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Hydroconversion of lignin-derived platform compound guaiacol to fuel additives and value-added chemicals over alumina-supported Ni catalysts

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ABSTRACT

Hydroconversion of guaiacol (GUA) over γ -Al₂O₃ and phosphatized- γ -Al₂O₃ (γ -Al₂O₃(P)) supported Ni catalysts was initiated by Lewis-sites and active Ni sites. Conversion proceeded via transmethylation and hydrodemethylation/hydrodemethoxylation as major and minor pathways, respectively, resulting in mainly catechol and methylcatechols, and via series of consecutive hydrodehydroxylation (HDHY) and ring hydrogenation (HYD) reactions leading to partially and fully deoxygenated, saturated, and unsaturated products. High Ni-loading and high H₂ pressure promoted the formation of cyclohexane and methyl-substituted cyclohexanes; however, above 300 °C the hydrogenation-dehydrogenation equilibrium favored the formation of benzene and methyl-substituted benzenes. Ni/ γ -Al₂O₃(P) showed suppressed HYD/HDHY activity resulting in pronounced formation of catechol and/or phenol and their methyl-substituted derivatives. Surface phenolate species were substantiated as surface intermediates of hydrodeoxygenation. Phosphatizing reduced the concentration of both basic OH and Lewis acid (Al⁺) – Lewis base (O⁻) pair surface sites of the γ -Al₂O₃ support and, thereby, suppressed phenolate formation and hydrodeoxgenation.

1. Introduction

Lignocellulosic biomass is the most abundantly available resource of renewable organic material. Converting lignocellulose into chemicals and fuels is of major interest to reduce dependence on fossil carbon resources [1-4]. Lignocellulose is composed of polymeric saccharides (cellulose, hemicellulose) and polymeric aromatics (lignin) [2,4]. Lignin is a three-dimensional, amorphous polymer built from methoxylated phenylpropane monomers (p-coumaryl alcohol, coniferyl alcohol, sinapyl alcohol) [5]. It is obtained in huge quantities as by-product of pulp and paper industry as well as of cellulosic ethanol industry and can be considered as an abundantly available renewable carbon source [6–11]. Its chemical and/or thermochemical depolymerization gives bio-oil that consists mainly of aromatic compounds. Because of their high oxygenate content, the bio-oils have low heating value, poor thermal stability, and are corrosive. Therefore, they need quality improving treatment before utilization or storage [11,12]. The catalytic hydrodeoxygenation (HDO) of the bio-oils gives value-added products, such as fuel additives, industrial solvents, and precursors for the

polymer and fine chemical industry [10–14].

Guaiacol (GUA) is a preferred model feedstock to investigate the processes of bio-oil HDO. It makes up a large proportion of oils of lignin origin and contains typical bio-oxygenate functionalities, such as, hydroxyl and methoxy groups, and contains three types of C–O bonds [10–12]. The C–O bonds must be cleaved in the HDO reaction. The dissociation energies of O–CH₃, C_{Ar}–OCH₃, and C_{Ar}–OH (where subscript Ar stands for aromatic) in GUA are 262–276, 409–421 and 466 kJ·mol⁻¹, respectively [15]. Note that the strength of these bonds will be lower, if the 6-member ring is saturated; however, the order of the dissociation energies remains the same [7]. These data suggest that demethylation is preferred over demethoxylation; however, steric constraints can be significantly higher for cleaving O–CH₃ bond than for C_{Ar} –OCH₃, resulting in the preferential braking of latter bond [15,16]. It seems to be the most difficult to make oxygen-free product if cleavage of C_{Ar} –OH bonds is needed [11,17].

The HDO reaction of GUA can result in a variety of fully or partially deoxygenated products, mainly derivatives of cyclohexane and benzene [11]. It was shown that primary reactions, such as ring hydrogenation,

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hydrodemethoxylation, hydrodemethylation, hydroand dehydroxylation could be accompanied by secondary transformations of the primary products [11,12]. Saturated hydrocarbon products like cyclohexane and methylcyclohexane can be used as fuel or non-polar solvent [11]. The partially reduced products like cyclohexanone and cyclohexanol are industrial precursors of nylons [11,18]. Aromatic products like benzene, toluene, and xylenes are important precursors of many commercial chemicals and polymers, such as, trinitrotoluene, nylons, rubbers and plastics [19]. Phenol serves as a precursor to a large array of drugs, herbicides, cosmetics, pharmaceuticals, and plastics [11]. Selectivity control is a major issue in designing HDO catalysts. The selectivity depends strongly on the balance of the hydrogenation and acidic functions of the catalyst and on the reaction conditions, mainly on the temperature and H_2 partial pressure [10–14,18,20].

Solid Brønsted acids, such as, H-Y zeolite, SiO₂-Al₂O₃, and sulfated ZrO₂-CeO₂ mixed oxides, carrying noble metal (Pt, Pd, Ru, Rh) were found to have high HDO activity and cycloalkane selectivity [21-23]. When metal oxides, such as ZrO₂, TiO₂, SiO₂ or CeO₂ were used as catalyst support, mainly cyclohexanol and/or cyclohexanone were formed [18,24,25]. Chang and coworkers [26] reported about high phenol or benzene yield using Mo/C catalysts. Similar results were obtained by Cai and coworkers [27]. Some supported transition metal catalysts (Ni, Co, Cu, Fe) were also active giving mainly unsaturated products, such as phenol and other aromatic compounds [19,28-32]. Among non-noble metal catalysts, the Ni and bimetallic Ni-containing catalysts have attracted significant attention due to their promising HDO potentials [10–12,20]. For example, hydrogenation of the benzene ring prevails at mild temperatures and reasonably high H₂ pressure, whereas higher temperatures (>300 °C) favor C-O bond hydrogenolysis. In the presence of strong acid sites, the latter reactions dominate even under mild reaction conditions [10]. It follows that the HDO reaction of GUA can be steered toward the desired reaction product by properly designed Ni-based catalysts and by applying suitable reaction conditions.

The stability of Ni-based catalysts in the HDO reaction is a major issue [10,12,32]. Sintering and/or leaching of the active metal can lead to activity loss; however, the main cause of deactivation is usually the deposition of aromatic polymers (catalyst coking), especially over the strong acid sites [10,12,32]. Deactivation due to sintering and coking is suppressed, if the hydrogenation and acid-base functions are well balanced and the required activity is achieved under moderate reaction conditions. Leaching of the active metal can be largely avoided by using solvent free, flow-through gas-phase reaction system [10]. The hydrogenation function of the catalyst can be controlled by controlling the metal particle size and metal loading, or by introducing a second metal as a promoter, e.g., for controlling the metal-support interaction [10-12]. The desired acid-base properties can be attained either by selecting a proper support material or by adjusting the acid-base properties of the support by surface modification. For instance, it was recently shown that phosphatizing of the γ -alumina support results in partial elimination of Lewis type acid-base pair sites and, thereby, in altering the HDO activity and selectivity of supported Pd catalysts in the hydroconversion of triglycerides [33].

The main objective of the present study is to better understand the HDO reactions of GUA model compound over Ni-based catalysts. The reaction was carried out using a fixed-bed flow-through microreactor. The hydrogenation function was varied by the metal loading, whereas the acid-base properties of the γ -Al₂O₃ support was modified by phosphatizing the catalyst surface. In a former study, related to the HDO of a triglyceride [33], we have shown that phosphatizing the γ -Al₂O₃ surface significantly decreased the number of those Lewis acid – Lewis base pair sites, responsible for the formation of surface intermediate of low reactivity, whereas the newly formed P–OH sites served as adsorption sites for forming active surface intermediate more prone to HDO reaction and enhanced formation of O-free paraffin products. In the present study, the modification of the acid-base properties of γ -Al₂O₃ by

phosphatization also resulted in a drastic change of the product distribution in the hydroconversion of GUA over Ni/ γ -Al₂O₃(P) catalysts. The effect of the reaction conditions on the catalytic activity and selectivity, such as, time-on-stream, space time, and temperature, was also studied. It will be shown how Ni loading and acidity of the catalyst affect the relative weights of the possible reaction pathways in the HDO reaction of GUA.

