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Ethanol Steam Reforming for Hydrogen Production over Bimetallic Pt–Ni/Al_2O_3

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Abstract Ethanol steam reforming was studied at 673–823 K over Pt–Ni/δ-Al_2O_3. Results indicate that bimetallic catalyst is resistant to coke deposition at steam-to-carbon ratios as low as 1.5 and higher ratios are beneficial for both ethanol conversion and hydrogen formation. About 773 K is the optimum since high H_2 production rates are accompanied by low CO and CH_4 production rates. A power-function rate expression obtained on the basis of intrinsic rates at 673 K gives reaction orders of 1.25 (±0.05) and –0.215 (±0.015) for ethanol and steam, respectively; the apparent activation energy is calculated as 39.3 (±2) kJ mol^{-1} between 673 and 723 K.

Keywords Ethanol steam reforming · Hydrogen production · Bimetallic catalysts · Pt–Ni

1 Introduction

One of the novel alternatives for clean energy generation is fuel cell technology. Polymer electrolyte membrane fuel cells (PEMFC) powered by hydrogen are well-suited for both vehicular and decentralized stationary facilities such as combined heat and power generation for houses and small-scale commercial applications [1, 2]. Since PEMFC operation requires a continuous supply of hydrogen, the use of an in situ catalytic fuel processor that will readily convert hydrocarbon fuels into hydrogen is a potentially feasible solution. Steam reforming (SR) is investigated in this context, since it has the highest efficiency for hydrogen production. Endothermic nature of steam reforming constitutes its main drawback given that an external source of heat is needed [3, 4].

The criteria for the selection of the optimal hydrocarbon source for small-scale energy production include either a well-established distribution network, as in the case of natural gas, and/or a liquid fuel for easy storage and transportation, as in the case of gasoline. Although natural gas, gasoline and methanol are usually mentioned as the likely sources for hydrogen production, their use does not reduce reliance on fossil fuels or emission of pollutants. Ethanol has recently received attention as a hydrogen source due to its crucial advantage of being producible from renewable sources such as biomass, plants or waste materials of agricultural and forestry industries. Hydrogen production from bio-ethanol offers a nearly closed carbon loop since the carbon dioxide produced is consumed for biomass growth [5]. Ethanol is widely available, easily transportable, safe to handle and less toxic compared to methanol. Higher temperatures (573–873 K) are required for ethanol SR because of its C–C bond, and this is the only disadvantage to be tackled.

Ethanol steam reforming is a highly endothermic reaction:

$$C_2H_5OH + 3\,H_2O \Rightarrow 2\,CO_2 + 6\,H_2 \quad \Delta H^{\circ}_{298} = 173\,kJ\,mol^{-1} \tag{1}$$

Even though the overall steam reforming reaction looks straightforward, the reaction scheme is complicated by the presence of other reactions occurring in the system, depending mostly on reaction temperature and catalyst composition and resulting in exit streams containing hydrogen, carbon monoxide, carbon dioxide, methane, ethylene, acetaldehyde etc [6, 7]. The most likely side

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reactions over Ni-based catalysts are ethanol SR with methane production, ethanol decomposition and methane SR:

$$C_2H_5OH + H_2O \Rightarrow 2\,CO_2 + CH_4 + 2\,H_2 \quad (2)$$

$$C_2H_5OH \Rightarrow CO + CH_4 + H_2 \quad (3)$$

$$CH_4 + H_2O \Leftrightarrow CO + 3\,H_2 \quad (4)$$

Methanation of carbon oxides may also be considered as a possibility. Comas et al. [7] studied ethanol SR over Ni/Al_2O_3 at 573–773 K to propose a reaction scheme. Fatsikostas and Verykios [8] investigated the effect of using different supports for Ni catalysts and reported that carbon deposition is significantly reduced by impregnating γ-Al_2O_3 with La_2O_3. Sun et al. [9] suggested that ethanol steam reforming on Ni catalysts is first-order with respect to ethanol and computed apparent activation energies between 1.87 and 16.88 kJ mol^{-1} depending on the type of catalyst support. Akande et al. [10] studied crude ethanol SR over Ni/Al_2O_3 and suggested a reaction order of 0.43 with respect to ethanol and activation energy of 4.41 kJ mol^{-1}. Although ethanol SR has recently received more attention, extended parametric and kinetic studies are scarce [11]. Intrinsic kinetics of ethanol SR studied over Ru/Al_2O_3 using excess water, on the other hand, showed that ethanol conversion was directly proportional to ethanol partial pressure and independent of steam partial pressure with apparent activation energy of 96 kJ/mol [12].

