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Influence of furanic polymers on selectivity of furfural rearrangement to cyclopentanone

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ABSTRACT

The influence of furanic polymers upon the activity and selectivity of Ni, Pd, Pt catalysts in rearrangement of furfural to cyclopentanone, and its consecutive hydrogenation to cyclopentanol in an aqueous phase has been studied. The coverage of surface of heterogeneous catalyst by the furanic polymers suppresses or almost completely inhibits hydrogenation of cyclopentanone to cyclopentanol. Furanic polymers are created on catalyst surface by partial polymerization reaction of furfuryl alcohol which is in aqueous medium catalyzed by H^+ protons formed by dissociation of water at reaction temperatures. Thermogravimetric and XPS measurements confirmed the presence of polymers on catalyst surface. Owing to the modification of catalyst surface by the polymer bearing furan moieties constituents the dominant reaction product is despite high reaction temperature (175 °C) and hydrogen pressure (80 bar), cyclopentanone, and not expected more stable cyclopentanol. Very high selectivity of furfural rearrangement to cyclopentanone can be achieved by influencing the balance between the rates of formation of furfuryl alcohol polymers on the catalyst surface and their decomposition.

1. Introduction

Selective catalytic hydrogenation of ketones, especially containing other unsaturated bonds or functional groups has already been the topic of many studies [1–3]. In the hydrogenation processes performed in the presence of heterogeneous metal catalysts, where ketones are desired products is the problem to obtain high selectivity because ketone can be further hydrogenated to the corresponding alcohol under reaction conditions. Typical example is the industrial production of cyclohexanone by a one-step catalytic hydrogenation of phenol, where subsequent hydrogenation of this reactive ketone to cyclohexanol can negatively influence the selectivity of the process. Several reports have suggested the methods how to influence the selectivity to cyclohexanone at high phenol conversion [4]. For instance the selectivity for cyclohexanone formation can be improved by the addition of alkali or alkaline earth metals to Pd/Al_2O_3 catalyst [5,6], by the promoting effect of Ce-dopant on amorphous alloy Pd-B catalysts [7] by changing the acid–base properties of the support [8–11] or its structure [4,12,13].

Recently, we have demonstrated [14] that at the reaction temperatures 150–175 °C and hydrogen pressure 30–80 bar furfural in aqueous medium is rearranged to cyclopentanone with very high selectivity. Despite very high reaction temperature and hydrogen pressure cyclopentanol is surprisingly formed only in low amounts. Moreover, high selectivity of cyclopentanone formation can be reached using various heterogeneous metal catalysts [15]. This experimental observation prompted us to elucidate the reasons for such peculiar behavior of metal catalysts.

In this paper we report that the modification of catalyst surface by the polymer bearing furanic moieties constituents positively influence the selectivity of furfural and furfuryl alcohol rearrangement to cyclopentanone. The polymers are formed in certain amounts during furfural hydrogenation by side polymerization reaction of intermediately formed furfuryl alcohol. Owing to the modification of metal catalyst by the polymers the subsequent hydrogenation of primary formed ketone is inhibited.

2. Experimental

2.1. Materials

Furfural (FA), furfuryl alcohol (FAL), tetrahydrofurfuryl alcohol (THFAL), 2-methylfuran (2-MeF), cyclopentanone (C_{PON}), cyclopentanol (C_{POL}), were purchased from Sigma-Aldrich. Furfural was purified by distillation and stored at −15 °C.

The commercial catalysts: 5% Pt/C (platinum on activated charcoal from Fluka), 5% Pd/C (Fluka), $Ni/SiO_2–Al_2O_3$ catalyst G-134 A (from Süd Chemie). The nickel catalyst was ground to fine powder

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Table 1
The physical properties of catalysts.

Catalysts	Metal (wt%)	S_{BET} ($m^2 g^{-1}$)	Pore diameter (BJH) (nm)	Particle size by XRD (nm)	Mean diameter of catalyst (μm)
G-134A	44	266	3.1	–	56
5% Pt/C	5	930	3.2	3.4	25
5% Pd/C	5	865	3.5	4.6	36

and in this form was used for experiments. The physical properties of catalysts are in Table 1.

