

A study of the selective catalytic hydroconversion of biomass-derived pyrolysis or fermentation liquids using propylamine and acetic acid as model reactants

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Abstract

Silica-supported P or In modified Ni catalysts were active in the hydrodenitrogenation (HDN) and hydrodeoxygenation (HDO) of reactant propylamine (PA) and acetic acid (AA), respectively, which reactants were selected to model platform molecules of biomass origin. The undesired C-C hydrogenolysis activity of supported Ni catalyst, resulting in low value gaseous products, could be reined by the modification, generating silica-supported Ni₂P and Ni₂In active phases.

Keywords: bio-oil conversion, acetic acid HDO, propylamine HDN, Ni₂In/SiO₂, Ni₂P/SiO₂

1. Introduction

The lignocellulosic materials, being mainly carbohydrate polymers, contain O as heteroatom [1], whereas the animal by-products, rich in proteins, which are polymers of amino acids, contain N-heteroatoms [2]. The processing of these kinds of biomasses to higher value fuel or chemicals involves combinations of mechanical, thermal, chemical, and biological operations to destruct the polymeric chains. The conversion to organic liquid of higher energy density requires partial or full removal of heteroatoms from the biomaterial. The product obtained in the primary destructive treatment has a lower average molecular weight and it can have already reduced heteroatom content. For instance, the product derived from lignocellulosic materials by either pyrolytic or common hydrolysis and fermentation treatment contains lower carboxylic acids [3-5]. The pyro-oil obtained from animal by-products contains only about 5 wt % organic oxygen and about 10 wt % organic nitrogen in N-heterocycles, nitriles, amides or amines [2,6,7]. The average molecular weight of the components of latter bio-oil is near to 150 [7,8].

The full HDO of lower C₂-C₄ carboxylic acids gives lower alkanes, which are relatively low value products compared to lower alcohols, which are products of partial HDO of the acids. A further advantage of the partial acid HDO is that it requires less costly hydrogen than the full HDO, moreover it gives lower amount of water, which is a worthless by-product of the HDO reaction. The selective heterogeneous catalytic HDO of lower carboxylic acids to alcohols needs

catalyst that has high activity in the hydrogenolysis of the C-O bonds and in the further hydrogenation of the obtained aldehyde intermediate, but relatively low activity in the hydrogenolysis of C-C bonds and in the dehydration of monohydric alcohols. In the present study the AA that is common product of biological acidogenic and acetogenic carbohydrate degradation was selected as model compound to study the acid conversion to alcohol by selective partial catalytic HDO.

The pyrolysis of animal by-products provides a pyro-oil having a carbon to nitrogen atomic ratio of about 9. The combustion of organic N-compounds involves environmental hazard due to emission of flue gas, containing nitric oxides. The generation of fuel from such pyro-oil, therefore, requires full denitrogenation, preferably without significant cracking of the hydrocarbon moiety of the molecules. In principle, the selective total HDN of the oil provides hydrocarbons and ammonia that can be used to obtain fuel and N-fertilizer, respectively. It is well known that the HDN of both nitriles and N-heterocycles proceeds through alkylamine intermediate [9]. Therefore, a simple amine, the PA was selected to study the processes of the catalytic HDN of nitrogen-rich pyro-oil.

For heteroatom removal from feedstock of fossil origin the petrochemical industry uses mostly sulfided Co,Mo/ γ -alumina and Ni,Mo/ γ -alumina catalysts [10,11]. However, bio-oils contain very different O- and N-compounds than petrochemical feeds. Moreover, the O and N content of the oils are much higher than those of the petrochemical feeds. The sulfide catalysts are not favorable for processing bio-oils because these reactants, in contrast to those of fossil origin, are virtually free of sulfur [12]. Precious metal and Ni catalysts are known to have high hydrogenation activity also in absence of sulfur, however, this property is paralleled by hydrodecarbonylation and/or cracking activity that is not desired if we want to get liquid with high yield.

