

# Extraordinary Activity of Nanodispersed Bimetallic NiFe Phosphide Catalysts for the Conversion of a Biomass Model Compound

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## ABSTRACT

The present work deals with the development of new catalysts, transition metal phosphides, which have outstanding activity for hydrodeoxygenation of pyrolysis oil. The study is significant as it leads to the production of high-energy content liquid fuels. Pyrolysis of biomass is a thermal conversion process that produces liquid fuels and chemicals, and is a promising technology to compete with and eventually replace non-renewable fossil fuels. The model substrate 2-methyltetrahydrofuran is studied by kinetic and spectroscopic methods to uncover the important steps involved in the reaction. On the most active catalyst, Ni<sub>2</sub>P, the studies indicate that the rate-determining step involves a single Ni atom. In situ infrared measurements are used to identify adsorbed reactive intermediates during reaction and give support for the reaction mechanism. The studies are important because they allow understanding of reactivity at a nanoscale level and lead to the design of more active catalysts.

**Keywords:** Hydrodeoxygenation, Biomass, Nickel phosphide, 2-Methyltetrahydrofuran, Reaction mechanism,

## 1 INTRODUCTION

Pyrolysis of biomass is a thermal conversion process that produces liquid fuels and chemicals, and is considered a promising technology to compete with and eventually replace non-renewable fossil fuel resources. Pyrolysis liquids are formed quickly and at relatively low temperatures, but contain significant oxygen (~40 wt.%) which causes drawbacks, including low heating value (about half that of petroleum liquids), high acid content (leading to corrosion problems), and low stability (resulting in increasing viscosity with storage). The subject of the present work is the development of new catalysts, transition metal phosphides, which have outstanding activity for removal of the oxygen in pyrolysis oil by hydrodeoxygenation (HDO) so as to produce high-energy content liquid fuels. The mechanism of catalytic action of the model substrate (2-methyltetrahydrofuran) is studied by kinetic, spectroscopic, and transient methods to uncover the

important steps involved in the reaction. The results summarized here have been presented in a full paper [1<sup>1</sup>].

## 2 EXPERIMENTAL/METHODOLOGY

A potassium ion-exchanged ultrastable Y zeolite (KUSY) was prepared as follows. A commercial HUSY zeolite (Si/Al=40, Zeolyst, CBV780) was stirred vigorously for 12 h in a diluted aqueous solution (0.5M) of potassium nitrate (KNO<sub>3</sub>, 99%) at 70 °C. The zeolite support was filtered off and washed with deionized water at room temperature, and then dried at 112 °C overnight and calcined in static air at 377 °C for 4 h.

The Ni<sub>2</sub>P and FeNiP catalysts were prepared by a temperature-programmed reduction method from supported phosphate precursors. Briefly, after impregnation and calcination the precursor was reduced from room temperature to 590 °C at a rate of 3 of 3°C/min and maintained at 590°C for 2 h. X-ray diffraction (XRD) patterns of the powder samples which were reduced and partially passivated were obtained with a diffractometer (Rigaku RINT 2400) operated at 40 kV and 100 mA, using Cu-K<sub>α</sub> radiation (λ = 0.15418 nm).

The measurement of CO uptakes was conducted using a pulse flow technique to estimate the number of active sites on the catalysts. Usually, 0.3 g of a passivated phosphide catalyst was loaded into a quartz reactor and pretreated with H<sub>2</sub> (100 ml/min) at 450 °C for 2 h. After cooling under He, pulses (25 μl) of CO were injected at room temperature in a He stream (100 ml/min) through a sampling valve. The detection of CO signal was carried out with a thermal conductivity detector (TCD). Specific surface area and pore volume of the samples were obtained from N<sub>2</sub> adsorption/desorption isotherms at -196 °C measured with a volumetric adsorption unit (BELSORP\_mini, BEL Japan). The measurements were carried out after evacuating and drying the passivated catalysts at 150 °C for 1 h. The surface areas were calculated from the linear portion of BET plots (P/P<sub>0</sub>=0.01-0.10).

Reaction was carried out in a continuous-flow quartz reactor after reduction in a H<sub>2</sub> flow at 450°C for 2 h. A mixture of 95 vol% of 2-MTHF and 5 vol% of n-heptane as an internal standard was vaporized and mixed with a H<sub>2</sub> gas

to give a reactant stream of 3 or 5 mol% 2-MTHF in H<sub>2</sub>. Analysis was by gas chromatography.