2. Experimental

2.1. Catalyst preparation

Commercial γ -Al₂O₃ (Alfa Aesar, 1/8" pellets) and its phosphatized derivative were used as support. The phosphatization of the commercial γ -Al₂O₃ was done using aqueous H₃PO₄ solution [33]. The γ -alumina pellets were first crushed and sieved to get a 0.316–0.63 mm particle size fraction, which was then dried at 110 °C for 12 h. Ten grams of the dried γ -Al₂O₃ grains were impregnated with 10 cm³ solution containing 1.1 ml of concentrated phosphoric acid (85% H₃PO₄, WVR) to achieve a P content of about 5 wt%. The impregnated support was dried at 110 °C for 16 h then it was calcined at 550 °C for 4 h to get the phosphatized γ -Al₂O₃ support [33]. The neat and the phosphatized supports are referred as γ -Al₂O₃(P) sample contains chemically bonded surface phosphate in forms of monomeric and mostly polymeric (about 75%) phosphate species [33].

Catalysts containing 5 or 20 wt% Ni were prepared by wet impregnation of the two alumina supports. The support material (10.4 g) was suspended in calculated amount of 0.26 M aqueous solution of Ni (NO₃)₂·6 H₂O (Aldrich, 98%) to get 5 or 20 wt% of Ni content in the catalyst. The suspension was slowly dried at 60 °C for 12 h then the Niprecursor compound was decomposed by temperature–programmed calcination. First, the dried solid was heated to 150 °C at a rate of 2 °C·min⁻¹ and held at this temperature for 1 h, then it was heated to 450 °C at a rate of 4 °C·min⁻¹ and held at this temperature for 4 h to decompose the Ni precursor compound and form NiO phase on the alumina support. The catalyst samples are designated as $5Ni/\gamma$ -Al₂O₃(P), 20Ni/ γ -Al₂O₃ and 20Ni/ γ -Al₂O₃(P), respectively. Before catalytic run, the calcined catalysts were reduced in-situ by at mospheric H₂ flow at 450 °C for 2 h.

2.2. Catalysts characterization

2.2.1. Elemental analysis

The P and Ni contents of the catalyst samples were determined by using Inductively Coupled Plasma Optical Emission Spectroscopic (ICP-OES) method (Spectro Genesis ICP-OES apparatus).

2.2.2. Specific Surface Area (SSA)

The specific surface area (SSA) of the samples was calculated from the N₂ adsorption isotherms using the BET method. Adsorption isotherms were measured at -196 °C using an automated gas sorption apparatus ("Surfer", Thermo Scientific). The samples were dehydrated in high vacuum ($\sim 10^{-6}$ mbar) at 250 °C for 2 h prior to the measurement.

2.2.3. X-Ray Powder Diffraction (XRPD)

The crystalline phases of the catalysts were identified by X-ray power diffraction (XRPD) measurements using a Philips PW 1810/3710 powder diffractometer, equipped with a graphite monochromator, applying Cu K_{\alpha} radiation (\lambda = 1.5418 Å) using steps of 0.02° 20, and scan time of 5.0 s. The X-ray tube was operated at 40 kV voltage and 35 mA current. The crystallite size was determined using the full profile fitting method based on the Scherrer equation.

2.2.4. Temperature-programmed H₂-reduction (H₂-TPR)

Reducibility of the Ni species in the calcined catalysts was studied by temperature-programmed H₂-reduction (H₂-TPR). About 100 mg of the catalyst precursor was pre-treated in 30 cm³·min⁻¹ O₂ flow at 500 °C for 1 h, then cooled to 40 $^\circ C$ and flushed with N_2 for 10 min prior to the TPR measurement. To obtain TPR curve, the N2 gas flow was switched to a $30\ \text{cm}^3 \cdot \text{min}^{-1}$ flow of 9.0 vol% H_2/N_2 mixture, and then the sample was heated up to 800 °C at a rate of 10 °C·min⁻¹. In a similar experiment, the TPR curve was measured up to 450 °C to determine the reduction degree of the Ni species that could be reached during the reduction of the catalyst before the catalytic run (vide infra). The reactor effluent was passed through a trap cooled by liquid nitrogen (-196 °C) to remove water from the gas flow. The rate of hydrogen consumption during the reduction process was followed by monitoring the H₂ concentration of the effluent gas using a thermal conductivity detector (TCD) next to the trap. The amount of H₂ consumed for the reduction (μ mol·g⁻¹_{cat}) was determined using a calibration value obtained by the reduction of a measured amount of Cu(II)O under the same conditions.

2.2.5. X-ray photoelectron spectroscopic (XPS) measurements

XPS measurements were performed by using an Omicron EA 125 electron spectrometer in the Fixed Analyser Transmission mode. The photoelectrons were excited by non-monochromatized ΜσΚα (1253.6 eV) and AlKa radiation. Spectra were recorded with a pass energy of 30 eV, providing resolution around 1 eV. The calcined catalyst samples were dispersed in isopropanol and droplets of the dispersion were dried onto stainless steel sample plates. Spectra of the calcined catalysts, as well as the reduced catalysts after 2 h annealing in 100 mbar H₂ at 450 °C (simulated reduction) were collected. The treatments were performed in a preparation chamber attached to the electron spectrometer. Spectra were processed with the CasaXPS software package [34], while quantitative evaluation of the data was performed with the XPSMultiQuant software package [35]. As the samples were insulating, charge compensation was performed by setting the binding energy of the Al 2p peak to 74.0 eV (a value frequently mentioned for Al₂O₃ [36]).

2.2.6. TEM measurements

Sample morphology was studied by a JEOL JEM 1011 transmission electron microscope (TEM), equipped with a side mounted Morada 11megapixel camera (Olympus). The accelerating voltage was set to 80 kV. The samples were suspended in distilled water and drop-cast onto a 300 mesh copper grid, coated by Formvar and lacey carbon support film.

2.2.7. Temperature-programmed CO₂ desorption (CO₂-TPD)

The basicity of the neat and phosphatized γ -Al₂O₃ supports was characterized by CO₂-TPD measurement. These measurements were carried out in the same apparatus as used for the H₂-TPD measurements. About 150 mg of the sample was placed into a quartz tube (6 mm ID) and activated in 30 cm³·min⁻¹ O₂-flow at 550 °C for 1 h. The sample was flushed with N₂ for 15 min at 550 °C after activation, then evacuated at the same temperature for 30 min and cooled to room temperature. The sample was contacted with CO₂ gas at 13.3 kPa for 15 min at room temperature, then flushed with a He flow of 30 cm³·min⁻¹ to remove the CO₂ gas from the system. The TPD measurement was initiated by raising the temperature from room temperature up to 700 °C at a rate of 10 °C·min⁻¹ in the same He flow. The CO₂ concentration in the effluent gas flow was monitored by thermal conductivity detector (TCD).

2.2.8. Fourier Transform Infrared Spectroscopy (FT-IR)

The acidity of the neat and phosphatized $\gamma\text{-}Al_2O_3$ supports was characterized by analyzing the Fourier-transform infrared (FT-IR) spectra of adsorbed pyridine (Py). The FT-IR spectra of the adsorbed species were recorded in transmission mode using a Nicolet Impact Type 400 spectrometer (Thermo Fisher Scientific) equipped with a homemade in-situ IR-cell. A self-supported wafer was prepared from the

support material. The wafer was pre-treated in high vacuum ($\sim 10^{-6}$ mbar) at 450 °C for 1 h in situ in the cell. The spectrum of the pre-treated sample was collected at room temperature and was used as a background spectrum. The sample was then contacted with the vapor of Py at 5.7 mbar and 200 °C for 30 min. The sample was then degassed by evacuation at this temperature for 30 min and a sample spectrum was recorded at room temperature. The evacuation was repeated at 400 °C and a second sample spectrum was recorded at room temperature. Spectra were collected by averaging of 32 scans at a resolution of 2 $\rm cm^{-1}$ and were normalized to a wafer thickness of 5 mg \cdot cm⁻². Difference spectra were generated by subtracting the spectrum of the wafer collected before Py adsorption from the spectrum of the Py-loaded wafer. The concentration of Lewis acid sites was calculated from the integrated absorbance of the band at 1450 cm⁻¹, characteristic of coordinately bound Py to Lewis acid sites. For the calculation, the integrated molar extinction coefficient of 1.65 $\text{cm} \cdot \mu \text{mol}^{-1}$ was used [37]. Acid site densities obtained after degassing the wafer at 200 $^\circ C$ and 400 °C are considered as the total concentration of Lewis acid adsorption sites and the concentration of strong Lewis acid adsorption sites, respectively.

