Selective oxidation of methane to methanol with molecular oxygen using aqueous Au-Pd colloids at low temperature

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In industry, CH4 is used as a feedstock by first indirectly converting it to methanol (CH3OH) via the production of synthesis gas (CO + H2) at high temperatures and pressures, an expensive and energy intensive process. The direct oxidation of CH4 to CH3OH, which is challenging as over oxidation must be avoided, has been the subject of intensive study for many decades. CH4 oxidation using supported AuPd nanoparticles (NPs) under mild aqueous conditions using H2O2 as oxidant at 50°C has been reported (1). The reaction proceeded through a radical mechanism. However, the relatively high cost of H2O2 for even stoichiometric oxidation of CH4 makes it difficult to be economically viable. Incorporation of O2 into the primary oxidation products would represent substantial progress toward a feasible CH4 to CH3OH process. Thus, this reaction has been performed here under mild conditions using colloidal AuPd NPs in the presence of both H2O2 and O2, with the selectivity to primary products reaching >90% with minimal CO2 produced.

Bimetallic Au-Pd nanoparticles were formed by standard colloidal method by using polyvinylpyrrolidone (PVP) as the stabilizing agent and NaBH4 as the reducing agent. In the methane oxidation experiments we first used H2O2 as an oxidant at 50°C and we found that when the unsupported AuPd colloid was used as a catalyst the level of decomposition of H2O2 was much lower than when the AuPd colloid was supported on TiO2. In view of this the products observed with the unsupported catalyst were substantial (Fig. 1). However, when molecular oxygen was added to the reaction gases the amount of products observed increased markedly. Use of isotopically labelled 18O2 showed that up to 70% of the methanol contained oxygen from the molecular oxygen. In this reaction the H2O2 acts as an initiator but more oxygenated products were formed than H2O2 consumed, suggesting that the controlled breakdown of H2O2 activates methane which subsequently incorporates molecular oxygen through a radical process as shown in scheme.

**Figure 1.** Conversion of methane using unsupported AuPd colloid with oxygen. And proposed reaction mechanism. Test conditions: 0.5 h, 50°C, H2O2 amount: 1000 μmol, 1500 rpm, P(CH4) = 30 bar, P(O2) = 5 bar, 6.6 μmol metal per reaction

Fresh and used catalyst were characterized using electron microscopy and XPS. Particles were found to be alloyed with icosahedral structure with no size dependent composition variation and no single atoms or clusters were detected in fresh and used catalyst. The catalyst was found to be stable for longer reactions and reuse. The reaction proceeded with same efficiency at room temperature and the activation energy for the reaction was found to be 39 kJ/mol. Using unsupported AuPd colloids with H2O2 as an initiator together with O2, methane can be oxidized to methanol where the oxygen in the methanol is derived from O2.

**References**


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