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Hydrodehalogenation of 4-chlorophenol and 4-bromophenol over Pd–Fe/Al_2O_3: influence of catalyst reduction conditions

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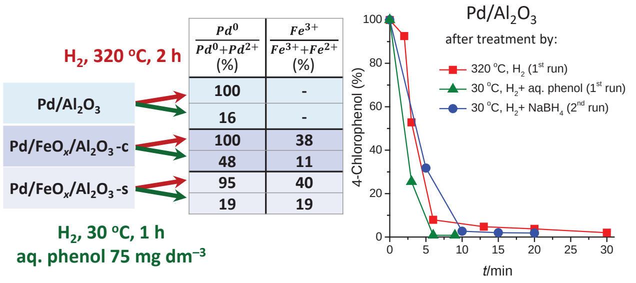
The reduction of monometallic Pd/Al_2O_3 and bimetallic PdFe/Al_2O_3 catalysts produced by co-impregnation or sequential impregnation of the support with metal salts was possible not only under high temperature hydrogen treatment but also at 30 °C under the action of aqueous phenol solution and hydrogen. According to the XPS data, both reduction routes provided sufficient degrees of Pd reduction required for fast hydrodehalogenation of 4-chlorophenol and 4-bromophenol to phenol in aqueous solutions. The degree of Pd reduction was higher in the co-impregnated bimetallic PdFe catalyst, which was more efficient in transformation of 4-bromophenol; the bimetallic catalysts were more stable than the monometallic Pd one in the conversion of 4-chlorophenol.



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Water purification for the removal of trace contaminants is a problem of considerable current importance.[1] Halogenated organic compounds (polychlorinated biphenyls, chlorinated pesticides, and pharmaceuticals[2]) are dangerous xenobiotics that affect the endocrine systems of humans and animals.[3,4] Trace chlorinated contaminants may result from water chlorination,[5] and catalytic hydrodechlorination (HDC) is a promising technique for converting these compounds without the formation of more toxic phosgene, dioxins, and molecular chlorine, which can be formed upon oxidative treatment.[6] This technique also reduces the toxicity because non-chlorinated counterparts of chlorinated compounds are usually much less dangerous.[7] For example, chlorophenols and bromophenols, which are widely used in industry, can be converted into phenol or cyclohexane over Rh-, Pd-, or Ni-containing catalysts.[8–10]

Palladium catalysts are active in the HDC of organic compounds, and a second metal is often added to them to enhance the catalyst activity because of the metal–metal interaction.[11,12] The addition of Fe to Pd catalysts facilitated the decomposition of organic residue after HDC.[13]

In this work, we compared monometallic 1 wt% Pd and 10 wt% Fe catalysts with bimetallic PdFe catalysts in the HDC of 4-chlorophenol and 4-bromophenol. The PdFe catalysts were prepared by the co-impregnation (sample PdFe/Al_2O_3-c) or sequential impregnation (impregnation with hexaaquairon(III) trinitrate followed by impregnation with palladium nitrate; sample PdFe/Al_2O_3-s) of a γ-Al_2O_3 support (Engelhard, S_{BET} = 190 $m^2\ g^{-1}$)[14] with metal nitrates (see Online Supplementary Materials, SM-1). After each impregnation step, the samples were dried at 150 °C and, finally, each catalyst was calcined in air at 400°C. The methods of physicochemical analysis of the catalysts were described earlier.[15]

The unreduced catalyst precursors were analyzed by temperature-programmed reduction with hydrogen (TPR-H_2) (Figure 1). A negative peak in the TPR-H_2 profile of Pd/Al_2O_3 at about 70 °C is associated with the decomposition of β-PdH_x due to the partial reduction of Pd even at room temperature. The remaining part of Pd was reduced below 400 °C. Iron oxides were completely reduced at about 700 °C, when the sintering of iron particles is most likely. At the reduction window of Pd (up to 400 °C), only a partial reduction of iron from Fe^{3+} to Fe^{2+} is

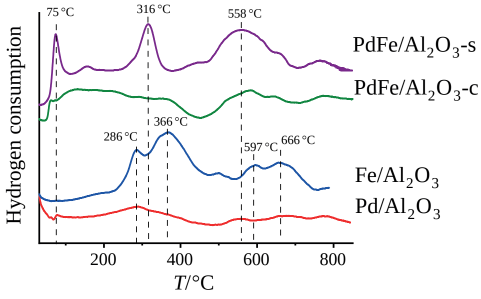

Figure 1 TPR-H_2 profiles of catalyst precursors (Unisit instrument, Russia; 10 K min^{-1}, 5% H_2 in Ar).

possible. The TPR-H_2 profiles suggest different reduction behaviors of the bimetallic catalysts: $PdFe/Al_2O_3$-c showed higher Pd–Fe interaction as the peaks of Pd and Fe reduction were less resolved in its TPR-H_2 profile. The TPR-H_2 analysis of the mono- and bimetallic catalysts revealed almost complete reduction of Pd under hydrogen treatment at 300 °C.