FT-IR spectra of phenol adsorbed on the neat and phosphatized γ -Al_2O_3 supports were collected in a similar way than the spectra of adsorbed pyridine, except that the activated sample pellet was contacted with phenol vapor at 0.2 mbar at room temperature for 30 min, then was evacuated consecutively at room temperature, 100, 200, 300, and 400 $^\circ C$ in high vacuum (10⁻⁶ mbar) at each temperature for 0.5 h. A spectrum was collected after each evacuation step at room temperature. The spectrum of the activated pellet was subtracted from each spectrum to get the spectrum of surface species formed from phenol adsorption.

2.3. Catalytic measurements

Hydrodeoxygenation (HDO) of guaiacol was investigated in a high pressure fixed-bed flow-through microreactor system using H₂ gas as hydrogen source. The stainless-steel reactor tube (12 mm ID) was filled with the 0.315–0.630 mm size sieve fraction of the catalyst grains. Before the catalytic run, the catalyst was reduced in situ in a H₂ flow of $100 \text{ cm}^3 \cdot \text{min}^{-1}$ at 450 °C for 2 h. The GUA reactant was fed into the reactor by a high-pressure liquid pump (Gilson, verity 3011), whereas the flow of H₂ was controlled by mass flow controller (Aalborg). The catalytic experiments were carried out in the 225-350 °C temperature range and in the total pressure range of 1-10 bar. The pressure of the catalytic system was set using a back pressure regulator. The space time of the GUA reactant was varied between 0.25 and 1.0 g_{cat} g_{GVL}^{-1} h by varying the amount of the catalyst in the reactor between 0.28 and 1.11 g, whereas the H₂/GUA molar ratio was set to 20. The steady state conditions were reached in one hour so that each measurement point required 2 hours. Since at least half of the measurement points were repeated, the total time-on-stream was about 12-18 hours in each experiments. The reactor effluent was passed through a water-cooled condenser to separate the gas and liquid phases. The effluent gas flow was further cooled using an acetone/dry ice trap placed downstream of the back pressure regulator. The gaseous products were analyzed using an on-line GC (Varian 3300) equipped with flame ionization detector (FID) and a 30 m long Supelco (alumina/chloride) capillary column. The hourly formed liquid product was collected and analyzed by GC-MS (Shimadzu QP2010 SE) applying a 60 m ZB-WAX PLUS capillary column. Response factors for GUA and the major reaction products, including cyclohexane, methyl-cyclohexane, catechol, phenol, benzene and toluene, were determined using pure compounds with known concentrations. The conversion of GUA and yield for each product were calculated as follows:

$$Conversion (\%) = \frac{(mols of GUA)_{in} - (mols of GUA)_{out}}{(mols of GUA)_{in}} \bullet 100\%$$
(1)

Yield of product
$$i$$
 (%) = $\frac{(mols of product i)}{(mols of GUA)_{in}} \bullet 100\%$ (2)

The material balance determined form the weight of the collected sample and the analysis results was always within \pm 5%. In each catalytic experiment, at least half of the measurement points were repeated. The difference between data points obtained under identical reaction conditions was always well within \pm 5% and thereby showing good reliability of the results.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Composition and surface area

The measured Ni and P contents of the catalysts are given in Table 1. Elemental analysis of the fresh and used catalyst samples confirms that the Ni content of the catalysts was retained during the catalytic reaction. Note that the hydroconversion reaction of GUA takes place in the gas phase under the applied reaction conditions.

Type IV nitrogen adsorption isotherms with H2 type hysteresis loop typical of mesopores were obtained for the support materials (Fig. S1). The impregnation with H₃PO₄ solution slightly reduced the specific surface area (SSA) of the neat γ -Al₂O₃ from 196 to 167 m²·g⁻¹ whereas the pore volume, determined using the Gurvich method from the adsorption capacity at p/p₀=0.95 was decreased from 0.52 to 0.43 cm³·g⁻¹. The pore-size distribution of the supports was calculated using the Barett-Joyner-Halenda (BJH) model. Both neat and phosphatized alumina support contain pores in the 2 – 15 nm range with an average pore diameter of about 7.5 nm (see insert in Fig. S1). Introduction of the active metal component did not affect the SSA (Table 1).

3.1.2. XRPD measurements

Fig. 1 presents the XRPD patterns of the neat and phosphatized alumina supports and the corresponding calcined, and reduced Ni catalysts. The characteristic broad lines of γ -alumina (ICDD 10–425) support at $2\theta = 37.6$, 39.5, 45.9 and 66.9° can be identified in each sample. The XRPD patterns of γ -Al₂O₃ and γ -Al₂O₃(P) are very similar suggesting that phosphatization did not cause any changes in the crystal structure of the alumina (Fig. 1A). Formation of crystalline cubic NiO phase (bunsenite, ICDD 47–1049) was confirmed by the appearance of high-intensity diffraction lines at $2\theta = 37.3^{\circ}$ (111), 43.3° (200), and 62.9° (220) in the pattern of the calcined catalysts having a Ni content of 20 wt

Table 1

Characterization of supports and catalysts.

% (Fig. 1B). When the Ni loading was near to 5 wt%, no characteristic diffraction lines for NiO phase appeared in the patterns of the calcined $5Ni/\gamma$ -Al₂O₃ and $5Ni/\gamma$ -Al₂O₃(P) (Fig. 1A). These results are consistent with previous findings [38,39] suggesting that at low or moderate Ni loadings (up to about 6 wt% NiO), Ni²⁺ species cannot be detected on γ -alumina by XRPD. It was shown that at low loading, impregnation of Ni species results in a highly dispersed, amorphous NiO phase without long-range order. H₂-TPR measurements, however, confirmed the exisof hard-to-reduce, highly dispersed tence NiO and/or non-stoichiometric surface Ni-aluminate phase (vide infra). The formation of the stoichiometric NiAl₂O₄ spinel phase (ICDD 78–1601) can be ruled out because the diffusion of Ni^{2+} ions into γ -Al₂O₃ lattice requires a significantly higher temperature (above 800 °C) than that we applied [38,39]. At high Ni loading, intense diffraction lines of the crystalline NiO phase appeared at $2\theta=37.3^\circ$ (111), 43.3° (200) and 62.9° (220) in the diffractogram of the calcined catalysts (20Ni/y-Al₂O₃ and 20Ni/γ-Al₂O₃(P)) (Fig. 1B).

When the catalysts were reduced at 450 °C, i.e., at the temperature of the reduction before the catalytic runs, cubic metal Ni⁰ phase (ICDD 04–0852) was identified in the XRPD patterns of the 20Ni/ γ -Al₂O₃ and 20Ni/ γ -Al₂O₃(P) catalysts. The corresponding high intensity diffraction lines appeared at 2 θ = 44.5° (111) and 51.9° (200) (Fig. 1B). The formation of larger Ni⁰ crystallites on the surface of the γ -Al₂O₃(P) support than on the neat γ -Al₂O₃ indicates that the interaction of NiO with the surface must be weaker in the presence of phosphate species, which is supported also by the results of the H₂-TPR measurements (*vide infra*).

As expected, no characteristic XRPD lines of Ni⁰ particles were detected in the pattern of the reduced $5Ni/\gamma$ -Al₂O₃ and $5Ni/\gamma$ -Al₂O₃(P) catalysts (Fig. 1A). The H₂-TPR analysis proved that the hard-to-reduce Ni²⁺ species originally present in the oxidized samples (also invisible by XRPD) can be partially or fully reduced to Ni⁰ depending on the applied reduction temperature (*vide infra*). It is important to note that the comparison of the XRPD patterns of the reduced fresh (Fig. 1) and used (Fig. S2) Ni catalysts did not show any noticeable structural change that could have been occurred during the catalytic runs.

