

# Effects of operating conditions and feedstock concentration on hydrogen production for methanol aqueous-phase reforming (P-14H)

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## 1. Introduction

Energy decarbonization is critically needed to mitigate climate change and contribute to economic growth and technological progress. H<sub>2</sub> has emerged as a potential energy vector for a clean energy transition [1]. However, an inexpensive infrastructure for storing and transporting hydrogen is yet to emerge [2]. Therefore, *in-situ* H<sub>2</sub> production from renewable fuels (e.g. alcohols) is a promising pathway to overcome the aforementioned challenges. Among other alcohols, methanol can be considered the most advantageous H<sub>2</sub> carrier with the highest H/C ratio besides being liquid under room conditions [3]. Apart from the conventional methanol steam-reforming (MSR) [4], methanol aqueous phase reforming (APR) is an emerging competitive pathway for H<sub>2</sub> production [5]. Methanol APR provides multiple advantages, namely elimination of the feed methanol aqueous solution evaporation and eliminates the carbon monoxide evolution. APR can produce H<sub>2</sub> and CO<sub>2</sub> at temperatures in the range of 200 °C - 250 °C and 1.5 MPa - 5.0 MPa [6].

Reforming and WGS reactions are kinetically favored by higher temperatures. Additionally, pressure plays a vital role in APR performance since APR is a multi-phase system with reaction kinetics often controlled by the diffusion of products through an aqueous phase. Therefore, it becomes necessary to evaluate the effects of operating conditions on methanol APR for optimal performance.

The purpose of this study is to explore methanol APR kinetic characteristics to propel much-needed research on novel catalysts and reactor design. In this work, we report the performance of a Pt/Al<sub>2</sub>O<sub>3</sub> catalyst under various operating temperatures, operating pressures, residence times, and feedstock concentrations in methanol APR.

## 2. Experimental

An in-house designed set-up was used to evaluate the performance of APR catalysts under different operating conditions. A 700 mg of commercial Pt/Al<sub>2</sub>O<sub>3</sub> (5 wt. % Pt) catalyst supplied by Sigma-Aldrich was placed in the mid-section of a fixed-bed reactor mixed with equal mass amounts of glass beads. The reactor was placed vertically in a temperature-controlled oven. The catalyst was reduced *in-situ* at 300 °C for 2 h in a flowing H<sub>2</sub>/N<sub>2</sub> (1:1) atmosphere. Afterward, the

reactor was purged with N<sub>2</sub> gas (30 mL·min<sup>-1</sup>) for 30 min to remove the adsorbed H<sub>2</sub>. Aqueous methanol solutions, with concentrations of 5 wt. % and 55 wt. % of methanol was fed to the reactor in an upward direction using an HPLC pump at a flow rate corresponding to a weight hourly space velocity (WHSV) between 0.1 h<sup>-1</sup> and 21.2 h<sup>-1</sup>. All these experiments were performed with N<sub>2</sub> co-feeding of 30 mL·min<sup>-1</sup>. The outlet stream was cooled down in a condenser at ca. 0 °C to separate liquid-phase components and gaseous products. The formed gaseous products were measured with online gas chromatography. A back pressure regulator was used to regulate the operating pressure of the reforming reaction. The catalytic performance of the methanol APR under various operating conditions was evaluated in terms of H<sub>2</sub> production rate (PR) (μmol·min<sup>-1</sup>·g<sub>catalyst</sub><sup>-1</sup>) as shown in Eq. (1); herein, *n* denotes the number of moles, and *m*<sub>catalyst</sub> is the mass of catalyst in grams.

$$\text{H}_2 \text{ production rate (PR)} (\mu\text{mol}\cdot\text{min}^{-1}\cdot\text{g}_{\text{catalyst}}^{-1}) = n(\text{H}_2) / (60 \times m_{\text{catalyst}}) \quad (1)$$

## 3. Results & Discussion

### 3.1 Effect of temperature

Fig.1 shows the H<sub>2</sub> production rate as a function of WHSV at 190 °C, 210 °C, and 230 °C, and 3.2 MPa for methanol feed concentration of 5 wt. %; and 6.0 MPa for methanol feed concentration of 55 wt. %. These conditions warranty liquid phase reaction for methanol and water.

