

Selective methanation of CO over supported noble metal catalysts: Effects of the nature of the metallic phase on catalytic performance

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ARTICLE INFO

Article history:

Received 19 February 2008

Received in revised form 28 March 2008

Accepted 28 March 2008

Available online 7 April 2008

Keywords:

CO methanation

CO₂ methanation

Selective methanation of CO

Noble metal catalyst

Ru

Rh

Pt

Pd

ABSTRACT

The catalytic performance of Al₂O₃-supported noble metal catalysts for the methanation of CO, CO₂ and their mixture has been investigated with respect to the nature of the dispersed metallic phase (Ru, Rh, Pt, Pd). Experiments have been conducted using feed compositions relevant to those of reformat gas streams, both in the absence and in the presence of water. It has been found that, for all experimental conditions investigated, Ru and Rh are significantly more active than Pt and Pd. Selectivity toward hydrogenation products depends strongly on the noble metal catalyst employed, as well as on whether solo- or co-methanation of CO/CO₂ is occurring. For hydrogenation of CO alone, selectivity toward CH₄ increases with increasing temperature at the expense of higher hydrocarbons. In presence of water in the feed, catalytic activity of Ru is not affected, while that of Rh is reduced. On the other hand, the performance of Pt and Pd is poor since they promote the undesired water-gas shift (WGS) reaction. In hydrogenation of CO₂ alone, selectivity toward higher hydrocarbons is negligible for all catalysts investigated but the reaction is accompanied by production of CO via the reverse WGS reaction. In all cases, addition of water in the feed results in decrease of catalytic activity. In combined hydrogenation of CO/CO₂ mixtures, conversion of CO₂ is completely suppressed until conversion of CO reaches its maximum value. Selectivity toward methane, which is typically higher than 70%, increases with increasing temperature and approaches 100% when CO₂ conversion is initiated. Addition of 30% water vapor in the feed does not affect CO hydrogenation over Ru and Rh catalysts but retards CO₂ hydrogenation, thereby expanding the temperature window of operation.

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1. Introduction

The methanation reaction has been widely used as a method of removal of carbon oxides from gas mixtures in hydrogen or ammonia plants, and for the purification of hydrogen streams in refineries and ethylene plants [1]. The selective methanation of CO may become attractive as a potentially effective means of reduction of CO content of hydrogen-rich reformat gases to extremely low levels, as required in fuel cell applications [2,3]. Fuel processors designed for use with polymer electrolyte membrane (PEM) fuel cells typically consist of a reformer, which converts the fuel into a hydrogen-rich gas stream, and a water-gas shift (WGS) unit, which reduces byproduct carbon monoxide to 0.5–1.0%, thus improving H₂ yield. An additional cleanup step is required to reduce CO levels to less than 50 ppm, as dictated by the poisoning limit of PEM fuel cell electrodes [4–7]. The preferential oxidation of CO (PROX) has been proposed for this purpose and studied by

many investigators [8–10]. However, this approach requires the addition of oxygen (air) in the hydrogen-rich gas stream, which may give rise to various problems related to reduced hydrogen yield, dilution, safety and restrictions in the operating parameters. Thus, CO methanation (Eq. (1)) is investigated as an alternative purification step [2,3,8,11]:



This approach has the advantage that no oxidizing and/or inert gases are mixed with the reformat stream and that the methane produced, which is inert to the PEM fuel cell, can be utilized in the afterburner. However, in order for this method to be effective, a suitable catalyst must be applied to promote selectively the CO methanation reaction at the expense of CO₂ methanation, which consumes significant quantities of hydrogen:



Thus, selectivity of the catalyst in promoting CO methanation versus CO₂ methanation ($S_{\text{CO}/\text{CO}_2}$) is of paramount importance. This parameter can be defined based on hydrogen consumption as

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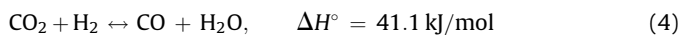
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follows:

$$S_{\text{CO}/\text{CO}_2} = \frac{3r_{\text{CO}}}{3r_{\text{CO}} + 4r_{\text{CO}_2}} \quad (3)$$

It is of interest to note that under methanation reaction conditions of CO/CO₂ mixtures, $S_{\text{CO}/\text{CO}_2}$ is relatively high at low temperatures because conversion of carbon dioxide is inhibited until the concentration of carbon monoxide has been reduced to about 200–300 ppm [1,3,12].

The reverse water-gas shift (RWGS) reaction may act as an obstacle in the complete, selective methanation of CO:



Consequently, it is important to develop selective CO methanation catalysts characterized by high activity at sufficiently low temperatures, able to retard both the CO₂ methanation and the RWGS reactions.

The methanation of CO, in the absence of CO₂, has been investigated over a variety of supported metal catalysts, including Ni [13–16], Ru [2,13,17], Pt [17] and Ni-Ru [18]. Nickel catalysts were found to exhibit high activity for the reaction [1], which is also affected by the nature of the support. Fujita et al. [13] reported that the methanation of CO proceeds more rapidly with the use of Ni/Al₂O₃ catalysts, compared to Ni/SiO₂ and Ru/SiO₂, whereas Görke et al. [2] reported that Ru/SiO₂ catalyst exhibits higher CO conversion and selectivity, compared to Ru/Al₂O₃. Concerning CO₂ methanation, a number of studies have been published dealing with the performance of supported Ru [18–21], Pt [19], Pd [19,22], Ir [19], Rh [19,23,24], Ni [25,26], Co [21] and Fe [21] catalysts. It is generally accepted that the hydrogenation of CO₂ proceeds through the formation and hydrogenation of CO, with higher selectivity toward methane, compared to CO hydrogenation reaction [13,22]. For example, Inui et al. [18] reported that the reaction rate for CO₂ methanation is higher than that of CO over Ni-La₂O₃ and Ni-La₂O₃-Ru catalysts. However, under conditions of simultaneous CO and CO₂ methanation, the coexistence of CO and CO₂ in the gas mixture, results in complete retardation of CO₂ methanation until CO has been totally converted to methane.

