268b Partial Oxidation of Methane Using Metal-Substituted Hexaaluminate Catalysts on Porous-Foam Supports

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This paper reports the results of a combined experimental and modeling effort to characterize partial oxidation of methane using metal-substituted hexaaluminate catalysts. The objective is to develop robust systems for the production of synthesis gas. The investigation considers two-stage combinations of Ni- and Rh-substituted hexaaluminates. The catalysts are supported on alumina-based porous-foam monolith structures, which are positioned within a tube furnace to control the nominal operating temperature.

The metal-substituted hexaaluminates have the general formulation AxB(1-x)Al11O18, where metal A is chosen to have good catalytic activity and metal B is used to enhance thermal stability [1]. In the work reported here metal A may be Ni or Rh and metal B may be La, Mn, or Sr. These catalysts are prepared using a process with alumoxane precursors [2,3]. The alumoxanes are prepared by refluxing a beohmite sol with a carboxylic acid (e.g., 1,6-diaminohexanoic acid) at a 12:1 molar ratio of boehmite to carboxylic acid. The metal cations are then introduced into the boehmite core of the carboxylato-alumoxane by heating an aqueous dispersion of the alumoxanes with a solution of metal acetylacetonates (acacs) at 90 ¢ªC for 16 hours. Two (or more) metals are exchanged with the Al by heating the alumoxane suspension with an appropriate mixture of both acacs simultaneously. After exchange the catalyst is loaded by dipping the foam monolith into the solution. After each dip-coating, the foam is dried and weighed. Several dip-dry cycles are used to develop a coating of approximately 30 microns. The foam assembly is then calcined at 1300 ¢ªC to form the substituted hexaaluminate structure.

The ceramic-foam structure is formed as a cylinder, 1.65 cm in diameter and 2.54 cm long. It has nominally 18 pores per centimeter (45 pores per inch), with a mean pore size of 400-600 microns. The porous ceramic is placed within a quartz tube that is housed within a temperature-controlled tube furnace. Mixtures of methane, oxygen, and helium, which are introduced into the tube at known flow rates, flow through the porous catalytic structure. Following cooling, the post-catalyst composition is measured via gas chromatography.

A reactive-flow model is based on a Dusty-Gas formulation for the porous-media transport and elementary multi-step reaction mechanisms to represent heterogeneous chemistry at the catalyst surfaces. The Dusty-Gas model considers molecular transport via ordinary and Knudsen diffusion and convective transport by Darcy flow [4]. Molecular transport properties are computed from the kinetic theory [5]. Structural and physical properties of the foam are used to determine needed parameters in the model, including porosity, permeability, and tortuosity [6]. The reaction mechanisms, which consider either Ni or Rh, were developed originally for metal washcoats, not hexaaluminates [7,8]. The model is a one-dimensional elliptic boundary-value problem with the independent variable being the distance through the foam structure. The dependent variables are the species composition and the surface coverages. The model is solved computationally using a hybrid Newton iteration strategy [5].

The experiments reported here consider Rh0.5Sr0.5Al11O18 and NiAl11O18 hexaaluminates. Initial experiments determined the performance of foam structures loaded uniformly with only the Rh-based catalyst. A second set of experiments used a combination of the Rh- and Ni-based catalysts. In all cases reported, the unreacted inlet composition is 12.2% CH4, 6.1% O2, and 81.7% He and the nominal inlet velocity is 450 cm/s. The nominal operating conditions were 1000¢ªC and atmospheric pressure.

According to model results, the Ni-based catalyst behaves initially as a full oxidation catalyst, producing primarily H2O and CO2 as long as there is O2 available. Once the O2 is fully consumed, the Ni behaves as a reforming catalyst, using H_2O and CO_2 to reform remaining CH_4 to H_2 and CO. For the flow conditions and catalyst loading here, the model predicts that the O_2 is fully consumed by about halfway through the foam structure. The Ni-based system accomplishes an indirect partial oxidation in the sense that full oxidation is followed by steam reforming.

The Rh catalyst behaves very differently from Ni. The Rh is much more active, causing much faster CH_4 conversion rates. Perhaps more importantly, in addition to H_2O and CO_2, the Rh-based reaction begins to produce CO right from the leading edge of the foam structure. In other words, the Rh behaves as a direct partial oxidation catalyst, even in the presence of O_2. Significant H_2 production rates are predicted as soon as the O_2 is consumed.

A very interesting result is obtained when the foam structure is coated with the Rh hexaaluminate on the upstream half and the Ni hexaaluminate on the downstream half. In this case, the selectivity to H_2 and CO is noticeably improved compared to the situation using only one of the catalysts. The high partial-oxidation activity of the Rh rapidly produces significant levels of H_2, CO, H_2O, and CO_2 in the early regions of the foam structure. However, as soon as there is sufficient H_2O available and the O_2 is depleted, the Ni behaves as a better reforming catalyst than the Rh. With the Rh-based catalyst in the entry regions, the Ni-based reforming in the downstream region begins with a significant base level of H_2 and CO already established. Thus, the overall performance is improved. Others have also reported performance improvements with two-stage catalyst structures for various applications [9,10]

Hexaaluminate-based catalysts offer some potentially important advantages compared to the equivalent metal washcoat analogs. The hexaaluminates may result in lower net metal incorporation, which results in lower cost for precious metals. Although they may be somewhat less active, the hexaaluminates are significantly more stable to temperature excursions [11]. This stability can be especially important in applications where reliability and lifetime are critical. As illustrated by the Rh-followed-by-Ni example, composite catalyst structures can significantly improve performance and reduce cost.

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