Catalysis Communications 95 (2017) 67–71

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

A reliable power-law type kinetic expression for PROX over Pt-Sn/AC under fully realistic conditions

B. Merve Eropak, A. Erhan Aksoylu *

Department of Chemical Engineering, Bogazici University, 34342 Bebek, Istanbul, Turkey

ARTICLE INFO

Article history:
Received 3 January 2017
Received in revised form 6 March 2017
Accepted 7 March 2017
Available online 11 March 2017

Keywords:
Preferential CO oxidation
PROX kinetics
Pt-Sn/AC
Hydrogen purification
Realistic conditions

ABSTRACT

The current experimental work is on PROX kinetics over Pt-Sn/AC catalyst at 383 K in the presence of H_2, CO_2, H_2O and CH_4, mimicking WGS outlet of a fuel processor, which is used in production of PEMFC-grade H_2 from hydrocarbons. Parameters of the power-law kinetic model were estimated to be used in PROX reactor modeling and design calculations; reaction orders with respect to CO and O_2 were found as 0.47 and (−0.57). The apparent activation energy of PROX over Pt-Sn/AC, was calculated as 45,300 J mol^{-1} in the temperature range of 383–403 K.

1. Introduction

The use of combined fuel processor-PEM fuel cell (FP-PEMFC) systems in small-scale stationary electricity production is expected to be well proliferated in foreseeable future as the part of distributed energy (DE) production systems connected to smart grids. On site hydrogen production via FP seems to be the most promising and suitable alternative to hydrogen storage, which still has technological hurdles. PEMFC is one of the most viable fuel cell type for small-scale stationary applications, like energy and/or combined heat and energy generation in houses, apartments, small scale businesses, etc. Operation at low temperatures also makes PEMFC preferable among all fuel cell types [1,2].

In hydrogen production from hydrocarbons by using FPs, significant amount of CO production is unavoidable as hydrogen is produced and enriched by the series of catalytic reforming and water-gas shift units of the fuel processor. The CO level in the downstream of the reformer is reduced by the shift reactions, but further CO removal is a necessity in order to decrease CO content to the required levels (between 10 and 50 ppm) for stable operation of PEMFC [3–5].

The catalysts showing the highest catalytic performance, while minimizing the hydrogen consumption is crucial for CO elimination units of FPs [6,7]; in case of reaction with minimal.

hydrogen loss, PROX units are preferable owing to their rapidness and ability to respond quickly to disturbances under operating conditions, and to their relatively simple implementation and lower operating costs as well [8].

The composition of the PROX feed, which is the exit stream of WGS reactor in an FP, is 60–65% H_2, 10–15% H_2O, 1–2% CO, and the rest is CO_2 and balance inert [9]. As hydrogen oxidation reaction is less exothermic than CO oxidation, the catalyst should be highly active and selective at low temperatures, i.e. slightly above water vapor condensation temperature, like at 383 K, under H_2-rich medium [3,10]. PROX catalysts are also required to show good resistance to deactivation caused by H_2O and CO_2 in the feed [6,11].

Researchers have focused on platinum group metal-based catalysts supported on alumina, zeolites or activated carbon as promising PROX catalysts. Since increasing oxygen supply for Pt sites via promoters like CeO_2 or SnO_2 enhances the selectivity, Pt/CeO_2 and Pt-Sn/AC catalysts were tested for CO oxidation reaction, and have shown superior activity and selectivity at low temperatures, which is a key point for catalyst selection [6,9,11–16]. It has been reported that HNO_3-oxidized AC (AC3) enhances Pt-CeO_x and Pt-SnO_x interaction and alloy formation [13]. In contrast to the studies conducted on other PROX catalysts, the addition of CO_2 led to an increase in CO conversion for 1%Pt-0.25%SnO_x/AC3, and the catalyst reached its highest performance (ca. 100% CO conversion) in the presence of CO_2 and/or (CO_2 + H_2O) in the feed [11,17]. The addition of a metal that can form an alloy with Pt, such as Sn to form Pt_3Sn, prevents the catalyst poisoning due to irreversible Pt-CO interaction [18,19]. Additionally, the presence of Pt_3Sn alloy on our Pt-Sn/AC catalyst allowed us to use low reaction temperatures, ca. 383 K in our studies [20]; the catalyst reached ca. 90% conversion for fully realistic PROX feed.

