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Ni/silica based bimetallic catalysts by solid state co-reduction of admixed metal oxides for acetic acid hydroconversion to ethanol

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Abstract Consecutive reduction of acetic acic (AA) to ethanol was investigated looking for advantageous bimetallic catalysts for the processing of VFAs (volatile fatty acids) that can be produced by thermochemical or biological biomass degradation. The reactant acid was hydrotreated in a flow-through reactor at 21 bar total pressure and 200-380 °C over fumed silica loaded with Ni main metal and Cu, Zn, Cd, Ga, In, Sn modifying metals. Varied these bimetallic composites prepared by solid state co-reduction of admixed metal oxide precursors the characteristic hydrodecarbonylation activity of nickel can be completely eliminated and high etanol yield can be attained selectively with exception of Zn and Cd. Low boiling point, high volatility of these two elements in Group IIb exclude formation of stable bimetallic composition. Indium and tin doping were found to be the most efficient. The lower reduction temperature of the In_2O_3 was found to be the advantage of novel In doping compared to well-known Sn-admission using oxide precursors for introduction of the second metal.

Keywords bimetallic catalysts, Ni/silica, indium or tin co-catalyst, acetic acid reduction

Introduction

Nowadays the research efforts of biomass conversion to chemicals and fuels have significantly increased, as the necessity for the utilization of renewable carbon sources has become more evident [1-6]. Degradation of biomass gives various platform molecules of high oxygen content. Upgrading to valuable products seems to be a challenge, where bimetallic catalysts can play important role. Abundant platform intermediates are the carboxylic acids (e.g. acetic acid) or various carboxylic group containing compounds [7]. Instead of the simple thermochemical routes (as pyrolysis), a novel way, a favorable biochemical destruction (on basis of the biogas process stopped after the rapid anaerobic acidogenic digestion stage) is suggested utilizing volatile fatty acids (VFAs) for production of biofuels and biochemicals [8-10]. Species of anaerobic bacteria, including members of the genus Clostridium, can convert directly sugar building units to AA from less expensive feeds, various wastes of food industry and agriculture:

$$C_6H_{12}O_6 \rightarrow 3\ CH_3COOH$$

The value of carboxylic acid reduction products depends on the catalytic selectivity. Short chain carboxylic acids can give either gaseous hydrocarbons or liquid phase alcohols, where latter is representing higher value. Complex bi- or tri-metallic heterogeneous catalysts seem to gain more and more significance in biomass upgrading technologies [7, 12].

From the 1960s, the unexpected properties of bimetallic catalysts inspired extensive investigations. Numerous studies were dealing with the effect of tin addition. Recently, advantageous influence of Sn-doping of alumina supported platinum catalyst was shown in acetic acid hydroconversion, too [12, 13]. However, use of non-precious metal catalysts seems to be a challenge initiated effortful research. Nowadays the adjacent indium (in the periodic table near the expansively studied tin) doping supported Ni-catalysts was found outstandingly efficient to suppress the total hydrogenation or hydrodecarbonylation of carboxylic acids resulting in selective consecutive reaction only to alcohols [14, 15]. The aim of present work was to apply non noble metal hydrogenating catalysts for selective reduction of carboxylic acids based on nickel main metal comparing impact of various modifying metals (Cu, Zn, Cd, Ga) formed from various oxides located around well-known tin and uncommon indium in the periodic table. Tin is a least rare element than the quite expensive indium. If tin could modify so favorably the non-precious main metals as indium in hydrodeoxygenation of platform molecules of biomass origin this study can show a significant practical impact, too.

Experimental

NiO/silica was obtained by incipient wetness impregnation on CAB-O-SIL M-5 (Cabot Corp.) fumed silica (BET: 200 m^2/g) using Ni(II)acetate, dried at 120 ^oC and calcined at 400 ^oC in air. Pt-catalyst was prepared on similar way with $H_2[PtCl_6]$ solution without calcination at 400 ^oC in air. The concentration of the main metals were 9 wt. % for Ni and 1 wt. % for Pt. Composite catalysts were prepared by adding various metal-oxides (10 wt. % CuO, ZnO, CdO, Ga_2O_3, In_2O_3, SnO) to the silica containing the main metal precursors and grinding the mixture in an agate mortar. The catalyst powders were compressed to tablets. The tablets were crushed and sieved to get the 0.63-1.00 mm size fraction used as catalyst in the catalytic experiments.

