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Rake mechanism for the deoxygenation of ethanol over a supported Ni_2P/SiO_2 catalyst

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ABSTRACT

The catalytic conversion of ethanol was studied on a metallic Ni_2P/SiO_2 catalyst, and comparison was made with an acidic HZSM-5 catalyst. Chemisorption probes indicated that the Ni_2P had substantial CO adsorption sites (134 µmol g⁻¹), while the HZSM-5 catalyst had large quantities of NH_3 adsorption sites (565 µmol g⁻¹). The catalytic activity in ethanol deoxygenation of the Ni_2P/SiO_2 was higher than that of the HZSM-5 catalyst on the basis of these chemisorptions sites.

In steady-state catalysis, contact time experiments indicated that for Ni₂P, acetaldehyde was a primary product and ethylene was a secondary product. However, this was not the result of a sequential oxidation reaction followed by a reduction process, but rather, it was due to the formation of a surface intermediate that could desorb as acetaldehyde or react further to produce ethylene. This rake-type mechanism was supported by a simulation of the reaction sequence that produced good agreement with the experimentally determined acetaldehyde and ethylene yields. The mechanism was also supported by in situ Fourier transform infrared measurements, which revealed the presence of signals compatible with adsorbed acetaldehyde, the likely surface intermediate species involved in the reaction. The present studies indicate that the reactions of alcohols on metallic catalysts like Ni₂P involve dehydrogenation/hydrogenation steps, rather than simple acid/base-catalyzed dehydration steps as occur in HZSM-5.

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1. Introduction

The utilization of biomass for the production of fuels and chemicals is currently an area of great activity because of the recognition that fossil fuels are a finite resource and because of the imminent threat of global warming from the release of carbon dioxide [1–6]. Among the major products of biomass conversion is ethanol, a commodity chemical derived from the fermentation of sugarcane or energy-rich crops such as corn [7,8]. Although ethanol is produced in large quantities as a substitute or supplement for fuels derived from crude oil, it is currently unlikely to replace much less expensive chemical feedstocks derived from petroleum or natural gas such as ethylene. Nevertheless, in a future with limited hydrocarbon supplies, there may be a role for ethanol as a primary feedstock [9] as recently demonstrated by the start-up of a 200,000 metric ton ethylene from ethanol plant in Brazil [10], and for this reason, research in ethanol conversion is warranted. It is also of interest to study ethanol for fundamental reasons. First, it is one of the simplest oxygenated compounds, and its deoxygenation can provide insight into oxygen removal from more complicated molecules. Second, it can react to produce different products and for this reason can be used as a probe to relate the reaction pathway to the properties of the catalysts, in particular their acid/base properties versus their metallic nature. This study is thus motivated in part to explore the catalytic chemistry of deoxygenation and in part to determine the role of intermediates in the reaction pathway. Use is made of a traditional acid catalyst, HZSM-5, which has been shown to be an effective agent for dehydration, and a metallic catalyst, Ni₂P, which has been demonstrated to have hydrogen transfer capabilities. The use of metallic catalysts is important because studies have shown that biomass conversion cannot be carried out by acid catalysts alone [2–4].

The decomposition of ethanol on solid catalysts typically occurs through competing reactions [8,11–13]: (1) intermolecular dehydration, which gives diethyl ether and water; (2) intramolecular dehydration, which yields ethylene and water; (3) dehydrogenation, which produces acetaldehyde and hydrogen; and (4) total decomposition into CO, H₂, CH₄, C, and O [7]. The acidity and basicity of the solid catalysts are two important factors that influence their activity and selectivity. Dehydration generally occurs on



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acidic catalysis [14–16], and dehydrogenation usually proceeds on basic sites [17,18].

An important pathway for ethanol conversion is dehydration to ethylene. Previous studies reported that HZSM-5 zeolite with strong Brønsted acid sites was an effective catalyst for this transformation [19]. However, deactivation by formation of coke on its surface led to decreasing activity and selectivity toward ethylene [20] and therefore made the process unsuitable for industrial applications [21]. Phillips and Datta [22] investigated the production of ethylene from hydrous ethanol over HZSM-5 under mild conditions and demonstrated that strong Brønsted acid sites led to rapid catalyst deactivation in the initial stages through the oligomerization of ethylene and the formation of carbonaceous species. However, moderating the acidity could reduce coke formation and enhance the steady-state catalytic activity of HZSM-5.

Another important pathway for ethanol decomposition is dehydrogenation to acetaldehyde and hydrogen, which is favored on basic [23] or metallic catalysts [24]. Chang et al. reported that copper catalysts supported on rice husk ash displayed high catalytic activity and selectivity toward dehydrogenation [24]. Much attention has been focused on preparing bifunctional catalysts with both acidic and basic sites in order to promote both dehydrogenation and dehydration [25–28]. Aramendía et al. [29,30] claimed that basic sites were responsible for dehydrogenation and both weak acid and basic sites were associated with dehydration.

Although there are a wide variety of catalysts for ethanol conversion, there has been no report on the decomposition of ethanol over transition metal phosphide catalysts. Transition metal phosphide catalysts possess excellent hydrogen transfer properties and have been investigated extensively in hydrotreating applications. They have also been used in hydrodeoxygenation studies and have shown promising results [31]. Therefore, it is of interest to determine the activity of transition metal phosphides in ethanol conversion. In the present study, a Ni₂P/SiO₂ catalyst was chosen for catalyzing the ethanol decomposition process because it is generally the most active of the transition metal phosphides for a variety of reactions (HDS, HDN, HDO) [32–36,31]. Comparison is made to HZSM-5, the most widely studied acid catalyst.

2. Experimental

2.1. Materials

The HZSM-5(Si/Al = 15) commercial catalyst was obtained from Zeolyst International. The transition metal phosphide Ni₂P/SiO₂ was prepared on a fumed silica EH-5 support provided by the Cabot Corp. The chemicals used in the synthesis of the catalyst were Ni(NO₃)₂·6H₂O (Alfa Aesar, 99%) and (NH₄)₂HPO₄ (Aldrich, 99%). The chemical utilized in the reactivity study was ethanol (Decon Laboratories, Inc., 200 Proof). The gases employed were H₂ (Airco, Grade 5, 99.99%), He (Airco, Grade 5, 99.99%), CO (Linde Research Grade, 99.97%), 0.5% O₂/He (Airco, UHP Grade, 99.99%), O₂ (Airco, UHP Grade, 99.99%), and NH₃ (Alexander Chemical Corporation, AH200).

2.2. Nickel phosphide (Ni₂P/SiO₂) synthesis

The Ni₂P/SiO₂ catalyst was prepared by temperature-programmed reduction (TPR), following procedures reported previously [38–40]. Briefly, the synthesis of the catalysts involved two stages. First, a solution of the corresponding metal phosphate precursor was prepared by dissolving appropriate amounts of Ni(NO₃)₂·6H₂O with ammonium phosphate in distilled water, and the solution was used to impregnate silica by the incipient wetness method. The obtained samples were dried and calcined at 773 K for

6 h, then ground with a mortar and pestle, pelletized with a press (Carver, Model C), and sieved to particles of 650-1180 µm diameter (16/20 mesh). Second, temperature-programmed reduction (TPR) was carried out on the pelletized precursor phosphate (typically 200 mg) placed in a U-shaped quartz reactor. The sample was heated from room temperature to 1073 K at 2 K min⁻¹ in flowing hydrogen at 100 cm^3 (NTP) min⁻¹ g⁻¹ to reduce the metal phosphate to the desired phosphide and to determine the peak maximum for reduction. A portion of the exit gas flow was sampled through a leak valve into a mass spectrometer (MS, Dycor/Ametek, model MA100), and the masses 2(H₂), 18(H₂O), 31(P), and 34(PH₃) were monitored during the experiment. For large the sample sizes, the sample was kept at the determined peak reduction temperature (883 K) for 2 h, followed by cooling to room temperature under He flow [100 cm³ (NTP) min⁻¹], and then passivated at room temperature in a 0.5% O₂/He for 4 h. The Ni molar loading was 1.16 mmol g^{-1} (mmol per g of support), corresponding to a weight loading of Ni₂P of 7.9 wt.% with an initial Ni/P ratio of 1/2.