---

* Corresponding author.
E-mail address: aksoylu@boun.edu.tr (A.E. Aksoylu).

http://dx.doi.org/10.1016/j.catcom.2017.03.003

The kinetics of PROX under ideal conditions has been studied over 1%Pt-0.25%SnO_x/AC3; the reaction rate was given as power-function with positive dependence on CO (0.96) and negative dependence on oxygen (−0.31) in the absence of H_2 [4]. There are limited studies on influence of both H_2O and CO_2 on the catalyst performance, although high water tolerance is critical for PROX reactor operation [21]. For the applicability of the obtained kinetic expression, it is critical to study selective CO oxidation under realistic feed gas mixtures simulating the effluent from a low-temperature WGS converter, which requires the addition of CO_2, H_2O and small amount of CH_4 to the ideal feed ($CO + O_2 + H_2$) of a PROX reactor.

Till now, highly active and selective catalysts have been developed for FP reactions; OSR, WGS and PROX, by our group. Kinetic expressions for OSR and WGS reactor design calculations have been obtained in our previous studies [22,23]. The aim of this work is to obtain a reliable, power-law type rate expression over 1 wt%Pt-0.25 wt%Sn/AC3 under fully realistic conditions, which is crucial for reactor modeling and design calculations.

2. Experimental

2.1. Catalyst preparation

Commercial activated carbon (AC), kindly supplied by NORIT (NORIT ROX), was crushed and sieved into 45–60 mesh size (344–255 μm). HNO_3-oxidized AC (AC3) and AC3 supported 1 wt%Pt-0.25 wt%Sn catalyst were prepared by following the procedures given in our previous studies [13,20].

2.2. Kinetic studies

The kinetic tests were carried out in a 4 mm ID tubular reactor under differential conditions at atmospheric pressure where reactants and products were mixed with balance He to keep a constant total flow rate (100 ml min^{-1}) at 383 K. The temperature of the catalyst bed was controlled (±0.1 °C) via a programmable temperature controller (Eurotherm 3216P). The feed stream included not only CO and O_2, but also H_2, CO_2, H_2O, CH_4 and balance He, which represent the realistic exit stream of WGS reactor of an FP. The flow rate of each gas is controlled by Brooks 5850E series mass flow controller with ±1% accuracy. It should be noted that when the flow range of any reactant used in the experiment is low, its MFC is chosen having a range with low maximum flow rate; as an example, MFC of CO has flow rate range of 0–20 ml/min. The flow rates of hydrogen, carbon dioxide, methane and water were kept constant at 60 ml min^{-1}, 15 ml min^{-1}, 3 ml min^{-1} and 10 ml min^{-1} respectively, while CO and O_2 concentrations were changed in the range of 1–2.5% and 1–1.5% respectively, aiming to analyze the effects of CO and O_2 concentration, in other words O:CO ratio in the feed, on rate. In the tests, O:CO ratio (λ) in the feed was in the range of 1–3. The tests were conducted in W/F_{CO} range of 0.0147–0.0489 $mg \cdot min \cdot \mu mol^{-1}$. The amounts of catalyst used in the experiments were 15 mg and 20 mg. It should be noted that 1st and 7th tests were also repeated over diluted 1 wt%Pt-0.25 wt%Sn/AC3 to check whether there is an exothermic effect on the reaction. Conversions obtained with diluted and pure catalyst beds were almost the same, i.e. 10.5% and 10.1% for the 1st test, 7.1% and 7.6% for the 7th test for diluted and undiluted cases, respectively.

