**CATALYSIS**

**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).

Metals that are active 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 < Pb. 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 < Pb < 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 \( E_a \) 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. S1C). The temperature in the top 5 cm of the bubble column was maintained.
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. The same reactor volume was used in all cases, including for Pb vapor. All compositions are molar percent. An asterisk (*) indicates that alloy is at the solubility limit of the dissolved active metal at 950°C.

<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>In</td>
<td>8.2 × 10⁻¹</td>
</tr>
<tr>
<td>Bi</td>
<td>8.2 × 10⁻¹</td>
</tr>
<tr>
<td>Sn</td>
<td>8.5 × 10⁻¹</td>
</tr>
<tr>
<td>Ga</td>
<td>3.2 × 10⁻¹</td>
</tr>
<tr>
<td>Pb</td>
<td>3.3 × 10⁻¹</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 × 10⁻⁸</td>
</tr>
<tr>
<td>17% Pt-Sn</td>
<td>1.6 × 10⁻⁸</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 × 10⁻⁸</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>
CH₄ conversion was constant through the time of saturation (figs. S2 and S3), indicating that the catalytic activity was not affected by the concentration of carbon on the melt. Constant conversion would be consistent with the cleavage of the C–H bond being the rate-limiting step.

To explore the behavior of carbon in the melt, we filled a U-shaped reactor (fig. S1B) with Ni₀.₂₇Bi₀.₇₃ and introduced CH₄ bubbles in one arm of the U tube and Ar bubbles in the other. The gas streams were isolated from each other using the HSE06 functional show that Pt₂,Pt₂ – 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 Pt₄ clusters (fig. S10) placed in molten Sn at 627°C. Both clusters dissociate in a few picoseconds to form isolated Pt₁ ions. This result is surprising for several reasons. Hybrid density functional calculations using the HSE06 functional show that Pt₂, Pt₄⁺, 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 hindered by a “cage effect”: The dissociation fragments must have enough energy to push 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 fill antibonding orbitals in Pt, which weakens the Pt-Pt bonds and charges the Pt atoms negatively, causing a “Coulomb explosion.”

On the basis of ab initio molecular dynamics calculations, the nickel within the melt is atomic with a partial negative charge. The atomic charge of the melt on each side 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).

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On the basis of ab initio molecular dynamics calculations, the nickel within the melt is atomic with a partial negative charge. The atomic charge in different alloys correlates to catalytic activity for CH₄ pyrolysis. If we can assume that the active site for methane activation is the dissolved active metal, the melts discussed here are “single atom” catalysts.
**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 atoms neighboring the Pt atom, and of all 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 Pt₂ cluster in molten Sn during an AIMD run. The two pictures show the charges on the Pt atoms of a Pt₂ cluster at two different times.

REFERENCES AND NOTES


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www.sciencemag.org/content/358/6365/917/suppl/DC1

Materials and Methods

Supplementary Text

Figs. S1 to S12, movies S1 and S2, and details of experiments and calculations are available as supplementary materials.


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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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