2.3. Characterization

Irreversible CO uptake measurements were used to provide an estimate of the active sites on the catalysts. Usually, 200 mg of a passivated Ni₂P/SiO₂ catalyst was loaded into a U-shaped quartz reactor, and then the sample was reduced in flowing H₂ [200 cm³ (NTP) min⁻¹] at 723 K for 2 h. For HZSM-5, the pretreatment temperature was 773 K using He as the purging gas. After cooling in He [200 cm³ (NTP) min⁻¹], pulses of CO in a He carrier at 43 µmol s⁻¹ [65 cm³ (NTP) min⁻¹] were injected at room temperature through a sampling valve. The mass 28 (CO) signal was monitored with a mass spectrometer (MS, Dycor/Ametek, model MA100). CO uptake was calculated by measuring the decrease in the peak areas caused by adsorption in comparison with the area of a calibrated volume (19.5 µmol).

Surface areas of the samples were obtained using the BET method based on adsorption isotherms at liquid nitrogen temperature, using a value of 0.162 nm² for the cross-sectional area of a N₂ molecule. The measurements were taken in a volumetric adsorption unit (Micromeritics ASAP 2000). X-ray diffraction (XRD) patterns of the samples were obtained with a PANalyticalX'pert Pro powder diffractometer operated at 45 kV, using CuK α monochromatized radiation (λ = 0.154178 nm).

Transmission infrared spectra of pyridine adsorbed on the Ni₂P/ SiO_2 catalyst and HZSM-5(Si/Al = 15) were collected to characterize the surface acidic sites. Fourier transform infrared (FTIR) spectra measurements were carried out with a Digilab Excalibur Series FTS 3000 spectrometer equipped with a liquid N₂ cooled mercury-cadmium-telluride detector. The IR cell was equipped with water-cooled KBr windows, connections for inlet and outlet flows, and thermocouples connected to a temperature controller to monitor and control the sample temperature. For the experiments, about 25 mg of finely ground Ni₂P/SiO₂ catalyst, or HZSM-5 samples were pressed into self-supporting wafers with a diameter of 13 mm (18.8 mg cm⁻²). Wafers were mounted vertically in a quartz sample holder to keep the incident IR beam normal to the sample. Before dosing pyridine, the sample of Ni₂P/SiO₂ was reduced in H₂, and HZSM-5 was purged in He flow at 723 K and 773 K, respectively, for 2 h at a flow rate of 100 μ mol s⁻¹ [150 cm³ (NTP) min⁻¹]. After pretreatment, the samples were slowly cooled in flowing He [200 cm³ (NTP) min⁻¹], and background spectra were collected at 423 K under He flow. The samples were dosed at atmospheric pressure and room temperature with 1.0 mol% pyridine in He carrier at a total flow rate of 140 μ mol s⁻¹ [200 cm³ (NTC) min⁻¹] until saturation was achieved. The samples were then purged with carrier gas for 0.5 h to remove gaseous and weakly adsorbed pyridine. Spectra

were acquired at 423 K and are shown with subtraction of the background contribution to highlight the pyridine adsorbate peaks.

Ethanol FTIR measurements were carried out with Ni_2P/SiO_2 catalyst in the same manner as with the pyridine experiments. After pretreatment, background spectra were collected under He flow, and then ethanol was introduced with He flow until saturation was achieved.

Ammonia, pyridine, and carbon dioxide temperature-programmed desorption (NH₃-TPD, pyridine-TPD, and CO₂-TPD) were used to determine the quantities of acid and base sites on the catalysts. TPD experiments were carried out by loading catalyst samples (200 mg) in U-shaped quartz reactors connected to a MS pretreating as in the CO uptake experiments, and then dosing NH₃ or CO₂ or a mixture of 2.6 mol% pyridine in dry He flow from a bubbler containing pyridine at room temperature onto the samples at room temperature until saturation. Then, samples were purged with pure He for 1 h at a flow rate of 200 cm³ (NTP) min⁻¹ to remove physisorbed NH₃ or pyridine or CO₂ and then heated from room temperature to 973 K at 10 K min⁻¹. The masses 17 (NH₃) or 79 (pyridine) or 44 (CO₂) were monitored by the MS during the experiments. Peak areas were quantified by comparison with the areas of calibrated pulses of the pure compounds.

Ethanol temperature-programmed desorption (EtOH-TPD) was used to compare the catalytic activity and product selectivity of ethanol over the two different catalysts. To start a reaction, catalysts (200 mg) were placed in a U-shaped reactor and pretreated at the same conditions as used for chemisorption. After pretreatment, a flow of He saturated with ethanol was introduced at 200 cm³ (NTP) min⁻¹ for 1 h at room temperature. After purging in He flow for 1 h, the temperature was raised at 10 K min⁻¹ to 1073 K in He flow [200 cm³ (NTP) min⁻¹]. The reaction products were analyzed using an online mass spectrometer (Dycor/Ametek, model MA100). The conversion of ethanol and the product selectivity for each sample were calculated and compared. The products were quantified using reaction response factors (RRF). The RRF were determined experimentally calibrating the mass spectrometer signals with pure standards of known concentration.

2.4. Reactivity studies

Activity tests were conducted in a U-shaped reactor at atmospheric pressure using catalyst amounts corresponding to 121 µmol of active sites. For nickel phosphide, the catalyst amount (903 mg) was based on the CO uptake (134 µmol g⁻¹), and for HZSM-5, the catalyst amount (214 mg) was based on the NH₃ uptake (565 µmol g⁻¹). To start, the catalyst was pretreated at the same conditions as used for chemisorption. After pretreatment, a mixture of 1.5 mol% ethanol in dry He flow from a bubbler containing ethanol at 273 K was passed onto the sample, and then the catalyst was stabilized for 0.5 h after the feed was introduced. Reactivity testing was performed as a function of temperature, starting at the highest temperature of 523 K, and was varied downward and upward with the initial temperature repeated at the end to establish catalyst stability. Mass balances closed within 5%.

Reactivity tests were also investigated as a function of contact time. The contact time is defined by the following equation, with the quantity of sites obtained from CO uptake experiment.

Contact time (s) =
$$\frac{\text{Quantity of sites } (\mu \text{mol } g^{-1}) \times \text{Catalyst weight } (g)}{\text{Reactant flowrate } (\mu \text{mol } s^{-1})}$$

The experiment started at the highest contact time of 270 s and was varied downward and upward with the initial contact time repeated at the end. Generally, it took about 10 h of on stream time to collect the rate data at several reaction temperatures or contact times, and the smoothness of the data indicated no deactivation.

The reaction products were analyzed using an online mass spectrometer (Dycor/Ametek, model MA100). The conversion and product yield were evaluated by determining the amount of ethanol reacted and products formed using the formulas below.

Conversion (%) =
$$\frac{N \text{ (ethanol)}_{in} - N \text{ (ethanol)}_{out}}{N \text{ (ethanol)}_{in}} \times 100$$

Yield (%) = Fractional conversion \times Selectivity \times 100

3. Results and discussion

3.1. Synthesis and basic characterization

The supported nickel phosphide was prepared in two stages as described in the experimental part. First, solutions of the nickel and phosphorous components were impregnated on the silica support, and the material was dried to form supported phosphate precursors. Second, the phosphate was transformed into a phosphide by temperature-programmed reduction (TPR). The TPR experiment was carried out to understand the phenomena involved in the reduction process and to determine the optimum reduction condition used for large-scale catalyst preparation (Fig. 1a). A sample of HZSM-5 was also included in the studies because it is among the most effective of reported catalysts and serves as a comparison with the Ni₂P material. Modification of ZSM-5, though interesting, would detract from the treated subject.



Fig. 1. Synthesis and XRD analysis of Ni_2P/SiO_2 : (a) mass 18 signal from TPR and (b) X-ray diffraction pattern.

Table 1 The true width at half-maximum of the peak and crystallite size of $\text{Ni}_2\text{P}/\text{SiO}_2$ catalyst.

