Steam reforming of ethanol over Al_2O_3 supported noble metal catalysts

Ph.D. Theses

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Preliminary and objectives

Hydrogen is considered to be a very promising energy carrier for the future because it burns cleanly without emitting any environmental pollutants, and in addition it possesses the highest energy content (120,7 kJ/g) compared to any of the known fuels. Before using any hydrogen-based energy carrier it is indispensable to solve the problems of production, transportation, storage and utilization of hydrogen.

In our environment hydrogen can be found in bound form in water and in organic compounds. Many chemical and biotechnological methods are known for its production. One of these is the fermentation of biomass to produce bio-ethanol, which during pyrolysis or burning produces the energy carrier needed. Great attention is paid nowadays to the energy production based on biomass to substitute fossil fuels and decrease the environmental problems.

As the bio-ethanol produced from biomass by fermentation has high hydrogen content, it is a good candidate for the hydrogen production originated from the biomass. This idea can be supported by many arguments. Bio-ethanol is considered to be a renewable energy source that is available in great amounts, and neither its transportation nor its storage causes significant problems. It is also a very important advantage that it is biodegradable and has no toxicity. It has to be mentioned as well that the carbon-dioxide produced by the decomposition of ethanol does not increase the CO_2 concentration in the atmosphere, because the carbon content of bio-ethanol originates from the carbon-dioxide that the plants have previously bonded from the atmosphere during photosynthesis. Because of these advantages great attention is paid to the hydrogen production from bio-ethanol. A lot of research work and experimenting aim to find the best and most efficient method.

The steam reforming of ethanol can be described by the following reaction scheme:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \quad \Delta H_r = 173{,}36\ \text{kJ/mol}$$

This reaction can be realized only in a catalytic way. According to the early studies the oxide supported metal catalysts presented good results in this process. Supported noble metals are very efficient in the catalytic hydrogenation but their price makes the processes very expensive. For this reason other metals (Cu, Ni, Fe, etc) are more favoured in the industry for this purpose, even though they may have lower efficiency in this process. Mainly metal oxides are used as supports not only to ensure the dispersion of the metal on the surface but to influence the route of the reactions.

At the beginning of our work we joined to the early researches of the catalytic steam reforming of ethanol. At that time the aim of these experiments was mainly to identify the products formed over different catalysts under various conditions. We began our study with the Al_2O_3 supported noble metals and based on the results obtained our interest was focused onto the Pt/Al_2O_3 catalyst. Our aim was not only the identification of the products that form in these reactions but also the examination of the interaction between the ethanol and the catalysts, that greatly influenced the whole process.

Experimental

The catalysts were prepared by impregnating the supports with the aqueous solutions of the metal-chlorides. The metal content of the catalysts was 1 m/m% in most cases. The same method was used to impregnate the 75-25%, 50-50% and 25-75% mixture of Al_2O_3 and ZrO_2. In the preparation of potassium doped $1\%Pt/Al_2O_3$ beside KNO_3 was also added in proper amount to yield 0.04, 0.2 and 0.4% K content. Before each experiment the catalysts were pre-treated by oxidation for 20 minutes and reduction for 60 minutes.

The catalytic tests were carried out in a fixed bed continuous flow reactor. 50 mg catalyst was used in each experiment. The pure ethanol or the mixtures of ethanol and water of 1:3 and 1:9 molar ratios were fed with the help of an infusion pump by 0.3 ml/h into 60 ml/min of Ar stream. The products were analysed by gas chromatography.

The carbon containing materials deposited during the catalytic run onto the surface of the catalysts were determined by temperature programmed reduction in which the catalysts were heated from 373 to 1173 K with 5 K/min heating rate in 40 ml/min of H_2 stream. The products formed in these experiments were also analysed by gas chromatography.

IR spectroscopy was used to identify the surface species formed during the adsorption of ethanol onto the catalyst. In these experiments the samples were treated in ethanol after the pre-treatments, then evacuated and the IR spectra of the surface were registered. By heating the samples to different temperatures the stability of these species could also be examined. The changes in the gas phase of the IR cell were monitored with the help of a mass spectrometer. The surface species formed during the catalytic reactions were monitored by an IR spectrometer equipped with a diffuse reflectance infrared cell (DRIFTS).

