NJC

PAPER

Check for updates

Cite this: New J. Chem., 2021, 45, 5023

Received 14th January 2021, Accepted 21st February 2021

DOI: 10.1039/d1nj00219h

rsc.li/njc

1. Introduction

Hydrogenation of aromatic ketones is a process of great importance because of the broad practical application of its products.^{1,2} Aromatic ketones can be efficiently hydrogenated using different metal catalysts.^{3–7} In hydrogenation studies, acetophenone (APh) is often used as a model substrate. The first product of APh hydrogenation is 1-phenylethanol (PhE), used in the cosmetic and pharmaceutical industry.^{8–10} Further hydrogenation of PhE can also occur, leading to ethylbenzene (EtB).^{10–14} In this reaction, the C–OH bond is converted to a C–H bond, which is a transformation of practical importance in organic synthesis, in particular in biomass conversion.^{15,16} Moreover, hydrogenolysis of PhE plays an important role in the manufacturing of propylene oxide in which PhE is an undesired waste product, while EtB can be recycled back into the process.¹²

Immobilized palladium catalysts were tested with good results for the hydrogenation of APh. In most cases, activated

Effect of solvent in the hydrogenation of acetophenone catalyzed by Pd/S-DVB⁺

Tomasz Bereta,^a Ewa Mieczyńska,^a Sylwia Ronka, ^b Włodzimierz Tylus^c and Anna M. Trzeciak ^{*}

A solvent effect was found in the hydrogenation of acetophenone catalyzed by a new Pd/S-DVB catalyst, immobilized on a styrene (S)/divinylbenzene (DVB) copolymer containing phosphinic groups. The porous structure of the catalyst was characterized by a specific surface area of 94.7 m² g⁻¹. The presence of Pd(II) and Pd(O) in Pd/S-DVB was evidenced by XPS and TEM. Pd/S-DVB catalyzes the hydrogenation of acetophenone (APh) to 1-phenylethanol (PhE) and ethylbenzene (EtB). The highest conversion of APh was obtained in methanol (MeOH) and in 2-propanol (2-PrOH), while in water it was lower. The conversion of APh correlates well with the hydrogen-bond-acceptance (HBA) capacity of the solvent. However, in all binary mixtures of alcohol and water the APh conversion and the yield of products significantly decreased. The observed inhibiting effect can be explained by the microheterogeneity of these mixtures and the blocking of the catalyst surface restricting access of the substrates to the Pd centers.

carbon (Pd/C)^{17,18} and inorganic oxides, Al₂O₃,¹⁹ TiO₂,²⁰ SiO₂, and AlPO₄,^{21,22} have been explored as supports. Pd loaded on a hierarchical FAU nanozeolite membrane catalyzed transfer hydrogenation using water as a solvent and sodium formate as the hydrogen and electron donor.²⁵ In contrast, organic polymers were scarcely used (Fig. 1).^{23,24}

Selective formation of PhE was achieved using Pd/POP2 (POP2 = spirofluorene-based porous organic polymer) at 25 bar of H_2 .²⁶ The catalytic activity of Pd/PVP (PVP = poly-4-vinylpyridine) was found to be comparable to that of Pd/Al₂O₃, while lower activity and selectivity were noted for Pd supported on electroactive PPY (PPY = polypyrrole).²³ Enantioselective APh hydrogenation was studied with cinchonidine [26] or proline modified catalysts.^{27,28}

Hydrogenation of APh with immobilized palladium catalysts was studied in various solvents, including water. By using Pd/C in water, high conversion of APh was obtained, which was further enhanced in the presence of CO_2 .¹⁸ A similar positive



Fig. 1 Products of acetophenone hydrogenation.



View Article Online

^a Faculty of Chemistry, University of Wroclaw, F. Joliot-Curie St. 14 St. 50-383 Wroclaw, Poland, E-mail: anna.trzeciak@chem.uni.wroc.pl

^b Department of Engineering and Technology of Polymers, Faculty of Chemistry, Wroclaw University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

^c Department of Advanced Material Technologies, Faculty of Chemistry, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27 St., 50-370 Wrocław, Poland