Peak (deg)	Direction	True width (rad)	Crystallite size (nm)
40.5	111	0.009	17
44.8	201	0.007	22
47.5	210	0.006	25
54.2	300	0.010	15
Average	-	0.008	20

The water evolution (mass 18) shows a reduction peak at 883 K. Only the results for mass 18 (H_2O) are shown, because the other monitored masses provided little additional information. This temperature was chosen for preparation of larger-scale samples used for characterization and testing.

Analysis of the product of TPR was carried out by XRD (Fig. 1b). The diffraction pattern for the silica-supported nickel phosphide shows three major peaks at 40.5°, 44.8°, and 47.5°, which line up well with the standard pattern for Ni₂P. The peaks are significantly broadened, indicating that small Ni₂P crystals were formed. The XRD pattern after reaction was essentially unchanged, indicating that the catalyst was stable.

The width at half-maximum was corrected for instrumental broadening (0.2°), and the crystallite size of the supported Ni₂P was calculated using the Scherrer equation, $D_C = K\lambda/\beta \cos(\theta)$, where *K* is a constant taken as 0.9, λ is the wavelength of the X-ray radiation (0.154178 nm), β is the peak width in radians at half-maximum, and 2θ is the Bragg angle. Table 1 reports the true width at half-maximum of the peak and the crystallite size.

There is no substantial anisotropy with crystallographic direction, indicating that the crystallites are spherical, in agreement with high-resolution transmission electron microscopy results from the group of Bussell [41].

The CO chemisorption and BET characterization results are reported in Table 2. Earlier studies have shown that uptakes of CO on SiO₂ and Al₂O₃ were negligible [42–44]. The CO chemisorption uptake of the Ni₂P/SiO₂ catalyst was 134 μ mol g⁻¹, which is in line with previous measurements. The CO uptake of HZSM-5 was small and was probably due to CO interaction with strong Lewis acid sites, as HZSM-5 does not contain metal. Both the phosphide and the HZSM-5 samples have high BET surface areas, 310 and 410 m² g⁻¹, respectively. The BET surface area of Ni₂P/SiO₂ is lower than that of the SiO₂ support of 350 m² g⁻¹, and this was likely caused by sintering during the preparation process. Additionally, Table 2 also lists the pore volumes of the two catalysts obtained from N₂ physisorption measurements and shows that the major types of pores in Ni₂P/SiO₂ and HZSM-5 catalysts are mesopores and micropores, respectively.

It has been reported [45] that micropores are associated with coke formation that results in the zeolite's loss of activity during the ethanol dehydration process. The micropore size limits the size of the channels, cavities, and channel intersections, trapping the species responsible for coking. Mesopores are more active in the ethanol reaction, for the larger size allows easier passage of the reactant for reaching the active sites and for the products to

Table 2	2
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Characterization	results	for	HZSM-5	and	Ni ₂ P	/SiO ₂	catalysts.
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Catalyst	CO uptake (umol g ⁻¹)	BET area $(m^2 g^{-1})$	Pore vo	Pore volume (cm ³ g ⁻¹)		
	(1	(8)	V _{micro} ^a	V _{meso} ^b	V _{tot}	
Ni ₂ P/SiO ₂	134	310	0.009	0.083	0.092	
ELSIVI-3	11	410	0.124	0.050	0.100	

^a Micropore volume from *t*-plot.

^b $V_{\text{total}} - V_{\text{micro}}$

leave. Gayubo et al. [46] studied the selectivity of olefin products from bioethanol and demonstrated that higher mesoporosity and moderate acid strength were suitable for the decomposition of bioethanol.

3.2. Temperature-programmed desorption (TPD) of NH_3 , pyridine, and CO_2

Measurements of NH₃ [47,48], pyridine, and CO₂ [49,50] temperature-programmed desorption (TPD) were carried out in order to clarify the relationship between the catalyst activity and the amount of acidic and basic sites on the catalysts. The results are shown in Figs. 2–4 and summarized in Table 3. Although the signal is reported with arbitrary units, the peaks were quantitated by injection of known quantities of NH₃, pyridine, and CO₂.

Relevant to the NH₃-TPD results, previous studies showed that [51] peak maxima, T_m , from 293 K to 473 K correspond to weak acidity sites, T_m from 473 K to 673 K to intermediate acidity sites, and T_m higher than 673 K to strong acidity sites. The HZSM-5 sample shows two peaks at T_m of 500 K and 724 K, respectively (Fig. 2), clearly suggesting the presence of moderate and strong acidic sites. The ratio of the moderate acidic sites to the strong ones is 0.75. Bi et al. [52] and Post and Hoof [53] reported that ethylene was easily polymerized on the strong Brønsted acid sites of HZSM-5 and suggested that elimination of the strong acidic sites could improve the stability of the catalyst. The Ni₂P/SiO₂ catalyst exhibits one broad peak from 402 K to 805 K with a maximum around 475 K, indicating that the catalyst has plenty of moderate acidity sites. The acid sites are prob-



Fig. 2. Mass 17 signal from NH₃-TPD.



Fig. 3. Mass 79 signal from pyridine-TPD.



Fig. 4. Mass 44 signal from CO₂-TPD.

ably associated with phosphorus on the support. In summary, the NH_3 -TPD characterization results show that Ni_2P has weak and moderate strength acid sites, while HZSM-5 has stronger acid sites the strongest of which might lead to side reactions.

Previous references noted that [54,55] pyridine is a strong base in the gas phase and requires higher temperature than ammonia for complete desorption from catalysts. Fig. 3 displays the pyridine-TPD profiles and shows that all peak maxima occur at higher temperature than the corresponding NH₃-TPD maxima (530 K for Ni₂P/SiO₂, 514 K and 991 K for HZSM-5, respectively). The conclusions are similar to those obtained with NH₃-TPD, with Ni₂P/SiO₂ exhibiting moderate strength acidic sites and HZSM-5 possessing both moderate and strong acidic sites in a ratio of 0.60.

Fig. 4 shows the TPD profiles of CO_2 from the Ni_2P/SiO_2 and HZSM-5 samples, with peak maxima located at 389 K and 373 K, respectively. Table 3 summarizes the quantity of acidic and basic sites. The results suggest that Ni_2P/SiO_2 has fewer acidic sites and more basic sites than HZSM-5. Previous FTIR characterization of acid sites indicates that there are Si—OH and P—OH groups on the support that contribute to the total acidity [56–58]. The quantity of probe molecules on HZSM-5 is generally larger than on the Ni_2P/SiO_2 , reflecting the large contribution of the total surface of the material to the adsorption.

The influence of acidic and basic centers on dehydration has been well studied. Basic and acidic sites are necessary for the dissociative adsorption of ethanol [59,60]. Golay et al. [61] investigated the influence of the catalyst's acid/base properties on the catalytic ethanol dehydration. They suggested that for the formation of ethylene, a simultaneous adsorption on both acidic sites and basic sites was necessary and that the dehydration was affected by both the surface acidity and the sorption kinetics on the basic sites.

3.3. Infrared spectroscopy of pyridine

Pyridine adsorption is often combined with in situ Fourier transform infrared spectroscopy (FTIR) to probe the surface acidic properties of supports and catalysts [62,63]. Characteristic bands in the FTIR spectrum are used to determine whether pyridine is protonated through the nitrogen atom by surface Brønsted acid sites or bonded to coordinative unsaturated metal sites (Lewis acids). Upon interaction with a Brønsted acid site, pyridine is protonated to a pyridinium ion and adsorbs with a characteristic band around 1545–1540 cm⁻¹. Interaction of pyridine with Lewis acid sites leads to a coordinatively bonded pyridinium complex with a well-resolved band centered around 1452–1447 cm⁻¹. A band located around 1490 cm⁻¹ is common to both adsorbed species. Many studies have employed this technique to gualitatively and quantitatively study the acidic properties of catalytic materials and the resulting effect on catalyst properties and activity. Fig. 5 displays FTIR spectra of adsorbed pyridine in He flow on HZSM-5 and Ni₂P/SiO₂ catalysts at 423 K and shows that both possess acidic sites. HZSM-5 contains mostly Brønsted acid sites, whereas Ni₂P/ SiO₂ has more Lewis acid sites.

