Selective, catalytic processes to convert methane into higher hydrocarbons or oxygenates are of great industrial importance because they would enable the conversion of abundant, remote natural gas reserves to useful petrochemicals and fuels. \(^1\) One of the most studied conversion processes is oxidative coupling, the formation of ethane, ethylene, and higher hydrocarbons (abbreviated as \(C_{2+}\)) from the reaction of methane with oxygen. \(^2\)–\(^{14}\) Alkali-promoted metal oxides are relatively selective catalysts for this conversion. A wide variety of oxides have been studied, including: basic oxides such as MgO, \(^7\) rare-earth oxides such as Sm\(_2\)O\(_3\), \(^9\)\(^{10}\) and transition metal oxides such as Mn oxides \(^2\)\(^{,3,11}\) and NiO. \(^12\)\(^{14}\) With all of these materials, deep oxidation of methane to CO\(_2\) and H\(_2\)O competes with oxidative coupling. The highest yields (methane conversion times selectivity to \(C_{2+}\)) achieved to date are below 30\%. It is estimated that methane conversions in excess of 60\% and \(C_{2+}\) selectivities greater than 80\% are necessary for an economic conversion process. \(^1\) One of the challenges in achieving better yields is to design or discover catalytic materials that have a high intrinsic selectivity for oxidative coupling, and a minimum activity for deep oxidation.
In order to design selective catalysts, it is necessary to understand the influence of catalyst structure on reaction pathway and reaction rate. Some of the fundamental aspects of oxidative coupling that need to be understood include: what is the nature of the surface site responsible for methane activation, how is this site produced by reaction of the material with gas-phase oxygen, what is the nature of the surface site for deep oxidation to produce CO₂, how is it produced, is it the same as the site for methane activation, how do these sites depend on catalyst structure? It is important to determine whether activation and oxidation occur on the same site. If they do, production of CO₂ is inescapable.

The variety and complexity of the structures of most catalysts make it difficult to determine the nature of the active sites and whether activation and deep oxidation occur at the same site. For alkali-doped MgO and CaO, Lunsford has shown a correlation between methane activation and the existence of O⁻ species, identified by ESR.7b,7d Under oxidative coupling conditions, this O⁻ site is produced to a significant extent only in the presence of gas-phase oxygen. No significant conversion occurs in the absence of gas-phase oxygen. Similar behavior is observed for other non reducible oxides. In contrast, a number of reducible metal oxides can for a time selectively convert methane to C₂⁺ hydrocarbons in the absence of gas-phase oxygen. This suggests that for these materials a lattice oxygen site at the surface is responsible for selective activation. (Lattice oxygen is subsequently replenished by reacting the reduced material with gas-phase oxygen.) Examples include supported and promoted manganese oxides, with C₂⁺ selectivities in excess of 80% at low methane conversion3,11 and LiNiO₂, for which C₂⁺ selectivities near 100% have been reported.12d The nature of the site responsible for deep oxidation is less well understood. It is possible that the active sites for reducible materials are different from those for non-reducible materials. In both cases however, it is clear that the reaction of dioxygen with these materials is a key step in producing active sites.

Of the wide range of catalyst materials studied, lithium-substituted nickel oxides are unusual in that they form sufficiently simple structures that a relatively complete characterization is possible.15-17 In addition, the origin of the selectivity imparted in nickel oxide by lithium substitution is particularly interesting. NiO readily reacts with CH₄ at temperatures above 873 K, but only CO₂ and H₂O are formed.12,22 This is quite different than the case of MgO, which has little or no reactivity toward methane without the addition of alkali metal. Somehow, substitution of Li cations for Ni cations converts nickel oxide from a material which is highly active and selective for complete combustion to one that can be highly selective for hydrocarbon production.

Recently, we have shown that the selectivity of lithium nickel oxides depends on the structure, especially on the long-range order of the cations.17 Here we report results on studies of the kinetics of reaction of gas-phase oxygen and of methane with an ordered structure that has high C₂⁺ selectivity. The catalyst material used in this study has the composition Li₀.₄₄Ni₀.₅₆O, close to the theoretical limit for complete substitution, Li₀.₅Ni₀.₅O. We confirm for this composition that lattice oxygen can be highly selective for methane activation and production of C₂⁺ hydrocarbons. However, a proper accounting of CO₂ that remains on the catalyst as a carbonate, reveals that the selectivity is only 75%, in contrast to an earlier study in which a nearly 100% C₂⁺ selectivity was reported.12d In addition, we identify a surface oxygen state in equilibrium with gas-phase oxygen that