Recent studies showed that modification of supported Ni/silica catalysts by In or P generates surface Ni₂In or Ni₂P phases [9,13]. Present work shows that introduction of In or P suppresses the undesired side reactions proceeding over the Ni/silica catalyst. Both Ni₂P and Ni₂In/silica catalysts are active and selective in the total HDN of amines to hydrocarbon and ammonia, whereas only the Ni₂In catalyst has enhanced activity and selectivity in the hydrogenation of carboxylic acids to alcohols.

2. Experimental

A microporous silica gel (Sylobead B127, Grace Davison; diameter of the pores: smaller than about 2 nm; specific surface area: 563 m²/g) was applied as catalyst support. The silica-supported nickel phosphide catalyst, Ni₂P/silica, was prepared by incipient wetness impregnation of the support by a solution of nickel phosphide precursor compounds, followed by drying, calcination

and controlled reduction according to ref. [9]. First an aqueous impregnating solution was prepared by adding chemicals $(\text{NH}_4)_2\text{HPO}_4$ (Fluka, +99%) and $\text{Ni}(\text{NO}_3)_2$ (Merck, +99%) to water in an amount to set their concentrations to 4.6 and 2.3 mol/dm³, respectively. Upon adding drops of concentrated nitric acid to the aqueous mixture a crystal clear green solution was obtained. Then, the dried silica was contacted with the impregnation solution by adding 0.5 cm³ of solution to each gram of the silica. The impregnated silica was dried at 120 °C for 6 h and calcined then at 400°C for 4 h. The calcined sample was used as precursor of the Ni₂P/silica catalyst. The supported Ni₂P was obtained by heating the precursor up to 650 °C at a heating rate of 2°C min⁻¹ in flowing H₂ (100 cm³ min⁻¹) and by continuing the H₂ treatment at this temperature for 3 h. Finally, the sample was cooled to room temperature in He flow (20 cm³ min⁻¹) and contacted with a flow of 1.0 % O₂/He (50 cm³ min⁻¹) at room temperature for 4 h to generate a phosphate-like surface layer over the pyrophoric Ni₂P particles to prevent the bulk of the particles from becoming oxidized when exposed to air [14].

The silica supported Ni catalyst, Ni/SiO₂, was prepared similarly as the Ni₂P/silica catalyst. The only difference was that the impregnating solution did not contain $(\text{NH}_4)_2\text{HPO}_4$. The impregnated silica was dried at 120°C for 6 h, calcined at 450°C for 4 h to get the oxide precursor of the Ni-catalyst. The catalyst was obtained by treating the precursor in H₂ flow at 500 °C for 3 h.

The Ni₂In/silica catalyst was prepared from the Ni/silica catalyst precursor. The incipient wetness impregnation method was applied to introduce indium in the Ni-containing preparation. Each gram of the Ni/silica precursor was impregnated with 0.5 cm³ In(NO₃)₃ solution, having In concentration of 2.3 mol/dm³, i. e., the Ni to In atomic ratio of the preparation corresponded to 2 to 1. The sample was dried, calcined to get the oxide precursor of the Ni₂In/silica catalyst. The catalyst was obtained by reduction of the precursor in H₂ flow at 450 °C for 1h. The chemical composition and the specific surface area of the catalyst samples are summarized in Table 1.

X-ray powder diffraction (XRD) examinations were carried out using a Philips PW 1810/3710 diffractometer equipped with an XRD cell that allowed in situ reduction of the catalyst precursors with hydrogen at selected temperatures. After H₂ treatments the XRD patterns were recorded at room temperature applying monochromatized CuKα ($\lambda=0.15418$ nm) radiation (40 kV, 35 mA) and a proportional counter.

The morphology of the samples was characterized by electron micrograph (TEM micrograph), moreover, by SSA and pore size distribution (PSD). The SSA and PSD were derived from the low-temperature (-196 °C) N₂ adsorption isotherms of the samples. The TEM pictures were obtained by a FEI Morgagni 268D type microscope, whereas the adsorption isotherms were

determined by Quantachrome NOVA Automated Gas Sorption Instrument. Before adsorption measurements the samples were evacuated at 350°C for 1 h.