The quantity of Brönsted acid sites and Lewis acid sites was calculated using the following equations [64], and the results are presented in Table 3:

$$C(B) = IMEC(B)^{-1} \times IA(B) \times \frac{\pi R^2}{W}$$
$$C(L) = IMEC(L)^{-1} \times IA(L) \times \frac{\pi R^2}{W}$$

where *C* is the concentration (μ mol/g catalyst), IMEC(B, L) the integrated molar extinction coefficients (cm/ μ mol), IA(B, L) the integrated absorbances (cm⁻¹), *R* the radius of catalyst disk (cm) and *W* is the weight of disk (mg).

Comparing the quantity of acid sites obtained by the TPD and FTIR methods, it is found that on Ni₂P, the NH₃ TPD amount (381 μ mol g⁻¹) is slightly larger than the pyridine FTIR amount (326 μ mol g⁻¹). This also is found on HZSM-5 where the TPD amount (565 μ mol g⁻¹) is larger than the pyridine FTIR amount (486 μ mol g⁻¹). There are two possible reasons for this. First, ammonia is smaller than pyridine, so it will pack more closely on the surface as well as enter more readily into smaller micropores.



Fig. 5. Infrared spectra of adsorbed pyridine over samples at 423 K.

Table 3 Acid and base properties of HZSM-5 and Ni_2P/SiO_2 catalysts.

Samples	CO_2 -TPD (µmol g ⁻¹)	NH ₃ -TPD (μmol g ⁻¹)	Pyridine FTIR					
			B (μ mol g ⁻¹)	L ($\mu mol \ g^{-1}$)	B + L (μ mol g ⁻¹)	B/L		
Ni ₂ P/SiO ₂ ^a HZSM-5	408 218	381 565	36 428	290 58	326 486	0.12 7.38		

^a The Ni₂P/SiO₂ CO₂-TPD amount is corrected by 149 μ mol g⁻¹ from the SiO₂ support, and the NH₃-TPD amount is corrected by 229 μ mol g⁻¹ from the SiO₂ support.

Second, the purge temperature of ammonia was room temperature, whereas that of pyridine in the FTIR measurements was 423 K, so that some weakly bound pyridine was desorbed.

Phillips and Datta [22] reported that Brønsted acid sites were involved in the HZSM-5-catalyzed ethanol dehydration to ethylene; however, oligomerization of ethylene also occurred at the same sites forming carbonaceous deposits that covered these sites and dramatically reduced the catalytic activity. Increasing Lewis acid sites and decreasing Brønsted acid sites were favorable for the catalytic decomposition of ethanol [65].

The number of sites titrated by CO₂ is surprisingly high. For Ni₂P, the quantity (408 µmol g⁻¹) exceeds the acidic sites (381 µmol g⁻¹) and the surface metal sites from CO chemisorption (134 µmol g⁻¹). For HZSM-5, the quantity of CO₂ adsorption (218 µmol g⁻¹) is about 1/3 the total acid amount (565 µmol g⁻¹). The adsorption of CO₂ is usually attributed to basic sites, but in this case for Ni₂P, there is likely to be some adsorption on the metallic sites. For both Ni₂P and HZSM-5, there are likely contributions from physisorption.



Fig. 6a. Signal of ethylene from EtOH-TPD.



Fig. 6b. Signal of acetaldehyde from EtOH-TPD.

3.4. Ethanol temperature-programmed desorption

Figs. 6a and 6b show the signal of ethylene and acetaldehyde, respectively, obtained from ethanol temperature-programmed desorption (EtOH-TPD). Fig. 6a shows that ethylene formation over HZSM-5 occurred at around 419 K and 533 K and over Ni₂P/SiO₂ occurred at around 407 K and 584 K. Thus, ethylene started to form and desorb from the Ni₂P/SiO₂ catalyst at a lower temperature than from HZSM-5.

Fig. 6b reveals the desorption of acetaldehyde. The formation of acetaldehyde over HZSM-5 occurred at around 422 K and 541 K. Over Ni₂P/SiO₂, acetaldehyde desorbed at 411 K and 497 K.

Table 4 summarizes the distribution of ethylene and acetaldehyde over different temperatures in the EtOH-TPD experiments over HZSM-5 and Ni₂P/SiO₂ catalysts.

Over HZSM-5, strong ethylene and acetaldehyde desorption was recorded at 530 K and 541 K, respectively. Over Ni_2P/SiO_2 , an almost similar amount of ethylene was observed at 407 K and 584 K, and acetaldehyde desorption occurred primarily at 497 K, with a smaller peak at 411 K. The Ni_2P/SiO_2 catalyst shows reactivity at lower temperature than HZSM-5 particularly for acetaldehyde, which indicates that it may be an initial product. This will be confirmed later.

Fig. 7 shows the conversion of ethanol and the selectivity toward products from EtOH-TPD over the two catalysts.

Overall, Ni₂P/SiO₂ has a little higher conversion of ethanol (57%) than HZSM-5 (56%), but also exhibits a higher selectivity toward acetaldehyde (21%) than HZSM-5 (4%), and a lower selectivity toward ethylene (57%) than HZSM-5 (96%). At the same time, carbon monoxide, a product of conversion from acetaldehyde, was detected at up to 20% in the product stream on the Ni₂P/SiO₂ catalyst along with a small quantity of methane (3%). In contrast, there was no carbon monoxide and methane detected from HZSM-5. The decomposition of ethanol has been studied extensively on different metallic catalysts such as Pt/Al₂O₃ [66], CuO with 5% CoO and 1% Cr₂O₃ [67], Pt/ZrO₂ [68], and supported Au [69], and it has been reported that the dehydrogenation of ethanol yielded acetaldehyde and hydrogen: C₂H₅OH \rightarrow CH₃CHO + H₂ (1). It is likely that the methane detected with the Ni₂P/SiO₂ came from



Fig. 7. Conversion and Selectivity from EtOH-TPD.

Table 4

Distribution of ethylene and acetaldehyde in different temperature ranges on EtOH-TPD.

Catalyst	HZSM-5	IZSM-5 Ni ₂ P/SiO ₂						
Maximum Temperature (K)	419	422	533	541	407	411	497	584
Percentage of ethylene (%)	20	-	80	-	50	-	-	50
Percentage of acetaldehyde (%)	-	16	-	84	-	28	72	-

an intermediate acetaldehyde which decomposed into methane and carbon monoxide: $CH_3CHO \rightarrow CH_4 + CO$ (2). It should be noted that in the presence of water (a dehydration by-product), the CH_4 steam-reforming reaction may also occur to produce CO and H_2 : $CH_4 + H_2O \rightarrow CO + 3H_2$ (3). Farkas and Solymosi [70] studied the adsorption, desorption, and dissociation of ethanol on MoC/Mo (100). They obtained a product mixture of 18% of ethylene, 12% of acetaldehyde, and 44% of carbon monoxide. The formation of methane, however, was not reported. They suggested the reason for no methane formation was that no CH_x species formed from rupture of a C–C bond on the catalyst surface during the dehydrogenation process. These results are in agreement with the finding from this study that the amount of methane was much smaller than that of carbon monoxide.

Under our conditions of EtOH-TPD, the Ni_2P/SiO_2 displayed better ability for the conversion of ethanol and selectivity toward dehydrogenation than HZSM-5. Dehydrogenation is generally accepted to occur on basic sites and metallic sites. On Ni_2P , the uptake of CO_2 is substantial (Table 3), but as discussed earlier, some of this may be due to chemisorption on metallic sites, and a considerable portion in physisorbed mode. It is more likely from the known hydrogen transfer capabilities of the phosphide that dehydrogenation is occurring on metallic sites.

In order to ensure that the TPD results were not affected by the lag time for gas to diffuse out of pores, an analysis was carried out using the criterion of Gorte [71] and Ibok and Ollis [72]. These researchers suggested that the effect of diffusion limitations could be ignored for a value of less than 0.01 for the group $\frac{\beta l^2 \varepsilon}{(T_f - T_0)D}$ where β is the heating rate (K/s), *l* is the width of catalyst slab (cm), ε is the porosity (cm³/cm³), T_f and T_0 are the final and initial temperature (K), respectively, and *D* is the effective diffusivity (cm²/s). For our conditions, a highest value of 6×10^{-5} is obtained (Table 5), and this indicates no diffusion limitations during the TPD experiments.

