



Calcined eggshell as an inexpensive catalyst for partial oxidation of methane



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ABSTRACT

Calcined eggshell was evaluated as an inexpensive catalyst for selective oxidation of methane. Experiments were conducted using a packed bed reactor to determine the effects of oxygen on methane ratio (1, 3 and 7), flow rate (0.4, 0.8 and 1.2 L/min), and temperature (650, 700, and 750 °C) on methane conversion and selectivity. Our results suggested that partial oxidation of methane on calcined eggshell yielded higher hydrocarbons (C₂–C₇) via oxidative coupling with an average fractional methane conversion of ~30%. Several factors including oxygen concentration, flow rate, and temperature were observed to influence fractional methane conversion and product selectivity. Catalyst characterization showed enhanced porosity and surface area upon calcination due to removal of organics and carbon dioxide. Surface deformation was observed in spent catalyst due to the physical impact of feed gas. Results from this research are expected to add value to eggshells and enhance agricultural waste management opportunities in areas where poultry industry is concentrated.

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1. Introduction

Alkanes such as methane are major components of natural gas and petroleum. In addition, methane is readily produced by anaerobic digestion of municipal, industrial, and agricultural waste [1]. Despite its availability, however, methane is not commonly converted directly into value-added products such as alcohols, aldehydes, and carboxylic acids because of its inertness [2]. High inertness requires large amounts of energy to break down the strong molecular bonds required to obtain high-value products. Abundant methane availability in remote areas along with its potential use as a raw material for fuels and chemicals synthesis has encouraged researchers to explore economical and efficient methods of handling methane for industrial and other commercial applications.

The difficulties associated with selective transformations of alkanes has led to the production of vital petrochemicals, especially oxygenates (alcohols, aldehydes, and carboxylic acids) from unsaturated hydrocarbons, such as, olefins. Olefins are produced from saturated hydrocarbons through energy intensive reactions via indirect conversion [2]. Thus it has become a prime focus of several researchers

to convert gaseous methane directly into value-added end products such as ethylene, methanol or aromatics.

The direct conversion of methane to useful end products has proven difficult for several reasons including high C–H bond energy of 425 kJ/mol, absence of any functional group, magnetic moment, and polar distribution in methane, which could have otherwise facilitated the conversion process under moderate reaction conditions [3]. Hence use of a catalyst has a crucial role in most processes for methane conversion. A wide variety of catalysts have been reported for the conversion of methane into various end products [3–5].

Oxidative coupling of methane (OCM) to form higher hydrocarbons such as ethylene, has gathered enormous attention for the past 3 decades because of the huge ethylene market [4–6]. The abstraction of hydrogen to activate methane forms the first step in OCM [4–6]. A large numbers of catalytic materials have been investigated for oxidative coupling of methane, which are divided into three major categories: alkali and alkaline earth metal compounds, compounds of lanthanide and actinide metals, and other metal compounds [6]. Pioneering work of Keller and Bhasin [5] concluded that low-melting metals of groups IIIA, IVA, VA and Mn of VIIB and Cd of IIB exhibit the highest activity for oxidative coupling of methane.

Though it has been suggested that pure alkali metal oxides are unsuitable catalysts because of the difficulty in their surface regeneration through dehydration, they have been investigated for several decades because of their ability to prevent overoxidation, a unique characteristic associated with the presence of non-labile oxide ions

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[7]. Alkaline metal oxides, particularly calcium oxide, have gained extensive attention for various catalytic properties in a broad spectrum of applications [8]. CaO as a catalyst is known to have several advantages such as high activity, mild working conditions, low catalyst cost, and long catalyst lifetime [9].

Eggshell, composed mainly of CaCO_3 , is one such renewable and inexpensive source of CaO, which can be easily obtained from CaCO_3 via calcination [10,11]. Hence, several recent studies have utilized eggshells as catalysts for transesterification reactions [11–13]. Eggshells have also been used as adsorbents in recovery of metals from aqueous solutions [10,14–16]. Favorable physical attribute associated with eggshell are low surface area and type II porosity (non-porous) characteristics. Several authors including Cullis [17], Tsai et al. [18], and Jimenez et al. [19] emphasized the importance of low surface area catalysts for promoting selective oxidation reactions. Because eggshell is known for low specific surface area, it may be able to enhance selectivity of desired products such as C_2 – C_6 hydrocarbons (C_2H_4 , C_3H_6 , C_6H_6 , etc.) and oxygenates (alcohols, aldehydes and

ketones). However, to our knowledge, eggshell has not been investigated as catalyst for partial oxidation of methane. We are especially interested in eggshell because of the large size of the poultry industry in Southeastern United States. The USA alone produces nearly a half million tons of eggshell annually [10,20]. Based on the surface chemistry and physical properties of the eggshell, we hypothesized that calcined eggshell will catalyze oxidation of methane. Hence, the goal of this research was to evaluate calcined eggshell as an inexpensive heterogeneous catalyst for selective oxidation of methane. The specific objectives were to (1) characterize the catalyst and (2) determine the effect of flow rate, methane:oxygen molar ratio, and temperature on selective oxidation of methane to value-added products.