2.2. Catalytic experiments

Catalytic experiments were performed using procedure and analytical methods described in our previous paper [14]. For a typical reaction, 20 ml of water, 0.5–1.0 g of reactant and given amount of metal catalyst was added to the reactor vessel. After sealing the reactor was several times flushed with low pressure hydrogen and then pressurized with hydrogen usually to 30–80 bar (ambient temperature). The reactor was then heated to the desired temperature and the stirring speed adjusted to 1500 rpm to eliminate external mass-transfer effects. After an appropriate reaction time the reactor was quickly cooled down, the reactor contents pour out to vial and the catalyst separated from the aqueous phase by centrifugation. The quantitative determination of the liquid products concentration was done using gas chromatography by the external standard method and using response factors of the corresponding standard compounds. A gas chromatograph–mass spectrometer combination was used to identify the organic compounds.

The yields of reaction products were calculated on the amount of the reactant charged into the reactor. In catalytic experiments where cyclopentanone simultaneously react with other reactant, e.g. furfural, which can be also converted to cyclopentanone and cyclopentanol, the amounts of cyclopentanone and cyclopentanol are in the tables expressed as grams of those compounds determined in the reaction mixture. The yields of other reaction products are expressed in the corresponding mol%, which are defined as

$$\frac{(\text{mol of product})}{(\text{mol of initial reactant})} \times 100\%$$

For the impregnation of fresh heterogeneous catalysts with furfuryl alcohol polymers two methods were used. By Method A the catalyst (100 mg) was impregnated with a defined amount of furfuryl alcohol polymers (FALP) dissolved in toluene or dimethylsulfoxide (DMSO). The FALP were prepared by polymerization of furfuryl alcohol (1.0 g) in freshly distilled water (20 ml) under nitrogen at the temperature of 175 °C for 70 min. The NMR analysis (Varian VNMRS-600) was used for determination of the molecular weight of FALP. In Method B the catalyst (100 mg) was added into a water solution of furfuryl alcohol (1 g in 20 ml of water) and heated at 175 °C for 70 min. The reactions were carried out in nitrogen atmosphere in a 100 ml Teflon lined stainless steel autoclave and the reaction mixture was mixed with a Teflon bar. After reaction the catalyst was separated, washed with water and then used for the catalytic reactions.

2.3. Characterization of catalysts

The surface areas and pore diameters were determined from BET nitrogen adsorption measurements (Micrometrics ASAP 2020). The samples were first degassed at 300 °C for 2 h before measurements. Metal particles sizes were determined from XRD data. The metal dispersion of catalyst was measured by hydrogen and CO chemisorption. A catalyst sample (50 mg) pre-exposed to air was placed in a glass tube connected to the instrument and stabilized at 100 °C under nitrogen flow. A volume of 50 μl pulses of pure H_2 or CO were injected in the flow until the catalyst was saturated with hydrogen or CO. Adsorption of gases was corrected for the adsorption by support under such conditions.

The XPS signals were recorded using a Thermo Scientific *K*-Alpha XPS system (Thermo Fisher Scientific, UK) equipped with a micro-focused, monochromatic Al $K\alpha$ X-ray source (1486.6 eV). An X-ray beam of 400 μm size was used at 6 mA × 12 kV. The spectra were acquired in the constant analyzer energy mode with pass energy of 200 eV for the survey. Narrow regions were collected with pass energy of 50 eV. Charge compensation was achieved with the system flood gun that provides low energy electrons (~0 eV) and low energy argon ions (20 eV) from a single source. The argon partial pressure was 3×10^{-7} mbar in the analysis chamber. The Thermo Scientific Avantage software, version 4.87 (Thermo Fisher Scientific), was used for digital acquisition and data processing. Spectral calibration was determined by using the automated calibration routine and the internal Au, Ag and Cu standards supplied with the *K*-Alpha system. The charge shift of the spectra was then corrected by setting the C 1s peak at 285 eV. The overlayer thickness was measured using the single overlayer calculator in the Thermo Scientific Avantage software, which uses the following equation to generate a fit to, derived from the Beer–Lambert Law:

$$\frac{1}{\cos\theta} = \frac{t}{\lambda} \times \ln[1 + K \times R] \qquad (1)$$

where t is the thickness of overlayer, $\theta$is the emission angle (measured from surface normal), λ is the attenuation length (the different attenuation lengths of the overlayer and substrate are considered), K is the ratio of atomic densities (element/overlayer) (and sensitivity factor if applicable), R is the measured intensity ratio (overlayer/element).

Temperature programmed reductions (TPR) were carried out using Micromeritics AutoChem 2910 instrument. Catalyst samples (30–50 mg) were heated up to 500 °C at a rate of 5 °C min^{-1} in a H_2–N_2 (10:90) gas flow (50 ml min^{-1}). Prior to measurements, the catalysts were dried in nitrogen atmosphere at 90 °C for 1 h. Thermal gravimetric analysis was conducted with a NETZSCH instrument. The samples (5–8 mg) were heated in flowing oxygen (50 ml min^{-1}) from room temperature to 600 °C at a rate of 5 °C min^{-1}.