3.1.3. H₂-TPR measurements

Previous studies reported that two types of NiO phase exist on the calcined precursor of the alumina-supported Ni catalysts, which can be distinguished by their reduction temperature [39–43]. Bulk NiO clusters weakly interacting with the alumina surface are reducible at around 400 °C, whereas highly dispersed NiO species, strongly interacting with alumina can be reduced only in the temperature range of 450 – 800 °C. It

Support and catalyst ID ^a	Ni, ^b wt%	P, ^b wt%	SSA, ^c m ² ·g ⁻¹	Reduction, ^d %, up to		d _{NiO} , ^e nm	d⁰ _{Ni} , ^f nm	Basicity, ^g µmol⋅g ⁻¹	Acidity, ^h μ mol \cdot g ⁻¹
				450 °C	800 °C				
γ -Al ₂ O ₃	-	-	196	-	-	-	-	125(35)	192(61)
5Ni/γ-Al ₂ O ₃	5.2 (5.1)	-	192	4.5	98	n.d.	n.d.	-	-
20Ni/γ-Al ₂ O ₃	19.9 (20.0)	-	190	68	99	16	11	-	-
γ -Al ₂ O ₃ (P)	-	4.8 (4.78)	167	-	-	-	-	7.1(1.3)	104(21)
$5Ni/\gamma$ -Al ₂ O ₃ (P)	5.1 (5.0)	4.8 (4.81)	165	0.9	98	n.d.	n.d.	-	-
$20Ni/\gamma$ -Al ₂ O ₃ (P)	20.2 (20.1)	4.8 (4.79)	160	65	100	27	14	-	-

^a The first number in the catalyst ID gives the nominal Ni content in wt%.

^b Ni or P content of the fresh and used catalysts (in parenthesis) after 37–40 h time-on-stream determined by elementar analysis.

^c Specific Surface Area (SSA), determined by the Brunauer-Emmett-Teller (BET) method.

^d Reduction degree, calculated from temperature-programmed H₂-reduction (H₂-TPR) curves.

^e Average NiO diameter calculated from the XRPD pattern of the catalysts calcined in air at 450 °C for 4 h.

 $^{\rm f}$ Average Ni⁰ diameter calculated from the XRPD pattern of the catalysts reduced at 450 $^{\circ}$ C for 1 h in H₂ flow.

 g The number of basic sites, calculated from the area of the overlapping CO₂-TPD peaks at around 80, 160, and 250 °C. The number of strong base sites (in parentheses) were obtained from the area of the peak at ~250 °C.

^h The integrated absorbance of the FT-IR band of adsorbed pyridine (Py) at 1450 cm⁻¹ was determined after degassing the support at 200 °C and also after subsequent degassing at 400 °C. The amount of the adsorbed Py was calculated using the integrated molar extinction coefficient of 1.65 cm·µmol⁻¹ [37]. The adsorbed amount was used to characterize the acidity. The Py retained after evacuation at 400 °C was considered to characterize the amount of strong acid sites (numbers in parenthesis).



Fig. 1. XRPD patterns (A) of the calcined, and reduced $5Ni/\gamma$ -Al₂O₃ and $5Ni/\gamma$ -Al₂O₃(P) catalysts, and the calcined γ -Al₂O₃ and γ -Al₂O₃(P) supports, and (B) of the calcined, and reduced $20Ni/\gamma$ -Al₂O₃ and $20Ni/\gamma$ -Al₂O₃(P) catalysts. Samples were calcined at 550 °C for 4 h. The Ni catalysts were reduced in H₂ at 450 °C for 1 h.

was evidenced that the reduction of the non-stoichiometric Ni-aluminate phases also takes place in latter temperature range [39], whereas the reduction of the stoichiometric NiAl₂O₄ phase requires temperature above 800 °C.

The H_2 -TPR curves measured for the calcined catalysts of the present study comprise overlapping broad reduction peaks in the temperature

range of 500–800 $^{\circ}$ C (Fig. 2A). Based on the above assignments, the peaks were attributed to reduction of highly dispersed NiO phase, strongly interacting with the support, and/or to reduction of non-stoichiometric Ni-aluminate phases. In the TPR curves of the catalysts having higher Ni content a strong peak also appeared at temperature lower than 500 $^{\circ}$ C, indicating the presence of more easily reducible NiO



Fig. 2. H_2 -TPR curves of the 5Ni/ γ -Al₂O₃, 20Ni/ γ -Al₂O₃, 5Ni/ γ -Al₂O₃(P) and 20Ni/Al₂O₃(P) catalysts. Samples were treated in O₂ flow (30 cm³·min⁻¹) at 500 °C for 1 h, then cooled to 40 °C and purged with N₂. TPR curves were obtained by heating the catalyst sample in a flow of 9.0 vol% H_2/N_2 mixture at a rate of 10 °C·min⁻¹ up to (A) 800 °C or (B) 450 °C.

phase (Fig. 2A). The peak is narrow for the $20Ni/\gamma$ -Al₂O₃(P) catalyst and is centered at 420 °C, whereas it is broader for the $20Ni/\gamma$ -Al₂O₃ sample and appears shifted toward higher temperatures. These results suggest that phosphatization reduced the strength of interaction between the NiO clusters and the support and made these NiO species easier to reduce.

The H/Ni atomic ratios were calculated from the hydrogen consumption, obtained in the TPR experiments shown in Fig. 2A, and the Ni content of the catalyst. The ratio was in the range of 1.95 – 2.0 corresponding to a reduction degree of 98–100% (Table 1). This means that Ni²⁺ in the surface species could be fully reduced to Ni⁰ up to 800 °C, precluding the presence of the stoichiometric NiAl₂O₄ phase in the catalysts.

The Ni⁰ content of the catalysts manifested in their hydrogenation activity (vide infra). Considering that the catalyst was pre-reduced in H₂ flow at 450 °C in situ in the catalytic reactor before any catalytic run, we determined the reduction degree of the catalysts up to the reduction temperature of 450 °C (Fig. 2B). At the lower Ni content only a small fraction (<5%) of the Ni²⁺ could be reduced to Ni⁰ (Table 1). At higher Ni content, however, the majority of the nickel was reducible to Ni⁰ (Fig. 2B). The reduction degree reached 68 and 65% for the 20Ni/ γ -Al₂O₃ and 20Ni/ γ -Al₂O₃(P) catalysts, respectively (Table 1). XRPD measurements confirmed the formation of Ni⁰ particles in these latter catalysts (Fig. 1B). In contrast, no Ni⁰ particles could be detected in the catalysts of low Ni content by XRPD (Fig. 1A) probably due to their small size below the detection limit (<5 nm) and/or owing to their very low concentration in the reduced catalyst. However, the TEM images of the reduced catalysts (Fig. S3) confirmed the presence of Ni⁰ particles in all catalyst samples. The 20Ni/y-Al₂O₃ and 20Ni/y-Al₂O₃(P) catalysts present Ni⁰ particles with a diameter of 10 - 12 nm and about 15 nm, respectively (Fig S3, at the bottom), which are in a good agreement with those average Ni⁰ diameters determined from the XRPD measurements (Table 1). On the contrary, only very few Ni⁰ particles having a size of around 5 nm were discernible on the TEM picture of 5Ni/y-Al2O3 and 5Ni/y-Al₂O₃(P) catalysts (Fig. S3, at the top), which remained

undetected by XRPD.

The results of the XPS measurements carried out on the supported Ni catalysts reduced at 450 °C (Fig. S4, and Table S1A,B) are qualitatively in agreement with the H₂-TPR results. The phosphatization of the γ -Al₂O₃ support somewhat affected the reduction of the highly dispersed NiO species to Ni⁰ species at low (5 wt%) Ni loading as shown by the lower reduction degree observed for the 5Ni/ γ -Al₂O₃(P) sample (Table 1). In contrast, phosphatization practically did not affect the reduction degree of NiO clusters mainly present at high (20 wt%) Ni loading in the catalysts (Table 1). It is important to note that XPS results excluded the formation of any nickel phosphide species under the applied reduction conditions.