The HDO and HDN reactions of acetic acid (AA) and propylamine (PA) model compounds, respectively, were studied over silica-supported catalysts using high-pressure flow-through microreactor. The HDO of AA was carried out at 1.0 h⁻¹ WHSV and 21 bar pressure, whereas the HDN of PA was carried out at 1.0 h⁻¹ WHSV and 30 bar pressure. The partial pressures of PA and AA were 2.7 and 2.1 bar, respectively. Each catalyst samples were tested for about two weeks in order to measure the temperature (200-400 °C) and space time (0.25-2.0 h×g_{catalyst}/g_{reactant}) dependence of the reactions, while several measurements at a given set of parameters were repeated in order to check the stability of the catalysts. All the catalysts showed stable activity during this time period. No coke deposition was perceptible to the eye on the catalysts removed from the reactor. The carbon content of the feed and the products was virtually equal.

The composition of the reactor effluent was analyzed by on-line gas chromatograph (Shimadzu GC-2010 Plus) equipped with an Equity-1 fused silica capillary column (Supelco) and a flame ionization detector.

3. Results and Discussion

The XRD patterns of the catalysts, obtained by in situ reduction of the catalyst precursors are shown in Fig. 1. The Ni/SiO₂ catalyst presents weak reflection lines at 44.5° and 52.0° characteristic of Ni metal particles. The reflections at 2θ degrees of 28.9 and 43.2° prove the presence of the Ni₂In phase in the Ni₂In/SiO₂ catalyst [13]. Note that neither In nor Ni phase was detectable. The 40.6, 44.6, 47.3, 54.2, and 54.9° XRD reflections stem from the crystalline Ni₂P phase of the Ni₂P/SiO₂ catalyst [9].

The average particle size of the active Ni, Ni₂In, and Ni₂P phases on the silica support was determined from the XRD data by the Scherrer equation (Table 1). The TEM pictures of Fig. 2 allowed us to draw conclusions also about the size distribution of the active particles (Table 1). The SSA of the silica support and that of the Ni/SiO₂ catalyst was nearly the same. In contrast, the Ni₂P/SiO₂ and Ni₂In/SiO₂ catalysts were of significantly lower SSA than the support (Table 1). The N₂ adsorption isotherm of the samples is of type I (Fig. 2D). Adsorption hysteresis is essentially absent, suggesting that the materials are purely microporous. The micropore structure was characterized by PSD curves, determined from the isotherms using the MP method (Fig. 2). The pores of about 1 nm diameter represent the highest pore volume in the support as well as in the catalysts. Therefore, the crystallites of active phase, having critical dimension commensurable with the pore sizes or much larger than those are. The smaller particles can block some of the micropores of the Ni₂In/SiO₂ catalyst from N₂ adsorption and might be responsible for the lower

surface area of the catalyst than that of the support (Table 1). The particles of the Ni₂P/SiO₂ are 20-60 nm size, i. e., they are much larger than the pore sizes. The TEM picture of the Ni₂P/SiO₂ catalyst (Fig. 2A) does not substantiate small particles that could block the micropores of the support. Nevertheless, the surface area of latter catalyst is much smaller than that of the support. Notice that the sample contains about three times as much phosphorus, than that, corresponding to the Ni₂P stoichiometry. Some pores of the silica must be blocked by surface bound PO_x species.