3.5. Reactivity

The conversion of ethanol as a function of temperature was compared for HZSM-5 and Ni_2P/SiO_2 with equal sites loaded in the reactor (121 µmol g⁻¹). For HZSM-5, the main product at all temperatures was ethylene, with some acetaldehyde, and a butylene isomer (not identified) also formed. On Ni_2P/SiO_2 , the main product was initially acetaldehyde, but this decreased with increasing temperature, and ethylene became the main product at high temperature. These results are consistent with previous studies [25–30]. In general, Ni_2P/SiO_2 exhibited higher activity than HZSM-5 at all temperatures. Turnover frequencies were obtained using the following formula:

$$\left(\text{Turnover frequency } (s^{-1}) = \frac{\text{Reactant flowrate } (\mu \text{mol } s^{-1}) \times \text{Conversion}}{\text{Quantity of sites } (\mu \text{mol } g^{-1}) \times \text{Catalyst weight } (g)}\right)$$

A summary is provided in Table 6. Calculations of the Weisz–Prater criterion (C_{WP}) were made to ascertain that no mass transfer limitations were present (see Supplementary Information). The highest C_{WP} gave $0.030 \ll 1$, indicating that internal mass transfer effects can be neglected at the conditions employed for the reactivity study in this paper.

Table 5	
Parameters in	the Gorte criterion.

β	Heating rate (K s ⁻¹)	0.17
1	Width of catalyst slab (cm)	0.09
3	Porosity (cm ³ cm ⁻³)	0.45
$T_f - T_0$	Temperature difference (K)	110
Ď	Effective diffusivity	0.1

Table 6

Catalyst	Conversion (%	Conversion (%)						
	448 K	473 K	498 K	523 K				
Ni ₂ P/SiO ₂ HZSM-5	41 9	54 25	86 68	100 91				
	Turnover free	uency (s ⁻¹)						
Ni ₂ P/SiO ₂ HZSM-5	0.0025 0.00057	0.0033 0.0016	0.0053 0.0042	0.0062 0.0056				

Apparent activation energies were calculated from fits to the conversion curves at low conversion and were 39 kJ mol^{-1} for HZSM-5 and 46 kJ mol^{-1} for Ni₂P/SiO₂.

Fig. 8 shows the ethanol conversion and product yields as a function of contact time over the HZSM-5 catalyst at 473 and 498 K. It can be seen that the conversion increased with time and temperature, as expected. The product formed in highest yield was ethylene. At 473 K (Fig. 8a), the ethylene decreased slightly at high contact time, and this was accompanied by a corresponding growth in butylenes, indicating that part of the ethylene might have been consumed to form the C4 products. Acetaldehyde was produced at low contact time together with ethylene, suggesting that these C2 species were produced in parallel. However, acetaldehyde did not grow appreciably with time, suggesting that it was an intermediate that also reacted to form the butylenes. At 498 K (Fig. 8b), ethylene grew monotonically with contact time. Acetaldehyde was formed in small amounts and went through a shallow maximum at short contact time, confirming that it is an intermediate. The butylenes were



Fig. 8. Variation of ethanol conversion and product yield as a function of reaction temperature at a contact time of 162 s: (a) HZSM-5 and (b) Ni_2P/SiO_2 .

formed in small but growing amounts, indicating that they were final products. Overall, the results indicated that ethylene and acetaldehyde were formed in parallel and reacted by a condensation reaction to form butylenes. At higher temperatures, the ethylene was the preferred product, and the acetaldehyde was largely consumed to form the butylenes, resulting in a smaller acetaldehyde yield than at lower temperatures.

Fig. 9 shows the ethanol conversion and yields of acetaldehyde and ethylene as a function of contact time at 473 and 498 K on Ni₂P/SiO₂. The curves are fits to the data that will be discussed later. The figure indicates that conversion and the yields of products increase with contact time. The data at 473 K (Fig. 9a) show both ethylene and acetaldehyde growing with time. From these data alone, it is not possible to deduce the sequence of reaction steps. Indeed, it could be that acetaldehyde and ethylene are produced in parallel. As will be shown, this is not the case. The data at 498 K (Fig. 9b) this time show that acetaldehyde goes through a maximum, while ethylene rises monotonically, behaviors characteristic of a sequential network. This result is in accordance with a previous report [73] in which the conversion of ethanol increased with increasing contact time along with a drop in acetaldehyde selectivity. As will be discussed in the modeling section, both sets of data can be described by a reaction sequence involving adsorbed intermediates undergoing consecutive reactions.

It should be emphasized that the measurements were carried out by varying the contact time up and down over a period of 10 h, so that the smoothness of the data provides evidence for the lack of deactivation. This fact and the obtention of a mass bal-



Fig. 9. Variation of ethanol conversion and product yield as a function of contact time on HZSM-5: (a) reaction temperature of 473 K and (b) reaction temperature of 498 K.

ance of $100 \pm 5\%$ indicate that the maximum acetaldehyde yield is not due to its consumption to form products such as butylenes (not detected) or heavy materials like polymers.

It should be noted that no ethane was detected. At the conditions of this study, the concentration of the ethanol reactant is low (1.5 mol%), and since the concentration of products is significantly lower, it is difficult for the hydrogen (from dehydrogenation) and ethylene (from dehydration) to come into contact to form ethane. Furthermore, the ethane formation reaction is favored by high temperature and pressure, which are not the conditions employed in our study. Thus, the lack of formation of ethane is understandable. Other studies report acetaldehyde and ethylene formation but not ethane [20,26].

Reaction temperature and contact time play important roles in the decomposition of ethanol, and their effect on the steady-state reactivity of HZSM-5 and Ni_2P/SiO_2 was examined. To summarize, on HZSM-5, the main product was ethylene with small amounts of acetaldehyde and butylenes. The formation of the ethylene can be attributed to acid sites, which NH_3 and pyridine titration showed to be plentiful, while the formation of acetaldehyde can be associated with basic sites, which also are present in smaller quantities. Butylenes formed at long contact time are likely formed by condensation of ethylene and acetaldehyde on strong Brønsted acid sites. The reaction network can be described as a parallel network in which ethylene and acetaldehyde are produced together by different mechanisms.

On Ni₂P/SiO₂, the main products of the ethanol reaction were ethylene and acetaldehyde with small amounts of carbon monoxide and trace quantities of methane, without ethane. The reaction likely starts with the formation of an ethoxide species on the silica which subsequently undergoes dehydrogenation/hydrogenation steps on the Ni₂P surface, due to the high reactivity of the metal centers in hydrogen transfer reactions. Acetaldehyde was formed as an intermediate compound, so the reaction network can be described as a sequential network.

The results in Fig. 10 suggest that there is a consecutive reaction: ethanol \rightarrow acetaldehyde \rightarrow ethylene. This seems odd, because this would entail the oxidation of ethanol before the formation of ethylene, which is unlikely at reductive conditions as used here. It was reasoned that a more likely possibility was that there existed a common species at the surface that could react to form both acetaldehyde and ethylene in a sequential manner. This led to the scheme above (Scheme 1).

Ethanol first adsorbs onto a vacant site to form an ethoxide species. This undergoes dehydrogenation through an alpha-H abstraction from the carbon proximal to the oxygen to form adsorbed acetaldehyde. The adsorbed acetaldehyde can desorb or can react further through an enolization reaction involving a beta-H abstraction from the carbon distal to the oxygen. This can then undergo hydrogenolysis with adsorbed hydrogen on active sites to form ethylene and an adsorbed OH group (not shown).

The catalytic reaction network was simulated based on the disappearance rate of ethanol and the formation rate of acetylene and ethylene. Details on the kinetic analysis are presented in the Supplementary Information. Ethanol, acetylene, and ethylene were noted as A, B, and C, and the corresponding adsorbed ethoxy, acetaldehyde, and vinyl alcohol are denoted as A^{*}, B^{*}, and C^{*}, respectively.