3. Results and discussion

The catalytic hydrogenation of furfural in aqueous solution at the temperatures 130–175 °C and hydrogen pressures 40–80 bar predominantly leads to the rearrangement of the furane ring. Under these conditions, cyclopentanone and partly cyclopentanol are formed as the main reaction products [14]. Peculiar is also the fact that by the prolongation of the reaction time the more reactive ketone is only slowly hydrogenated to cyclopentanol. However, when after hydrogenation of furfural was in the reaction mixture containing mainly cyclopentanone exchanged the spent catalyst with the fresh one and this reaction mixture was again hydrogenated at the same conditions, almost all cyclopentanone and other intermediates were converted to the corresponding reaction products (Table 2 runs 2 and 3). The products of partial hydrogenolysis of alcohols were also detected by GC/MS. The retardation of subsequent cyclopentanone hydrogenation cannot be associated

Table 2
Recycling of catalysts Reaction conditions: 1 g FA, 0.100 g catalyst, 20 g water; reaction temperature 175 °C, hydrogen pressure 80 bar, reaction time 30 min.

Run	Catalyst		Conversion (%)	Yield (mol%)					
				C_{PON}	C_{POL}	FAL	THFAL	2-MeF	2-MeTHF
1	5% Pt/C	Fresh	100	40.2	36.2	0	0.3	5.0	9.4
2	5% Pt/C	Re-used	100	43.2	33.6	3.5	0.9	4.6	4.3
3[a]	5% Pt/C	Fresh	–	2.9	56.8	0	7.7	0	5.6
4	G-134A	Fresh	100	57.3	6.9	0	9.7	0.2	1.6
5	G-134A	Re-used	99.4	60.1	3.1	3.7	5.2	1.4	0.2
6[b]	5% Pd/C	Fresh	97.8	67.0	0.7	0	2.0	2.4	6.1
7[b]	5% Pd/C	Treated by Method B	95.9	66.4	0.1	2.7	3.9	2.1	2.4

FA—furfural; FAL—furfuryl alcohol; THFAL—tetrahydrofurfuryl alcohol; 2-MeF—2-methylfuran; 2-MeTHF—2-methyltetrahydrofuran; C_{PON}—cyclopentanone; C_{POL} cyclopentanol.

[a] Reaction mixture from run 2 was after separation of spent catalyst hydrogenated using fresh 5% Pt/C catalyst.

[b] At 160 °C, 30 bar hydrogen and 60 min.

with deactivation of the heterogeneous metal catalyst which can proceed during furfural hydrogenation. As seen from the results in Table 2 the spent catalysts recycled to the next runs exhibited the same activity and produced practically the same yields of cyclopentanone and the distribution of products as the fresh catalysts. In these recycling experiments the catalysts after reaction were separated from the reaction mixtures by centrifugation and without washing or using other purification procedures were directly used in the next runs.

Since both the metal and the support of the catalyst can influence the catalytic activity and in our case also the selectivity to the reactive ketone, the heterogeneous catalysts with different metals were tested in the competitive hydrogenation of the mixture of furfural with cyclopentanone. Both these reactants are during reaction absorbed on transition metals via different bonding configurations which could be the reactive intermediate leading to different surface reaction pathways with neighbouring activated surface hydrogen [16]. Furfural prefers adsorption through the furan ring while cyclopentanone probably through the η^2(C,O) adsorption mode [3,16].

Over tested catalysts the hydrogenation of furfural in the aqueous solution yields cyclopentanone and cyclopentanol [15]. In experiments with the mixture of furfural/cyclopentanone the latter can be formed from furfural and by consecutive hydrogenation of cyclopentanone. For simplicity, in Table 3 are the results of the competitive hydrogenation of furfural and cyclopentanone expressed as grams of cyclopentanone and cyclopentanol determined in the reaction mixtures. In all these runs the conversion of furfural was complete. The higher amounts of cyclopentanone detected in the reaction mixtures after competitive hydrogenation of furfural/cyclopentanone mixtures revealed that on the Pt, Pd and Ni catalysts the hydrogenation of cyclopentanone (the initial amount was 0.50 g) to cyclopentanol is under reaction conditions slower than its formation by the furfural rearrangement. The highest inhibition of cyclopentanone hydrogenation was observed in the reaction catalyzed by the nickel catalyst. However, when instead of furfural tetrahydrofurfuryl alcohol or 2-methylfuran was used in the mixture with cyclopentanone the inhibition was not observed and cyclopentanone was almost completely hydrogenated to cyclopentanol (Table 3 runs 2 and 3).

