Reaction network and kinetic analysis of ethanol steam reforming over a Ru/Al$_2$O$_3$ catalyst

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A B S T R A C T

Ethanol steam reforming, a potential technology of hydrogen production for fuel cell application, has attracted great research attention recently. Because ethanol can be produced from biomass cheaply, using bioethanol with large excess of water as the direct feed of steam reforming is believed to be a promising technology to produce hydrogen for fuel cells. Although various catalyst systems were used for ethanol steam reforming, detailed reaction kinetics was not investigated thoroughly. In the analysis of heterogeneous catalytic kinetics, reaction mechanism including adsorption step of reactants, reaction step of the adsorbed species, and desorption step of the products were usually proposed. Then a suitable rate determining step was assumed to allow the derivation of the rate equation as a function of reactant and/or product concentrations. In this study, the general rate equations for cyclic reaction networks with multiple pathways were applied to derive the rate equation and hydrogen yield equation for ethanol steam reforming. The derived rate and yield equations were used to analyze the kinetic data of Vaidya and Rodrigues. The results showed that the experimental ethanol conversions and hydrogen yield ratios at varying space times and reaction temperatures could be satisfactorily predicted by the model equations. The rate controlling steps are water reaction with the adsorbed ethanol, water reaction with the adsorbed acetaldehyde, and CO desorption. Furthermore, for temperature lower than 923 K, the overall reaction is also controlled by desorption of ethanol and desorption of acetaldehyde; for temperature higher than 923 K, the overall reaction is also controlled by the dehydrogenation of the adsorbed ethanol. The averaged activation energy of three sequential reaction steps was found to be 110 kJ/mol, compared with the overall activation energy 96 ± 17 kJ/mol determined by Vaidya and Rodrigues.

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1. Introduction

Ethanol steam reforming, a potential technology of hydrogen production for fuel cell application, has attracted great research attention recently [1–15]. Because ethanol can be produced from biomass cheaply, using bioethanol with large excess of water as the direct feed of steam reforming is believed to be a promising technology to produce hydrogen for fuel cells [16]. Although various catalyst systems were used for ethanol steam reforming, reaction rate and yield equations were not investigated explicitly [9,16–19]. The desired overall reaction of steam reforming is

$$C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 \qquad (1)$$
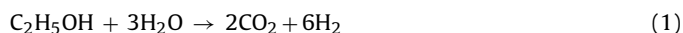
However, if other side reactions are also considered, the reaction network becomes very complicated and thus makes kinetic data analysis very difficult.

Vaidya and Rodrigues studied catalytic steam reforming of ethanol over a Ru/γ-Al$_2$O$_3$ catalyst in the temperature range 873–973 K and found the ethanol reaction rate was first order with respect to ethanol and independent of water [16]. They proposed a possible reaction mechanism for ethanol steam reforming and derived a rate expression assuming that the decomposition of an activated complex formed during reaction into intermediate products was the rate determining step. Using the derived rate expression and packed-bed reactor model, they obtained an equation to calculate the ethanol conversion as a function of catalyst weight (W) and volumetric feed flow rate (Q_0). Although the equation was used to fit the ethanol conversion versus W/Q_0 data with satisfactory agreement, it cannot be used to interpret other kinetic data such as hydrogen yield.
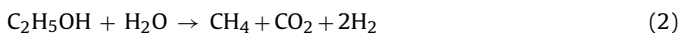
With the advancement of spectroscopy and other surface analysis techniques, most researches about heterogeneous catalysis focus on catalyst preparation, characterization, and performance tests. Nevertheless, for a given catalyst system an adequate rate equation reflecting the elementary reaction step is very useful for reactor scale-up and process design. In the analysis of heterogeneous catalytic kinetics, reaction mechanism including adsorption

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step of reactants, reaction step of the adsorbed species, and desorption step of the products were usually proposed. Then a suitable rate determining step was assumed to allow the derivation of the rate equation as a function of reactant and/or product concentrations. Because of complicated reaction steps involved in heterogeneous catalysis, empirical power-law rate equation is usually used. For example, Soyal-Baltacioğlu et al. [9] used a power-law rate equation to analyze the kinetic data of ethanol steam reforming over Pt–Ni catalysts. In this study, the general rate equations for cyclic reaction networks with multiple pathways [20] and pyramidal topology [21] were applied to derive the reaction rate and yield ratio equations for ethanol steam reforming. The derived rate and yield ratio equations were used to analyze the kinetic data of Vaidya and Rodrigues to elucidate how to apply the general rate equations for heterogeneous reaction network analysis.