The kinetic tests have been performed for different CO and O_2 partial pressures with two different W/F values in a differential reactor in order to obtain reaction rates ($-R_{CO}$) via using conversion versus residence time ($W_{cat}/F_{CO,in}$) data (Eq.(1)) with, and for calculating reaction orders in (Eq.(2)). PROX experiments, tabulated in Table 1, were performed to collect intrinsic kinetic data in the initial rates region. GHSV values used in the experiments were 300,000 ml g^{-1} h^{-1} and 400,000 ml g^{-1} h^{-1} for the 0.020 gcat and 0.015 gcat, respectively. The tests for apparent activation energy calculations were performed additionally at 388, 393 and 403 K.

$$(-R_{CO}) = \frac{x_{CO}}{W/F_{CO_{in}}} \tag{1}$$

$$-r_{CO} = \left[k_0 \exp\left(-\frac{E_A}{RT}\right)(P_{H_2})^{\psi}(P_{H_2O})^{\gamma}(P_{CO_2})^{\theta}(P_{CH_4})^{f}\right](P_{CO})^{\alpha}(P_{O_2})^{\beta} \tag{2}$$

CO and O_2 conversion levels were determined via Thermo CO Analyzer and Agilent Technologies 6850 Series II Gas Chromotograph, respectively. Kinetic data were fitted to a linear equation (validated by R^2 values given in Table 1) ensuring that the reactor is differential.

The adsorption and desorption tests were conducted by using a gravimetric analyzer, which gives adsorbent weight change vs pressure data with a resolution of 0.1 μg. The adsorption and desorption isotherms were obtained within 0–1000 mbar pressure range for each 100 mbar step at room temperature and 383 K. The flowrates of CO_2 and CO used in the tests were 50 ml/min and 20 ml/min respectively. Prior to the adsorption tests, samples were outgassed overnight at room temperature to eliminate humidity and trapped gases.

3. Results and discussion

The form of general power-law type rate expression of CO oxidation for realistic feed is given in Eq.(2). In this study, the primary aim is to obtain a simple, CO and O_2 partial pressure dependent rate expression, which can be used in the design of PROX reactor of a fuel processor. In all experiments, concentrations of H_2, CO_2, H_2O and CH_4 in the feed were kept fixed at 60%, 15%, 10%, and 3% mimicking the PROX inlet of a practical fuel processor. Therefore, the power-law type rate expression can be written assuming the terms including H_2, CO_2, H_2O and CH_4 partial pressures in Eq.(2) were constant, and all the related terms are lumped in k' of the rate expression as in Eq. (3).

$$-r_{CO} = k' \; (P_{CO})^{\alpha} \, (P_{O_2})^{\beta} \tag{3}$$

A sample graph is given in Fig. 1 to show the initial rate calculation of experiments 1a–b. A non-linear multivariable optimization was conducted by using "Lsqnonneg" function provided in MATLAB toolbox to estimate the parameters, k′, α and β of Eq.(3) within ±20% error

Table 1

Experimental sets conducted over 1%Pt-0.25%Sn/AC3 catalyst.

Exp no*	T (K)	O:CO ratio	CO flow rate (ml/min)	O_2 flow rate (ml/min)	P_{CO} (kPa)	P_{O2} (kPa)	λ	$(-R_{CO})_0$ (μmol mg^{-1} min^{-1})	R^2
1a–b	383	2	1	1	1.013	1.013	2	2.148	0.994
2a–b	383	2.5	1	1.25	1.013	1.267	2.5	1.988	0.833
3a–b	383	3	1	1.5	1.013	1.520	3	1.648	0.942
4a–b	383	2.5	1.2	1.5	1.216	1.520	2.5	1.586	0.937
5a–b	383	2	1.25	1.25	1.267	1.267	2	2.362	0.953
6a–b	383	1	2	1	2.027	1.0133	1	2.402	0.960
7a–b	383	1.5	2	1.5	2.027	1.520	1.5	2.198	0.990
8a–b	383	1	2.5	1.25	2.533	1.267	1	3.428	0.925

* Experiments in series a and b were performed by using 20 and 15 mg of catalyst, respectively, to have initial rate data at two different W/F_{CO} ratios, for each reaction condition.