The reduction of the samples was studied using temperature-programmed H_2-reduction (H_2-TPR) using a flow-through quartz microreactor. Around 30 mg catalyst was pretreated in a flow of 30 ml min^{-1} nitrogen at 350 °C for 1 h. The pretreated sample was then cooled to room temperature in the same N_2 flow thereafter contacted with a 30 cm^3 min^{-1} flow of 9.7 % H_2/N_2 mixture. The reactor temperature was ramped up at a rate of 10 °C min^{-1} to 800 °C and maintained for 1 h at this temperature. The effluent gas was passed through a liquid nitrogen trap and a thermal conductivity detector (TCD). Data were recorded and processed by computer.

The XRD patterns of the catalysts were recorded by Philips PW 1810 diffractometer at elevated temperatures in hydrogen flow using a high temperature XRD cell (HT-XRD). The crystalline phases were identified using the ICDD database.

Nitrogen adsorption measurements were carried out at -196 °C using Quantochrome Autosorb 1C instrument. The specific surface area did not changed significantly after loading the metals.

All the catalysts were activated (reduced to form metallic active surface) in hydrogen flow in situ in the reactor for 1 h in order to generate active supported metal prior to the catalytic test. Routine reduction temperature was 450 °C except catalysts shown in Fig. 4 and 5. The catalytic hydrogenation of acetic acid was carried out in a high-pressure fixed bed flow-through reactor at 21 bar total pressure in the reaction temperature range of 200-380 °C. The inner diameter of the flow reactor was 16 mm, the maximum height of catalyst bed can be 120 mm. Dilution of the bed by inert material was not applied. Position of the thermocouple can be changed inside the catalyst bed in an inner sleeve. The WHSV of acetic acid was 1 h^{-1} and its partial pressure was 2.1 bar. Hydrogen feeding was half as big again as needed to full reduction of AA to ethane. The reaction was allowed to run for 1 h at each temperature to attain steady state and for second hour to collect reactor effluent for analysis. Ageing of the catalysts was not detected, consequently whole temperature profile was measured using the same load of catalyst The reactor effluent was cooled down and the liquid and gas phase products were separated. The liquid was analyzed using a gas chromatograph (GC, Shimadzu 2010) equipped with flame ionization detector and a Restek Rt-U-Bond capillary column. The gas was analyzed by an on-line GC (HP 5890) equipped with thermal conductivity detector and Carboxen 1006 PLOT capillary column. The activity and the selectivity of the catalysts were characterized by product distributions represented by stacked area graphs. In this representation, the distance between two neighboring curves gives the yield of the specified product in mol percent.

Results and Discussion

Over monometallic hydrogenating catalysts (e.g. nickel or noble metal platinum as shown in Fig. 1A and 1C) hydrogenolysis can be a characteristic reaction attacking C-C bonds. In such cases, hydrodecarbonylation may be the main reaction route hardly producing alcohols in the carboxylic acid hydroconversion. However, appearance of indium atoms on the active metal surface (Ni [14] or Pt [15] supported on alumina, and on silica shown in Fig. 1B and 1D) results in a drastic mechanism change produced alcohols at high yield selectively as demonstrated in Fig. 1. Nickel and indium containing bimetallic catalysts can be easily formed with admixed In_2O_3 by the solid state co-reduction at 450 °C. The appearance of Ni_2In phases seemed to be responsible for the significant enhancement of the desired, high hydrogenation activity and alcohol selectivity in comparison with the corresponding properties of the monometallic forms. Indium co-catalyst applied with a noble metal, platinum has been found also extremely efficient for the selective reduction of acetic acid to ethanol (see Fig. 1D and [14]). Question of this study is what about the efficiency of adjacent tin compared to indium when this modifying metal can be also admitted to nickel by co-reduction of SnO precursor similarly to the simple In-doping technique.

Formation of bimetallic active phases in the studied catalysts is demonstrated in Fig. 2 using H_2-TPR technique and shown by HT-XRD method in Fig. 3. NiO loaded on fumed silica can be completely reduced in hydrogen flow at quite low temperature (see Fig. 2a) contrary to In_2O_3 where three reduction steps can be distinguished in a higher and wider temperature range (Fig. 2b). Low temperature formation of nickel can activate interaction of molecular hydrogen with indium(III)oxide resulting in complex TPR peaks between signals of monometallic forms (Fig. 2c). The situation is qualitatively quite similar admixing SnO or Ga_2O_3 however these oxides needed higher reduction temperatures resulting in the multiple TPR peaks of bimetallic samples at significantly higher temperature (Fig. 2d).