2. Proposed reaction network

Consider the following main reactions involved in ethanol steam reforming:

$$C_2H_5OH + H_2O \rightarrow CH_4 + CO_2 + 2H_2 \tag{2}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{3}$$
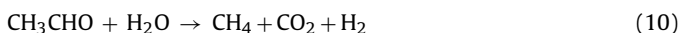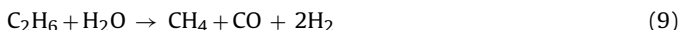
$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{4}$$

Reaction (2) is the steam reforming reaction of ethanol that is predominant at these temperatures. Reactions (2)–(4) together denote the overall steam reforming reaction of ethanol. Ethanol dehydrogenation to acetaldehyde and ethanol dehydration to ethylene also occur in the presence of Ru/Al$_2$O$_3$ [16]:

$$C_2H_5OH \rightarrow CH_3CHO + H_2 \tag{5}$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \tag{6}$$

The formation of ethane observed during ethanol steam reforming may result from ethylene hydrogenation:

$$C_2H_4 + H_2 \rightarrow C_2H_6 \tag{7}$$
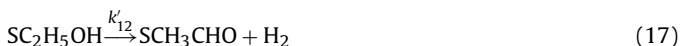
The intermediates such as C_2H_4, C_2H_6, and CH_3CHO also possibly undergo steam reforming to produce CO_2 and H_2:

$$C_2H_4 + H_2O \rightarrow CH_4 + CO + H_2 \tag{8}$$

$$C_2H_6 + H_2O \rightarrow CH_4 + CO + 2H_2 \tag{9}$$

$$CH_3CHO + H_2O \rightarrow CH_4 + CO_2 + H_2 \tag{10}$$

The produced CH_4 and CO can be converted to CO_2 and H_2 by Reactions (3) and (4).

The following reaction mechanism is proposed for the above overall reactions:

$$S + C_2H_5OH \underset{k_{10}}{\overset{k_{01}}{\longleftrightarrow}} SC_2H_5OH \tag{11}$$

$$SC_2H_5OH + H_2O \overset{k_{12}}{\longrightarrow} SCH_4 + 2H_2 + CO_2 \tag{12}$$

$$SCH_4 \underset{k_{02}}{\overset{k_{20}}{\longleftrightarrow}} S + CH_4 \tag{13}$$

$$SCH_4 + H_2O \overset{k_{23}}{\longrightarrow} SCO + 3H_2 \tag{14}$$

$$SCO \underset{k_{03}}{\overset{k_{30}}{\longleftrightarrow}} S + CO \tag{15}$$

$$SCO + H_2O \overset{k_{34}}{\longrightarrow} S + H_2 + CO_2 \tag{16}$$

$$SC_2H_5OH \overset{k'_{12}}{\longrightarrow} SCH_3CHO + H_2 \tag{17}$$

$$SCH_3CHO \underset{k'_{02}}{\overset{k'_{20}}{\longleftrightarrow}} S + CH_3CHO \tag{18}$$

$$SCH_3CHO + H_2O \overset{k'_{23}}{\longrightarrow} SCH_4 + H_2 + CO_2 \tag{19}$$

$$SC_2H_5OH \overset{k''_{12}}{\longrightarrow} SC_2H_4 + H_2O \tag{20}$$

$$SC_2H_4 \underset{k''_{02}}{\overset{k''_{20}}{\longleftrightarrow}} S + C_2H_4 \tag{21}$$

$$SC_2H_4 + H_2 \overset{k''_{23}}{\longrightarrow} SC_2H_6 \tag{22}$$

$$SC_2H_4 + H_2O \overset{k''_{24}}{\longrightarrow} SCH_4 + H_2 + CO \tag{23}$$

$$SC_2H_6 \underset{k''_{03}}{\overset{k''_{30}}{\longleftrightarrow}} S + C_2H_6 \tag{24}$$