### 3 RESULTS

Fig. 1 shows the XRD patterns scanned over the broad range of 8-82° for Ni<sub>2</sub>P/KUSY, NiFeP(3:1)/KUSY, NiFeP(1:1)/KUSY, NiFeP(1:3)/KUSY and FeP/KUSY. As references, the XRD patterns for KUSY, bulk Ni<sub>2</sub>P, bulk Fe<sub>2</sub>P, and the powder diffraction file (PDF) for FeP is also shown. The assignments of the peaks and the structures are available from the literature. FeP adopts the MnP orthorhombic B31 structure and Fe<sub>2</sub>P takes the hexagonal C22 structure. Sharp peaks were observed in the range of 7 to 35 ° for all supported catalysts which correspond to the diffraction lines of the USY zeolite. This indicates that the well-crystallized KUSY support has maintained its structure even after impregnation, calcination and reduction.

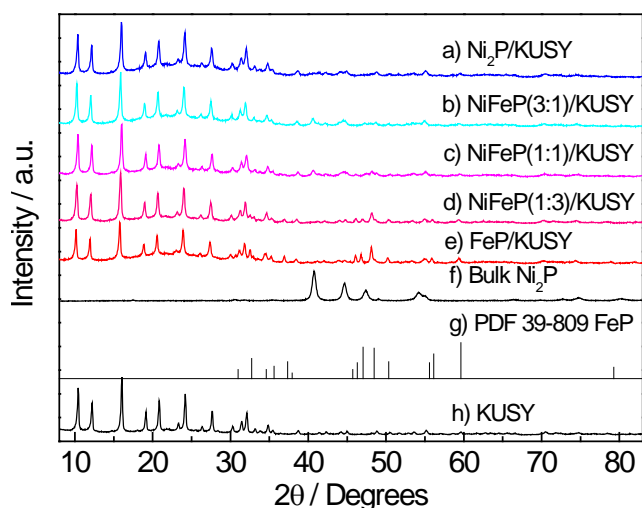


Figure 1. Broad-scan X-ray diffraction patterns of a) Ni<sub>2</sub>P/KUSY; b) NiFeP(3:1)/KUSY; c) NiFeP(1:1)/KUSY; d) NiFeP(1:3)/KUSY; e) FeP/KUSY; f) Bulk Ni<sub>2</sub>P; g) PDF 39-809 FeP; h) KUSY

For the phosphide-containing samples, the presence of signals cannot be seen easily probably because they are highly dispersed on the support. To improve the sensitivity, the 2θ range of 39.3 to 52.0 ° was scanned again with a smaller step size of 0.02 and the measurement was repeated five times. Fig. 2 shows that there are distinct peaks visible. Pattern a) for Ni<sub>2</sub>P/KUSY shows the characteristic peaks of the hexagonal Ni<sub>2</sub>P phase. The strong Ni<sub>2</sub>P signal has been scaled down in intensity to bring it to the same level as the other patterns, so does not show appreciable USY signals. Pattern b) for NiFeP(3:1)/KUSY shows predominantly Ni<sub>2</sub>P and the USY support. FeP if present should be highly dispersed. Pattern c) for NiFeP(1:1)/KUSY also shows predominantly Ni<sub>2</sub>P and the USY support, but in addition

some peaks due to FeP. Pattern d) for NiFeP(1:3)/KUSY and pattern e) for FeP/KUSY show some distinct peaks between 46 and 52 ° which are mostly due to bulk FeP. The peaks assigned to FeP are displaced to higher angle indicating small lattice constants. Also, the peak intensity of the (220) plane is relatively weak compared to that of the (211) plane in the FeP crystal.

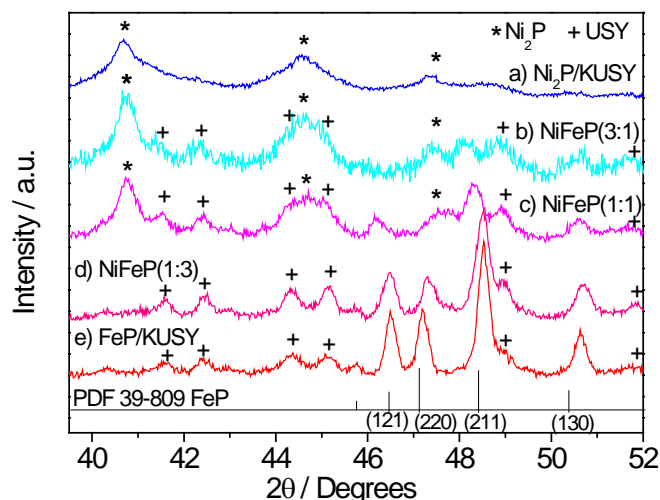


Figure 2. Narrow scan X-ray diffraction patterns of a) Ni<sub>2</sub>P/KUSY; b) NiFeP(3:1)/KUSY; c) NiFeP(1:1)/KUSY; d) NiFeP(1:3)/KUSY; e) FeP/KUSY