 $[\]dagger$ Electronic supplementary information (ESI) available. See DOI: 10.1039/ d1nj00219h

effect of CO₂ was also noted in MeOH.¹⁸ Water was found to be a superior solvent in APh hydrogenation using Pd/Al₂O₃ and Pd/C.¹⁹ The APh hydrogenation efficiency of these catalysts was correlated with the hydrogen-bond-acceptance (HBA) capacity (β) and hydrogen-bond-donor (HBD) capacity (α), depending on the support.^{19,29} An enhancement of the hydrogenation activity of the Ru/FCN (FCN = methacrylate-styrene resin) catalyst in water/MeOH and water/i-PrOH systems was rationalized by increased solvation of the reaction product and its accelerated desorption from the catalyst surface in these media.³⁰

Herein, we present the application of a new palladium catalyst immobilized on a porous *P*-functionalized polymer for APh hydrogenation. Considering the results cited above, we expected a solvent effect on the hydrogenation yield and selectivity. In particular, it was interesting to study mixed solvents of the ROH/water type. Such mixtures, which significantly deviate from the ideal solutions,^{31,32} have not yet been applied in APh hydrogenation with Pd catalysts. In fact, we found for the first time significant inhibition of the catalytic reaction in MeOH/water and i-PrOH/water binary mixtures.

2. Experimental

2.1. Preparation of the Pd catalyst

The styrene (S) and divinylbenzene (DVB) copolymer was prepared by typical suspension polymerization using 0.5 wt% benzoyl peroxide as an initiator. The nominal crosslinking degree of the S-DVB copolymer was 20 wt%. Synthesis of the polymer was carried out in the presence of nonsol and sol solvents, heptane/ toluene 1:9 v/v, in order to obtain a porous structure. The obtained polymer beads were washed with hot and cold water and acetone and dried. Then, the polymer was swollen in toluene and heated with this solvent for 9 h in a Soxhlet apparatus.

The S-DVB copolymer was then modified by phosphorylation. Thus, dry polymer beads were placed in a round bottom flask together with an excess of PCl_3 and swollen for 30 minutes. Then, powdered aluminum chloride was added and the entire mixture was refluxed for 6 h. After that, the beads were filtered, washed briefly with dioxane and dropped into a beaker containing ice and a solution of sodium chloride. After washing with distilled water, the beads were transferred to a *ca.* 3 M NaOH solution and left in it overnight followed by standard conditioning with distilled water, 1 M HCl, distilled water, 1 M NaOH, distilled water, 1 M HCl and finally with distilled water. The synthesis of S-DVB with phosphinic acid groups is presented in Fig. 2.

Palladium was introduced to the phosphorylated polymer using an aqueous solution of $K_2[PdCl_4]$ and applying a 2-fold metal excess with respect to the phosphinic groups. The palladium solution was put in contact with the phosphorylated S-DVB copolymer for 5 days (shaking at 150 rpm at room temperature). During this time, the color changed from yellow to black due to the reduction of Pd(n) to Pd(0). The resulting Pd/S-DVB material was washed with deionized water to remove the palladium excess and dried.



Fig. 2 Schematic representation of the polymer S-DVB synthesis.

2.2. Methods

The acid capacity in the polymer support was measured by immersing a known amount of the centrifuged polymer (in protonated form) in 50 mL of 0.1 M sodium hydroxide solution for 24 h and titrating the resultant solution with 0.1 M hydrochloric acid. The water regain of the resin was investigated using the centrifugation method.

The phosphorus content in the polymer support and in the catalytic material was determined by digesting a sample (*ca.* 20 mg) in hot concentrated sulfuric acid followed by analysis of the solution using the standard molybdate blue method. Readings were taken at 700 nm.

The palladium concentration was measured using the atomic absorption spectrometry method (AAS) on a GBC Avanta instrument with the wavelength set at 244.8 nm for Pd, and a slit of 0.2 nm.

The morphological features of the synthesized catalyst were obtained using a scanning electron microscope (JEOL, JSM-6610LVnx).

The XPS spectra were measured on a SPECS UHV/XPS/AES system with a dual Mg/Al X-ray source and a hemispherical PHOIBOS 100 analyzer operated in fixed analyzed transmission (FAT) mode. The spectra were processed using the CasaXPS v.2.2.19 program. The background was determined by the Schirley method.