3.1.4. Acid-base properties

The concentration and base-strength distribution of sites on the surface of the supports were determined by CO₂-TPD measurements. Adsorption of CO₂ was shown to result in formation of different carbonate-like surface species, such as, bicarbonates and bidentate, monodentate, and bridged carbonate species having different thermal stability [44,45]. It was shown that TPD peak around 80 °C was due to the decomposition of bicarbonate species formed on weak basic sites, whereas the strongly overlapping peaks around 160 and 250°C could be attributed to the decomposition of chelating bidentate carbonate species formed on medium strength basic sites and monodentate carbonate species formed on strong basic sites, respectively [45]. The thermally most stable bridged carbonate species, if present, would give a desorption peak over about >320 °C [45].

The amounts of weak, medium strength, and strong base sites were calculated from the area of the component bands at 80, 160, and 250 °C, resolved by peak fitting (Fig. 3 A). (Strong base sites, binding bridged carbonate species were not considered, since no peak was discernible above 300 °C.) The concentrations of total and strong base sites (in parenthesis) are given in Table 1. Results show that more than 90% of the basic adsorption sites and also the strong base adsorption sites, originally present in the γ -alumina support, were eliminated by



Fig. 3. (A) CO₂-TPD curves and (B) FT-IR spectra of adsorbed pyridine recorded for the neat (γ -Al₂O₃) and the phosphatized alumina (γ -Al₂O₃(P)) supports. Prior to the CO₂-TPD run, the sample was activated in O₂ flow at 550 °C. Adsorption was carried out at room temperature at 133 mbar CO₂ pressure. Prior to pyridine adsorption, the sample was activated in high vacuum (10⁻⁶ mbar) at 450 °C for 1 h. Sample was contacted with pyridine vapor at 5.7 mbar and 200 °C for 30 min, then evacuated at this temperature (a200, b200) and consecutively at 400 °C (a400, b400) for 30 min. Spectra were recorded after each evacuation step at room temperature.

phosphatization. Former studies showed that phosphatization of alumina consumes the basic surface OH-groups via acid-base reaction [46,47] and also reduce the concentration of the Lewis acid (Al^+) – Lewis base (O⁻) pair sites [33].

The FT-IR spectra of adsorbed pyridine (Py) was used to characterize the surface acidity of neat and phosphatized y-alumina supports (Fig. 3B). The pairs of bands at 1624/1455 and 1617/1450 cm⁻¹ (Fig. 3B, a200) stem from the 8a and 19b ring vibration modes, which are the most sensitive regarding the nature of interactions between the Lewis acid sites and the lone pair electrons of the Py nitrogen. The Lewis acidity of γ -Al₂O₃ comes from coordinately unsaturated surface Al³⁺ ions [48]. The band pair of 1624/1455 cm⁻¹ is assigned to Py adsorbed on tetrahedral Al³⁺ cations with coordinative unsaturation, which represent the strongest Lewis acid sites of γ -Al₂O₃. The assignment of the other pair of bands at $1617/1450 \text{ cm}^{-1}$ is still a matter of debate. The adsorption sites are likely to be pentacoordinated Al³⁺ (octahedral Al with one coordinative unsaturation) or tetracoordinated aluminum ions (octahedral Al with two coordinative unsaturation), which may also have OH groups in their vicinity [48,49]. Upon evacuation at 400 °C latter pair of bands practically disappeared indicating that a fraction of the Py was bound to weak acid Lewis sites. The strong acid Lewis sites (pair of bands at 1624/1455 cm¹) still could retain significant amount of Py (Fig. 3B, a400).

In the spectra of the phosphatized alumina, both pair of bands appeared with significantly lower intensities (cf., Fig. 3B, a200 and b200) suggesting that phosphatization extensively reduced the number of Py-adsorbing Lewis acid sites. As expected, after evacuation at 400 °C only the strong Lewis acid sites could retain Py (Fig. 3B, b400). The concentrations of the Lewis acid adsorption sites were determined from the integrated absorbance of the band around 1450 cm⁻¹ (19b vibration) obtained after degassing the sample at 200 and 400 °C, respectively, using the molar extinction coefficient given in ref. [37]. Results indicate that phosphatization eliminated approximately half of the Lewis acid adsorption sites and within this about two-third of the strong acid Lewis sites (Table 1).

The FT-IR spectra of adsorbed Py on γ -Al₂O₃ and on the reduced 5% Ni/ γ -Al₂O₃ obtained under identical conditions were compared (Fig. S5). The close resemblance of the spectra suggests that the presence of Ni has no significant effect on the acidity of the γ -Al₂O₃ support.

3.2. Catalytic results

The nickel-free γ -Al₂O₃ and γ -Al₂O₃(P) catalysts have no hydrogenation activity, and therefore, neither hydrogenated nor HDO products appeared in the product mixture from GUA conversion. The main products obtained are catechol and its methyl-substituted derivatives (Fig. 4, Table S2), showing that demethylation - methyl substitution are the main reaction routes. Appearance of some phenolics (mainly 2methoxy-5-methylphenol and 2-methoxy-3-methylphenol, Table S2) indicates that methyl substitution on the aromatic ring of GUA also takes place in some extent. In the transmethylation reaction O-CH₃ bond cleavage occurs. This is the weakest C-O bond in GUA [15]. The reaction was shown to be catalyzed by Lewis acid sites [50-52]. We have shown that Lewis acid sites are present in both the γ -Al₂O₃ and γ -Al₂O₃(P) materials (Fig. 3 A, Table 1). The lower activity of the γ -Al₂O₃(P) could be attributed to the decreased concentration of Lewis sites (Fig. 4, Table 1) caused by phosphatization [33]. Former studies suggested that after heterolytic cleavage of the O-CH₃ bond, the positively charged methyl group participates in the electrophilic substitution of the aromatic ring in the ortho-position [51,53]. The surface reaction was suggested to take place within one adsorption complex (intramolecular transmethylation) [51]. The simultaneous appearance of catechol and its methyl-substituted derivatives (containing 1-3 methyl groups) in the product mixture (Table S2) indicates that methyl substitution proceeds not only within a single GUA molecule, but also via bimolecular pathways (intermolecular transmethylation). As expected the catalytic activity decreased relatively quickly in absence of hydrogenation activity (Fig. 4) due to acid catalyzed formation of coke deposits (aromatic polymers) on the catalyst surface [10,12,32].

In presence of hydrogenation function, both saturation of the



Fig. 4. Conversion of GUA and product yields over (A) γ -alumina (γ -Al₂O₃) and (B) phosphatized γ -alumina (γ -Al₂O₃(P)) support in the function of time-on-stream. Reaction conditions: 300 °C, 10 bars, W/F = 1 g_{cat}. g_{GUA}^{-1} -h, and H₂/GUA molar ratio of 20. (GUA: guaiacol reactant; reaction products CAT der.: catechol and its methyl-substituted derivatives; PHE der.: phenolates, mainly methylated GUA derivatives).

benzene ring and the HDO reaction of the thus obtained saturated intermediate readily proceeded. At the lowest applied reaction temperature cyclohexanol and cyclohexane and their methyl-substituted derivatives were the main products over the $5\text{Ni}/\gamma$ -Al₂O₃ catalyst (Fig. 5A). The phenol conversion to O-free cycloalkanes was shown to proceed through cyclohexanol intermediate over catalysts of high hydrogenation activity, such as catalysts containing Ni or noble metal [10, 12,21–23,30].

