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In-situ ETEM Observation of Competing Mechanisms for Filamentous Carbon Gasification

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Metal catalyst deactivation caused by carbon deposition, also known as coking, is a significant problem in various industrial catalytic processes, such as the conversion of methane to syngas and hydrogen. A common characteristic of carbon deposits over typical methane conversion catalysts such as supported Ni and supported Fe involves the formation of filamentous carbon. Despite different approaches to control carbon deposition, catalytic activity loss is often inevitable, and eventually, the removal of carbon via gasification is necessary to regenerate spent (supported) metal catalysts. However, the current regeneration approach relies on single-step thermal carbon gasification, often leading to irreversible deactivation due to metal sintering and incomplete carbon removal.

Various mechanisms have been proposed to describe filamentous carbon gasification. The most frequently mentioned are: 1) carbon bulk diffusion, where carbon dissolution at the carbon-catalyst interface diffuses through the metal for gasification; 2) oxygen/hydrogen spillover, where gas species are adsorbed and dissociated on the metal catalyst, which can then migrate to the nearby carbon for gasification; 3) the redox mechanism, where lattice oxygen oxidizes the carbon deposited on metals; and 4) in the case of non-redox supports, the oxide particles migrate towards carbon deposition for gasification. All these conventional mechanisms rely on carbon-catalyst interaction.

In this work, we performed the first in-situ ETEM gasification of filamentous carbon at 750 °C in 1 bar $1O_2/4He$. As shown in Figure 1, a representative HRTEM image of the spent Ni-W/CeO_2 partial oxidation of methane (POM) catalyst shows that some filamentous carbon is metal-free, and some encapsulate the metal catalyst. Our ETEM experiments were conducted using an atmospheric MEMS-based gas cell (DENSsolution, Climate G+ system), which mimics the technically relevant industrial catalyst regeneration usually carried out under atmospheric pressure. Interestingly, as shown in Figure 2, we observed both immobile and highly mobile catalyst particles during the gasification and filamentous carbon that is gasified both with and without carbon-catalyst interaction. In particular, we found that the non-catalyzed filamentous carbon gasification is reproducible. This directly contradicts the conventional mechanisms via metal-carbon interaction as required for carbon gasification. A similar conclusion was made in a recent in-situ optical microscopy study on char gasification, where successful gasification was achieved without carbon-alkali contact [1]. These novel in-situ real-space observations suggest that there are probably several different mechanisms at play during the process of removing filamentous carbon through thermal gasification and that these mechanisms may compete with each other and affect the rate of the carbon gasification reaction. In summary, in-situ ETEM is a powerful technique that facilitates direct assessment of the predominant and/or the combination of regeneration mechanism(s) for spent catalyst regeneration under different carbon gasification conditions [2].

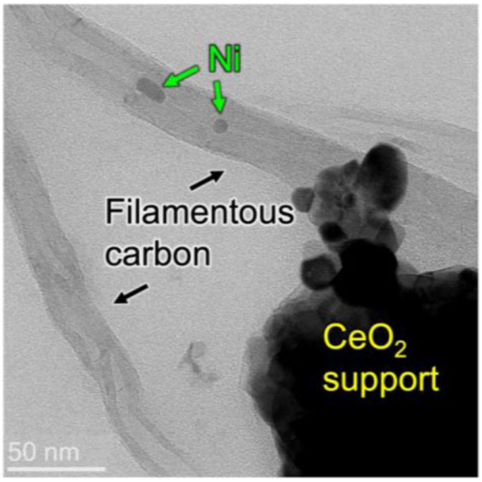

Fig. 1. HRTEM of the filamentous carbon in a spent Ni-W/CeO_2 POM catalyst.

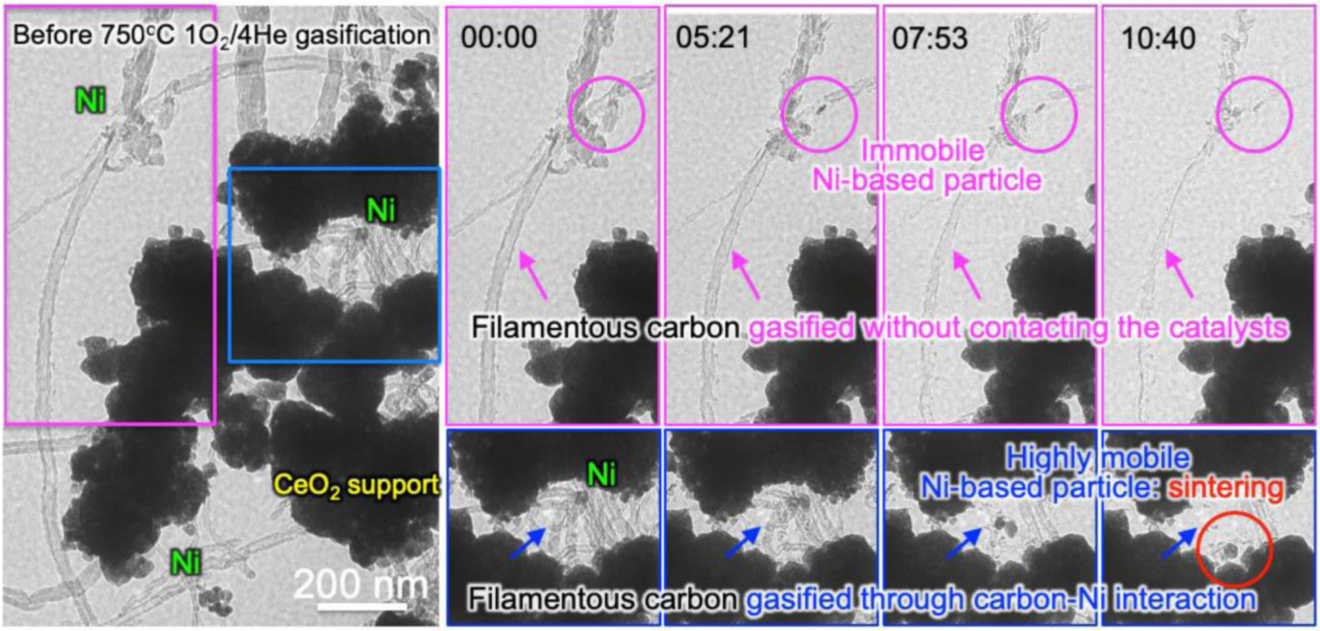

Fig. 2. In-situ ETEM filamentous carbon gasification, suggesting a new competing mechanism.

References

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