The porous structure of the synthesized material examined by nitrogen adsorption at liquid nitrogen temperature gave no measurable surface area. Therefore, the pore size and surface area were characterized by benzene and carbon dioxide adsorption. A high-vacuum gravimetric apparatus with McBain–Bakr quartz spring balances was used. Adsorption isotherms were taken at 25 °C. Each sample was degassed at 250 °C for 3 h in a vacuum before starting the measurement. The micropore volume was determined by applying the Dubinin–Radushkevich (DR) equation. The values of the specific surface area (S_{BET}) were calculated on the basis of the Brunauer, Emmett and Teller (BET) equation from the adsorption branches of the benzene isotherms.

2.3. Hydrogenation experiments

The catalytic experiments were carried out in AMTECH corp. personalized autoclaves with PID and magnetic stirring providing precise control of the pressure and temperature.

0.00395 g of the palladium catalyst (containing 1×10^{-5} mol Pd), 0.1 mL (8.57 × 10⁻⁴ mol) of acetophenone and 3 mL of solvent were added to a 15 mL stainless steel autoclave under an N₂ atmosphere. The autoclave was pressurized to 15 bar of N₂. After pressure release, the autoclave was pressurized to 10 bar H₂ (in *ca.* 30 min), and then heated to 80 °C. After the reaction was completed, the autoclave was cooled down over 30 min, the pressure was released and 10 mL of methanol was added to the mixture. Next, 0.1 mL of mesitylene was added as an internal standard and the organic products were analyzed by the GC-FID and GC-MS methods (Shimadzu QP 2010 SE).

3. Results and discussion

3.1. Synthesis and characterization of Pd/S-DVB

The obtained Pd/S-DVB catalyst was characterized by benzene and carbon dioxide adsorption–desorption experiments. The results indicate that the synthesized polymer support is predominantly submicroporous (pores with diameters between 0.4 and 0.7 nm). The mesopore structure of the investigated product is poorly developed. Its specific surface area and the volume of pores are 94.7 m² g⁻¹ and 0.059 cm³ g⁻¹, respectively. The Pd to P ratio is close to 1 and the experimental data are comparable with the theoretical P and Pd atom content (2.5–2.6 mmol g⁻¹) (Table 1).

XPS analysis of the obtained Pd/S-DVB catalyst evidenced the presence of Pd(π) and Pd(0) attached to the polymer. Thus, Pd(π) was in part reduced to Pd(0) in the reaction with the polymeric support and simultaneously the phosphinic groups on the polymer surface were oxidized to phosphonate ones. Both forms of Pd are stabilized on the surface of the polymer by interactions with P = O and OH groups. Due to the small diameter of the pores, the bonding of Pd inside the pores is less likely.

Fig. 3 shows the Pd 3d spectra of the surface of the fresh catalyst. The Pd:P ratio was estimated as 0.26, significantly lower than in the AAS analysis. It can be assumed that part of the palladium was localized inside the polymer, not on its surface. Before analysis, the surface of the catalyst sample was cleaned with an Ar+ beam (Ar sputtering) using minimal energy over a short time period (1 keV, 1 min, 1.3 μ A cm⁻²).

Table 1 Characteristics of the Pd/S-DVB catalyst	
Pd content [mmol g^{-1}] Phosphorus content [mmol g^{-1}] S. $(s_{-m})^{a} [m^{2} \sigma^{-1}]$	2.6 2.5 94.7 (5.3)
$V_{\rm t} \left(V_{\rm BET}\right)^a \left[{\rm cm}^3 {\rm g}^{-1}\right]$	0.059 (0.002)

 a $S_{\rm t}/V_{\rm t}$ – the total surface area/volume of the pores calculated as the sum of the surface areas of submicropores, micropores and mesopores; $S_{\rm BET}/V_{\rm BET}$ – the BET surface area/volume of pores calculated from benzene adsorption isotherms.



Fig. 3 XPS spectra: Pd 3d core level spectrum of the sample before the reaction (left) and Pd 3d core level spectrum of the sample after the reaction (right).

The optimal fit was obtained for the presence of three palladium forms, namely Pd(0) with a binding energy of 335.1 eV for Pd $3d_{5/2}$, PdO with a binding energy of 336.6 eV and Pd(II) with a binding energy 338.0 assigned to the non-reduced PdCl₄^{2–} precursor.³³ The content of these palladium forms was 21.0, 57.4 and 21.6%, respectively. The presence of PdO can be explained by the oxidation of Pd NPs in air.

