Catalytic molten metals for the direct conversion of methane to hydrogen and separable carbon

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Metals that are active catalysts for methane (Ni, Pt, Pd), when dissolved in inactive low-melting temperature metals (In, Ga, Sn, Pb), produce stable molten metal alloy catalysts for pyrolysis of methane into hydrogen and carbon. All solid catalysts previously used for this reaction have been deactivated by carbon deposition. In the molten alloy system, the insoluble carbon floats to the surface where it can be skimmed off. A 27% Ni–73% Bi alloy achieved 95% methane conversion at 1065°C in a 1.1-meter bubble column and produced pure hydrogen without CO2 or other by-products. Calculations show that the active metals in the molten alloys are atomically dispersed and negatively charged. There is a correlation between the amount of charge on the atoms and their catalytic activity.

Hydrogen is an important chemical intermediate and could be used as a CO2-free energy carrier in many applications that currently rely on fossil hydrocarbons. Steam methane (CH4) reforming (SMR) followed by the water-gas shift reaction is the most common process for large-scale hydrogen production today (1). Although commercially optimized for decades, the endothermic SMR process is expensive; high capital costs and high energy consumption are unavoidable (2). Furthermore, the process produces stoichiometric CO2, which may impose additional costs because of the need for sequestration or because of a possible carbon tax. Despite the fundamental economic and environmental limitations of SMR, none of the presently deployed renewable power sources, including hydrogen from electrolysis, can compete with the SMR process for large-scale H2 production (3).

Alternatively, H2 can be produced by pyrolysis of CH4 without producing CO2:

\[ \text{CH}_4(g) \rightarrow \text{C}(s) + 2\text{H}_2(g) \Delta H^\circ = 74 \text{ kJ/mol} \]  

(1)

Only half as much H2 is produced per mole of CH4 compared to SMR; however, considerably less energy input is required and solid carbon is coproduced rather than CO2. The solid carbon can be safely stored in perpetuity; some may be valuable for use in electrodes or as additives to materials (e.g., concrete, asphalt, rubber). Further, direct CH4 pyrolysis can be done in a relatively simple (and potentially low-cost) commercial process in a single reaction step. Small amounts of unconverted CH4 can be tolerated in most downstream processes. For ammonia production or in a fuel cell, for example, H2 may contain small amounts of CH4 whereas carbon oxides produced from the SMR process will poison the catalysts and must be completely removed.

Early interest in CH4 pyrolysis made use of gas-phase radical reactions. Reaction equilibrium favors high temperature and low pressure to achieve high CH4 conversion, and high-temperature gas-phase chemistry coproduces a mixture of H2 along with ethane, ethylene, acetylene, and aromatics, which are expensive to separate (4). The only commercially practiced processes use gas-phase reactions in thermochemical or plasma reactor systems (5) to produce specialty carbons; however, CH4 pyrolysis has not been used commercially specifically for H2 production. Steinberg (6) and others (7–15) have proposed using inert molten metals as thermochemical reaction media and as a heat transfer fluid for pyrolysis of CH4. In molten metals, the low-density carbon produced by gas-phase pyrolysis at high temperature floats to the surface of the melt where it can be removed. The highest H2 yield of 78% at 1175°C was obtained in a 1-m bubble column containing molten tin, which is not thought to be catalytic (15). Technoeconomic analyses using several heating strategies show that H2 can potentially be produced by pyrolysis at approximately the same cost as that of H2 produced by SMR (6), and that using a catalytically active and selective molten metal catalyst producing continuously separable carbon could make the cost of H2 competitive with SMR even without a CO2 tax (16).

Metallic catalysts (e.g., Ni, Pd, Pt) achieve high conversion and selectivity to H2 at moderate temperatures; however, their melting temperatures are extremely high and as solids, they are rapidly deactivated by solid carbon (coke) (6, 8, 17–19). The only report of the use of a molten metal as a catalyst for CH4 pyrolysis described pure liquid magnesium (Mg), which was used to achieve ~30% of the equilibrium conversion, at 706°C (20). Higher conversions, at higher temperatures, were not possible because of Mg evaporation.