The fuel processor/fuel cell system proposed by Avci et al. [13] for hydrogen production from different hydrocarbons was modified to investigate ethanol conversion to hydrogen by a series of thermodynamic analyses and computer simulations [14]. Hydrogen production was considered to occur over a bimetallic catalyst (such as Pt–Ni) by indirect partial oxidation (IPOX) which combines steam reforming and total oxidation reactions as well as water–gas shift (WGS) as a beneficial side reaction. In IPOX, the external energy demand of endothermic SR is minimized by the highly exothermic total oxidation. The thermodynamic approach was used, because suitable rate equation(s) for ethanol SR are lacking. The results indicated that H_2 yields up to 65% of the theoretical (1 mol ethanol can yield up to 6 mol H_2) can be obtained with an ethanol total oxidation conversion of about 13% at a steam-to-carbon ratio of 3.3 and an IPOX reactor exit temperature of 873 K [14].

The present work focuses on ethanol SR over bimetallic Pt–Ni/δ-Al_2O_3, which is a successful IPOX catalyst that has potential for fuel processor applications associated with PEM fuel cells [15, 16]. A parametric study was conducted to reveal the effects of water-to-ethanol ratio and temperature on ethanol conversion and hydrogen formation, and a kinetic study was carried out in order to propose a power-function rate expression for ethanol conversion by steam reforming over Pt–Ni/δ-Al_2O_3.

2 Experimental

2.1 Catalyst Preparation

δ-Al_2O_3 was used as support material because of its thermal stability and suitable total surface area. Bimetallic 0.2 wt%Pt–15 wt%Ni/δ-Al_2O_3 was prepared by drying γ-Al_2O_3 (Alcoa) at 423 K, calcination at 1,173 K to get δ-Al_2O_3, sequential incipient-to-wetness impregnation using aqueous $Ni(NO_3)_2.6H_2O$ (Merck) and $Pt(NH_3)_4(NO_3)_2$ (Aldrich) solutions with an intermediate calcination at 873 K and a final calcination at 773 K. The BET surface area of 82 $m^2\ g^{-1}$ was determined using a Micromeritics Flowsorb II-2300 apparatus. The details of the preparation procedure have been reported elsewhere [17].

2.2 Reaction Experiments

Reaction experiments were conducted using 4 mm-i.d. stainless steel tubular down-flow microreactors placed in the constant-temperature zone of a 2.4-cm i.d. tube furnace controlled to ±0.1 K by a Shimaden FP-21 programmable controller. In all experiments, 25 mg of 250–422 μm (40–60 mesh) fresh catalyst particles were diluted with inert δ-Al_2O_3 to a total bed weight of 250 mg. Silane-treated glass wool (Alltech) was used to hold the catalyst bed in a fixed position. Preliminary experiments showed that the stainless steel reactor, glass wool and δ-Al_2O_3 were inert under the conditions used. Catalyst particle size and gas space velocity are important factors affecting mass transport in a solid-catalyzed system. Particles of 250–422 μm size were found to be sufficiently small for avoiding internal diffusion effects under the present reaction conditions [18]. Experiments at constant contact time but varying gas flows with the same composition showed that external mass transfer effects were insignificant. In order to eliminate axial dispersion, the $D_{tube}/D_{particle} > 10$ and $L_{bed}/D_{particle} > 50$ criteria were also satisfied [19].

Nitrogen and hydrogen flows were regulated by Omega Model 5878 and Aalborg GFC171S series mass flow controllers, respectively. Liquid reactants were premixed according to the water/ethanol ratio specified, and the liquid mixture was introduced at constant flow rate using a Jasco PU-1580 intelligent HPLC pump into a stream of diluent nitrogen flow. The mixing section and the

connecting lines to the reactor were kept at 423 K by a heating tape plus temperature controller system for achieving evaporation and avoiding condensation. The liquid flow rate metered on the HPLC pump was converted into total and individual gas flow rates by assuming ideal gas behavior and utilizing water/ethanol ratios, molecular weights and liquid densities [17].

