Fe and Ni-based Oxygen Carriers for CO_2 activation via Chemical Looping

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Abstract:

'Chemical Looping Combustion' (CLC) is an emerging clean combustion technology which offers an efficient and elegant route for fossil fuel combustion with inherent CO_2 capture based on the cyclic oxidation and reduction of an "oxygen carrier" (typically a metal) with air and a fuel, respectively. We have recently shown that this process can also be used for CO_2 activation by replacing air with CO_2 as the oxidant for the process, thus enabling the reduction of CO_2 to CO (which has many uses in the chemical industry) as an alternate pathway to carbon sequestration. We had identified Fe as the most suitable metal for the process due to its good reactivity with CO_2 at realistic process operating conditions. However, Fe shows poor reactivity with methane as a typical fuel for this process. Ni and NiO, on the other hand, is well known as an efficient catalyst for methane combustion, but cannot be oxidized with CO_2. We hence hypothesized that a bimetallic Fe/Ni oxide would show combined good reactivity with both CH_4 and CO_2 in the reduction and oxidation half cycles, respectively.

Supported Ni, Fe, and Ni/Fe oxygen carriers with 40wt% metal loading were synthesized using a simple wet-impregnation procedure. Three different ratios of the Fe to Ni were studied for their performance. Thermo-gravimetric analysis (TGA) of the carriers combined with X-Ray Diffraction (XRD) gave insight into oxidation states, carrier conversions, and reaction rates were evaluated in fixed-bed reactor experiments. We found that bimetallic oxides can indeed show activity for both methane combustion and CO_2 reduction; albeit the individual rates of oxidation are lower than for monometallic Fe carriers, and rates of reduction are lower than for monometallic Ni carriers. For comparison, physical mixtures of monometallic Fe and Ni carriers with the same metal weight loadings were prepared to isolate the oxidation characteristics of the individual metal oxides during the reactive processes. Remarkably, a significantly higher rate of carrier conversion obtained with the physical mixture—not only in comparison to the bimetallic carriers, but also in comparison to either monometallic carrier—suggested that the steps involved were quite different from those in case of a mixed oxide. The remarkable behavior can

be explained based on a synergistic reaction sequence between the two carrier materials, which will be discussed in detail in the presentation. Overall, our study thus identifies a very simple, yet highly promising carrier system for an efficient chemical looping process for CO_2 activation.