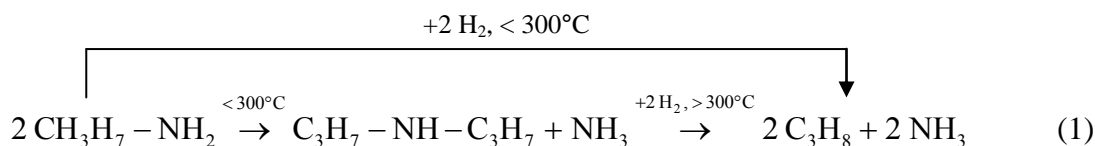
The Ni/silica catalyst shows both HDO and HDN activities (Figs. 3A,B). The AA conversion increased with the increasing reaction temperature (Fig. 3A). A fraction of the ethanol, formed as hydrogenation product, gave ester by reacting with the non-converted acid. The yield of ethanol paralleled the increase of the conversion, whereas the ethyl acetate yield changed in opposite direction suggesting that ester is a secondary source of ethanol. The formation of methane in significant amount indicates that the Ni-catalyst has high hydrogenolysis/hydrogenation activity. A possible route of methane formation is the decarboxylation of the AA reactant or hydrodecarbonylation the acetaldehyde intermediate of the reaction [15]. If CO₂ and CO was formed at all they must have been readily converted to methane over the active Ni/silica hydrogenation catalyst.

Below about 300 °C the main products of PA hydroconversion over the Ni/silica catalyst were dipropylamine (DPA) and ammonia (Fig. 3B). These are products of PA disproportionation generally observed on supported Ni catalysts [16]. Minor amounts of tripropylamine (TPA) and propane were also obtained. Full hydrodenitrogenation was achieved above 350 °C only. However, besides the desired products of propane and ammonia, methane and ethane was also formed in significant amount. The appearance of latter products shows that the Ni/silica catalyst is active in the C-C bond hydrogenolysis.

In the HDO reaction of AA the Ni₂P/silica catalyst showed similar catalytic properties than the Ni/silica catalyst, except that not only methane but methane and CO in equal amounts were formed (cf. Figs. 3A and 3C). These results indicate that phosphorus modification did not decrease the hydrogenation activity of Ni to an extent to prevent the attack of the C-C bond between the methyl and carbonyl group in the AA or the acetaldehyde molecules. The HCOOH or HCOH primary products of the C-C bond hydrogenolysis must have been rapidly decomposed to give CO₂ and CO. Methanization of latter products did not proceed, explaining the equivalency of methane to carbon monoxide in the product mixture.

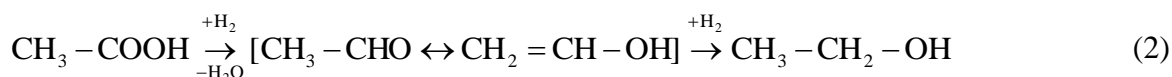
In the HDN of PA the Ni₂P/silica catalyst was less active than the Ni/silica below about 300 °C (cf. Figs. 3B and 3D). The main reaction was PA disproportionation to DPA and ammonia. The propane yield was minor. At temperatures above about 300 °C the hydrodenitrogenation of the

DPA intermediate speeded up and lower steady-state DPA intermediate concentrations were established (Eq.1).



At a reaction temperature of about 400 °C the PA conversion was near to 90 %, mainly ammonia and propane was formed in about equal molar amounts. It is to be noted that methane and ethane could not be detected in the reactor effluent. The Ni₂In/silica catalyst showed nearly the same catalytic properties in the HDN of PA as the Ni₂P/silica catalyst (cf. Figs. 3D and 3F), except that it showed higher activity below about 300 °C. Unlike to the Ni/silica catalyst neither Ni₂P/silica, nor Ni₂In/silica shows activity in the hydrogenolysis of aliphatic C-C bonds.

The AA hydroconversion, parallel with the ethanol yield, increases more rapidly with the temperature over the Ni₂In/silica than over the Ni/silica catalyst (cf. Figs. 3A and 3E). This infers that the In modification increased the activation energy of the AA conversion. Already at about 350 °C near to full conversion was obtained. The only products were practically ethanol and water. Minor amounts of acetaldehyde and ethyl acetate were also formed. In contrast, acetaldehyde and ethyl acetate were the main products at low conversions below about 330 °C. Former is the intermediate of alcohol formation whereas latter is a side product coming from the reaction of the product alcohol and the non-reacted acid [15]. At higher temperatures both were hydrogenated to alcohol. It is to be noticed that no methane, CO or CO₂ were formed. The main reaction proceeds through acetaldehyde/vinyl alcohol tautomers (Eq.2).