The appearance of O-free aromatic products (benzene and its methylsubstituted derivatives) in the lower temperature range (<250 °C), where the ring dehydroxylation via hydrogenolysis of phenolic C-OH bond or hydrogenation/dehydrogenation equilibrium favors ring hy-[54,55], drogenation suggest that tautomerization/hvdrogenation/dehydration pathways [56,57] also proceeds to some extent. Since we could not detect neither keto-tautomer nor cyclohexadienol intermediate over our γ -alumina supported Ni catalysts, the direct hydrodehydroxylation of the phenolic C-OH bond seems to be more likely. Note that hydrogenolysis of the C-OH bond of a cyclohexanol or methylcyclohexanols is more favored than that of the phenolic C–OH bond due to the lower bond strength of the former one [7]. Ring hydrogenation-hydrodehydroxylation reactions and direct hydrodehydroxylation of the phenolic C-OH bond result in O-free saturated and unsaturated six-membered ring hydrocarbons, respectively. Both reactions were significantly accelerated at temperatures above 250 °C; however, the yield of unsaturated O-free HDO products (benzene and its methyl-substituted derivatives) significantly increased over 300 °C (Fig. 5A) due to the shift of the ring hydrogenation/dehydrogenation equilibrium toward dehydrogenation [54, 55]. Similar behavior of the catalyst of higher Ni content was observed, except that the enhanced ring hydrogenation activity resulted in higher yield of cycloalkanes in the temperature range below 300 °C (Fig. 5B). The enhanced ring hydrogenation activity at higher Ni content can be attributed to the higher surface hydrogen concentration during reaction, which shifted the product distribution toward more saturated O-free products. These results indicate that as function of reaction temperature the product distribution was controlled by both the ring hydrogenation–dehydrogenation equilibrium and the relative hydrodehydroxylation rate of phenol and cyclohexanol type C–OH bonds.

Detailed analysis showed that products with and without methyl substitution(s) on the ring appeared in the product mixture (Table S2). The main products were the cyclohexane and its methyl-substituted derivatives over both neat alumina supported Ni-catalysts (Table S2). The significant amount of methyl-substituted and multiply methylsubstituted products in the product mixture suggests that methyl group of GUA was largely preserved in these reaction products. Hydrodemethylation of GUA can result in catechol and methane, whereas hydrodemethoxylation gives phenol and methanol. However, only minor amount (<5%) of methanol and/or methane was detectable in the studied temperature range, indicating that hydrodemethoxylation and/or hydrodemethylation reaction represent a minor reaction route. Note that the ratio of methanol to methane was affected by the reaction conditions. More methanol (2-3%) and less methane (1-2%) was formed under mild conditions (<250 °C and low hydrogenation activity), whereas methane formation (2-5%) significantly exceeded that of methanol under more severe conditions (>300 °C and high hydrogenation activity). This may indicate the preference of energetically more favored hydrodemethylation over hydrodemethoxylation in the higher temperature range; however, the possible hydrodeoxygenation of the product methanol to methane cannot be excluded.

The appearance of significant amount of methyl-substituted and multiply methyl- substituted products in the product mixture (Table S2) and the insignificant quantity of hydrogenolysis products methanol/ methane suggested that transmethylation reactions had a decisive role in the conversion of GUA. These reactions were shown to readily proceed on Lewis acid sites (Fig. 4 and Table S2). In contrast, both hydrodemethylation and hydrodemethoxylation reactions, representing minor pathways, require hydrogenation activity of the catalyst (presence of metal and hydrogen) and lead to the formation of catechol and



Fig. 5. Hydroconversion of GUA and product yields over (A) $5Ni/\gamma$ -Al₂O₃ and (B) $20Ni/\gamma$ -Al₂O₃ catalysts in the function of reaction temperature. Reaction was carried out at 10 bars, W/F= 1 g_{cat}·g_{GUA}⁻¹h, and a H₂/GUA molar ratio of 20. (GUA: guaiacol reactant; reaction products CHL der., BEN der., and CHN der.: cyclohexanol, benzene, and cyclohexanone and their methyl-substituted derivatives; Cycloalkanes: saturated products consisting of cyclohexane and its methyl-substituted derivatives; Others: mainly methyl-guaiacol and dimethoxy-benzene below 250 °C, also include 2–5% methane + methanol).

phenol, respectively. The possible reaction network of GUA hydroconversion is shown in Scheme 1. The non-substituted and methylsubstituted products are intermediates that can be further transformed in ring hydrogenation and/or hydrodehydroxylation reactions on metal sites [10,11,58]. It is important to note, that due to the presence of hydrogenation function, both the $5Ni/\gamma$ -Al₂O₃ and $20Ni/\gamma$ -Al₂O₃ catalysts showed good stability up to 40 h time on stream (Fig. S6A, B).

The activity of the γ -Al₂O₃-supported Ni catalysts was studied in the function of space time at the lowest applied reaction temperature (225 °C) to avoid reaching full GUA conversion (Fig. 6). The GUA conversion and the yield of cyclohexanes (cyclohexane and its methyl-substituted derivatives) increased parallel with the increased space times over both catalysts, whereas the yield of cyclohexanols (cyclohexanol and its methyl-substituted derivatives) hardly changed. Note that at 225 °C the ring hydrogenation/dehydrogenation equilibrium favors ring hydrogenation [54,55]; therefore, only minor amount of O-free aromatic products (benzene and its methyl-substituted derivatives) could be formed via direct hydrodehydroxylation from phenols (phenol and its methyl-substituted derivatives) because the hydrogenolysis of the cyclohexanol and methylcyclohexanol C-OH bond is favored to the phenolic C–OH bond [7]. Above results substantiate that cyclohexanols are intermediate products of the formation of cyclohexanes (Scheme 1). Earlier studies have also shown that HDO reaction of phenolic compounds to cycloalkanes proceeds through cyclohexanol intermediate [10,12,21-23,30]. The HDO reaction of latter intermediate to cyclohexanes can proceed either by direct hydrogenolysis of the C-OH bond or by dehydration to cyclohexenes, which are then hydrogenated to the final cycloalkane products. The dehydration is a possible HDO route [56], even if cyclohexenes are not detected as intermediate due to the high enough hydrogenation activity of the catalyst.

The effect of hydrogen pressure on the activity of the catalysts at 300 °C are shown in Fig. 7. In line with former observations [11,31], the hydrogen pressure significantly affected the selectivity of GUA conversion. At atmospheric pressure catechol, phenol and their methyl-substituted derivatives were the main products on $5Ni/\gamma$ -Al₂O₃ catalyst (Fig. 7A). If H₂ pressure was increased the yield of phenols significantly increased at the expense of catechols. These results suggest

that catechols, formed on the acid sites of the support via demethylation - methyl substitution reactions, were partially hydrodehydroxylated to phenols on metallic sites (Scheme 1). On further increase of pressure, the product distribution shifted to saturated and aromatic O-free products due to the further acceleration of both ring saturation and C-O bond hydrogenolysis reactions (Fig. 7A). Due to the higher hydrogenation activity of the 20Ni/y-Al₂O₃ catalyst, catechols were completely hydrodehydroxylated to phenols at atmospheric pressure resulting in a very high yield (>90%) of phenols (Fig. 7B). Phenols are then completely hydrogenated/hydrodehydroxylated to cycloalkanes and hydrodehydroxylated to benzene derivatives at a total pressure of 5 bars. The yield of cyclohexanes further increases at the expense of benzenes at 10 bars (Fig. 7B) as higher hydrogen pressure at 300 °C probably favors more the former ring hydrogenation/hydrodehydroxylation pathway due to sufficiently high hydrogenation activity of the 20Ni/y-Al₂O₃ catalyst. These results are consistent with the reaction sequence shown in Scheme 1 (catechols - phenols - benzene and cyclohexane derivatives). At 300 °C, where the ring hydrogenation is not hindered significantly by the ring hydrogenation-dehydrogenation equilibrium, the product distribution shifted from unsaturated products (phenols and benzene derivatives) to saturated products (cyclohexane derivatives) at increasing hydrogen pressures.

Catalytic results obtained on the phosphatized-alumina-supported Ni-catalysts are shown in Fig. 8. Mainly catechol, phenol and their methyl-substituted derivatives were formed together with a minor amount of saturated and aromatic O-free compounds on $5Ni/\gamma$ -Al₂O₃ catalyst (Fig. 8A, Table S2). These results suggest that the activation of GUA follows similar pathways than over the phosphate-free Ni/ γ -Al₂O₃ catalysts starting with transmethylation reactions on Lewis acid sites. The yield of catechols goes through a maximum as a function of the reaction temperature, while the yield of phenols continuously increases at the expense of catechols, suggesting that phenols were mainly formed by partial hydrodehydroxylation of catechols (Scheme 1).