2. Materials and methods

2.1. Catalyst preparation

Raw eggshell (2–4 mm) were thoroughly washed with deionized water and calcined for 4 h in a furnace (with air) maintained at 1000°C to remove carbon dioxide and organic material from eggshell matrix. Subsequently the calcined shell was stored in airtight containers until further use.

2.2. Characterization

The specific surface area and pore volume of the catalyst were determined using a Micrometrics Gemini VII 2390 analyzer using liquid nitrogen (-196°C) after degassing the catalyst samples at 150°C for 2 h.

The surfaces of the fresh and spent catalyst were analyzed using a variable pressure scanning electron microscope (VPSEM) (Hitachi S3200). Prior to analysis, the catalyst samples were coated (~ 35 nm) with gold (60%) and palladium (40%) to enhance the surface conductivity. An electron beam and a pressure of 20 keV and $\sim 10^{-6}$ Torr, respectively, were used to collect images of the surface.

Catalyst surface was also analyzed via a time-of-flight secondary ion mass spectroscope (TOF-SIMS) (ION TOF, Inc. Chestnut Ridge, NY, USA) equipped with a Bi_n^{m+} ($n = 1-5$; $m = 1, 2$) liquid metal ion gun and operated below 5.0×10^{-9} mbar. A $500 \mu\text{m} \times 500 \mu\text{m}$ area was selected to procure mass spectral images (256 by 256 pixels) using a Bi^+ primary ion beam. The secondary ions were extracted into a TOF mass spectrometer with post acceleration to improve detection sensitivity.

2.3. Catalyst testing

Ten grams of catalyst were loaded into a 304 stainless steel tubular reactor (2.5 cm dia) to a packing height of 15 cm (empty bed residence time = 0.06–0.18 min). Methane (99 %) and oxygen (99.5 %) were co-fed into the reactor that was heated to a predetermined temperature using a microprocessor controlled furnace (Iguana, Paragon Industries, TX, USA). Prior to each experiment, the catalyst was activated by heating the reactor to 650°C for 1 h.

Experiments were performed to study the effect of molar ratio of methane to oxygen set to 1, 3, and 7 using 10 g catalyst at 650°C . Further, flow rates of 0.4, 0.8, and 1.2 L/min (at a temperature of 650°C) and temperatures of 650, 700, 750°C (at a flow rate of 0.8 L/min) were also studied using a reactor packed with 10 g catalyst and operating at a molar ratio $\text{CH}_4:\text{O}_2$ of 3.0. Inlet and outlet gas samples were collected at 10 min and 15 min (in 1-L Tedlar bags) and analyzed using a gas chromatograph equipped with mass spectrometer (HP-5 MS) and thermal conductivity detector (Carbosieve SII).

The fractional conversion of methane was determined as:

$$\text{Conversion}(\%) = \left\{ \frac{(\text{Total flow rate} \times \text{mol.methane})_{\text{inlet}} - (\text{Total flow rate} \times \text{mol.methane})_{\text{outlet}}}{(\text{Total flow rate} \times \text{mol.methane})_{\text{inlet}}} \right\} \times 100$$

In addition, selectivity was calculated by accounting for the number of carbon atoms as:

$$\text{Selectivity}(\%) = \left\{ \frac{\alpha \times \text{moles of product formed}}{\beta \times \text{moles of methane consumed}} \right\} \times 100$$

Where α = Stoichiometric coefficient of reactant (methane) and β = Stoichiometric coefficient of product

3. Results and discussion

3.1. Catalyst characterization

As expected, TOF-SIMS analysis of calcined eggshell confirmed the presence of CaO phase in the form of CaO and $\text{Ca}(\text{OH})_2$ (Fig. 1). Calcium oxide may have reduced to corresponding hydroxide form because of exposure to moisture in the air [13]. High density of CaO

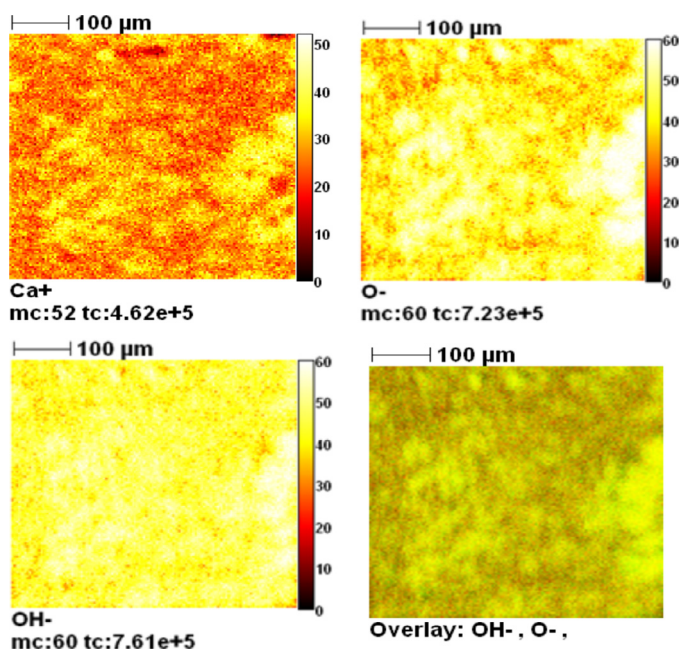


Fig. 1. TOF-SIMS analysis of calcined eggshell catalyst.

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