Curves of AA and PA hydroconversion over Ni₂In/silica and Ni₂P/silica catalysts were compared as a function of space time (Fig. 4). The yields of acetaldehyde, ethyl acetate (Fig. 4A), and DPA (Fig. 4B) passed through maximum indicating that these products were intermediates of a consecutive hydroconversion process.

The Ni₂In/silica catalyst exhibited high selectivity in the HDO of AA to ethanol and nearly the same high selectivity in the HDN of PA to propane and ammonia. In contrast, the Ni₂P/silica catalyst was very selective in the PA HDN reaction but had undesired hydrodecarbonylation activity in the HDO of AA. The suppressed C-C hydrogenolysis and CO hydrogenation of the modified catalysts could be due to the insertion of P or In atoms between the surface Ni atoms decreasing the electron density of the surface and, thereby rendering reactant and C-C, C-O, and

H-H bond activation more difficult than over pure Ni surfaces. The In modifier does not only rein the hydrogenation activity of Ni, but direct the HDO reaction from the hydrogenolysis/hydrogenation to the hydrogenation/dehydration pathway.

4. Conclusions

The present paper shows that a highly active Ni/silica hydrogenation catalyst is not favored for HDO and HDN reactions because they initiate undesired hydrogenolysis/hydrogenation side reactions giving alkanes, having lower carbon number than the reactant aliphatic carboxylic acid or amine. However, the Ni alloying with In or P gives Ni₂In and Ni₂P phases on the silica support that are active and selective in the partial or full removal of heteroatoms in a hydroconversion process without breaking C-C bonds.

The results obtained for the catalytic hydroconversion of AA suggest that it is possible to obtain high yields of lower alcohols from biocarboxylic acids by selective catalytic partial hydrodeoxygenation under relatively mild reaction conditions using Ni₂In/silica catalysts. It was also shown that PA can be selectively hydroconverted to propane and ammonia over both Ni₂P/silica and Ni₂In/silica catalysts under relatively mild reaction conditions. The presented results suggest that N-containing organic compounds, such as pyro-oil from animal by-products, can be hydroconverted to valuable hydrocarbon mixture and ammonia.

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Figure captions

Fig. 1. X-ray diffractograms of catalyst (a) Ni₂P/SiO₂, (b) Ni/SiO₂, and (c) Ni₂In/SiO₂. The samples were pretreated in situ in H₂ flow using a high-temperature XRD cell at the indicated temperature prior recording the XRD patterns at room temperature.

Fig. 2. TEM micrographs of (A) Ni₂P/SiO₂, (B) Ni/SiO₂, and (C) Ni₂In/SiO₂ catalysts. Segment D shows the N₂ adsorption isotherms of the support and the In and P-modified supported Ni catalysts at -196 °C, whereas segment E shows the PSD of micropores determined from the isotherms using the MP method.

Fig. 3. The hydroconversion of (A,C,E) AA and (B,D,F) PA over (A, B) Ni/silica, (C, D) Ni₂P/silica, and (E,F) Ni₂In/silica catalysts as function of temperature. The HDO of AA was carried out at 1.0 h⁻¹ WHSV and 21 bar pressure, whereas the HDN of PA was carried out at 1.0 h⁻¹ WHSV and 30 bar pressure. The partial pressures of PA and AA were 2.7 and 2.1 bar, respectively.

Fig. 4. The hydroconversion of (A) AA over Ni₂In/silica and (B) PA over Ni₂P/silica catalyst as a function of space time. The HDO of AA was carried out at 21 bar pressure and 350 °C. The HDN of PA was studied at 375 °C at a total pressure of 30 bar. The partial pressures of PA and AA were 2.7 and 2.1 bar, respectively.