The interaction of ethanol and the catalysts was studied by temperature programmed desorption (TPD). After the adsorption of ethanol at room temperature. the samples were heated from 300 K to 900 K in pure or wet (3% water) He. The desorbed products were analysed with the help of a mass spectrometer.

Novel results

1. The results of IR and TPD studies on the interaction of the ethanol and the catalysts

1.1. After the adsorption of ethanol at room temperature molecularly adsorbed ethanol and ethoxy groups were identified on the surface of the supported noble metals. Besides these species another form of adsorbed ethanol was found that coordinated to the surface OH species of the support with hydrogen bridge bond. According to our results the stability of these surface forms decreased with the increase of the temperature.

1.2. Surface reactions caused the occurrence of other species beside the ethanol and ethoxy groups, like adsorbed CO that was identified already at room temperature. It was found that the nature of the metal greatly influenced the formation of CO_a. The intensity of the CO_a band increased up to 473 K, but at higher temperatures it decreased either because of the desorption of CO or of the less amount of surface species that produced CO in surface reactions.

1.3. It was found that beside CO_a surface acetate also formed above 373 K that was present in the greatest amount at 573 K on the surface of all catalysts independent of the nature of the metal. We concluded that the acetate was located mainly on the support while the metal particles were the active sites for the adsorption of CO.

1.4. From the surface of Al_2O_3 the products desorbed in one stage. At the supported noble metals a second stage above 650 K was also observed. The product distribution at lower temperatures was nearly the same both in the case of the Al_2O_3 and the Al_2O_3 supported metals, although the main product on Al_2O_3 was ethylene while it was detected only in traces on the supported noble metals.

1.5. It was established that in the second desorption stage on supported noble metals the formation of carbon-dioxide and methane was due to the decomposition of the acetate species. It was found that these surface forms were most stable on Pt/Al_2O_3 among the Al_2O_3 supported noble metals.

1.6. The presence of potassium did not cause changes in the first desorption stage, but decreased the stability of surface acetate species.

2. The results of the catalytic tests

2.1. In the catalytic decomposition of ethanol over the supported noble metals ethylene was nearly the only product. In the reactions of ethanol and water in 1:3 and 1:9 molar ratios the selectivities of H_2 and CO_2 decreased in time while that of ethylene gradually increased. In our experiments the greatest change of the product selectivities was observed in the reactions over Pt/Al_2O_3. It was concluded that the changes in the product distribution in time were due to the inhibiting effect of the acetate species.

2.2. The results of the experiments carried out on Pt/Al_2O_3 proved that less carbon containing materials, including acetate species formed when less ethanol was fed into the reactor in unit of time.

2.3. It was found that in the reactions carried out on catalysts with different platinum loading under the same conditions similar amounts of surface acetate formed but their inhibiting effect weakened because of the increased number of the metallic sites.

2.4. According to our results increasing the reaction temperature from 723 to 823 and 923 K the formation of ethylene was suppressed and the rate of changes in the selectivities of H_2 and CO_2 decreased. This was attributed to the fact that at higher reaction temperatures the formation of acetate species was not favoured or rather the already existing acetate groups decomposed and could not further deactivate the catalyst.

2.5. According to the DRIFTS spectra registered in the course of the reactions the intensities of the acetate bands significantly increased in the first minutes while that of the adsorbed CO increased. This result supports the inhibiting effect of the acetate groups.

2.6. In the presence of potassium hydrogen, carbon-dioxide and methane formed with higher selectivity than in the case of pure Pt/Al_2O_3 and the forming rate of ethylene decreased. Our results showed that the alkali metal increased the rate of the reforming reactions over Al_2O_3 and decreased the stability of acetate species.

2.7. Increasing the amount of ZrO_2 in the Al_2O_3+ZrO_2 supported platinum the selectivity of hydrogen in the steady state increased compared to the pure Pt/Al_2O_3, while that of ethylene decreased in the same order. As the formation of acetate on the surface of ZrO_2 containing samples was not favoured, the amount of these species decreased in proportion with the ZrO_2 content and they could not further inhibit the formation of hydrogen.