HT-XRD technique was proven really powerful in earlier studies to show interactions of indium modifier with hydrogenating main metals (e.g. nickel or copper [14, 16-17]) parallel to dynamic methods as H_2-TPR. NiO (●) formed during calcination of impregnated Ni-acetate can be fully reduced to nickel bellow 450 ^{o}C (the routine pretreatment temperature prior to catalytic investigations) (see in Fig. 3, a and a1 diffractograms). HT-XRD measurements were carried out in H_2 flow by increasing linearly the temperature to selected values then keeping constant for 30 minutes. Half hour was found to be sufficient for total reduction of investigated samples on a characteristic temperature. Using CAB-O-SIL M-5 fumed silica support on the average nickel particles diameters of 17 nm were determined from the XRD patterns using the Scherrer equation. Shape of these particles was spheric and a quite wide particle size distribution was observed in some TEM images /not shown/.

In presence of indium one of the Ni-In alloys, specified as Ni_2In intermetallic compound can be formed [14] (using Ni:In=2 atomic ratio presence of pure Ni or In phases cannot be detected). Using SnO modifying agent quite different picture can be observed (see in Fig. 3). Contrary to indium tin oxide can be reduced only between 450 and 550 °C, where SnO and NiO equally cannot be see in the diffractogram (see in Fig. 3 b2).. However there are no any new lines which can be assigned to one of the six existing intermetallic compounds of tin and nickel. Only nickel diffraction lines can be detected but with much lower intensity than prior to SnO reduction reflecting decreased transmittance. Tin has similarly low melting point as indium mostly below the 450 °C routinely applied pretreatment temperature. Cooling done the reduced NiSn/SiO_2 sample from 550 °C to room temperature tin diffraction lines can be well observed reflecting only the presence of pure tin phase (see in Fig. 3 b3). Interestingly nickel with indium and tin can form numerous intermetallic compounds with the same composition only with one exception: tin cannot form Ni_2Sn with atomic ratio two. Contrary appearance Ni_2In was characteristic for the most efficient In-doped catalysts. However, from catalytic point of view it can be satisfactory, if only the outer surface or layer of the main metal contains Sn atoms forming the desired phase composition. Most of the tin atoms can be dispersed standing apart Ni particles causing only lower transmittance for X-ray.

Further discrepancies were also found with other investigated oxides during the solid state co-reduction: Ga_2O_3 can be only reduced at high temperature, above 600 °C, however some kind of NiGa intermetallic compounds can be detected by HT-XRD /not shown/. Zinc and mainly cadmium oxides can be reduced easily at low temperature however the low boiling point and high volatility of these elements exclude formation of stable bimetallic composition. Ultimate problem is the impoverishment of the support consequential from the high volatility of these metals. Thus introduction of Cd and Zn precursors cannot result in any influence for Ni/silica reactivity at routine reaction temperatures.

Although tin doping can reach only the upper layers of nickel particles the catalytic influence is perfectly accordant with indium admission (compare Fig. 4A and 1A, B). More active catalyst seems to be produced with tin than indium (compare the conversion curves in Fig. 4A /dashed line is obtained on Ni_2In/silica catalyst/). To eliminate the undesired hydrodecarbonylation reaction route enough tin atom can be produced from the oxide phase above 400 ^{o}C co-reduction temperature. Applying only one tenth of routine modifying metal oxide content, the side reaction can be completely eliminated however the activity for the selective consecutive reduction of acetic acid to ethanol is quite low similarly to copper or gallium admission (Fig. 5). Cu and Ga can eliminate the hydrodecarbonylation side reaction, but give low activity level in ethanol production. Using SnO as the precursor of second metal for efficient bimetallic catalyst co-reduction should take place at much higher pretreatment temperature than applied in routine procedure earlier. However the choice of the suitable catalysts is expanded and a further improvement can be attained by optimization of the preparation technique.