Table 1. Characterization of the catalysts

Sample	SSA, ^a m ² g ⁻¹	ΣV_p , ^b cm ³ g ⁻¹	Ni, wt%	P, wt%	In, wt%	D, ^c nm
SiO ₂	563	0.41				
Ni/SiO ₂	558	-	6.76	-	-	2-10 (11)
Ni ₂ P/SiO ₂	268	0.15	5.04	4.11	-	20-60 (49)
Ni ₂ In/SiO ₂	299	0.19	6.76	-	8.3	2-10 (10)

^a SSA= specific surface area, determined by the Brunauer-Emmett-Teller (BET) method.

^b ΣV_p = total pore volume. The volume of liquid N₂, equivalent with the saturation N₂ adsorption capacity, was assumed to be equal with ΣV_p .

^c Diameter of particles of the active phase observed in the TEM micrograph (particle size determined from XRD by Scherrer equation is given in parentheses).

Fig. 1.

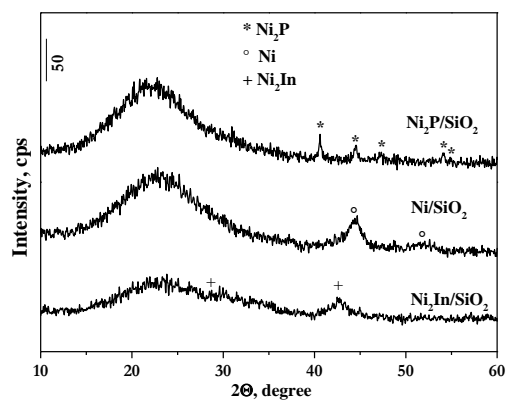


Fig. 2.

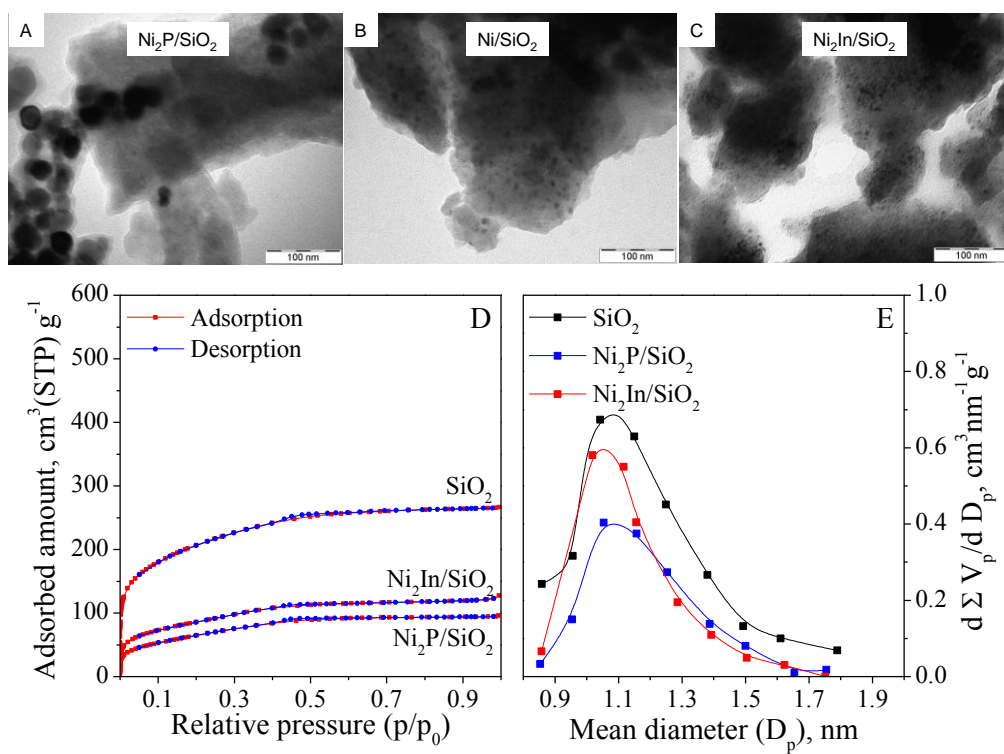


Fig. 3.