We prepared liquid alloys of active metals in low-melting-temperature metal “solvents” (Sn, Pb, Bi, In, and Ga) using known equilibrium phase behavior to produce catalysts that melt at <1000°C, and examined the catalytic properties of such melts. We used density function theory to explore physical properties of atoms and clusters of atoms introduced into melts as they relate to the catalytic activity of the melt. The melts are used in molten-metal bubble columns, where carbon continuously floats to the surface where it can be removed (Fig. 1).

A differential reactor (fig. S1A (21)) was used to compare the specific activities for CH4 pyrolysis for 21 metals and alloys (Table 1). Four trends are notable. First, low-melting-temperature metal “solvents” had some activity, in the order In < Bi < Sn < Ga < Pd. Second, the addition of an active component increased the reaction rate, and the magnitude of this increase depends on the solvent metal used. For example, the activity of melts containing 17 mol% of Ni increased as the solvent changed, the order being In < Sn < Ga < Pd < Bi. Third, the activity increased with the amount of the active metal; for example, 73 mol% of Ni in In was more active than 17 mol% of Ni in In. Fourth, Ni was always more active than Pt, for the same solvent, whereas solid Pt and solid Ni have approximately the same activity (18). Of the compositions that we tested, 27 mol% of Ni dissolved in molten Bi (Ni0.27Bi0.73) was the most active catalyst that we found, and further experimental work focused on this alloy.

An effective activation energy EE of 208 kJ/mol was determined for the Ni0.27Bi0.73 melt from the data in the Arrhenius plot shown in Fig. 2A obtained in a 15-cm bubble column (Fig. 2B). This value is lower than the activation energy for CH4 pyrolysis in Bi liquid or for the uncatalyzed gas-phase reaction, but it is higher than that for carbon or solid Ni catalysts (see Fig. 2B). This difference indicates that Ni dissolved in Bi is different from Ni solid, and that Ni0.27Bi0.73 is different from Bi solid, or a physical mixture of Ni and Bi.

We observed 95% CH4 conversion in a 1.1-m bubble column containing molten Ni0.27Bi0.73 (Fig. 3A) at 1065°C. Under these reaction conditions, the equilibrium conversion is 98%. When the temperature was reduced to 1040°C, the CH4 conversion decreased to 86%. The effect of residence time was measured by adjusting the depth at which gas was introduced in the 1.1-m bubble column (see fig. SIC). The temperature in the top 5 cm of the bubble column was maintained...
cooler by ~100°C, to minimize reactions in the gas headspace above the melt. Procedures and concerns related to the safe operation of molten-metal bubble columns are addressed in the supplementary materials.

Kinetic data obtained in a differential bubble column reactor were used to model a large-scale reactor. The rate expression was determined by using the activation energy from the Arrhenius plot (Fig. 2A), and the first-order pressure dependence was determined in a separate experiment (Fig. 3B and C). The conversion as a function of the surface area was then calculated at 1040°C and plotted with the experimental data (Fig. 3A).

At 1065°C in the 11-m bubble rise column, only H₂ was observed in the product effluent; no by-products were detectable. In a separate experiment, propane was also observed to completely decompose to hydrogen and carbon at 1000°C in a 12-cm column. Higher pressures resulted in less selectivity to hydrogen (Fig. 3C) in a differential reactor; which may be due to gas-phase reactions occurring; however, at longer residence times, the lack of by-products suggests that any other products pyrolyze at least as rapidly as methane. The CH₄ data were used to make an estimate of ~600 m³ for the reactor required for a 200 kilotons per annum H₂ plant, operating at 10 atm, with 95% CH₄ conversion at 1065°C, assuming 25% gas-phase holdup, continuous carbon removal, and approximately spherical, 1-cm-diameter, bubbles (see supplementary information).

The stability of Ni₀.₂₇Bi₀.₇₃ as a catalyst for CH₄ pyrolysis was determined by measuring pyrolysis activity over time. The activity of a bubble column of molten Ni₀.₂₇Bi₀.₇₃ did not change over 170 hours (fig. S2). Over this time period, carbon dissolved into the melt and approached a steady state with the rate of precipitation out of the melt. A solid nickel catalyst deactivated in 1 hour (fig. S3), likely forming a carbon-covered surface.