Conclusions

Modification of supported Ni particles with In, Sn, Cu or Ga by a novel co-reduction process of the oxide forms effectively directs hydrodeoxygenation of carboxylic acids to alcohol production in consecutive reduction steps and the presence of these metals hinders the hydrodecarbonylation, the chain shortening of bioacids. This study reveals that In and Sn doped Ni/silica catalysts are highly efficient bimetallic composites. The needed lower reduction temperature of the In_2O_3 containing precursor mixture and the potential of well-defined Ni_2In active phase formation are main advantages of use indium doped bimetallic catalysts for selective alcohol production from carboxylic acids. Contrary tin promotes formation of more active bimetallic catalyst using cheaper precursor (SnO).

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References

1 G.W. Huber, S. Iborra, A. Corma, Chem. Rev. **106**, 4044 (2006)

2 J.N. Cheda, G.W. Huber, J.A. Dumesic, Angew. Chem. Int. Ed. **46,** 7164 (2007)

3 M. Stöcker, Angew. Chem. Int. Ed. **47,** 9200 (2008)

4 D. Kubicka, Collect. Czech. Chem. Commun. **73,** 1015 (2008)

5 M. F. Demirbas, Appl. Energy **86,** S151 (2009)

6 S.N. Naik, V.V. Goud, P.K.Rout, A.K. Dalai, Renew. Sustain. Energy Rew. **14,** 578 (2010)

7 J. C. Serrano-Ruiz, R. Luque, A. Sepúlveda-Escribano, Chem. Soc. Rev. **40,** 5266 (2011)

8 M.T. Holtzapple, C.B. Granda, Appl. Biochem. Biotech. **156,** 525 (2009)

9 H.N. Chang, N.J. Kim, J. Kang, C. M. Jeong, Biotechn. Bioproc. Eng. **15,** 1 (2010)

10 V. Pham, M.T. Holtzapple, M.El-Halwagi, J. Ind. Microbiol. Biotech. **37,** 1157 (2010)

11 D.M. Alonso, S.G. Wettstein, J. Dumesic, Chem. Soc. Rev. **41** (2012) 8075.

12. R. Alcala, J.W. Shabaker, G:W. Huber, M.A. Sanchez-Castillo, J. Dumesic, J. Phys. Chem. **109** (2005) 2074.

13. K. Zhang, H. Zhang, H. Ma, W. Ying, D. Fang, Catal. Lett. **144** (2014) 691.

14. Gy. Onyestyák, Sz. Harnos, D. Kalló, Catal. Comm. **16,** 184 (2011)

15. Gy. Onyestyák, Cat. Com., **38**, 50(2013)

16. Gy. Onyestyák, Sz. Harnos, Sz. Klebert, M. Stolcova, A. Kaszonyi, D. Kalló, Appl. Catal. **A 464-465**, 313 (2013)

17. Gy. Onyestyák, Sz. Harnos, D. Kalló, Catal. Comm. **26,** 19 (2012)

Figure captions

Figure 1. Stacked area graphs of product distribution of AA hydroconversion as a function of the reaction temperature at 21 bar and 1 $g_{AA}\cdot/g_{cat.}\cdot h$ WHSV over Ni/silica (A), Pt/silica (C) catalysts and their In-doped forms (B, D).

Figure 2. H_2-TPR fingerprints demonstrating the reduction of NiO (a), In_2O_3 (b), NiO + In_2O_3 (c), and NiO + SnO (d) silica loaded catalyst precursors.

Figure 3. HT-XRD patterns of the indium free NiO/silica (a, a1) and NiO/silica + 10 wt% In_2O_3 mixture (b, b1, b2, b3) catalyst precursors, treated in H_2 flow for 30 min at different temperatures.

Figure 4. Stacked area graphs of product distributions obtained in the hydroconversion of AA over NiO/silica + 10 wt% SnO mixture catalysts after co-reduction at 550 ^oC (A), 500 ^oC (B), 400 ^oC (C), and NiO/silica + 1 wt% SnO mixture reduced at 550 ^oC (D) depending on the reaction temperature characteristic for SnNi/silica catalyst. The total pressure was 21 bar and the WHSV of AA was 1 h^{-1}. (The dashed line in Fig. 4A is the conversion curve from Fig.1B characteristic for InNi/silica catalyst.)

Figure 5. Stacked area graphs of product distributions obtained in the hydroconversion of AA over NiO/silica + 10 wt% Ga_2O_3 mixture catalysts after co-reduction at 550 ^oC (A) and NiO/silica + 10 wt% CuO mixture reduced at 450 ^oC (B) depending on the reaction temperature. The total pressure was 21 bar and the WHSV of AA was 1 h^{-1}.

Figure 1.