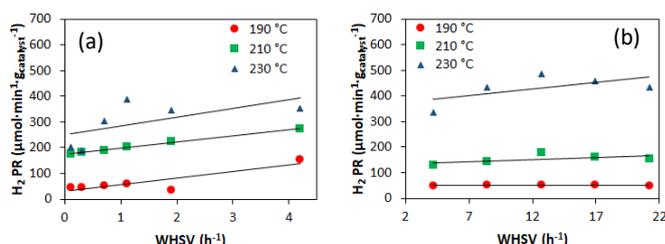


Fig. 1. H<sub>2</sub> production rate (PR) vs residence time in APR with 5 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> at operating temperatures of 190 °C, 210 °C, and 230 °C. (a) 5 wt. % methanol aqueous solution and 3.2 MPa of operating pressure; (b) 55 wt. % methanol aqueous solution 6.0 MPa.

Fig. 1 shows an increase in H<sub>2</sub> production rate as a function of the temperature and WHSV. However, the H<sub>2</sub> production

rate did not increase significantly when using high methanol concentration (55 wt. % of methanol). At higher methanol concentration, the contact time between reactants and catalyst decreases, which adversely affects the H<sub>2</sub> production rate [7]. For lower operating temperatures, the reforming reactions are inhibited and catalyst deactivation due to carbon deposition becomes possible [8].

### 3.2 Effect of pressure

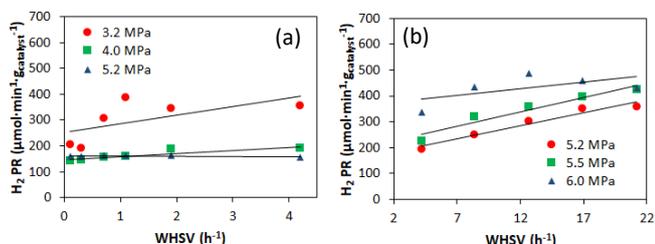


Fig. 2. H<sub>2</sub> production rate (PR) vs residence time in APR with 5 wt. % Pt/Al<sub>2</sub>O<sub>3</sub> at operating temperatures of 230 °C. (a) 5 wt. % methanol aqueous solution and operating pressure of 3.2 MPa, 4.0 MPa, and 5.2 MPa; (b) 55 wt. % methanol aqueous solution and operating pressure of 5.2 MPa, 5.5 MPa, and 6.0 MPa

Fig.2 shows the effect of the operating pressure on the H<sub>2</sub> production rate at 230 °C. For 5 wt. % methanol feed concentration, at 4.0 MPa and 5.2 MPa of operating pressure, the catalyst activity is almost constant with WHSV. This was assigned to the high partial pressures of the products and unavailability of active sites (caused by high H<sub>2</sub> concentration on the catalyst surface) [6,9]. The catalyst is more sensitive to changes in the pressure near the bubble point pressure of the aqueous feed, as the H<sub>2</sub> production stays nearly constant beyond 4.0 MPa, even for high WHSV. This indicates that APR may suffer from mass transfer limitations as operating pressure is increased. Additionally, N<sub>2</sub> has a critical pressure of 3.4 MPa. Therefore, it loses its function as a sweep gas in operating pressures beyond 3.4 MPa.

For 55 wt. % methanol feed concentration, H<sub>2</sub> production rate increase as the operating pressure is increased. The reason for this could be decreased mass transfer limitation, due to the formation of smaller gas bubbles with increasing pressure. H<sub>2</sub> production also increased with WHSV. As the feed flow rate increases, more gaseous products are dragged out of the reactor, which eventually accelerates the H<sub>2</sub> production rate.

## 4. Conclusions

Kinetic characterizations were performed for methanol APR over Pt/Al<sub>2</sub>O<sub>3</sub> catalyst using two different feedstock concentrations at various temperatures, pressures, and residence times. H<sub>2</sub> production increased with the temperature and decreased with the operating pressure for methanol feed concentration of 5 wt. %. However, the effects of pressures were less pronounced for feed concentration of 55 wt. %.

Using various dopant and novel supports for catalyst development can yield a higher H<sub>2</sub> production rate since the current APR catalysts suffer from poor performance. Mass

transfer limitation also presents a huge hurdle that limits APR performance. Hence, various reactor designs should be studied that allows higher mass transfer rates for increased H<sub>2</sub> production.

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