The kinetic rate law equations are the following:

$$\frac{V}{S}\frac{d[A]}{d\tau} = -k_{A}[A][*] + k_{-A}[A^{*}]$$
(1)

$$\frac{V}{S}\frac{d[B]}{d\tau} = -k_{\rm B}[B][*] + k_{-\rm B}[B^*]$$
(2)



Fig. 10. Variation of ethanol conversion and product yield as a function of contact time on Ni_2P/SiO_2 . The curves are fits from a simulation model discussed in the text: (a) reaction temperature of 473 K and (b) reaction temperature of 498 K.

$$\frac{V}{S}\frac{d[C]}{d\tau} = -k_{\rm C}[C][*] + k_{\rm -C}[C^*]$$
(3)

The rate of consumption of A, $-r_A = \frac{V}{S} \frac{d[A]}{d\tau}$, has units of mol m⁻²s⁻¹, in which $V(m^3)$ is the bed volume and $S(m^2)$ is the catalyst surface area. This rate is generally expressed as $-r_A = [L]kf(Y)$ where [L] (mol m⁻²) is the total concentration of sites, k is a rate constant, and f(Y) is a dimensionless function of concentrations.

The bed volume is given by $V = w/\rho_A$, where ρ_A (0.3 g cm⁻³) is the apparent density. The total surface area of Ni₂P (m²) is given by S = awf, where a (42 m² g⁻¹) is the Ni₂P effective surface area, obtained from the equation $a = \frac{6}{\rho D_C}$, w (0.900 g) is the weight of catalyst, f (0.079) is the fractional weight loading of the Ni₂P, ρ



Scheme 1. "Rake" mechanism for ethanol reaction.

$$\frac{d[\mathbf{A}^*]}{d\tau} = k_{\mathbf{A}}[\mathbf{A}][*] - (k_{-\mathbf{A}} + k_1)[\mathbf{A}^*] + k_{-1}[\mathbf{B}^*] = \mathbf{0}$$
(4)

$$\frac{d[\mathbf{B}^*]}{d\tau} = k_{\mathbf{B}}[\mathbf{B}][*] + k_1[\mathbf{A}^*] - (k_{-\mathbf{B}} + k_{-1} + k_2)[\mathbf{B}^*] + k_{-2}[\mathbf{C}^*] = \mathbf{0}$$
(5)

$$\frac{d[C^*]}{d\tau} = k_2[B^*] - (k_{-C} + k_{-2})[C^*] + k_C[C][*] = 0$$
(6)

Use was made of an active site balance, where [L] is the total concentration of active sites:

$$[L] = [*] + [A^*] + [B^*] + [C^*]$$
(7)

This kind of scheme is known in the literature as a "rake" mechanism because the adsorption and desorption steps when written out as in Scheme 1 resemble the prongs of the device used to gather leaves. The rake mechanism was first described by Cormerais et al. [74] and has been suggested to apply to many types of reactions [75,76], but in the early days of its introduction 30 years ago, the solution of the equations was not readily possible. Even to this day, many kinetic studies still use simple first-order analysis of networks that ignore the existence of the adsorption steps. In this case, the equations were solved numerically (Table 7) to obtain plots of acetaldehyde and ethylene yields and conversion versus time.

As can be seen by the curves shown in Fig. 10a and b, the simulation results are in good agreement with the experimental points, even though the behavior of the species is different at each temperature. At 473 K, the acetaldehyde yield grows together with that of ethylene, while at 498 K, there is a clear maximum in the acetaldehyde yield. The rate constants are reasonable, with smaller values at lower temperature as expected. The closeness of the fits indicates that the proposed mechanism describes the physical situation accurately.

In order to further check the reasonableness of the mechanism, measurements of adsorbed surface intermediates were taken. Data were taken at different temperatures with ethanol adsorbed using He as carrier (Fig. 11).

Table 8 summarizes the assignments in the spectra. At high wavenumber, two sharp negative bands at 3746 and 3665 cm⁻¹ are due to SiO-H and PO-H stretching vibrations and appear negative because the hydroxyls are being consumed [56]. At 2990, 2940, and 2900 cm^{-1} , a cluster of peaks appear that are due to C-H stretching vibrations for methyl and methylene groups. Next in the center of the spectrum appear bands at 2365 and 2330 due to gas-phase CO₂ interference. For the highest temperature data, weak broad bands are present at 1930 and 1830 cm⁻¹, which are attributed to combination bands. A small feature at 1750 cm⁻¹ is due to adsorbed aldehyde CHO. At 1580 cm⁻¹, a small peak is observed that grows with temperature. This position is characteristic of a C=C double bond. An oddly shaped feature at 1400 cm^{-1} followed by a negative peak at 1366 cm⁻¹ is due to background subtraction. A feature at 1260 cm⁻¹ corresponds to a CH₂ wag. Peaks at 1070 and 890 cm⁻¹ are assigned to the SiO₂ support. Peaks at lower wavenumber are obscured by interference from the silica.

Overall, in He atmosphere, the diminution of OH bands and the growth of C—H stretching vibrations are consistent with the formation of ethoxide species bound to Si—OH and P—OH hydroxyl func-

Table 7	
Rate constants use	ed in the simulation.

Temperature (K)	$k_{\rm A} ({\rm cm}^3{ m mol}^{-1}{ m s}^{-1})$	$k_{-A} (s^{-1})$	$k_{\rm B} ({\rm cm^3}{ m mol^{-1}}{ m s^{-1}})$	$k_{-B} (s^{-1})$	$k_{\rm C} ({\rm cm}^3{\rm mol}^{-1}{\rm s}^{-1})$	$k_{-C} (s^{-1})$	$k_1 ({ m s}^{-1})$	$k_{-1} (s^{-1})$	$k_2 ({ m s}^{-1})$	$k_{-2} ({ m s}^{-1})$
473 498	$\begin{array}{c} 2.80\times10^7\\ 3.50\times10^7\end{array}$	8.50 9.00	$\begin{array}{l} 3.50\times10^7\\ 4.00\times10^7\end{array}$	6.75 12.0	$\begin{array}{c} 2.75\times10^7\\ 3.25\times10^7\end{array}$	2.25 30.0	9.00 17.0	4.50 5.00	3.75 5.50	3.00 3.50



Fig. 11. EtOH FTIR over Ni₂P/SiO₂ with 0.15% EtOH in He flow.

tionalities. There is also evidence for an adsorbed acetaldehyde species with a band at 1750 cm^{-1} and the formation of an ethylene or vinyl alcohol species contributing to the C=C signal at 1580 cm^{-1} .

In order to obtain more information on the behavior of the adsorbed species, a transient experiment was carried out. The objective was to approximate the contact time measurements shown in Fig. 10b. A Ni_2P/SiO_2 sample was exposed to the ethanol reactant stream (1.5%), and then the flow was switched to He. The spectra of ethanol FTIR at 497 K as a function of time are shown in Fig. 12.

The assignments in Fig. 12 are the same as in Fig. 11. In Fig. 12, vertical lines have been placed at 1750 cm^{-1} (position for an aldehyde functionality, HC=O) and at 1580 cm^{-1} (position for an olefin double bond). The experiment starts at time zero with the steady-steady ethanol reaction, so the expected main species is adsorbed ethoxide on the silica surface, together with acetaldehyde and eth-

Table 8	
Summary of FTIR assignments.	

ylene precursors on the Ni₂P. When the flow is switched to He, the species on Ni₂P desorb and are replaced with species from the ethoxide pool on the silica. Examination of the signal due to an aldehyde at 1750 cm⁻¹ shows that the peak increased significantly in size at a contact time of 60 s but then disappeared at a contact time of 300 s. The behavior is mirrored in the C-H stretch region at 2900-2800 cm⁻¹. These findings essentially agree with the reactivity results for acetaldehyde in Fig. 10b, which show a maximum close to 60 s and then a decrease. Consideration of the signal at 1580 cm⁻¹ due to an olefin (C=C) shows that it is present at time zero. When the atmosphere is switched to He, its intensity decreases slightly at 60 s and then increases at 300 s. The increase is understandable as the acetaldehyde is converted to an ethylene precursor. These results are also consistent with the results in Fig. 10b and the proposed rake mechanism in which the adsorbed acetaldehyde is an intermediate that is converted to an ethylene precursor on the surface of the catalyst. There was no growth in the band at 2075 cm^{-1} due to adsorbed carbon monoxide (CO). This further indicates that the adsorbed aldehyde did not decompose into CH₄ and CO but was converted to ethylene.