$$SC_2H_6 + H_2O \overset{k''_{34}}{\longrightarrow} SCH_4 + 2H_2 + CO \tag{25}$$
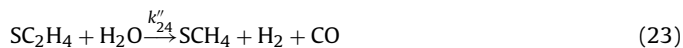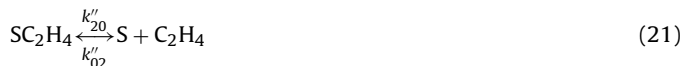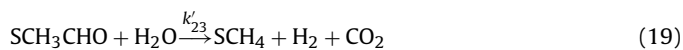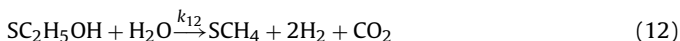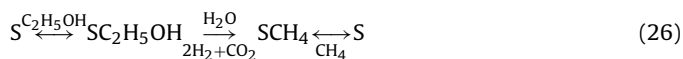
According to the proposed mechanism, ethanol steam reforming starts with the adsorption of ethanol on the catalyst as shown by Reaction (11). The adsorbed ethanol reacts with water in the gas phase to form the methane-adsorbed species and releases carbon dioxide and hydrogen as shown by Reaction (12). The adsorbed methane can desorb from the catalyst as shown by Reaction (13) or reacts with water in the gas phase to form the CO-adsorbed species and release hydrogen as shown by Reaction (14). The adsorbed CO can desorb from the catalyst as shown by Reaction (15) or reacts with water in the gas phase to release carbon dioxide and hydrogen as shown by Reaction (16).

The adsorbed ethanol can release hydrogen and form the acetaldehyde-adsorbed species as shown by Reaction (17). The adsorbed CH_3CHO can desorb from the catalyst or react with water in the gas phase to release carbon dioxide and hydrogen and form the CH_4-adsorbed species as shown by Reactions (18) and (19), respectively. The adsorbed ethanol can also release water and form the ethylene-adsorbed species as shown by Reaction (20). The adsorbed C_2H_4 can desorb from the catalyst, reacts with hydrogen in the gas phase to form the C_2H_6-adsorbed species or reacts with water in the gas phase to release CO and hydrogen and form the CH_4-adsorbed species as shown by Reactions (21)–(23), respectively. The adsorbed ethane can desorb from the catalyst or react with water in the gas phase to release CO and hydrogen and form the CH_4-adsorbed species as shown by Reactions (24) and (25), respectively.

A reaction network, shown in Fig. 1, can be drawn to show the reaction pathways of the mechanism schematically. As shown in Fig. 1, the overall reactions involved in ethanol steam reforming can be obtained from the following reaction routes with the co-reactants and co-products shown above and below the arrows, respectively:
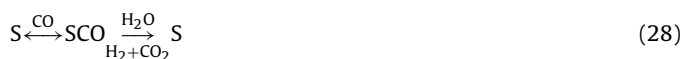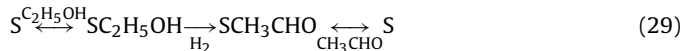
For Reaction (2),

$$S \overset{C_2H_5OH}{\longleftrightarrow} SC_2H_5OH \underset{2H_2+CO_2}{\overset{H_2O}{\longrightarrow}} SCH_4 \underset{CH_4}{\longleftrightarrow} S \tag{26}$$

For Reaction (3),

$$S \overset{CH_4}{\longleftrightarrow} SCH_4 \underset{3H_2}{\overset{H_2O}{\longrightarrow}} SCO \underset{CO}{\longleftrightarrow} S \tag{27}$$

For Reaction (4),

$$S \overset{CO}{\longleftrightarrow} SCO \underset{H_2+CO_2}{\overset{H_2O}{\longrightarrow}} S \tag{28}$$

For Reaction (5),

$$S \overset{C_2H_5OH}{\longleftrightarrow} SC_2H_5OH \underset{H_2}{\longrightarrow} SCH_3CHO \underset{CH_3CHO}{\longleftrightarrow} S \tag{29}$$