Table 1 summarizes the BET surface areas, pore volumes and quantities of CO adsorbed on the samples. The surface areas and pore volumes of all the catalysts decreased compared to KUSY. Table 1 also shows that the CO uptakes decreased with increasing contents of Fe, and with Ni<sub>2</sub>P/KUSY showing the highest value and FeP/KUSY exhibiting the lowest value. The low uptake of FeP compared to Ni<sub>2</sub>P is an intrinsic property of the Fe and has been observed before. The lowering of the CO uptake with increasing Fe content is consistent with the formation of an alloy with Fe occupying a substantial part of the Ni surface.

	BET area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	CO uptake (μmol/g)
Ni <sub>2</sub> P/KUSY	504	0.392	69
NiFeP(3:1)/KUSY	-	-	47
NiFeP(1:1)/KUSY	543	0.417	33
NiFeP(1:3)/KUSY	-	-	14
FeP/KUSY	539	0.407	4
KUSY	733	0.456	-

Table 1. BET surface area, total pore volume and CO uptakes of KUSY-supported samples

## 4. DISCUSSION

A model biofuel feedstock containing 95 vol% 2-MTHF and 5 vol% of *n*-heptane as an internal standard was used to test the HDO activity of the samples. Fig. 3a shows the conversions of 2-MTHF as a function of temperature for the various catalysts. The overall conversion was highest for the catalysts with the largest amount of Ni. The five conversion curves (Fig. 3a) show a consistent progression with iron content, and using the statistically-based rule-of-four-or-five [2] we conclude that there is a 97% chance that the results obtained are not random. Fig. 3b shows the turnover frequency (TOF) of 2-MTHF on the same catalysts, which is calculated by the following equation, where the quantity of sites is given by the number of surface metal atoms as titrated by CO chemisorption.

TOF = Reactant flow rate x conversion/Sites x catalyst wt.

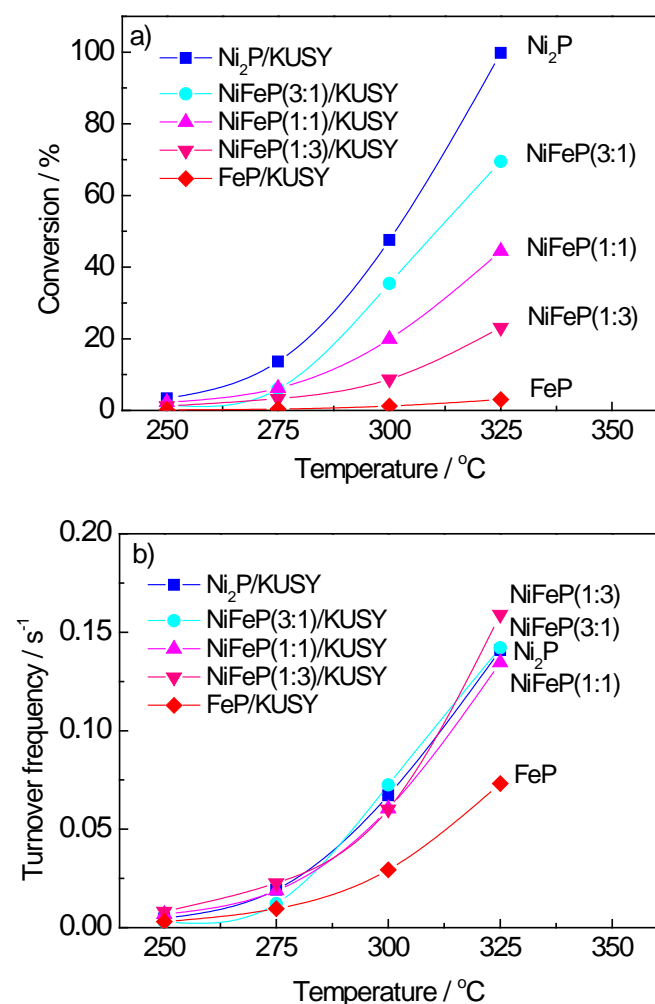


Figure 3. HDO of 2-MTHF over Ni<sub>2</sub>P/KUSY, NiFeP(3:1)/KUSY, NiFeP(1:1)/KUSY, NiFeP(1:3)/KUSY and FeP/KUSY a) Conversion; b) Turnover frequency