Table 3
Effect of catalyst (0.100 g) on the hydrogenation of mixture of 0.50 g of cyclopentanone and 0.50 g of furfural in 20 ml of water reaction temperature 175 °C, hydrogen pressure 80 bar, reaction time 30 min.

Run	Catalyst	Determined in the reaction mixture (g)[c]	
		C_{PON}	C_{POL}
1	5% Pt/C	0.67	0.21
2	5% Pt/C[a]	0.03	0.46
3	5% Pt/C[b]	0.02	0.47
4	5% Pd/C	0.72	0.20
5	G/134A	0.81	0.12

[a] THFAL instead of furfural.

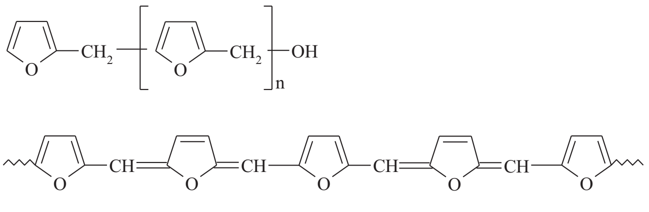
[b] 2-MeF instead of furfural.

[c] Theoretically from 0.5 g FA can be formed 0.44 g of C_{PON} or 0.45 g C_{POL}; the reaction mixture contains also other products which are not shown.

Since the inhibition of cyclopentanone hydrogenation cannot be associated with catalyst deactivation (Table 2) and this reaction is not inhibited by the presence of tetrahydrofurfuryl alcohol or 2-metylfuran it suggests that the adsorption of simple furanic molecules on catalytic centers is not responsible for inhibition. This is valid also for furfural which at given reaction conditions is very quickly hydrogenated to furfuryl alcohol and other furan ring saturated products.

To elucidate the origin of inhibition, the hydrogenation of cyclopentanone alone was studied using spent catalysts and catalysts impregnated with furfuryl alcohol polymers. Namely, as we have demonstrated [18] furfuryl alcohol, the primary product of furfural hydrogenation, in water at higher temperatures (>130 °C) is partly polymerized to water insoluble polymers probably having conjugated diene structures [17,20] (Scheme 1). The NMR analysis confirmed, that depending on the temperature and reaction time these polymers usually contains from 5 to 30 furanic rings in the chain. In toluene are preferably dissolved FALP with lower molecular weights, while in DMSO also FALP with longer chains. As can be seen from Table 4, the spent catalysts from the hydrogenation of furfural or the mixture of furfural/cyclopentanone reused for the hydrogenation of cyclopentanone alone at the same conditions are significantly less active (runs 2 and 9) than the fresh catalysts (runs 1 and 8). A similar inhibition effect as the spent catalysts have the catalysts impregnated by solutions of FALP in toluene (runs 3 and 11) or in DMSO (run 4).

These results confirmed that for the high selectivity of cyclopentanone formation in the furfural rearrangement in an aqueous solution is responsible the adsorption of furfuryl alcohol polymers on the surface of heterogeneous metal catalyst. Moreover, it can explain why the spent catalysts from furfural or furfuryl alcohol rearrangement in water inhibit the hydrogenation of cyclopentanone to cyclopentanol. The evidence for this assumption was



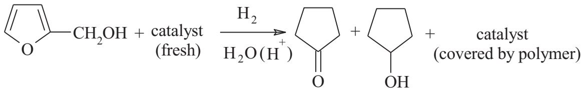
Scheme 1. Structures of furfuryl alcohol polymers [17,20].

Table 4
Hydrogenation of cyclopentanone (1.0 g) in water (20 g) catalyzed by 0.100 g G-134A catalyst at 130 °C, 40 bar hydrogen for 30 min.