The catalyst was reduced under 20 cm^3 min^{-1} pure hydrogen flow at 773 K for 4 h prior to each reaction experiment. After reduction, the reactor temperature was raised to the reaction temperature (623, 673, 723, 773 or 823 K) under inert nitrogen flow, and nitrogen was trapped within the reactor for 2 h while the reactant flow rates that were diverted to the bypass line reached steady-state. The feed composition and residence time were adjusted to give water/ethanol molar ratios of 3.0–6.0 (corresponding to steam-to-carbon ratios of 1.5–3.0) and W/F_{Eo} values of 2.8–5.2 (mg s μmol^{-1}), respectively.

Product samples were collected and analyzed 1.5, 3, 4 and 5.5 h after the reaction mixture was introduced into the microreactor. Ethanol and other hydrocarbons were analyzed using a Shimadzu GC-14A gas chromatograph with a TCD, a Porapak Q column and He as carrier gas. A Shimadzu-8A gas chromatograph with a TCD, a Molecular Sieve 5A column and Ar as the carrier gas was used for analyzing H_2 and CO.

In kinetic experiments, 20–25 mg fresh 0.2 wt%Pt–15 wt%Ni/δ-Al_2O_3 samples were diluted with δ-Al_2O_3 to a total bed weight of 250 mg. A temperature of 673 K was selected for kinetic analysis in the initial rates range using different feed concentrations. Various water/ethanol molar ratios in the range of 3.0–6.0 and W/F_{Eo} values of 0.90–3.70 (mg s μmol^{-1}) were used in duplicate experiments with feed having ethanol mole fractions between 0.05 and 0.15. The temperature dependence of the rate constant and the activation energy were calculated by repeating these experiment sets at 698 and 723 K.

3 Results and Discussion

3.1 Effect of Temperature

Considering the stoichiometry of Reaction 1, and in order to eliminate coke deposition on the Pt–Ni catalyst, the water/ethanol molar ratio was fixed at 5.0 for investigating the effect of temperature on ethanol conversion and product distribution. Figure 1 shows the notable effect of reaction temperature on ethanol conversion. The lowest conversion (ca. 12%) was obtained at 623 K whereas the highest one (ca. 100%) was achieved at 823 K. The most significant difference among the conversion levels in the same reaction time zone was observed in going from 723 to

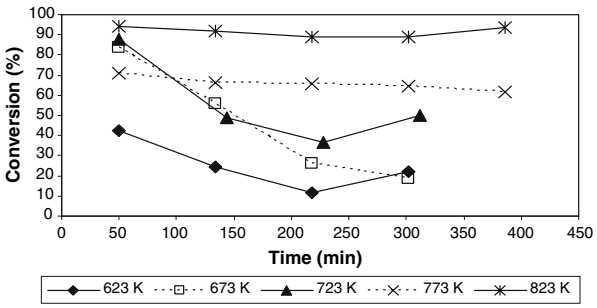

Fig. 1 Effect of temperature on ethanol conversion

773 K at around 230 min, which may be explained by considering possible side reactions, i.e. Reactions 2, 3 or 4. The production rates of two competing products, hydrogen and methane, are plotted in Fig. 2. Hydrogen production increases remarkably with increasing temperature from about 40 μmol/g cat-s at 623 K to about 185 μmol/g cat-s at 823 K while the highest methane production of ca. 8 μmol/g cat-s is observed at 723 K as compared to ca. 4 μmol/g cat-s at 623 K. These results, when combined with the data on CO_2 and CO production rates (Fig. 3), suggest that ethanol SR with methane formation becomes

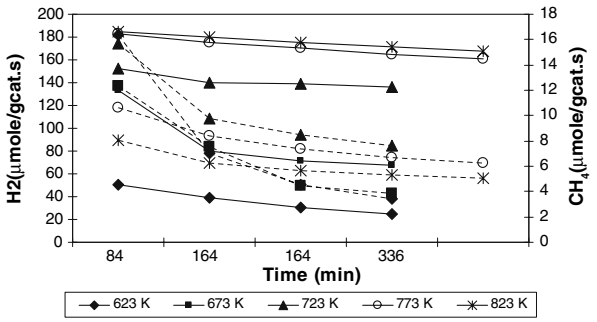

Fig. 2 The variation of hydrogen and methane production rates with temperature (solid lines and left *y*-axis represent H_2 production, dotted lines and right *y*-axis represent CH_4 production)