After hydrogenation, the Pd:P ratio decreased to 0.08, indicating palladium leaching or its transfer inside the polymer (Fig. 3). At the same time, the amount of Pd(0) on the surface increased to 41.5% while the amount of PdO decreased to 8.9% due to Pd reduction in the presence of H_2 .

Fig. S3 (ESI[†]) presents the P 2p spectra of three Pd/S-DVB samples before and after hydrogenation. The binding energies, BE 133.4 eV and BE 134.36 eV, were attributed to P $2p_{3/2}$ and P $2p_{1/2}$, respectively, and they are characteristic of phosphonate groups.^{34,35} The shape and position of the peaks were the same for all three measurements, indicating that the polymer was not changed during the reaction.

The presence of Pd(0) in the studied catalyst was additionally evidenced by XRD measurements before and after hydrogenation (Fig. 4). The XRD pattern presented four peaks at 40°, 46.7°, 68°, and 82°, corresponding to Pd(0) crystallized in the *Fm3m* space group (JCPDS card number 5-681).

The presence of Pd NPs in the Pd/S-DVB analyzed after the hydrogenation reaction was confirmed by TEM. The size of the Pd NPs varied from 12 to 26 nm, with an average of *ca.* 17 nm,



Fig. 4 XRD patterns of the as prepared Pd/S-DVB.

7

11

15

10

16

53

54

18

77

65

0.88

indicating some aggregation under the reaction conditions (Fig. 5).

Fig. 6 presents the SEM micrograph of the Pd/S-DVB catalyst, which has a regular spherical shape. Mapping of the catalyst surface showed a uniform distribution of palladium and phosphorus (Fig. 6).

3.2. Catalytic activity

3.2.1. Effect of solvents. The immobilized Pd/S-DVB catalyst was employed in the hydrogenation of acetophenone (APh) with H_2 (10 bar) in various solvents (Table 2). The reaction performed in DMF produced a mixture of two products, EtB and PhE, with the latter being the main one. Similar low selectivity was obtained in toluene, with 28% PhE and 18% EtB. In MeOH and in BuOH, APh was hydrogenated mainly to EtB with yields of 72% and 77%, respectively. An even higher amount of EtB was produced in i-PrOH (81%). Hydrogenation of APh in water proceeded with lower efficiency, and 66% conversion was achieved after 4 h with 52% EtB (Table 2).

To rationalize the effect of the solvent on the APh conversion, different correlations were analyzed and the best one was obtained for the HBA ability expressed by the β parameter.²⁹ The β -scale presents a measure of the solvent ability to accept a proton. Correlation of the APh conversion with the β parameter was noted for Pd/Al₂O₃ and Rh/Al₂O₃ having OH groups on the surface, but not for Pd/C and Rh/C.^{19,36} In our case, the interaction of the solvent molecules with OH groups present on the surface of the Pd/S-DVB catalyst influenced the catalytic activity. Attraction of protons by the stronger HBA solvents modified the surface, facilitating coordination of APh and its hydrogenation. With the increase in the β value, the conversion of APh also increased (Fig. 7). This trend is opposite to that noted for Pd and Rh catalysts.^{19,36} On the other hand, attempts



Fig. 5 TEM micrograph of Pd/S-DVB after the hydrogenation of APh.



Fig. 6 (a) SEM micrograph of the Pd/S-DVB catalyst; (b) Pd mapping; and (c) P mapping on the surface.

Table 2 Effect of solvents on the hydrogenation of acetophenone							
Solvent (mL)	X _i H ₂ O	APh conv. (%)	EtB yield (%)	PhE yield (%)	β^{29}		
DMF		69	28	41	0.69		
MeOH		91	72	14	0.66		
1.5 H ₂ O/1.5 MeOH	0.69	24	18	6			
0.25 H ₂ O/2.75 MeOH	0.17	18	12	3			
0.5 H ₂ O/2.5 MeOH	0.31	33	23	8			
2.75 H ₂ O/0.25 MeOH	0.96	62	56	6			
H_2O		66	52	4	0.18		
i-PrOH		90	81	7	0.95		

61

68

33

87

80

0.46

0.81

0.25 H₂O/2.75 i-PrOH 0.28

0.25 H2O/2.75 BuOH 0.32

0.5 H₂O/2.5 i-PrOH

1.5 H₂O/1.5 i-PrOH

BuOH

 Toluene
 48
 18
 28
 0.11

 Reaction conditions: APh 0.1 mL (8.3×10^{-4} mol), Pd (1×10^{-5} mol), 4
 h, 80 °C, 10 bar H₂.