The picture that emerges from the FTIR measurements is consistent with the reaction scheme presented earlier. Ethanol adsorbs on hydroxyl species on the silica to form ethoxide species. Substantial work [77,78] indicates that alkoxide species on silica are highly mobile so these can readily move to the Ni₂P surface, which is excellent in hydrogen transfer reactions [34–44]. A first reaction that occurs is dehydrogenation to form an adsorbed acetaldehyde (growth in band of 1750 cm⁻¹). Subsequently, in He, the acetaldehyde undergoes an enolization to vinyl alcohol (growth in band at 1580 cm⁻¹). This set of steps accounts for the main species formed and the main catalytic pathway in the reaction. There is also a side reaction, which is not major in the steady state, but which proceeds in temperature-programmed reaction, namely the formation

Sammary of Fine dosignments.				
Band (cm ⁻¹)	Assignment	Species	Reference	
3746 (neg)	SiO—H stretch	Si—OH	[56]	
3665 (neg)	PO—H stretch	Р—ОН	[56]	
2990, 2940, 2900	C—H stretch	CH ₃ CH ₃ , CH ₂ =CH-OH CH ₃ CHO, CH ₃ CH ₂ OH, CH ₂ =CH ₂	[79,80]	
2075	C=0	CO	[41,56]	
1930, 1830	Combination			
1750	HC=0	НСНО	[77,78]	
1580	C=C	CH ₂ =CH-OH	[80]	
1400	OH bend		[77]	
1366 (neg)	Background subtraction			
~1310, 1260	CH ₂ wag	CH ₃ CH ₂ OH	[79]	
$\sim \! 1160$	C—C stretch	CH ₃ CHO, CH ₃ CH ₂ OH	[80]	
	Combination	CH ₂ =CH-OH		
~ 1070	Si—O	SiO ₂		
~890	Si—O—Si	SiO ₂		
~990	C=C wag	CH ₂ =CH ₂		
	C—C stretch	CH_3CH_3 , CH_3CH_2OH	[79,80]	
790–830	CH ₃ rock	CH_3CH_3 , CH_3CHO	[77,79]	
	CH ₂ rock	CH ₂ =CH ₂		
\sim 760	C—H bend	CH ₃ CHO	[79]	
~ 600	$CH_2 = C OPLA$	CH ₂ =CH-OH	[78]	
\sim 500	C—C—O deform	CH ₃ CHO	[79]	
300-400	Torsion	CH ₂ =CH-OH	[78]	



Fig. 12. EtOH FTIR over Ni₂P/SiO₂ in He at 497 K.

of adsorbed CO. This is likely the result of the decomposition of adsorbed acetaldehyde in the presence of H_2 (not He) to a methyl species and CO. The hydrogen is likely adsorbed atomic hydrogen, and the driving force is the formation of methane and strongly bonded CO. Although not a primary path in the steady-state reaction, this pathway accounts for the observation of CH_4 and CO in the ethanol TPD spectra (Fig. 7).

The reaction of ethanol on HZSM-5 and Ni_2P/SiO_2 provides information on the reaction pathways on a typical acid catalyst and a metal catalyst. The acid catalyst, HZSM-5, carries out simple dehydration to form ethylene. The metal catalyst also forms mainly ethylene, but through a non-direct pathway in which an adsorbed ethoxide species is first dehydrogenated to a surface acetaldehyde species, which undergoes enolization to a vinyl alkoxide and subsequent hydrodeoxygenation. This route is non-direct and occurs because of the strongly metallic hydrogenation/dehydrogenation properties of the Ni₂P. It is important because the pathway may also be involved in the reactions of more complex molecules, and for this reason, its participation should be considered in the study of their conversion.

4. Conclusions

The experiments described in this work lead us to the following conclusions:

- 1. Comparison between the properties of commercial HZSM-5(Si/ Al = 15) and synthesized Ni₂P/SiO₂ catalysts showed that HZSM-5 possesses higher surface area and stronger acidic sites than the Ni₂P/SiO₂ catalyst. The Ni₂P/SiO₂ catalyst essentially has more mesopores and moderate acid and basic sites. Infrared spectroscopy of pyridine reveals that acidity of HZSM-5 and Ni₂P/SiO₂ catalysts consists mainly of Brønsted and Lewis acid sites, respectively. In the ethanol temperature-programmed desorption process (EtOH-TPD), the Ni₂P/SiO₂ catalyst exhibited a higher selectivity toward dehydrogenation products (acetaldehyde) than HZSM-5.
- 2. Steady-state reaction results confirm that the Ni₂P/SiO₂ produces both acetaldehyde and ethylene, and contact time studies indicate that acetaldehyde is a primary product and ethylene is a secondary product. The reaction, however, does not consist of an oxidation reaction followed by a reduction reaction, but involves sequential reactions on the surface, namely a rake mechanism. Analysis of the reaction sequence and simulation of the results give support for this interpretation. Measurements by in situ Fourier transform infrared spectroscopy also give evidence for the presence of the suggested intermediate,

adsorbed acetaldehyde on the surface of the catalyst at reaction conditions. Measurements at increasing contact times show that it increases and then disappears, in agreement with the corresponding reactivity results.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2012.02.001.