The carbon produced by CH₄ pyrolysis in a Ni₀.₂₇Bi₀.₃₂ bubble column accumulated as a fine powder at the top surface of the melt (Fig. 1A and B). Raman spectroscopy indicated that most of the carbon was graphite [0.594 I(D)/I(G), Fig. 1C]. A sharp peak at 284.5 eV in x-ray photoelectron spectroscopy (fig. S4) also suggested that most of the carbon was graphitic. Energy-dispersive x-ray spectroscopy showed that the powder was mostly carbon (92% of atoms) with small amount of Bi and Ni (total <4% of atoms) (fig. S6). The metal was deposited by evaporation from the liquid and deposition on the floating carbon layer (fig. S7). If the carbon layer was submerged in the melt, the Ni and Bi dissolved and clean carbon floated on the surface, where it could be removed (fig. S8). Carbon also deposited slowly on the walls of the reactor via precipitation from the saturated melt; carbon was observed on walls that were never in contact with the CH₄ bubbles (fig. S5). The rate of deposition on the reactor walls depended initially on the reactor material. However, once carbon formed, the carbon-on-carbon deposition decreased with time.

X-ray fluorescence measurements of cooled Ni₀.₂₇Bi₀.₇₃ alloy, after 170 hours of methane pyrolysis, showed that 1.5 mol % of carbon has dissolved in the melt. Based on an assumed saturation of 1.5 atom % carbon, the time required to reach saturation in a bubble column is 5 hours; however,

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Table 1. Comparison of activity for methane pyrolysis at 1000°C when CH₄ is flowed over 38.5 mm² of molten metal as described in fig. S1a.

<table>
<thead>
<tr>
<th>Liquid catalyst</th>
<th>Rate of hydrogen production (mol H₂ produced × cm⁻² s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>8.2 × 10⁻¹²</td>
</tr>
<tr>
<td>Bi</td>
<td>8.2 × 10⁻¹²</td>
</tr>
<tr>
<td>Sn</td>
<td>8.5 × 10⁻¹⁵</td>
</tr>
<tr>
<td>Ga</td>
<td>3.2 × 10⁻⁹</td>
</tr>
<tr>
<td>Pb</td>
<td>3.3 × 10⁻⁹</td>
</tr>
<tr>
<td>Ag</td>
<td>4.3 × 10⁻⁹</td>
</tr>
<tr>
<td>Pb vapor</td>
<td>2.1 × 10⁻⁹</td>
</tr>
<tr>
<td>17% Cu-Sn*</td>
<td>3.1 × 10⁻⁹</td>
</tr>
<tr>
<td>17% Pt-Sn</td>
<td>1.6 × 10⁻⁹</td>
</tr>
<tr>
<td>17% Pt-Bi</td>
<td>4.2 × 10⁻⁹</td>
</tr>
<tr>
<td>62% Pt-Bi*</td>
<td>6.5 × 10⁻⁹</td>
</tr>
<tr>
<td>17% Ni-In</td>
<td>4.7 × 10⁻⁹</td>
</tr>
<tr>
<td>17% Ni-Sn</td>
<td>5.6 × 10⁻⁹</td>
</tr>
<tr>
<td>73% Ni-In*</td>
<td>6.4 × 10⁻⁹</td>
</tr>
<tr>
<td>17% Ni-Ga</td>
<td>7.9 × 10⁻⁹</td>
</tr>
<tr>
<td>17% Ni-Pb</td>
<td>8.3 × 10⁻⁹</td>
</tr>
<tr>
<td>17% Ni-Bi</td>
<td>9.0 × 10⁻⁹</td>
</tr>
<tr>
<td>27% Ni-Au*</td>
<td>1.2 × 10⁻⁸</td>
</tr>
<tr>
<td>27% Ni-Bi*</td>
<td>1.7 × 10⁻⁸</td>
</tr>
<tr>
<td>27% Ni-Bi* (replicate)*</td>
<td>1.7 × 10⁻⁸</td>
</tr>
</tbody>
</table>

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Fig. 1. Hydrogen production with a Ni-Bi molten catalyst. (A) Reactor for CH₄ conversion to H₂ and carbon in a molten-metal bubble column with continuous carbon removal. (B) Scanning electron microscopy image of the carbon produced. (C) Raman spectrum of surface carbon. The dashed line labeled “D” is at 1350 cm⁻¹, and the dashed line labeled “G” is at 1582 cm⁻¹. (D) Ab initio molecular dynamics simulation showing an orbital (green) of a Pt atom dissolved in molten Bi (gray) alloy.
operation at 1050°C, most of the carbon formed accumulated above the surfaces of the melt—on both sides of the tube. This observation is consistent with carbon formation from CH₄ pyrolysis at the surfaces of the CH₄-containing bubbles, saturating the metal alloy liquid with carbon such that precipitation occurs at all heterogeneous interfaces (including the surfaces of both CH₄ and Ar bubbles).