Run	Catalyst	Conversion to cyclopentanol (%)
1	Fresh	62.9
2	Re-used from run 5, Table 2	23.6
3	Impregnated in toluene by Method A	42.1
4	Impregnated in DMSO by Method A	36.0
5	Treated by Method B	32.3
6	Re-used from run 5, Table 3	30.4
7	Treated by Method B and reduced[a]	89.4
8	Fresh[b]	96.4
9	Re-used from run 5, Table 3[b]	51.7
10	Fresh[c]	57.9
11	Impregnated in toluene by Method A[c]	21.7
12	Treated by Method B[c]	24.9
13	5% Pd/C treated by Method B[d]	5.8
14	5% Pt/C re-used from run 2, Table 3[b]	97.1

[a] Catalyst treated by Method B was reduced in a flow of hydrogen (30 ml min^{-1}) at 400 °C for 2 h.
[b] At 175 °C and 80 bar hydrogen.
[c] At 160 °C, 8 bar, 80 min.
[d] At 30 bar and 60 min.

experiments with catalysts treated in aqueous solution of furfuryl alcohol at temperatures comparable to those of catalytic reactions. It is known, that at these temperatures water molecules dissociate, i.e. the aqueous solution becomes acidic [19] and catalyzes the polymerization of furfuryl alcohol [17,18,20]. A part of thus in-situ formed FALP is adsorbed on the surfaces of the heterogeneous catalysts, and influence their catalytic properties (Scheme 2). The polymers are water insoluble and owing to their electron-rich, usually conjugated structures [17] they are strongly adsorbed on the catalyst surface. The catalysts modified by the in-situ formed furfuryl alcohol polymers inhibited cyclopentanone hydrogenation in similar extent as the spent catalysts (Table 4, runs 5 and 12) or catalysts impregnated by FALP solutions (runs 4 and 11). Depending on the reaction conditions and type of metal catalyst the FALP adsorbed on the surface of catalyst are continuously hydrogenated and hydrogenolyzed to saturated products which are weakly adsorbed on the catalyst and thus easily removed from the catalyst surface. A similar effect has also prolongation of the reaction time which is exhibited by the proportionally increasing and decreasing concentrations of cyclopentanol and cyclopentanone in the reaction mixture [15]. These results explain why the inhibition effects of spent catalysts (Table 4, compare runs 2 and 9) and also catalysts impregnated with FALP (runs 11 and 3) are smaller at higher hydrogen pressures. Additionally, the results indicate that the selectivity of cyclopentanone formation during rearrangement of furfural or furfuryl alcohol in aqueous systems, i.e. the inhibition of its consecutive hydrogenation to cyclopentanol determines the balance between formation of FALP on the catalyst surface and their removal by hydrogenation/hydrogenolysis reactions. An example is almost the same and very high selectivity of cyclopentanone formation obtained during transformation of furfural with fresh and spent 5% Pt/C catalyst (Table 2, runs 1 and 2) at the temperature of 175 °C and hydrogen pressure 80 bar. On the other hand, the spent catalyst from the run 2 (Table 3) at the same conditions almost completely hydrogenates cyclopentanone to cyclopentanol (Table 4, run 14). The latter results revealed that under these reaction conditions furfuryl alcohol polymers present on the spent platinum catalyst are only removed from the surface of spent catalyst by hydrogenolysis. Since in this experiment furfuryl alcohol is not present in the reaction mixture the decrease of FALP on the catalyst surface cannot be compensated by its polymerization. It causes that the effect of FALP to inhibit cyclopentanone hydrogenation to cyclopentanol is eliminated. It is also in agreement with the results of cyclopentanone hydrogenation using fresh catalysts which were not modified with FALP (Table 4). However, when in the reaction mixture is present also furfuryl alcohol or its precursor (furfural) the lost of FALP caused by the hydrogenation/hydrogenolysis is compensated by the partial polymerization of furfuryl alcohol which proceeds continuously during reaction. It supports the results of cyclopentanone hydrogenation in the mixture with furfural which show (Table 3) that owing to the possibility to generate continuously FALP the metal catalyst remains permanently modified with the polymers, and as a result cyclopentanone present in the reaction mixture is not hydrogenated to cyclopentanol, or only in less extent. If instead of furfural cyclopentanone is hydrogenated in the mixture with tetrahydrofurfuryl alcohol or 2-methylfuran, which under reaction conditions cannot be polymerized to FALP or similar types of polymers and thus modify metal catalyst, cyclopentanone is almost completely converted to cyclopentanol (Table 3, runs 2 and 3), i.e. the performance of catalyst is similar as in the experiment with cyclopentanone alone (Table 4, run 14).



Scheme 2. Conversion of furfuryl alcohol in water.