Fig. 7 Dependence of the APh conversion on the β value of the solvents.

to correlate the APh conversion with the α parameter expressing the HBD ability failed. Similarly, there is no correlation between the conversion and H₂ solubility in the studied solvents.

3.2.4. Binary solvent mixtures. Next, binary mixtures of the ROH/H₂O type were investigated as solvents for APh hydrogenation. A decrease in APh conversion was observed for MeOH/H₂O mixtures when compared to the pure solvents. For example, 0.25 mL of water added to 2.75 mL of MeOH decreased the conversion to only 18%. Interestingly, a further increase in the amount of water caused a slow increase in the conversion up to 62% in the presence of 2.75 mL of water. A similar, non-linear dependence of the APh conversion on the amount of water was also found for i-PrOH/H2O mixtures. The minimal conversion in the studied series was 38% and in all cases the conversion of APh was lower than in i-PrOH or water only. Interestingly, in a mixed system of BuOH/H2O, the inhibiting effect was much smaller and hydrogenation was only slightly less efficient than in pure BuOH with the conversion decreasing by 7%.

Analysis of the product's composition led to the conclusion that the EtB/PhE ratio, illustrating the hydrogenation selectivity, changed only slightly when the composition of the solvents changed. In general, the highest EtB/PhE value was noted in pure water because of the low amount of PhE formed in this solvent. In the binary mixtures, the EtB/PhE values were lower than for solely water or solely alcohol.

The most intriguing feature of the studied system is the nonlinear dependence of the APh conversion on the amount of water in the MeOH/H₂O and i-PrOH/H₂O mixtures (Fig. 8 and 9). For an explanation, one can consider the microheterogeneous structure of the ROH/H₂O mixtures derived from the presence of hydrated alcohol clusters, stabilized by hydrogen bonding.^{31,32} As a result, the ROH/H₂O mixtures are separated at a molecular level and deviate from the ideal mixture. The extent of this phenomenon depends on the kind of alcohol. Thus, clusters of BuOH are less hydrated than clusters of i-PrOH or MeOH. Therefore, water strongly influenced the catalytic reactions carried out in i-PrOH and MeOH binary mixtures, while a weaker effect was observed in BuOH.

The observed solvent effects differ from those reported for other systems, most probably because of the specifity of the S-DVB support. In our system, protic solvents of the highest β values, such as alcohols, provided the best results.

The addition of water to ROH changed the structure of the solvent by forming hydrated clusters, in particular in the case of short-chain ROH. As a result, the HBA capacity of the mixed solvent system also decreased and the reaction slowed down.

The inhibiting effect observed in the ROH/H₂O mixture can be significantly reduced by adding a small amount of α -cyclodextrin. Thus, the conversion of APh increased from 18% to 78% when 10 mol% α -cyclodextrin was added to the reaction carried out in 2.75 MeOH/0.25 H₂O. Cyclodextrin changed the solvent structure and facilitated hydrogenation. In the analogous experiment performed with addition of [^{*n*}Bu₄N]Br, known as a phase transfer agent, the conversion of APh only slightly increased, to 24%.



Fig. 8 Conversion of APh (left) and the EtB/PhE ratio (right) at different mole fractions of water for APh hydrogenation in MeOH.



Fig. 9 Conversion of APh (left) and the EtB/PhE ratio (right) at different mole fractions of water for APh hydrogenation in i-PrOH.



Fig. 10 Hydrogenation of differently substituted acetophenones.

Table 3 Hydrogenation of differently substituted acetophenones (Fig. 10)

R=	R-APh conv. (%)	R-PhE (%)	R-EtB (%)
Н	91	24	67
3-Me	82	25	57
2-Me	59	11	48
2,5-Me	59	10	49
3-NO ₂	33	30	3
$2 - NO_2$	13	7	6
$3-NH_2$	36	34	2
$2-NH_2^2$	9	7	2

3.2.5. Hot filtration test. In order to check the heterogeneous nature of the hydrogenation process the hot filtration test was performed.³⁷ The solid catalyst was removed after 1 h of the catalytic reaction, and the remaining solution was subjected to further heating (4 h). The GC analysis evidenced that the composition of the reaction mixture did not change due to the non-activity of the solution after catalyst separation. Thus, hydrogenation occurred with an immobilized Pd/S-DVB catalyst.