The low concentration of saturated and unsaturated O-free compounds in the product mixture suggests that the phosphate-containing Ni catalysts, being less acidic than the corresponding phosphate-free catalysts (Table 1), have lower activity in both ring hydrogenation



Scheme 1. Reaction network of GUA hydroconversion over γ -Al₂O₃ and γ -Al₂O₃(P)-supported Ni catalysts.



Fig. 6. Hydroconversion of GUA and product yields over (A) $5Ni/\gamma$ -Al₂O₃ and (B) $20Ni/\gamma$ -Al₂O₃ catalysts as function of space time. Reaction was carried out at 225 °C, 10 bars and H₂/GUA molar ratio of 20. (GUA: guaiacol reactant; reaction products CHL der., PHE der., BEN der., and CHN der.: cyclohexanol, phenol, benzene, and cyclohexanone, and their methyl-substituted derivatives; Cycloakanes: saturated products consisting of cyclohexane and its methyl-substituted derivatives; Others: mainly dimethoxybenzene and methylguaiacol, include 2–3% methanol and 1–2% methane as minor products).



Fig. 7. Hydroconversion of GUA and product yields over (A) $5Ni/\gamma$ -Al₂O₃ and (B) $20Ni/\gamma$ -Al₂O₃ catalysts in the function of total pressure. Reaction was carried out at 300 °C, W/F= 1 g_{cat}·g₋⁻G₀⁻A⁻h, and a H₂/GUA molar ratio of 20. (GUA: guaiacol reactant, reaction products CHL der., CAT der., PHE der., BEN der., and CHN der.: cyclohexanol, catechol, phenol, benzene, and cyclohexanone, and their methyl-substituted derivatives; Cycloalkanes: saturated products consisting of cyclohexane and its methyl-substituted derivatives; Others: mainly dimethoxybenzene and methylguaiacol and their partially saturated derivatives, include 2–5% methane + methanol as minor products).



Fig. 8. Hydroconversion of GUA and product yields over (A) $5Ni/\gamma$ -Al₂O₃(P) and (B) $20Ni/\gamma$ -Al₂O₃(P) catalysts in the function of reaction temperature. Reaction was carried out at 10 bars, W/F= 1 g_{cat}. g_{GUA}^{-1} -h, and a H₂/GUA molar ratio of 20. (GUA: guaiacol reactant, reaction products CAT der., PHE der., BEN der., and CHN der.: catechol, phenol, benzene, and cyclohexanone, and their methyl-substituted derivatives; Cycloalkanes: saturated products consisting of cyclohexane and its methyl-substituted derivatives; Others: mainly methylguaiacol and dimethoxybenzene, include 2–5% methane + methanol).

and hydrodehydroxylation. The enhanced hydrogenation activity of the catalyst, having higher Ni content allowed the formation of more phenols and O-free products, mainly cyclohexanes (Fig. 8B, Table S2). However, the high concentration of phenols indicates that both the ring hydrogenation and hydrodehydroxylation activity remained also strongly hindered. Since the concentration and the size of Ni⁰ particles on the non-phosphatized and phosphatized support was hardly different (Table 1, Fig. S3) the radically different catalytic selectivities can be related mainly to the differences in the acid-base properties of the support, which strongly affected the further conversion of phenols to O-free products.

Note that the GUA conversion over the phosphatized-aluminasupported Ni catalysts decreased only slightly with the time on stream (Fig. S6C, D), whereas the selectivity for the less hydrodeoxygenated products increased at the expense of partially and/or fully hydrodeoxygenated products. (See the growing concentration of catechols at the expense of phenols and O-free products over the 5%Ni/ γ -Al₂O₃(P), or the rising concentration of catechols and phenols at the expense of the O-free products on 20% Ni/y-Al2O3(P) in the function of time on stream). These results suggest that the catalyst surface was somewhat poisoned during the reaction, probably due to formation of polyaromatic deposits from abundant aromatic reaction intermediates affecting both the active sites on the support and the active metal sites. However, the possible coke formation seems to have a less pronounced effect on the facile demethylation - methyl substitution reactions on the Lewis acid - Lewis base pair sites, than on the hydrogenation activity of the catalysts.

3.3. Effect of acid-base properties on product distribution

Former studies suggest that the most difficult step to form oxygenfree product is the cleavage of C_{Ar} –OH [11,17], although the saturation of the benzene ring weakens the C–OH bond and thereby facilitates the hydrodehydroxylation reaction [7,10,12]. Because the different activities of the catalysts in the activation of GUA can be related mainly to the differences in the surface properties of the support, we wanted to elucidate the reason of the much lower hydrogenation activity, especially the much lower six-membered carbon ring hydrogenation activity of the Ni/ γ -Al₂O₃(P) than that of the Ni/ γ -Al₂O₃ catalyst. In the presence of similar hydrogenation function in these catalysts, the observed radically different selectivities are most probably related mainly to the changes in the surface properties of the support caused by phosphatization, which presumably strongly affected the further hydroconversion of reaction intermediates, especially the hydroconversion of phenols to O-free products. It was presumed that on the phosphatized alumina support the formation of active surface intermediate, necessary for reaching full HDO, became hindered. Therefore, the adsorption complex formed from phenol was investigated by FT-IR spectroscopy.

The spectra of surface species obtained from the adsorption of phenol on the neat and the phosphatized γ -alumina support are shown in Fig. 9. The strong bands at 1598 and 1499/1491 cm⁻¹ can be assigned to aromatic ring vibrations, $\nu(CC_{ring})$, whereas the broad bands with maxima at 1296 and 1261 cm⁻¹ can be attributed to the C–O stretching vibration, ν (CO), of surface phenolate species formed on activated neat γ -Al₂O₃ support (Fig. 9, above group) [59–61]. A ν (CC_{ring})+ δ (OH) combination band [60,61] appears as a weak shoulder at 1470 cm⁻¹ in the spectra of phenol, surface-bound on both supports (Fig. 9, RT spectra) that can indicate that molecularly adsorbed phenol is also present on the surface when the surface coverage is relatively high. This band readily disappears upon degassing at higher temperature and only surface phenolate species are retained. Taylor et al. [59] reported about weak out-of-plain combination bands, obtained from phenol adsorption, in the range of $2000 - 1650 \text{ cm}^{-1}$. The absence of such bands in our spectra suggests that the benzene ring of the phenolate may parallel the adsorbent surface. The phenolate, bound to the catalyst support nearby to active metal particles could be the active surface intermediate of phenol hydroconversion [62,63].

The characteristic $\nu(CC_{ring})$ and $\nu(CO)$ bands of phenolate species



Fig. 9. FT-IR spectra of phenol adsorbed on γ -Al₂O₃ and phosphatized γ -Al₂O₃ support. Sample pellet was activated in situ in the IR cell in high vacuum (10⁻⁶ mbar) at 450 °C for 1 h. The pellet was contacted with phenol vapor at 0.2 mbar and room temperature for 30 min, then was evacuated consecutively at room temperature, 100, 200, 300, and 400 °C in high vacuum at each temperature for 0.5 h. A spectrum was collected after each evacuation step at room temperature. The spectrum of the activated pellet was subtracted from each spectrum to get the spectrum of surface species formed from phenol adsorption.

were much weaker for the phosphatized than for the neat γ -Al₂O₃ support (Fig. 9). The phenolate concentration decreases as the evacuation temperatures is raised. The surface phenolate species are more easily released from the phosphatized alumina than from the neat alumina support (Fig. S7). These results suggest that interaction of the phenol with the γ -Al₂O₃(P) is much weaker than with the neat γ -Al₂O₃.

The ν (CO) vibration of phenolate species formed on the neat alumina gave bands at 1296 and 1261 cm⁻¹ (Fig. 9, above group) suggesting formation of two kinds of phenolate species in chemisorption process. Note that the latter band seems to be missing from the spectra obtained using phosphatized support as adsorbent.