Constant-temperature ab initio molecular dynamics was used to investigate the electronic properties of the molten alloys. Initial calculations were performed for a melt containing one active metal atom in 82 atoms of inert material. In all cases, the active metal atom becomes negatively charged. Figure 1D shows that, for Pt in Sn, the negative charge occupies an orbital whose shape is similar to that of a d-orbital. Because the system is liquid, the shape of the orbital and its energy fluctuate (movie S1). The Bader charges of the active atoms in several melts are shown in table S1. Figure 4A shows that the calculated charge on the active atom is correlated with the catalytic activity measured experimentally for CH₄ pyrolysis: The lesser the negative charge, the higher the activity. The electron charge on the active metal comes from the neighboring Sn atoms, each having a slightly more positive Bader charge than when they are alone in the melt (Fig. 4, B and C). The average charge per atom is –0.91 electron, and no Pt-Pt bonds are formed. In retrospect, this finding is not surprising: Pt is an electrophilic metal, and barium and cesium platinides are known compounds in which Pt is a negative ion (22, 23). The addition of Bi to Pt-group metals has also been observed to weaken the binding strength of aromatic hydrocarbons to the surface (24).

In simulations, we followed the evolution of Pt₂ (Fig. 4D and movie S2) and Pt₈ clusters (fig. S10) placed in molten Sn at 627°C. Both clusters dissociate in a few picoseconds to form isolated Pt⁻ ions. This result is surprising for several reasons. Hybrid density functional calculations using the HSE06 functional show that Pt₂, Pt₂⁻, and even Pt₄⁻ are stable in the gas phase and have a binding energy 0.5 eV. None would dissociate spontaneously in the gas. Further, dissociation of a molecule in a liquid is normally associated with the solvent out of the way. Thus, Pt-cluster dissociation should be an activated process occurring on a time scale longer than a nanosecond. The only explanation for the rapidity of the dissociation is that electrons from Sn move rapidly to the active metal atom in 82 atoms of inert material. The electron charge on the active atom is correlated with the catalytic activity measured experimentally for CH₄ pyrolysis: The lesser the negative charge, the higher the activity. The electron charge on the active metal comes from the neighboring Sn atoms, each having a slightly more positive Bader charge than when they are alone in the melt (Fig. 4, B and C). The average charge per atom is –0.91 electron, and no Pt-Pt bonds are formed. In retrospect, this finding is not surprising: Pt is an electrophilic metal, and barium and cesium platinides are known compounds in which Pt is a negative ion (22, 23). The addition of Bi to Pt-group metals has also been observed to weaken the binding strength of aromatic hydrocarbons to the surface (24).
**Fig. 4. Theoretical results.** (A) Activity for pyrolysis at 1000°C plotted versus calculated Bader charge on the active element. In all experiments, 17 mol % of platinum or nickel was used. The calculations used 1.2 mol % Pt or Ni, at 627°C. (B) The time evolution of the Bader charge on a Pt atom dissolved in molten Sn, and the sum of Bader charges on nearest-neighboring Sn atoms during an ab initio molecular dynamics (AIMD) run. (C) Projected density of states of a Pt atom, of the Sn all atoms, and of nearest-neighboring Sn atoms. The graph also shows, in green, the shape of one Pt orbital. The boundaries of the simulation box are shown in blue. (D) The graph shows the distance between Pt atoms in a Pt$_2$ cluster in molten Sn during an AIMD run. The two pictures show the charges on the Pt atoms of a Pt$_2$ cluster at two different times.

**REFERENCES AND NOTES**

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Hydrogen from methane in molten metal

The hydrogen used in making ammonia and other industrial reactions is produced mainly through steam reforming of methane over nickel catalysts. This high-temperature process also releases carbon dioxide, a greenhouse gas. Upham et al. used nickel dissolved in molten bismuth to pyrolyze methane to release hydrogen and form carbon, which floats to the surface of the melt, where it can be removed. Carbon formation on steam-reforming catalysts is usually a deactivating side reaction, but in the new process, the carbon can be stored or incorporated into composite materials. 

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