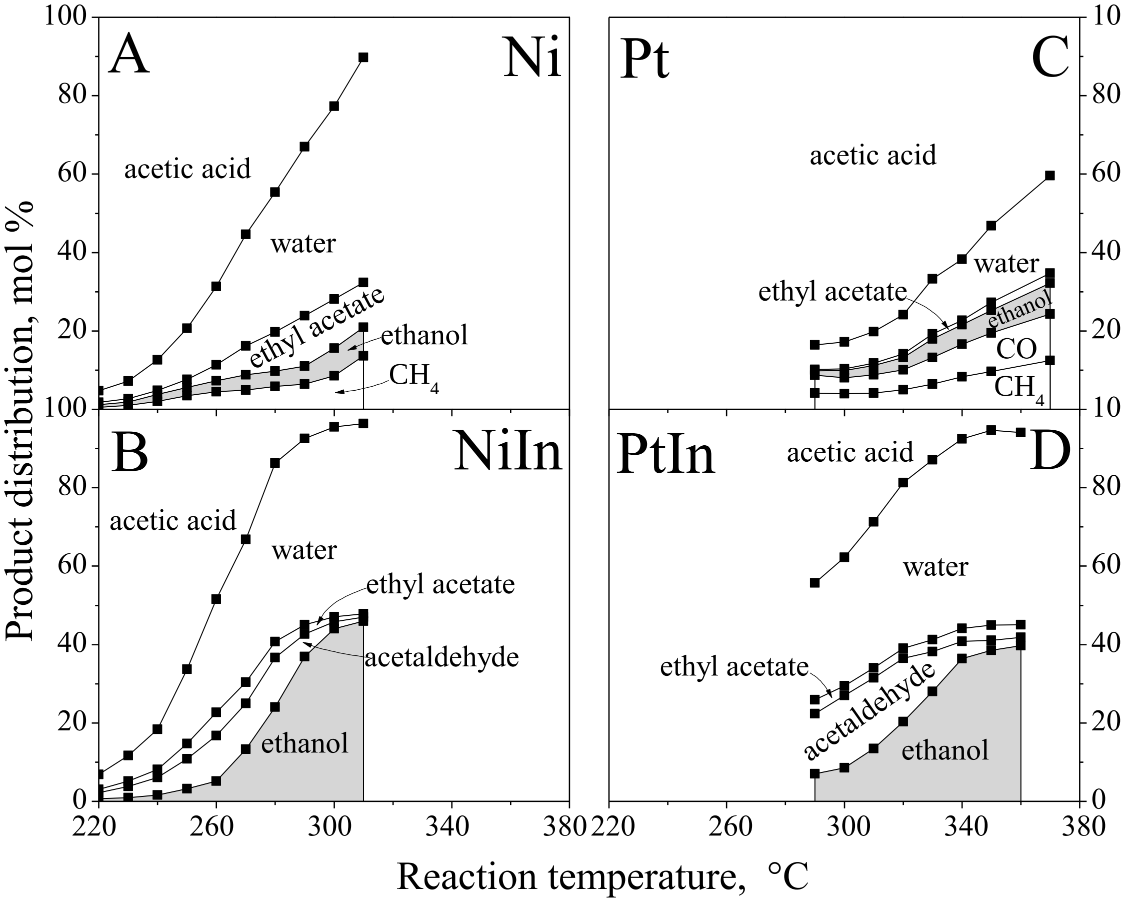


Figure 2.