3.2.6. Hydrogenation of different acetophenones. In the next stage of the study, differently substituted acetophenones were used as substrates in hydrogenation performed with Pd/S-DVB for 1 h in MeOH (Table 3). By using a shorter reaction time, we expected to see differences between the applied substrates. The highest conversion was obtained for non-substituted APh, while the presence of substituents, in general, resulted in a decrease in the yields of the products. Considering the electronic effect of the substituents, higher conversions were obtained in the presence of Me groups of weaker donor character than with the stronger donor NH₂ substituent. It should be noted that the products obtained from NO₂ and NH₂ substituted APh were the same, with the main one being aminophenylethanol. This is because the NO₂ group was fully hydrogenated to the NH₂ group under the applied conditions.

These experiments produced additional data concerning hydrogenation selectivity. In the reaction of APh and its Me-substituted derivatives, hydrogenolysis of R-PhE occurred efficiently leading to the formation of R-EtB as a main product. The stronger donor group NH_2 increased the selectivity for R-PhE and only a small amount of R-EtB was formed.

The steric effect of the substituents was responsible for higher conversion when the substituent was present in the 3-position rather than the 2-position, promoting the smaller steric hindrance.

Conclusions

The new Pd/S-DVB catalyst immobilized on a P-functionalized porous polymer efficiently catalyzed the hydrogenation of APh,

mainly forming EtB. The selectivity for the R-PhE product was higher for NH₂-APh as a result of the increased electron-donor properties.

The conversion of APh correlated well with the HBA capacity of the solvent used and the best results were obtained using protic solvents such as MeOH, i-PrOH and BuOH. Our results confirmed the earlier conclusion that interactions between the solvent and the catalyst support play an important role in the hydrogenation of aromatic ketones. The addition of water to these solvents caused a strong inhibiting effect and a significant decrease in conversion. This can be explained by the specific interactions of the binary mixtures with the porous Pd/S-DVB catalyst. Such a strong inhibiting effect was observed for the first time in these studies. It can be explained by the presence of hydrated clusters of ROH and the microheterogeneity of the reaction medium. Deviation from an ideal solution is stronger for short-chain alcohols, such as MeOH or i-PrOH, and weaker for BuOH. As a result, the inhibiting effect of the water present in BuOH is much smaller than in MeOH.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The financial support of the National Science Foundation (NCN) with grant 2017/25/B/ST5/00394 is gratefully acknowledged. The authors are grateful to Mr Marek Hojniak (Faculty of Chemistry, University of Wroclaw) for GC and GC-MS analysis, and to Dr Wojciech Gil (Faculty of Chemistry, University of Wroclaw) for performing SEM measurements.

References

- 1 J. Magano and J. R. Dunetz, *Org. Process Res. Dev.*, 2012, 16, 1156.
- 2 Z. Wang, K.-D. Kim, C. Zhou, M. Chen, N. Maeda, Z. Liu, J. Shi, A. Baiker, M. Hunger and J. Huang, *Catal. Sci. Technol.*, 2015, 5, 2788.
- 3 D. Duraczyńska, E. M. Serwicka, A. Drelinkiewicz,
 R. P. Socha, M. Zimowska, L. Lityńska-Dobrzyńska and
 A. Bukowska, *Mol. Catal.*, 2019, 470, 145.
- 4 W. Wu, J. Li, Z. Chen, W. Chen, H. Pang, K. Ma and J. Zeng, *J. Catal.*, 2019, 373, 209.
- 5 X. B. Zhang, W. N. Lu, J. L. Wang, B. H. Liao, Y. H. Qin,
 Y. J. Zhang, B. Zhang and S. A. Xin, *Catal. Commun.*, 2019, 119, 124.
- 6 D. C. Costa, A. L. Soldati, G. Pecchi, J. F. Bengoa,
 S. G. Marchetti and V. Vetere, *Nanotechnology*, 2018,
 29, 215702.
- 7 X. Bo Zhang, React. Kinet., Mech. Catal., 2011, 102, 417-424.
- 8 G. D. Yadav and R. K. Mewada, *Catal. Today*, 2012, **198**, 330–337.