The origin of the two phenolate species on neat alumina adsorbent is still not fully understood. It was shown that both basic surface hydroxyl groups and Lewis acid (Al⁺) – Lewis base (O⁻) pair sites of γ -Al₂O₃ are involved in phenolate formation [59,61]. Phenolate formation on basic hydroxyl groups was proposed via an acid-base reaction between the proton of the phenolic OH group and a basic hydroxyl group giving monodentate phenolate, attached to a surface Al³⁺ ion, and water [59]. Note, that similar mechanisms were substantiated for the formation of monodentate phosphate species on the y-alumina support used in a former study [33]. The negative ν_{OH} bands in the spectra of the phenol-loaded neat and phosphatized $\boldsymbol{\gamma}\text{-alumina}$ supports confirm that surface hydroxyls were involved in the adsorption (Fig. S8). The intensity of the negative OH bands (except the band at 3685 cm⁻¹ assigned to bridging OH groups) practically did not change at elevated evacuation temperatures, indicating that these OH groups were consumed during phenolate formation and water was released from the surface. Similar observations were made by Taylor and co-workers [59], who found that basic OH-groups, consumed in phenolate formation, can be recovered only by exposing the sample to water vapor at high temperatures. It should be noted that on the phosphatized alumina, mostly the

surface the P-OH groups (band at 3677 cm^{-1} in Fig. S8) are involved in the adsorption interaction; however, these sites are almost fully recovered at elevated evacuation temperatures, suggesting that probably they form a strong H-bond with the adsorbate, but not consumed in the interaction.

Phenolate species were also shown to form via heterolytic dissociation of the O–H bond of phenol on Lewis acid (Al⁺) – Lewis base (O⁻) pair sites of γ -alumina [59–61]. It was substantiated that the proton of the phenolic OH group coordinates to the oxide ion, whereas its conjugate base, the phenoxide anion (C₆H₅O⁻), coordinates to the adjacent Al³⁺ ion, forming a monodentate phenolate. Upon evacuation the phenolate formed over the pair sites recombine more easily with the concomitantly formed surface protons (H⁺) and is released as phenol than the phenolate, formed in reaction of phenol and strongly basic surface hydroxyl groups.

Based on our current results, we assume that the formation of phenolate species proceeds on both basic surface hydroxyls and Lewis acid – Lewis base pair sites. The observed two ν (CO) bands might be related to these two kinds of phenolates. While one of the ν (CO) bands is present at 1296 cm⁻¹ in the spectrum of phenol bound to the phosphatized alumina the other band at 1261 cm⁻¹ is hardly discernable in the spectrum, because dissociative phosphate chemisorption efficiently annihilated Lewis type pair sites, which would be needed for dissociative phenol adsorption (Table 1). Moreover, if the 1296 cm⁻¹ band was originated from dissociative phenol adsorption, the band would have had to be disappeared due to phenol recombination and desorption at elevated temperature. We assume that the 1261 cm⁻¹ band is related to phenolate species formed on Lewis sites, whereas the band at 1296 cm⁻¹ can be attributed to phenolate species formed in reaction with basic hydroxyl groups. In contrast, Popov et al. [60,61] assigned similar ν (CO) bands to monodentate and bidentate alumina-bound phenolate species. However, it was also shown that the lower frequency ν (CO) band was not obtained, if the phenol was adsorbed over alumina that was doped with potassium carbonate. The thermally decomposed carbonate $(K_2CO_3 \rightarrow 2 \text{ K}^+ + \text{O}^{2-} + \text{CO}_2)$ was poisoning Lewis base O⁻ surface sites and terminating coordinative unsaturation of surface Al^{3+} ions [60]. Latter finding seems to substantiate our identification of the phenolate ν (CO) bands.

Results of the phenol adsorption experiments suggest that the lower aromatic ring hydrogenation activity of the phosphatized-aluminasupported Ni catalysts is probably related to the lower concentration of surface phenolate intermediates as compared to that of the neat alumina-supported Ni catalyst. These species, adsorbed in the vicinity of metal particles, were considered as active species in phenol hydrogenation [62,63] and probably also play important role in the formation of O-free products from GUA via hydrodehydroxylation reactions. Partial elimination of basic hydroxyls and Lewis acid (Al⁺) – Lewis base (O⁻) pair sites of alumina by the surface phosphate species substantially reduced the concentration of sites for phenolate formation, which is necessary for further deoxygenation. Since the reaction rate depends on the rate constant and the surface concentration of the active intermediate, the significantly reduced phenolate concentration over the phosphatized-alumina-supported catalyst resulted in lower activity in the ring hydrogenation and hydrodehydroxylation reactions.

The above results suggest that formation of active phenolate surface species is necessary to reach full HDO and obtain O-free products (cyclohexane, benzene and their methyl-substituted derivatives). Phenolate formation requires the presence of basic hydroxyls and Lewis acid (Al⁺) – Lewis base (O⁻) pair sites on the surface of the γ -alumina. It was interestingly found that by the (partial) elimination of these sites the reaction can be steered towards the selective formation of phenol (and its methyl-substituted derivatives). These results signify that the role of acid-base properties of the support material in the reaction deserves further investigation. Experiments using different neutral and acidic supports containing Brønsted acid sites of different strength are in progress.

4. Conclusions

The conversion of guaiacol (GUA) over γ-alumina proceeds over Lewis acid-Lewis base pair sites by demethylation - methyl substitution (DME/MES) reactions resulting in catechol (CAT) and its methylsubstituted derivatives (Me_n-CAT, n=1-4). In the presence of Ni⁰ particles on the y-alumina the hydrodemethylation (HDME) and hydrodemethoxylation (HDMO) reactions, resulting in minor amount of methane and catechol or methanol and phenol, respectively, also contributed to the conversion of GUA, however, the methyl groups of GUA were largely preserved in the liquid product due to the dominance of DME/MES reactions. This reaction was followed by a series of hydrodehydroxylation (HDHY) and ring hydrogenation (HYD) reactions resulting in partially and fully deoxygenated, saturated, and unsaturated products with yield, depending on the hydrogenation activity of the catalyst, as well as, on the reaction conditions. High hydrogenation activity, associated with high Ni loading and high H₂ partial pressure, favored the formation of saturated O-free products, such as, cyclohexane (CHA) and its methyl-substituted derivatives (Me_n-CHA, n=1-4) up to about 300 °C. At higher reaction temperatures the product distribution shifted towards unsaturated O-free products, such as, benzene (BEN) and its methyl-substituted derivatives (Me_n-BEN, n=1-4) due to shift of reaction equilibrium towards dehydrogenation of six-membered carbon rings and the acceleration of the direct HDHY reaction of phenols. It is important to note that the latter hydrogenolysis reaction of the C-OH bond (in contrast to the ring hydrogenation) is not limited thermodynamically in the studied temperature range and accelerates at higher reaction temperatures.

The phosphatized-alumina-supported Ni catalysts showed suppressed HYD and HDHY activity as compared to the neat aluminasupported catalysts, while the hydrogenation function of the catalysts was not much different. Consequently, formation of CAT and/or phenol (PHE) and their methylated derivatives was significantly enhanced mainly at the expense of saturated O-free products. The suppressed HYD and HDHY activity of these catalysts can be explained by the significantly reduced surface concentration of the active phenolate intermediate species. Formation of phenolate species proceeded on both basic OH groups and Lewis acid (Al⁺) – Lewis base (O⁻) pair sites, the concentration of which were significantly reduced by phosphatization of the γ -alumina support.

CRediT authorship contribution statement

Hanna E. Solt: Visualization, Investigation, Conceptualization. Gyula Novodárszki: Visualization, Project administration, Investigation, Conceptualization. Magdolna R. Mihályi: Writing – review & editing, Writing – original draft, Project administration, Funding acquisition, Data curation. Róbert Barthos: Investigation, Data curation. Ferenc Lonyi: Writing – review & editing, Writing – original draft, Supervision, Project administration, Conceptualization. Balázs Csík: Visualization, Investigation. Dhanapati Deka: Funding acquisition, Conceptualization. Zoltán Pászti: Visualization, Investigation, Data curation. József Valyon: Writing – review & editing, Funding acquisition. Anna Vikár: Visualization, Investigation, Data curation. Yuting Shi: Visualization, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors do not have permission to share data.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcata.2024.119757.

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