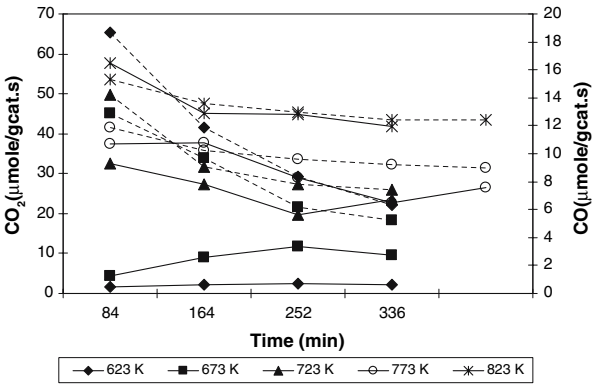

Fig. 3 The variation of carbon dioxide and carbon monoxide production rates with temperature (solid lines and left *y*-axis represent H_2 production, dotted lines and right *y*-axis represent CH_4 production)

significant at 723 K, since CH_4, H_2 and CO_2 productions are all favored (Reaction 2). CO, CO_2 and CH_4 production trends as well as the H_2/CH_4 ratios (Figs. 2–4) at this temperature do not suggest significant methanation. At 823 K, CH_4 production decreases while CO and H_2 productions increase, indicating that the effluent composition may be affected by the thermodynamic equilibrium of methane steam reforming (Reaction 4). Furthermore, considering that mainly CO rather than CO_2 is produced at 623 K (Fig. 3), together with H_2 and some CH_4, it may be said that ethanol decomposition is significant at this temperature. The reaction mechanisms suggested at these temperatures coincide well with the overall reaction scheme proposed by Comas et al. [7] for bio-ethanol SR over monometallic Ni/Al_2O_3.

It is evident that hydrogen production should be as high as possible at the optimum reaction temperature. Figure 2 indicates maximum H_2 production at 823 K; however, this is also the temperature at which maximum CO production occurs. Since CO acts as a poison for fuel cell electrodes, the level of CO in the reformer effluent has to be minimized. Therefore, optimum reaction temperature must be selected on the basis of the H_2/CO production ratio, i.e. the point selectivity for H_2 (Fig. 4), rather than the hydrogen production rate. In this respect, 723 and 773 K stand out as better reaction temperatures than 823 K. The H_2/CH_4 point selectivity is also important, since CH_4 is an undesired byproduct that uses up hydrogen. CH_4 production rate is highest at 723 K and decreases as the temperature is raised to 823 K (Fig. 2) with the highest H_2/CH_4 point selectivity occurring at 823 K.

The selectivity data are also in good agreement with the reaction scheme outlined above. For instance, at 723 K, the high H_2 and the low CO levels resulting from Reaction 2 lead to a high H_2/CO production ratio whereas at 823 K, since both CO and H_2 are produced by Reaction 4, the selectivity stays at a relatively lower value. CH_4 steam reforming, which was suggested to be dominant at 823 K, causes the H_2/CH_4 point selectivity to be the highest at this temperature; on the contrary, CH_4 production from ethanol steam reforming at 723 K gives a much lower selectivity. As a result, the optimum reaction temperature may be proposed as 773 K, since both CO and CH_4 production rates are relatively low while that of H_2 is remarkably high (185 μmol/g cat-s).

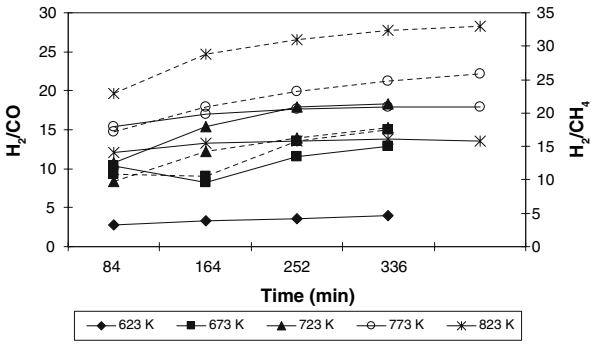

Fig. 4 Effect of temperature on hydrogen to carbon monoxide and hydrogen to methane selectivity's (solid lines and left *y*-axis represent H_2/CO selectivity, dotted lines and right *y*-axis represent H_2/CH_4 selectivity)