- 9 J. Masson, S. Vidal, P. Cividino, P. Fouilloux and J. Court, *Appl. Catal.*, *A*, 1993, **99**, 147.
- 10 V. Vetere, M. B. Faraoni, G. F. Santori, J. Podestá, M. L. Casella and O. A. Ferretti, *J. Catal.*, 2004, 226, 457.
- 11 M. G. Musolino, F. Mauriello, C. Busacca and R. Pietropaolo, *Top. Catal.*, 2015, **58**, 1077.
- 12 B.-S. Kwak, T.-J. Kim and S.-I. Lee, *Appl. Catal., A*, 2003, 238, 141.
- 13 P. Tundo, S. Zinovyev and A. Perosa, J. Catal., 2000, 196, 330.
- 14 J. Feng, Y. H. Zhong and S. H. Dai, *IOP Conf. Ser.: Mater. Sci.* Eng., 2018, 292, 012117.
- 15 M. Schlaf, Dalton Trans., 2006, 4645.
- 16 J. Muzart, Tetrahedron, 2005, 61, 9423.
- 17 T. Sato, O. Sato, K. Arai, F. Mine, N. Hiyoshi, C. V. Rode and M. Shirai, *J. Supercrit. Fluids*, 2006, 37, 87.
- 18 N. Hiyoshi, O. Sato, A. Yamaguchi and M. Shirai, *Chem. Commun.*, 2011, 47, 11546.
- 19 S-i Fujita, Y. Onodera, H. Yoshida and M. Arai, *Green Chem.*, 2016, **18**, 4934.
- 20 X. Gao, L. He, J. Xu, X. Chen and H. He, *Catalysts*, 2019, 9, 513.
- 21 M. A. Aramendia, V. Borau, C. Jiménez, J. M. Marinas, M. E. Sempere and P. Urbano, *Appl. Catal.*, 1988, 43, 41.
- 22 M. A. Aramendia, V. Borau, J. F. Gomez, A. Herrera, C. Jimenez and J. M. J. Marinas, *J. Catal.*, 1993, 140, 335.
- 23 A. Drelinkiewicz, A. Waksmundzka, W. Makowski,
 J. W. Sobczak, A. Król and A. Zieba, *Catal. Lett.*, 2004,
 94, 143.
- 24 M. M. Trandafir, L. Pop, N. D. Hadade, I. Hristea, C. M. Teodorescu, F. Kumeich, J. A. van Bokhoven, I. Grosu and V. I. Parvulescu, *ChemCatChem*, 2019, **11**, 538.
- 25 R. Molinari, C. Lavorato, T. F. Mastropietro and P. Argurio, *Molecules*, 2016, 21, 394.
- 26 L. O. Nindakova, V. O. Strakhov and S. S. Kolesnikov, *Russ. J. Gen. Chem.*, 2018, 88, 199.
- 27 I. Schrader, J. Warneke, J. Backenköhler and S. Kunz, *J. Am. Chem. Soc.*, 2015, 137, 905.
- 28 N. Su, X. Gao, X. Chen, B. Yue and H. He, J. Catal., 2018, 367, 244.
- 29 M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877.
- 30 D. Duraczyńska, A. Drelinkiewicz, E. Bielańska,
 E. M. Serwicka and L. Lityńska-Dobrzyńska, *Catal. Lett.*,
 2011, 141, 83.
- 31 P. Tomza, W. Wrzeszcz, S. Mazurek, R. Szostak and M. A. Czarnecki, *Spectrochim. Acta, Part A*, 2018, **197**, 88.
- 32 P. Tomza and M. A. Czarnecki, J. Mol. Liq., 2015, 209, 115.
- 33 M. Mart, W. Tylus and A. M. Trzeciak, *Mol. Catal.*, 2019, 462, 28.
- 34 F. Li, H. Zhong, G. Zhao, S. Wang and G. Liu, *Appl. Surf. Sci.*, 2015, 353, 856.
- 35 R. Zhao, P. Rupper and S. Gaan, Coatings, 2017, 7, 133.
- 36 H. Yoshida, Y. Onodera, S.-I. Fujita, H. Kawamori and M. Arai, *Green Chem.*, 2015, 17, 1877.
- 37 N. T. S. Phan, M. van Der Sluys and C. W. Jones, *Adv. Synth. Catal.*, 2006, **348**, 609.