A detailed investigation is being carried out in this laboratory in an attempt to identify the key parameters which determine the performance of supported noble metal catalysts for the title reaction and to explore reaction kinetics and mechanism. The objective is to develop active, selective and stable methanation catalysts, able to efficiently and selectively remove CO from reformate gases to levels lower than those dictated by the poisoning limits of fuel cells. In the present study, the effects of the nature of the dispersed metallic phase on the catalytic performance of Al₂O₃-supported noble metal catalysts is investigated for the methanation of CO, CO₂ and their mixtures.

2. Experimental

2.1. Catalyst preparation and characterization

Supported noble metal catalysts were prepared by impregnation of γ -Al₂O₃ (Alfa Products) powder with an aqueous solution of the corresponding metal precursor salt (Rh(NO₃)₃, Ru(NO)(NO₃)₃, (NH₃)₂Pt(NO₂)₂, (NH₃)₂Pd(NO₂)₂) (Alfa Products). The resulting slurry was heated slowly to 70 °C under continuous stirring and maintained at that temperature until nearly all the water evaporated. The solid residue was dried at 110 °C for 24 h and then reduced at 300 °C (400 °C for Ru catalysts) in H₂ flow for 2 h. The metal loading of the catalysts thus prepared was 0.5 wt.%.

Dispersed noble metal catalysts were characterized with respect to their specific surface area employing nitrogen physisorption at the temperature of liquid nitrogen (B.E.T. method). Metal dispersion and mean crystallite size were estimated by selective chemisorption of H₂ at 25 °C for Rh and Pt, 60 °C for Pd and 100 °C for Ru samples. Details of the equipment and procedures used for catalyst preparation and characterization can be found elsewhere [27].

2.2. Catalytic performance tests and kinetic measurements

Catalytic performance tests have been carried out using an apparatus, which consists of a flow measuring and control system, the reactor and an on-line analysis system. The flow system is equipped with a set of mass-flow controllers (MKS) to measure and control the flow of the gases (CO, CO₂, H₂, He) and a set of valves, which allows introduction of the gas mixture to the reactor or to a by-pass loop, through stainless steel tubing. When desired, water is introduced to the system with the use of an HPLC pump (Marathon Scientific Systems), vaporized in a stainless steel evaporator maintained at 170 °C and mixed with the gas stream coming from the mass-flow controllers. The resulting gas mixture is then fed to the reactor through stainless steel tubing maintained at 150 °C by means of heating tapes. The reactor consists of a 40-cm long quartz tube (6 mm O.D.) with an expanded 1-cm long section in the middle (8 mm I.D.), in which the catalyst sample is placed. Reaction temperature is measured in the middle of the catalyst bed by means of a K-type thermocouple placed within a quartz capillary well, which runs through the cell. The reactor is placed in an electric furnace, the temperature of which is controlled using a second K-type thermocouple placed between the reactor and the walls of the furnace. A pressure indicator is used to measure the pressure drop in the catalyst bed.

The analysis system consists of a gas chromatograph (Shimadzu) interfaced to an integrator. The chromatograph is equipped with two packed columns (Porapak-Q, Carboxen) and two detectors (TCD, FID) and operates with He as the carrier gas. The injection of the gas mixture to the desired column is achieved by means of two six-port valves. The response factors of the detectors were measured with the use of gas streams of known composition (Scott specialty gas mixtures). Reaction gases (He, 15% CO/He, CO₂, H₂) are supplied from high-pressure gas cylinders (Messer Griesheim GMBH) and are of ultra-high purity.

In a typical experiment, 150 mg of fresh catalyst (0.18 mm < d < 0.25 mm) is placed in the reactor and reduced *in situ* at 300 °C for 1 h under hydrogen flow of 60 cc/min. The temperature is then lowered to 180 °C under He flow and the flow is switched to the reaction mixture, which consists of either 1% CO + 50% H₂ (CO hydrogenation) or 15% CO₂ + 50% H₂ (CO₂ hydrogenation) or 1% CO + 15% CO₂ + 50% H₂ (combined methanation of CO/CO₂), in He. When water was added in the feed, part of the balance gas (He) was replaced by water vapor (30% H₂O). The catalyst is conditioned at 180 °C for 1 h and then the conversions of reactants and products are determined using the analysis system described above. Selectivities to hydrogenation products were calculated using the following expression:

$$S_i = \frac{C_{i,\text{out}}}{\sum_i C_{i,\text{out}}} \quad (5)$$

Similar measurements are obtained following a stepwise increase of temperature up to 470 °C. In all cases, data points are averages of at least three measurements. All experiments were performed at near atmospheric pressure.

Measurements of intrinsic reaction rates were obtained in separate experiments where the conversions of reactants were

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