The different effect of Pt, Pd and Ni catalysts on hydrogenation of cyclopentanone/furfural mixture (Table 4) is probably associated with their different effects on the (i) polymerization of furfuryl alcohol, and (ii) hydrogenation/hydrogenolysis of FALP on catalyst surface. The polymerization of furfuryl alcohol in water is acid catalyzed reaction. This reaction is influenced by water dissociation which at reaction temperatures 130–180 °C becomes acidic (pH < 6) [19] and also by the acid–base properties of heterogeneous catalyst. Moreover, the metal-support interaction in the catalyst can lead hydrogen to spill over from the metal onto the support material, forming protic sites on the support surface and consequently an increase pool of H$^+$ in the system. The latter factors probably also enhance the adsorption of FALP on Pt and Pd catalysts supported on activated carbon. On the other hand the removal of FALP from the catalyst surface by hydrogenation/hydrogenolysis reactions depends at constant reaction conditions on the metal and the interaction of the metal/support. Since dissociation of water is temperature dependent, the differences among catalysts at constant temperatures are influenced mainly by their effects on both furfuryl alcohol polymerization and decomposition of FALP. However, it is hardly to distinguish between these effects of the catalyst.

From the results described above becomes clear that by providing equilibrium between the rates of FALP formation and their decomposition on the catalyst surface by optimization of reaction conditions and catalyst properties it is possible to achieve very high selectivity of furfural conversion to cyclopentanone.

The deposition of polymers on the catalyst surface can negative influence its activity (rate reaction) by blocking catalytically active sites. However, as is seen from the results of furfural rearrangement using fresh and spent catalysts or with Pd/C catalyst modified by FALP (Table 2), practically the same conversion of furfural and product distribution was reached. In contrary to furfural hydrogenation the lower conversions of cyclopentanone to cyclopentanol observed using spent catalysts or catalysts modified with FALP (Table 4) can be attributed to the retardation of cyclopentanone hydrogenation due to different adsorption of the ketone and its reactivity toward hydrogenation on metals.

The presence of FALP on the surface of the spent nickel catalyst was studied using XPS and NMR analysis. Fig. 1 shows the XPS spectra in the C 1s region of the spent nickel catalysts and the XPS spectra of furfuryl alcohol polymer prepared by polymerization of furfuryl alcohol in water at 175 °C. In the C 1s peak of

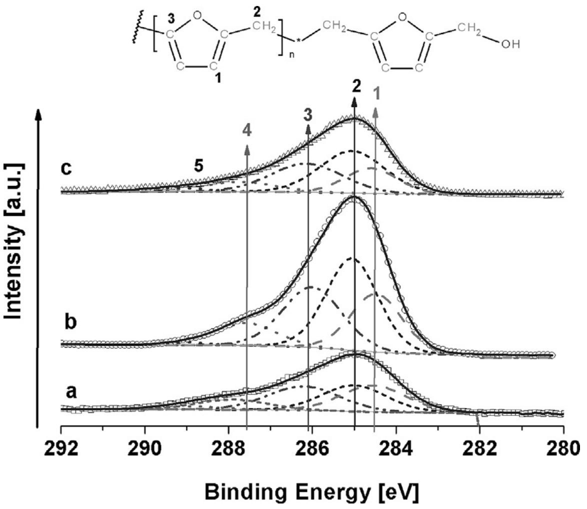


Fig. 1. The XPS of (a) spent nickel catalyst from run 6, Table 3; (b) furfuryl alcohol polymers; (c) spent nickel catalyst from run 5, Table 2, (–) Fit envelope.

the spent nickel catalysts obtained at different reaction conditions was by deconvolution clearly recognized the characteristic peaks of furfuryl alcohol centered at ~284.5 eV, ~285.0 eV, and ~286.0 eV corresponding to C=C, C–C, and C–O bonding, respectively. Besides these characteristic peaks also peak at ~287.6 eV attributed to carbonyl groups (C=O) and a very small peak at about 288.9 eV attributed to O–C=O bonding was detected. These results are consistent with the XPS studies of the bulk furfuryl alcohol polymer used as the reference (see Fig. 1b). The thickness of furfuryl alcohol polymer film on the Ni catalyst was about 0.5 nm as calculated by the single overlayer calculator from XPS results. The presence of FALP on the spent nickel and Pt/C catalysts was also studied by NMR analysis. The polymers were from water washed spent catalysts extracted by DMSO and the concentrated extracts analyzed by NMR. The XPS and NMR analysis confirmed that on the catalyst surface are in the course of furfural hydrogenation present furfuryl alcohol polymers.

From the thermogravimetric analysis of some spent catalysts was determined that the amount of the polymer deposited on the catalyst was usually about 4–11 wt%.