The broad-scan x-ray diffraction patterns of the samples (Fig. 1) show retention of the sharp USY crystalline peaks indicating that the support was stable to the thermal treatment used for the preparation of samples. The narrow-scan diffraction patterns (Fig. 2) show the presence of Ni<sub>2</sub>P and FeP in the pure compounds and coexistence of the two phases in the mixed compounds.

The CO chemisorption results show that the uptake amount decreases with Fe content to a very small value for FeP/KUSY (Table 1). This indicates that Fe phosphide does not chemisorb CO appreciably, possibly due to a strong interaction of Fe with P on the surface.

The reactivity results showed that the conversion decreased with increasing iron content with Ni<sub>2</sub>P/KUSY having the largest conversion and FeP/KUSY having the lowest (Fig. 3a). Interestingly, when the conversion data were normalized by the CO uptakes the resulting turnover frequencies did not change appreciably with composition (Fig. 3b). Although the differences are very small, at the highest temperature the two most active catalysts are NiFeP(1:1)/KUSY and NiFeP(1:3)/KUSY, which is surprising, as these have the largest content of Fe, and Fe phosphide by itself is the least active. However, the TOF is based on the chemisorption of CO on Ni sites, so this must mean that the activity of each Ni site is slightly enhanced by the presence of Fe. It is deduced that there is a very slight ligand effect.

The finding that the TOF was not much affected by the alloying (Fig. 3b) indicates that there is only a weak ligand effect for the surface Ni. It also indicates that the steps that are important in setting the rate of reaction are not much dependent on the surroundings of the Ni atoms, that is, that these steps are structure-insensitive. Consistent with this, it is expected that a single Ni atom will be involved in the initial activation. A plausible possibility is that the initial ring-opening is the rate-determining step (Fig. 4).

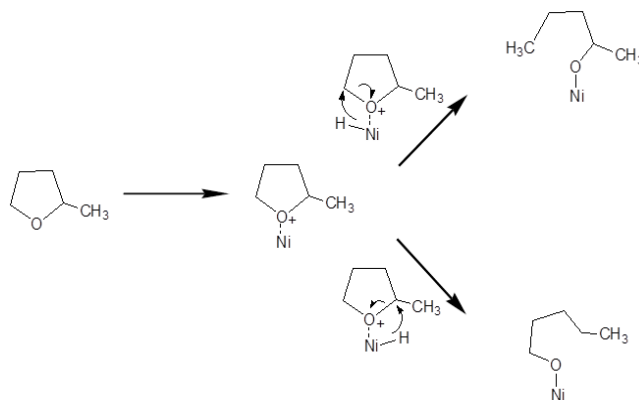


Figure 4. Rate-determining ring-opening steps on a single Ni center to produce 2-pentoxide or 1-pentoxide.

## 5. CONCLUSIONS

In this study, bimetallic NiFe phosphide catalysts supported on potassium ion-exchanged ultrastable Y zeolites (USY) were synthesized with different Ni and Fe molar ratios and were evaluated for the hydrodeoxygenation (HDO) of 2-methyltetrahydrofuran (2-MTHF). The synthesized NiFe phosphides contained highly dispersed Ni<sub>2</sub>P and FeP phases. The pure Ni supported catalyst, Ni<sub>2</sub>P/KUSY, showed the highest conversion for the HDO of 2-MTHF which decreased with increasing Fe content in the samples. On the other hand, the turnover frequency (TOF) based on active sites titrated by CO uptakes were very close for all the Ni-containing catalysts, indicating the involvement of a single surface Ni atom in the rate-determining step. The step involved is likely the ring-opening step of 2-MTHF HDO which can proceed to produce either a 2-pentoxide species or a 1-pentoxide species. These results demonstrate that bimetallic NiFe phosphide catalysts exhibit a weak ligand effect on the rate. The performance of the Ni<sub>2</sub>P/KUSY samples is exceptional because of the high TOF for the total rate coupled with a high selectivity for HDO products.

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