3.2 Effect of Water/Ethanol Ratio

The effect of the water/ethanol molar ratio (W/E) on the steam reforming performance of Pt–Ni/δ-Al_2O_3 was studied at two temperatures, 673 and 773 K. No coke formation was observed at either temperature and even at the lowest water/ethanol ratio of 3.0 corresponding to a steam/carbon ratio of 1.5, which is well below the limit claimed to eliminate coke deposition over monometallic Ni catalysts. The resistance of bimetallic Pt-Ni to coke formation under these conditions may be explained by the presence of Pt despite its low weight percentage. The variation in total ethanol conversion with the water/ethanol ratio at 773 K is presented in Fig. 5, while the corresponding hydrogen and methane production trends are shown in Fig. 6. Ethanol conversion and hydrogen production are both improved by increasing the water/ethanol ratio from 5.0 to 6.0. On the contrary, CH_4 production is suppressed with increasing W/E ratios, suggesting that methane reforming may be promoted at water/ethanol ratios greater than 4.0.

3.3 Kinetics of Ethanol Steam Reforming over Pt–Ni/δ-Al_2O_3

The general form of the empirical power-function rate expression for ethanol conversion by steam reforming is postulated as follows:

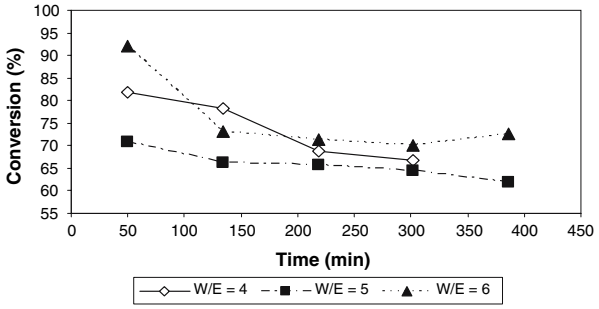

Fig. 5 Effect of water to ethanol ratio on ethanol conversion

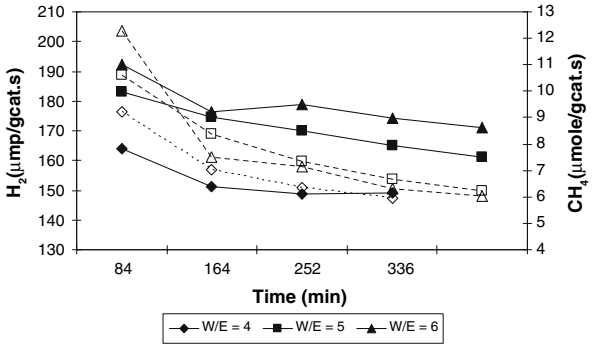

Fig. 6 The variation of hydrogen and methane production rates with water to ethanol ratio (solid lines and left *y*-axis represent H_2 production, dotted lines and right *y*-axis represent CH_4 production)

$$-r_{C_2H_5OH} = \left[k_0 \exp\left(-\frac{E_A}{RT}\right)\right](P_{C_2H_5OH})^{\alpha}(P_{H_2O})^{\beta} \qquad (5)$$

Evaluation of the rate parameters, i.e. α, β, k_0 and E_A, involves the calculation of reaction rates from ethanol conversion versus residence time data. Representative initial rate data obtained from duplicated experiments conducted at 673 K are presented in Table 1 along with the corresponding reactant partial pressures in the feed. Reaction orders were estimated using Eq. 5 and non-linear regression analysis in the MATLAB^{TM} environment (Table 2). The effect of products was neglected since data were collected in the initial rates region. Reaction orders show that the rate of ethanol steam reforming is directly proportional to the partial pressure of ethanol and is mildly inhibited by steam partial pressure. These results are in agreement with previous research on steam reforming of ethanol over Ni-based catalysts in so far as a positive reaction order close to unity is observed for ethanol [9, 11]. The mechanism proposed for ethanol SR over Ru/Al_2O_3 with excess water [12] implicates a surface complex between adsorbed ethanol and water from the gas phase, and the decomposition of this complex is taken as rate limiting to explain the first order dependence on ethanol. The reaction orders obtained in the present study would indicate a reaction occurring on a surface that is mostly covered by adsorbed water with relatively weak ethanol adsorption. The dependence of ethanol steam reforming rates on steam partial pressure has not been sufficiently addressed in the literature; however, the negative dependence observed in this study is in line with general trends observed in steam reforming of alkanes [17].