List of publications

Publications related to the Ph.D. theses:

Impact Factors:

1. J. Raskó, **M. Dömök**, K. Baán, A Erdőhelyi
   FTIR and mass spectrometric study of the interaction of ethanol and ethanol–water with oxide-supported platinum catalysts
   Appl. Catal. A: General 299 (2006) 202
   IF: 2.630
   Citations: 6

2. A. Erdőhelyi, J. Raskó, T. Kecskés, M. Tóth, **M. Dömök,** K. Baán
   Hydrogen formation in ethanol reforming on supported noble metal catalysts
   Catal. Today 116 (2006) 367
   IF: 2.148
   Citations: 10

3. **M. Dömök**, M. Tóth, J. Raskó, A. Erdőhelyi
   Adsorption and reactions of ethanol and ethanol–water mixture on alumina-supported Pt catalysts
   Appl. Catal. B: Environmental 69 (2007) 262
   IF: 3.942
   Citations: 4

4. **M. Dömök**, T. Kecskés, K. Baán, K. Fodor, A. Erdőhelyi:
   Steam reforming of ethanol on K-doped Pt/Al_2O_3 catalysts
   Proceedings of the 8th Pannonian International Symposium on Catalysis, Szeged, 2006

5. **M. Dömök,** K. Baán, T. Kecskés, A. Erdőhelyi:
   Promoting mechanism of potassium in the reforming of ethanol on Pt/Al_2O_3 catalyst
   Submitted for publication, Catal. Letters

Summed impact factors: 8.720

Presentations and posters:

1. A. Erdőhelyi, J.Raskó, **M.Dömök**:
   Hydrogen Formation in the Reforming of Ethanol on Different Supported Pt Catalysts
   International Hydrogen Energy Congress & Exhibition, Istanbul, Turkey, 2005.

2. A. Erdőhelyi, J. Raskó, M. Tóth, **M. Dömök**:
   Hydrogen Formation in the Reforming of Ethanol on Different Supported Noble Metal Catalysts
   „Science and Art in Europe“ Catalysis: Nanotechnology with Past, Berlin, Germany, 2005.

3. A.Erdőhelyi, J. Raskó, T. Kecskés, M. Tóth, **M. Dömök**, K. Baán:
   Hydrogen Formation in the Reforming of Ethanol on Different Supported Noble Metal Catalysts
   2nd European Hydrogen Energy Conference, Zaragoza, Spain, 2005.

4. A. Erdőhelyi, J. Raskó, M. Tóth, **M. Dömök**:
   The Effect of Nano Structured Noble Metals on the Decomposition and on the Reforming of Ethanol
   Cost D 15 Evaluation Meeting, Maribor, Slovenia, 2005.

5. K. Fodor, J. Raskó, **M. Dömök**, M. Tóth, T. Kecskés, A. Erdőhelyi:
   The Reactivity of Surface Species Formed in the Ethanol + Water Reaction on Supported Pt Catalysts
   American Chemical Society 232nd National Meeting & Exposition Advances in Hydrogen Production, San Francisco, USA, 2006.

6. **M. Dömök**, M. Tóth, T. Kecskés, K. Fodor, J. Raskó, A. Erdőhelyi:
   Hydrogen Formation in the Ethanol + Water Reaction on Supported Noble Metal Catalysts
   First Budapest International Hydrogen Energy Forum, Budapest, 2006.

7. **Dömök M.**, Erdőhelyi A.:
   Etanol és etanol-víz reakciója Pt/Al_2O_3 katalizátoron
   Kémiai Előadói Napok, Szeged, 2006.

8. Erdőhelyi A., **Dömök M.**, Tóth M., Raskó J.:
   Az etanol reformálása hordozós nemesfém katalizátorokon
   Fizikai-kémiai és Szervetlen Kémiai Bizottság ülése, MTA SZAB Székház*,* 2006.

9. **M. Dömök**, T. Kecskés, K. Baán, K. Fodor, A. Erdőhelyi:
   Steam Reforming of Ethanol on K-doped Pt/Al_2O_3 Catalysts
   8th Pannonian International Symposium on Catalysis, Szeged, 2006.