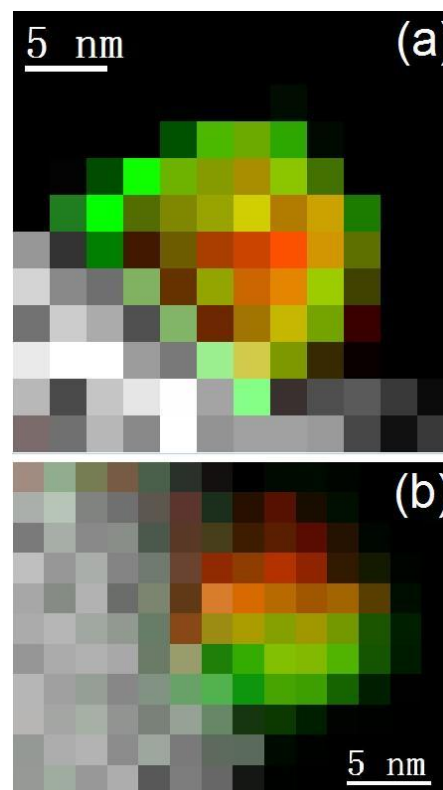


Figure. 2 (Color). EELS spectrum image (Grey–Si, Red–Co, Green–Mn) for the Mn^{SEA}/Co/SiO₂ catalyst (a) calcined and (b) reduced.

Figure. 3

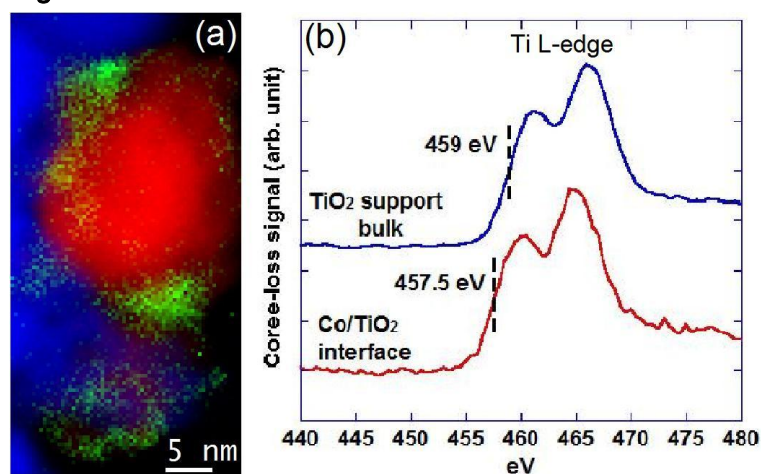


Figure. 3 (Color). (a) EELS spectrum image (Blue–Ti, Red–Co, Green–Mn) for the reduced Mn^{SEA}/Co/TiO₂ catalyst. (b) Ti *L*-edges extracted from (a) at the TiO₂ support and Co/TiO₂ interface.

Figure. 4

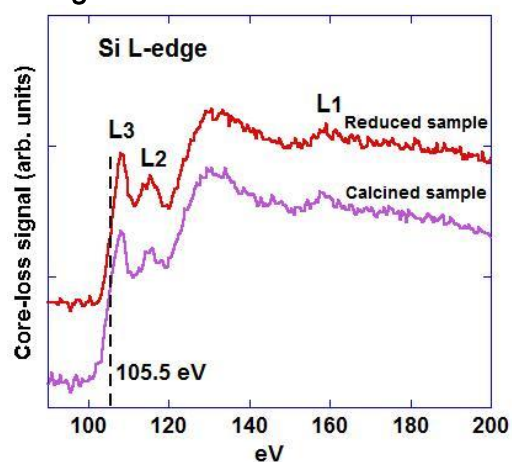


Figure. 4 (Color). The comparison of Si *L*-edges acquired at the Co/Si interfaces from Mn^{SEA}/Co/SiO₂ samples after calcination and after reduction. The dash line indicates the edge onset at 105.5 eV.