Table 1 Representative initial rate data over Pt–Ni/δ-Al_2O_3 (673 K and 1 atm)

Experiment No.	W/F_{E0} (mg s µmol^{-1})	C_2H_5OH (kPa)	H_2O (kPa)	N_2 (kPa)	Rate ($\times 10^3$ mol gcat^{-1} s^{-1})
1	2.932	5.05	25.25	70.70	0.0348
2	3.665	5.05	25.25	70.70	0.0518
3	1.466	8.42	33.67	58.92	0.0428
4	1.833	8.42	33.67	58.92	0.0479
5	1.955	6.31	37.88	56.81	0.0354
6	2.443	6.31	37.88	56.81	0.0479
7	0.978	11.22	37.41	52.37	0.0569
8	1.222	11.22	37.41	52.37	0.0582
9	1.173	9.35	41.15	50.50	0.1415
10	1.466	9.35	41.15	50.50	0.1535
11	1.173	10.52	31.56	58.92	0.1662
12	1.466	10.52	31.56	58.92	0.1317

Table 2 Kinetic parameters of ethanol steam reforming (673–723 K)

Parameter	Units	Estimates
k_0	mol gcat^{-1} s^{-1} kPa$^{-1.07}$	0.013
E_A	kJ mol^{-1}	39.3 (±2.1)
α		1.25 (±0.05)
β		–0.215 (±0.015)

The last four data sets reported in Table 1 for ethanol SR at 673 K were repeated in duplicate at 698 and 723 K, in order to estimate the apparent activation energy (E_A) and the pre-exponential factor (k_0). These data are plotted in Fig. 7 and the parameter estimates are given in Table 2. The E_A value of 39.3 ± 2.1 kJ mol^{-1} is not in agreement with those reported in the literature for ethanol steam reforming on *Ni-based* catalysts but is comparable with E_A values for steam reforming of alkanes [17, 19]; furthermore, its magnitude confirms that kinetic experiments were conducted under reaction-controlling conditions. The low E_A values reported in the literature for ethanol SR and their irregularity [9–11] indicate that external and/or internal diffusion effects may be significant under the experimental conditions used in those studies.

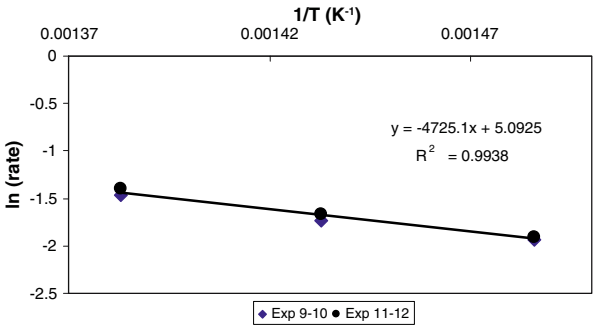

Fig. 7 Arrhenius plot of ethanol steam reforming over Pt–Ni/δ-Al_2O (1 atm)

4 Conclusions

Ethanol steam reforming was studied at 673–723 K over bimetallic Pt–Ni/δ-Al_2O_3, which is a successful IPOX catalyst with potential for use in fuel processors. The parametric study conducted indicates that the Ni-based bimetallic catalyst is resistant to coke deposition even at a steam-to-carbon ratio as low as 1.5 (W/E = 3.0); higher water-to-ethanol ratios have a positive effect on both ethanol conversion and H_2 formation. About 773 K is selected as the optimum reaction temperature, since high H_2 production rates are accompanied by low CO and CH_4 production rates, thus yielding favorable H_2/CO and H_2/CH_4 production ratios at this temperature. An empirical power function rate equation is proposed on the basis of intrinsic rates evaluated at 673 K over Pt–Ni/δ-Al_2O_3. Reaction orders are calculated as 1.25 (±0.05) and –0.215 (±0.015) with respect to ethanol and steam, respectively. The apparent activation energy and the pre-exponential factor between 673 and 723 K are found to be 39.3 (±2.1) kJ mol^{-1} and 0.013 mol g cat^{-1} s^{-1} $kPa^{-1.07}$, respectively.

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