As is evident from the TPR measurements of fresh and by polymer-modified nickel catalysts (Fig. 2) the polymer deposited on the catalyst is at temperatures above 200 °C gradually removed. When such reduced catalyst was used in the hydrogenation reaction, in contrast to the unreduced catalyst the hydrogenation of cyclopentanone was significantly enhanced (Table 4, runs 5 and 7).

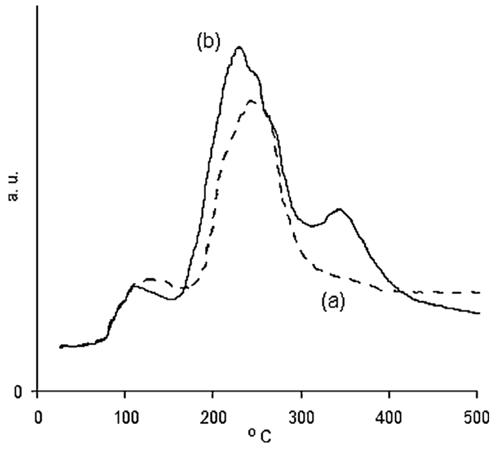


Fig. 2. TPR profiles of fresh (a) and by polymers modified (b) nickel catalyst.

The presented experimental data revealed that very high selectivity of furfural transformation to cyclopentanone in water, which under reaction conditions can be further hydrogenated to cyclopentanol was caused by the inhibition effect of furfuryl alcohol polymers. The polymers are formed on the catalyst surface continuously by partial polymerization of intermediately formed furfuryl alcohol. It is generally accepted that bonding of reaction groups (e.g. C=C, C=O) to the surface of the catalyst is the main factor determining the selectivity in hydrogenation of unsaturated ketones and aldehydes [1,3,21]. Furthermore, the different adsorption–desorption properties of reactants and products on the catalyst in various solvents implies that the change of these properties might potentially affect the product selectivity [21,22]. We assume that the role of FALP present on the catalyst surface is to enhance desorption of cyclopentanone from the metal surface where it is formed by the rearrangement of furfural. The enhancement of cyclopentanone desorption is attributed to a reduction in the chemisorbed bond strength due to competitive absorbate–adsorbate interaction between the furfuryl alcohol polymer and cyclopentanone. The interaction of furfuryl alcohol polymers on metal centers can occur through π-bonds of furan rings and the extended π-conjugation along the molecular backbone. This interaction creates on catalyst surface a polymeric layer and electron-rich metal centers. As a result, the adsorption strength of cyclopentanone on metal is weakened what promotes desorption of formed cyclopentanone from the surface. Cyclopentanone is adsorbed on metals through the keto-carboxyl moiety, probably in a η^2(C,O) mode while furfural and furfuryl alcohol are strongly bound due to the relatively strong interaction of the π-bonds of the furan ring with the d orbitals of the metal [23,24]. These factors influence cyclopentanone against its consecutive hydrogenation to cyclopentanol.

The mechanism of enhancement of the selectivity of the hydrogenation reaction by the use of some organic additives was suggested by several authors to explain the great improvement of the catalytic activity and the selectivity. In the liquid-phase hydrogenation of benzene to cyclohexene in the presence of ruthenium catalysts, the selectivity was significantly enhanced by the addition of amines and alcohols. Struijk and Scholten [25] and Suryawanshi and Mahajani [26] explained the modifying action by the formation of a hydrogen bond between cyclohexene and the modifier. Fan et al. [27] suggested that the metal and the additive interact creating a water layer around the active metal centers, which promote desorption of cyclohexene. Jiang et al. [28] explained the increase of selectivity to geraniol and nerol in the ruthenium catalyzed hydrogenation of citral, using some organic additives by the increased hydrophilicity of metal particles, which favored the adsorption of the citral C=O bond over the adsorption of the conjugated C=C bond.