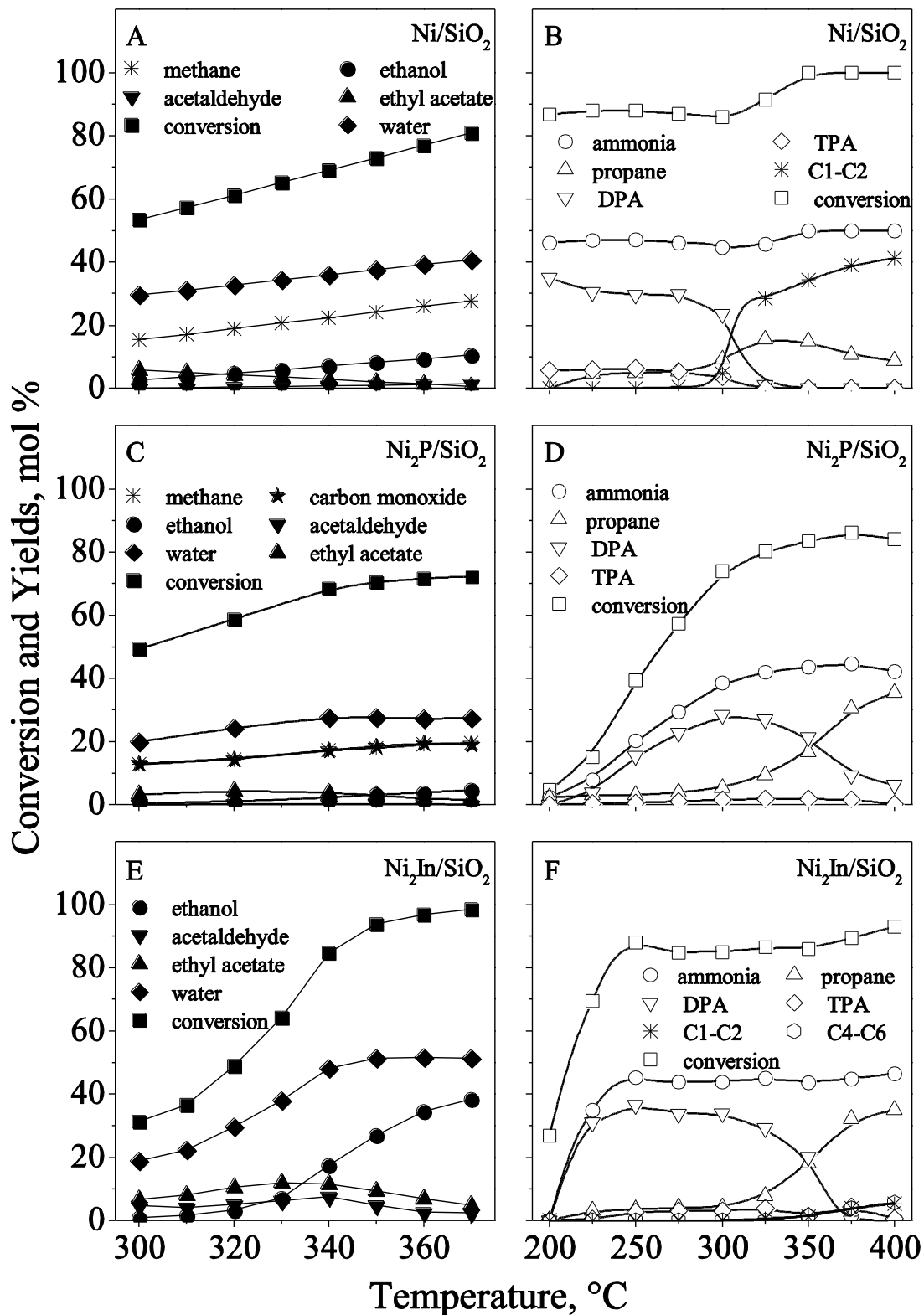


Fig. 4.