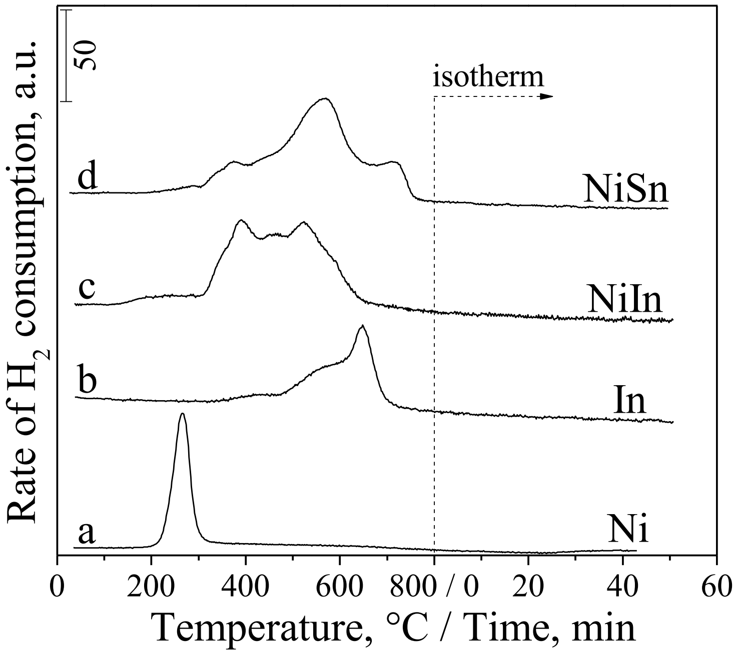


Figure 3.

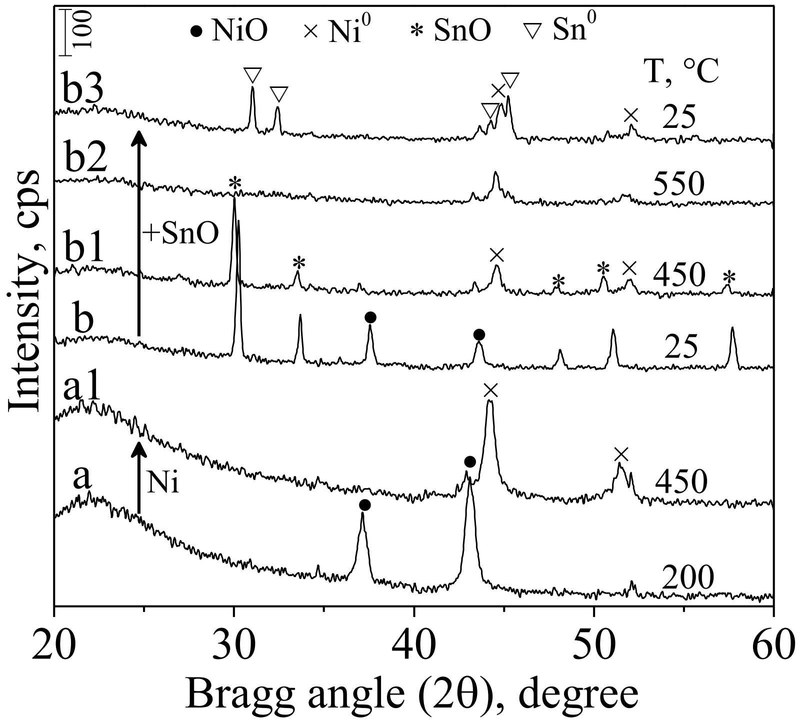


Figure 4.