4. Conclusions

Catalytic rearrangement of furfural in an aqueous solution exhibited high selectivity to cyclopentanone. Although the reaction was performed at high reaction temperature and hydrogen pressure (175 °C, 80 bar) the consecutive hydrogenation of cyclopentanone to cyclopentanol was inhibited. Responsible for this effect was modification of catalyst surface with furfuryl alcohol polymers, which are formed gradually on catalyst surface by partial polymerization of intermediately formed furfuryl alcohol. The polymerization reaction is catalyzed by H^+ protons created by autodissociation of water at reaction temperatures and by acid centers of catalyst support. Since under reaction conditions the polymeric layer is gradually decomposed by hydrogenation/hydrogenolysis reactions, important for keeping very high selectivity of cyclopentanone formation is to provide the balance between the rates of formation and decomposition of polymers on the catalyst surface. The presence of furfuryl alcohol polymers on catalyst surface was confirmed by XPS analysis of spent catalyst. The TG and NMR analyzes have shown that on the catalyst are usually present 4–11% of water insoluble polymers which contains from 5 to 30 furanic moieties in the chain. The inhibition effect of furanic polymers present in the spent catalysts and the catalysts impregnated with solutions of such types of polymers was confirmed also in hydrogenation of cyclopentanone alone. The mechanism of action of furfuryl alcohol polymers was attributed to the enhancement of cyclopentanone desorption from the catalyst surface as a result of reduction in the chemisorbed bond strength due to competitive interaction between the polymers and cyclopentanone.

References

[1] V. Ponec, Appl. Catal., A 149 (1997) 27–48.
[2] G.M.R. van Druten, V. Ponec, Appl. Catal., A 191 (2000) 163–176.
[3] A. Vargas, S. Reimann, S. Diezi, T. Mallat, A. Baiker, J. Mol. Catal. A: Chem. 282 (2008) 1–8.
[4] Y. Pérez, M. Fajardo, A. Corma, Catal. Commun. 12 (2011) 1071–1074.
[5] G. Neri, A.M. Visco, A. Donato, G. Milone, M. Malentacchi, G. Gubitosa, Appl. Catal., A 110 (1994) 49–59.
[6] S. Scire, S. Minico, C. Crisafulli, Appl. Catal., A 235 (2002) 21–31.
[7] H. Li, J. Liu, H. Li, Mater. Lett. 62 (2008) 297–300.
[8] S. Watanabe, V. Arunajatesan, Top. Catal. 53 (2010) 1150–1152.
[9] Y.Z. Chen, C.W. Liaw, L.I. Lee, Appl. Catal., A 177 (1999) 1–8.
[10] H. Liu, T. Jiang, B. Han, S. Liang, Y. Zhou, Science 326 (2009) 1250–1252.
[11] J. Matos, A. Corma, Appl. Catal., A 404 (2011) 103–112.
[12] P. Makowshi, R.D. Cakan, M. Antonietti, F. Goettman, M.M. Titirici, Chem. Commun. (2008) 999–1001.
[13] Y. Wang, J. Yao, H. Li, D. Su, M. Antonietti, J. Am. Chem. Soc. 133 (2011) 2362–2365.
[14] M. Hronec, K. Fulajtarova, Catal. Commun. 24 (2012) 100–104.
[15] M. Hronec, K. Fulajtarova, T. Liptaj, Appl. Catal., A 437–438 (2012) 104–111.
[16] S.H. Pang, J.W. Medlin, ACS Catal. 1 (2011) 1272–1283.
[17] T. Kim, R.S. Assary, Ch.L. Marshall, D.J. Gosztola, L.A. Curtiss, P.C. Stair, ChemCatChem 3 (2011) 1451–1548.
[18] M. Hronec, K. Fulajtarova, T. Sotak, J. Ind. Eng. Chem. (2013), http://dx.doi.org/10.1016/j.jiec.2013.05.029.
[19] A.V. Bandura, S.N. Lvov, J. Phys. Chem. Ref. Data 35 (2006) 15–30.
[20] M. Choura, N.M. Belgacem, A. Gandini, Macromolecules 29 (1996) 3839–3850.
[21] U.K. Singh, M.A. Vannice, Appl. Catal., A 213 (2001) 1–24.
[22] Y. Xiang, L. Ma, Ch. Lu, Q. Zhang, X. Li, Green Chem. 10 (2008) 939–943.
[23] M.K. Bradley, J. Robinson, D.P. Woodruff, Surf. Sci. 604 (2010) 920–925.
[24] S. Sittisa, D.E. Resasco, Catal. Lett. 141 (2011) 784–791.
[25] J.J.J. Struijk, F. Scholten, Appl. Catal., A 82 (1992) 177–287.
[26] P.T. Suryawanshi, V.V. Mahajani, J. Chem. Tech. Biochem. 69 (1997) 154.
[27] G.Y. Fan, R.X. Li, X.J. Li, H. Chen, Catal. Commun. 9 (2008) 1394–1397.
[28] H.J. Jiang, H.B. Jiang, D.M. Zhu, X.L. Zheng, H.Y. Fu, H. Chen, R.X. Li, Appl. Catal., A 445–446 (2012) 351–358.