References

- [1] T.V. Choudhary, C.B. Phillips, Appl. Catal., A 397 (2011) 1.
- [2] J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, Chem. Rev. 110 (2010) 3552.
- [3] A. Wawrzetz, B. Peng, A. Hrabar, A. Jentys, A.A. Lemonidou, J.A. Lercher, J. Catal. 269 (2010) 411–420.
- [4] O. Casanova, S. Iborra, A. Corma, J. Catal. 275 (2010) 236-242.
- [5] J.J. Bozell, G.R. Petersen, Green Chem. 12 (2010) 539.
- [6] J.C. Serrano-Ruiz, D. Wang, J.A. Dumesic, Green Chem. 12 (2010) 574.
- [7] A. Birot, F. Epron, C. Descorme, D. Duprez, Appl. Catal., B 79 (2008) 17-25.
- [8] J. Rass-Hansen, R. Johansson, M. Moller, C.H. Christensen, Int. J. Hydrogen Energy 33 (2008) 4547–4554.
- [9] E.B. Pereira, P. Ramírez de la Piscina, N. Homs, Bioresource Technol. 102 (2011) 3419-3423.
- [10] A.H. Tullo, Chem. Eng. News 89 (May 16) (2011) 24-25.
- [11] R.L. Guenard, L.C.F. Torres, B. Kim, S.S. Perry, P. Frantz, S.V. Didziulis, Surf. Sci. 515 (2002) 103–116.
- [12] P.A. Clayborne, T.C. Nelson, T.C. De Vore, Appl. Catal., A 257 (2004) 225–233.
 [13] B.M. Nagaraja, A.H. Padmasri, P. Seetharamulu, K.H.P. Reddy, B.D. Raju, K.S.R.
- Rao, J. Mol. Catal. A 278 (2007) 29–37. [14] E.A. El-Katatny, S.A. Halawy, M.A. Mohamed, M.I. Zaki, Appl. Catal., A 1999
- (2000) 83–92. [15] N.R.C.F. Machado, V. Calsavara, N.G.C. Astrath, C.K. Matsuda, A.P. Junior, M.L.
- Baesso, Fuel 84 (2005) 2064–2070.
- [16] V. Calsavara, M.L. Baesso, N.R.C.F. Machado, Fuel 87 (2008) 1628-1636.
- [17] N. Takezawa, C. Hanamaki, H. Kobayashi, J. Catal. 38 (1975) 101-109.
- [18] Y. Matsumura, K. Hashimoto, S. Yoshida, J. Catal. 117 (1989) 135-143.
- [19] I. Takahara, M. Saito, M. Inaba, K. Murata, Catal. Lett. 105 (2005) 249-252.
- [20] X. Zhang, R. Wang, X. Yang, F. Zhang, Micropor. Mesopor. Mater. 116 (2008) 210-215.
- [21] J. Schulz, F. Bandermann, Chem. Eng. Technol. 17 (1994) 179-186.
- [22] C.B. Phillips, R. Datta, Ind. Eng. Chem. Res. 36 (1997) 4466-4475.
- [23] J.M. Vohs, M.A. Barteau, Surf. Sci. 211 (1989) 590-608.
- [24] F.W. Chang, W.Y. Kuo, K.C. Lee, Appl. Catal., A 246 (2003) 253-264.
- [25] M.A. Aramendía, V. Borau, C. Jiménez, J.M. Marinas, A. Porras, F.J. Urbano, J. Catal. 161 (1996) 829-838.
- [26] Y. Shinohara, T. Nakajima, S. Suzuki, J. Mol. Struct. 460 (1999) 231-244.
- [27] M.M. Doheim, H.G. El-Shobaky, Colloids Surf. A 204 (2002) 169-174.
- [28] F.S. Ramos, A.M. Duarte de farias, L.E.P. Borges, J.L. Monteiro, M.A. Fraga, E.F. Sousa-Aguiar, L.G. Appel, Catal. Today 101 (2005) 39-44.
- [29] M.A. Aramendía, V. Boráu, C. Jiménez, J.M. Marinas, A. Porras, F.J. Urbano, React. Kinet. Catal. Lett. 65 (1998) 25–31.
- [30] M.A. Aramendíra, V. Boráu, I.M. García, C. Jiménez, A. Marinas, J.M. Marinas, A. Porras, F.J. Urbano, Appl. Catal., A 184 (1999) 115–125.
- [31] H.Y. Zhao, D. Li, P. Bui, S.T. Oyama, Appl. Catal., A 391 (2011) 305-310.
- [32] Y. Shu, Y.-K. Lee, S.T. Oyama, J. Catal. 236 (2005) 112-121.
- [33] T. Kawai, K.K. Bamdo, Y.-K. Lee, S.T. Oyama, W.-J. Chun, K. Asakura, J. Catal. 241 (2006) 20–24.
- [34] X. Wang, P. Clark, S.T. Oyama, J. Catal. 208 (2002) 321-331.
- [35] S.T. Oyama, X. Wang, Y.-K. Lee, K. Bando, F.G. Requejo, J. Catal. 210 (2002) 207– 217.
- [36] S.T. Oyama, T. Gott, H. Zhao, Y.-K. Lee, Catal. Today 143 (2009) 94-107.
- [37] S.T. Oyama, J. Catal. 216 (2003) 343-352.
- [38] S.T. Oyama, X. Wang, F. Requejo, T. Sato, Y. Yoshimura, J. Catal. 209 (2002) 1–5.
- [39] S.T. Oyama, X. Wang, Y.-K. Lee, W.-J. Chun, J. Catal. 221 (2004) 263–273.
- [40] S.T. Oyama, X. Wang, Y. Lee, K. Bando, F.G. Requejo, J. Catal. 210 (2004) 207-217.
- [41] S.J. Sawhill, K.A. Layman, D.R. Van Wyk, M.H. Engelhard, C. Wang, M.E. Bussell, J. Catal. 231 (2005) 300–313.

- [42] P.A. Clark, X. Wang, P. Deck, J. Catal. 210 (2002) 116-126.
- [43] P.A. Clark, S.T. Oyama, J. Catal. 218 (2003) 78-87.
- [44] S.T. Oyama, Y.-K. Lee, J. Catal. 258 (2008) 393-400.
- [45] M. Guisnet, P. Magenoux, Stud. Surf. Sci. Catal. 88 (1994) 53-68.
- [46] A.G. Gayubo, A. Alonso, B. Valle, A.T. Aguayo, J. Bilbao, Appl. Catal., B 97 (2010) 299-306.
- [47] P. Berteau, B. Delmon, Appl. Catal. 70 (1991) 307-323.
- [48] W. Wang, S.P. Wang, X.B. Ma, J.L. Gong, Catal. Today 148 (2009) 323-328.
- [49] S.R. Jagtap, Y.P. Patil, Appl. Catal., A 341 (2008) 133-138.
- [50] A.S. Ndou, N. Plint, N.J. Coville, Appl. Catal., A 251 (2003) 337-345.
- [51] P. Berteau, B. Delmon, Catal. Today 5 (1989) 121-137.
- [52] J.D. Bi, X. W Guo, M. Liu, X.S. Wang, Catal. Today 149 (2010) 143-147.
- [53] J.G. Post, H.G.V. Hoof, Zeolites 4 (1984) 9-14.
- [54] D.J. Parrillo, C. Lee, R.J. Gorte, Appl. Catal., A 110 (1994) 67-74.
- [55] H.G. Karge, V. Dondur, J. Weitkamp, J. Phys. Chem. 95 (1991) 283-288.
- [56] Y.-K. Lee, S.T. Oyama, J. Catal. 239 (2006) 376-389.
- [57] T. Gott, S.T. Oyama, J. Catal. 263 (2009) 359-371.
- [58] S.T. Oyama, T. Gott, K. Asakura, S. Takakusagi, K. Miyazaki, Y. Koike, K.K. Bando, J. Catal. 268 (2009) 209–222.
- [59] K.M.A. El-Salaam, E.A. Hassan, Surf. Technol. 16 (1982) 121-128.
- [60] F.F. Roca, L.D. Mourgues, Y. Trambouze, J. Catal. 14 (1969) 107–113.
 [61] S. Golay, L. Kiwi-Minsker, R. Doepper, A. Renken, Chem. Eng. Sci. 54 (1999) 3593–3598.
- [62] R.L. Mao, T.S. Le, M. Fairbairn, A. Muntasar, S. Xiao, G. Denes, Appl. Catal., A 185 (1999) 41–52.
- [63] M. Lenarda, M.D. Ros, M. Casagrande, L. Storaro, R. Ganzerla, Inorg. Chim. Acta 349 (2003) 195-202.

- [64] C.A. Emeis, J. Catal. 141 (1993) 347-354.
- [65] G.A.M. Hussein, N. Sheppard, J. Chem. Soc. Faraday Trans. 87 (1991) 2661– 2668.
- [66] M. Dömöka, M. Tótha, J. Raskób, A. Erdőhelyi, Appl. Catal., B 69 (2007) 262– 272.
- [67] J. Franckaerts, G.F. Froment, Chem. Eng. Sci. 19 (1964) 807-818.
- [68] T. Yamazaki, N. Kikuchi, M. Katoh, T. Hirose, H. Saito, T. Yoshikawa, M. Wada, Appl. Catal., B 99 (2010) 81–88.
- [69] A. Gazsi, A. Koos, T. Bansagi, F. Solymosi, Catal. Today 160 (2011) 70-78.
- [70] A.P. Farkas, F. Solymosi, Surf. Sci. 601 (2007) 193-200.
- [71] R.J. Gorte, J. Catal. 75 (1982) 164-174.
- [72] E.E. Ibok, D.F. Ollis, J. Catal. 66 (1980) 391-400.
- [73] B.M. Abu-Zied, A.M. El-Awad, J. Mol. Catal. A 176 (2001) 227-246.
- [74] F.X. Cormerais, G. Perot, F. Chevalier, M. Guisnet, J. Chem. Res. S (1980) 362-363.
- [75] S. Lars, T. Andersson, J. Catal. 98 (1986) 138-149.
- [76] M. Stöcker, Mesopor. Micropor. Mater. 29 (1999) 3-48.
- [77] M. Seman, J.N. Kondo, K. Domen, R. Radhakrishnan, S.T. Oyama, J. Phys. Chem. B 106 (2002) 12965–12977.
- [78] M. Seman, J.N. Kondo, K. Domen, R. Radhakrishnan, S.T. Oyama, Chem. Lett. 11 (2002) 1082–1083.
- [79] T. Shimanouchi, Molecular vibrational frequencies, in: P.J. Linstrom, W.G. Mallard (Eds.), NIST Chemistry WebBook, NIST Standard Reference Database Number 69, 37 National Institute of Standards and Technology, Gaithersburg, MD 20899. http://webbook.nist.gov> (retrieved 23.06.11).
- [80] M. Hawkins, L. Andrews, J. Am. Chem. Soc. 105 (1983) 2523-2530.