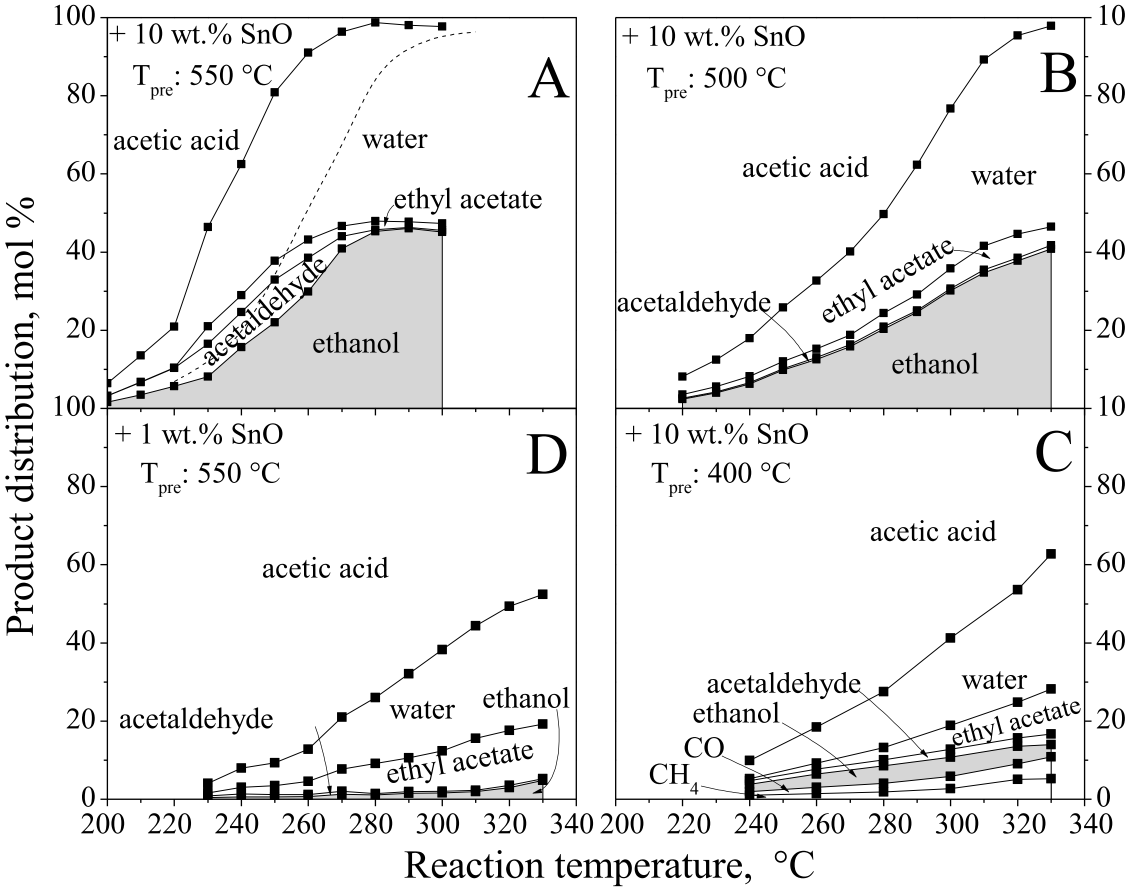
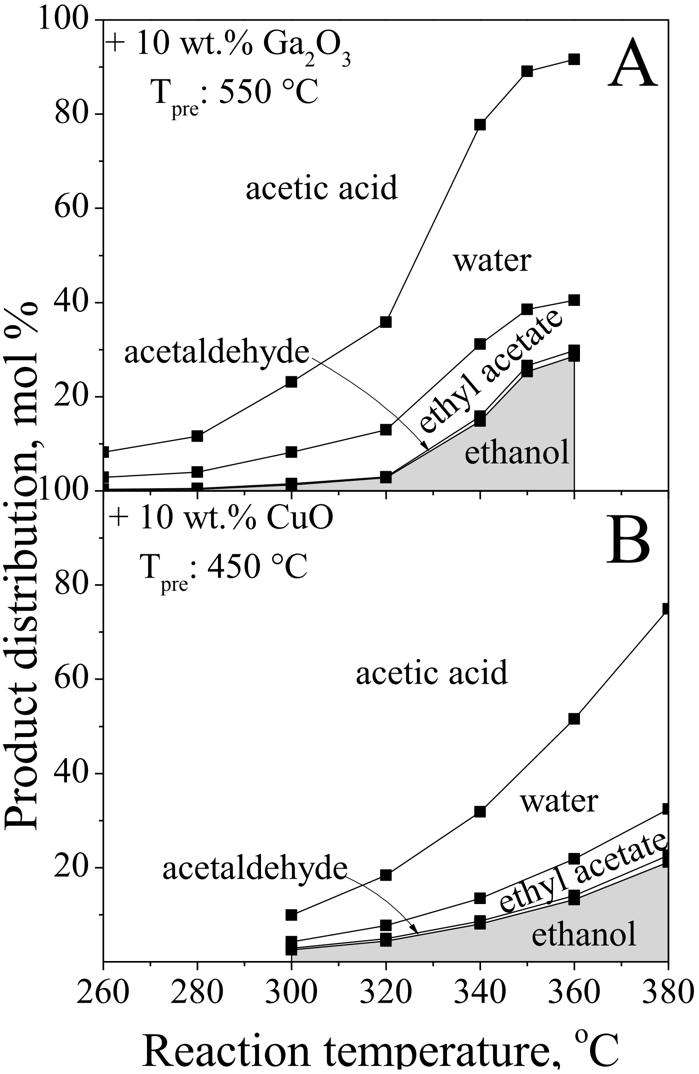


Figure 5.


A
+ 10 wt.% Ga_2O_3
T_{pre}: 550 °C
acetic acid
water
acetaldehyde
ethyl acetate
ethanol
B
+ 10 wt.% CuO
T_{pre}: 450 °C
acetic acid
water
acetaldehyde
ethyl acetate
ethanol
Product distribution, mol %
100
80
60
40
20
0
Reaction temperature, °C
260
280
300
320
340
360
380