Tunable Hierarchical Support for Enhancing the Activity and Stability of metal Catalysts

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Abstract:

Numerous reports in literature show the important effect of the support material on catalytic performance. In cases where for example one support material provides good catalytic activity but less than optimal selectivity or low catalyst stability the task of finding the right support becomes critical. This work focuses on trying to bridge this gap by constructing a hierarchical support that allows tuning the interactions between the support and the metal catalyst such that optimal catalysis is obtained. Herein, we use the nickel catalyzed dry reforming as an example for controlling the activity, selectivity and stability of the catalyst.

Keywords: metal support interaction, methane reforming, catalyst synthesis.

1. Introduction

The dry reforming of methane (MDR) is a highly attractive route to produce syngas. Supported nickel catalysts were identified as a cost effective and active catalyst for MDR. However, the high concentrations of carbon species in MDR and the absence of water make carbon deposition on the nickel catalyst the thermodynamically favored path. This stimulates the use of even higher reaction temperatures, which was shown thermodynamically to limit carbon formation.[1] Unlike most rare earth metals, for which the T_{Tam} (Tammann temperature) is above the desired reaction temperature (600 °C -800 °C), Ni has a lower T_{Tam} (590 °C), making it highly prone to sintering. On the one hand supporting nano-size Ni on a strongly interacting support (SIS) produces a more stable catalyst, but may also block important active sites.[2] On the other hand, if the same nano-sized Ni is supported on a weekly interacting support (WIS), although activity can be higher the stability is much lower. To mitigate this challenge we have constructed an hierarchal support material, which is composed of thin (<2 nm) platelets of a SIS, which is supported on a second WIS. We show for the hierarchical material, where the Ni is supported only on the SIS platelets, the obtained catalyst is more active and more stable at the same time, while exhibiting a selectivity that is more typical to the underlying support material. This unique hierarchical configuration allows us to control reaction performance and suggests that the underlying support and the Ni, despite having no physical contact, can 'talk' through the mediating SIS layer.

2. Experimental

The synthesis of these new catalyst platforms relies on the coupling between positively charged clay-like metal-oxide nano-platelets (hydrotalcite (HT)) and a negatively charged secondary oxide surface (i.e. zirconia (Zr), silica and graphene oxide) acting as the underlying support. To this end we have developed a nucleation and growth methodology to control the size of layered double hydroxide nanoparticles.[3] The nano-platelets and Ni are then grafted on the secondary support using conventional impregnation techniques. Catalysts are characterized by HR-TEM, HR-STEM, SAXS, PXRD, TPR and XPS and tested under relevant MDR conditions.

3. Results and discussion

Results for the Zirconia system shows that for MDR the hierarchical catalyst is ~2 fold more active and more stable than the Ni on ZrO_2 and over 7 fold more active than the Ni on HT, see Figure 1. These results are correlated to a significant changes in the reduction temperature of Ni, which was found to be lower by ~50 °C on the hierarchal support as compared to Ni on HT, see Figure 2. We further show that the catalyst on the hierarchal support undergoes only minor deactivation over 40 h. Moreover, because Ni can be reduced at a significantly lower temperature the catalyst can be recycled several times, each time regaining the same performance as a fresh catalyst. Reaction results are explained with respect to calculated apparent activation energy of the various catalysts. The effect of Ni loading and dispersion are assessed with respect to catalytic performance.

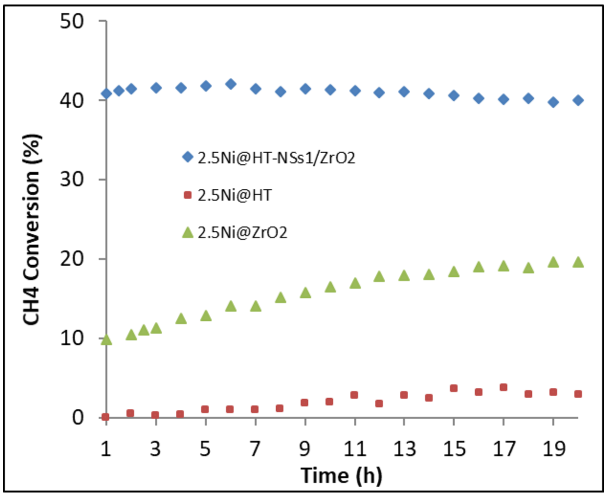

Figure 1. Methane conversion during dry reforming at 800 °C for catalysts reduced at 600 °C with

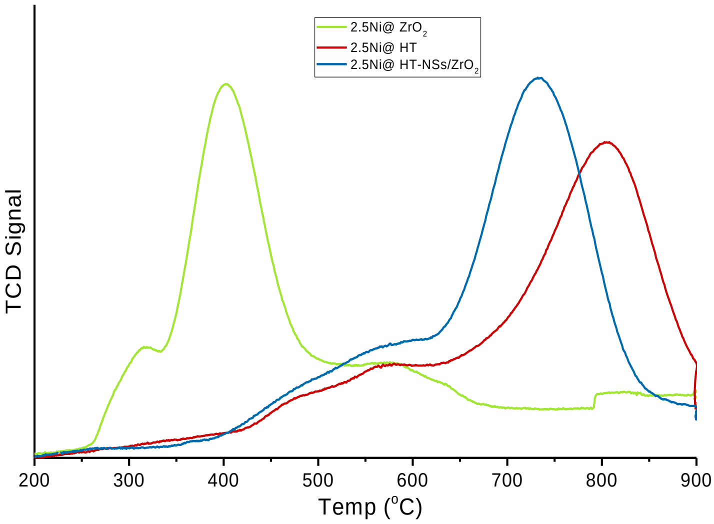

Figure 2. Temperature program reduction profile for the various catalysts

4. Conclusions

The work here presents a new way to tune the catalyst properties such that enhanced MDR catalytic performance is obtained. The highlight of these results comes from the relatively high tunability of the materials and the simple synthesis procedure, which we believe can be easily extended to various other catalytic reactions.

References

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