The catalysts were reduced (see Online Supplementary Materials, SM-2) and tested in a batch reactor equipped with a magnetic stirrer (HDC of chlorophenol: 0.1 g of catalyst, 30 °C, 0.6 dm^3 h^{-1} of H_2, 15 cm^3 of a solution of 4-chlorophenol, $C_{4\text{-ClPh}}$ = 75 mg dm^{-3}) (see Online Supplementary Materials, SM-3). Reaction products were analyzed by HPLC on an Agilent 1100 instrument[15] (Online Supplementary Materials, SM-4). The palladium-containing catalysts showed high efficiency after high-temperature reduction (320 °C, H_2, 2 h; see SM-2): 4-chlorophenol was completely converted into phenol in 10 min [Figures 2(*a*–*c*)]. At the same time, the conversion of 4-chlorophenol over Fe/Al_2O_3 was < 30% after 2 h. Almost no by-products (<1%) were detected in all cases. The reduction of Fe/Al_2O_3 with hydrogen at 515 °C for 2 h led to a 79% conversion of 4-chlorophenol after 2 h of catalytic test; the main product was cyclohexane, and the phenol content of the products was only 4.7%.

The Pd-containing catalysts were stable during five runs without additional reduction [Figure 2(*d*)]. Moreover, the bimetallic catalysts showed higher stability than that of monometallic Pd/Al_2O_3, the activity of which slightly decreased in 4th and 5th cycles.

We attempted to reduce the catalysts with a solution of $NaBH_4$ in water (30 °C, 1 h, $NaBH_4$ to PdO molar ratios of 2 : 1 and 6 : 1 for the reduction of Pd/Al_2O_3 and the bimetallic catalysts, respectively) and an additional H_2 flow of 0.6 dm^3 h^{-1} (see SM-2). The reduced catalysts showed a relatively low initial rate of 4-chlorophenol conversion [Figures 2 (*a*–*c*)]. However, after an induction period of about 30 or 60 min for Pd/Al_2O_3 or the bimetallic catalysts, respectively, the reaction rate significantly increased, probably, due to the additional reduction of the catalysts under the action of reaction mixture components. Pd/Al_2O_3 was the most efficient in the first run after low-temperature reduction: the complete conversion of 4-chlorophenol was achieved in 60 min. Longer conversion times were observed with the bimetallic catalysts. The activity of monometallic Fe/Al_2O_3 in HDC after H_2 + $NaBH_4$ treatment was low [Figure 2(*a*)] and nearly the same in both the first and second runs.

The acceleration of the HDC reaction under the action of reaction medium should lead to the high activity of the catalyst in the second run. Indeed, the Pd-containing catalysts demonstrated very short induction periods (< 10 min) in the second run without additional pretreatment. The longest induction period was observed for $PdFe/Al_2O_3$-c. The reaction rate over this catalyst [Figure 2(*b*)] was very high after the induction period and close to that over the catalysts reduced at 320 °C. Moreover, its activity remained high in the next runs [Figure 2(*e*)]. The activity of $PdFe/Al_2O_3$-s gradually increased in first three runs [Figure 2(*e*)]. The complete 4-chlorophenol conversion was observed in the third run after 9 min. Other Pd-containing catalysts were highly active even in the second run. The activity of the catalysts slightly decreased during 7–10 runs [see Figure 2(*e*) for $PdFe/Al_2O_3$-c], probably, because of the partial removal of catalysts from the reaction medium during HPLC sampling.

The leaching and chlorination of Pd can deteriorate the catalytic activity in a prolonged catalyst test. This effect should be less pronounced in dilute substrate solutions. To analyze the influence of these factors, the Pd/Al_2O_3 sample tested after mild reduction in three consecutive cycles of 4-ClPh transformation was studied by XPS (Figure 3). On the catalyst surface, the Cl/Pd ratio was about 1.4, but 87% Pd still occurred in the non-oxidized state [Figure 3(*a*)]. Therefore, chlorine on the spent catalyst surfaces was mainly bonded to elements other than Pd. Both covalent bonding to carbon and ionic bonding of chlorine are observed in the Cl2p spectrum [Figure 3(*b*)]. Ionic Cl species can be attributed to terminal Cl atoms on the alumina surface.

The reaction mixture collected after three cycles was analyzed by AAS. The extent of Pd leaching was only 0.2%.

The HDC of 4-chlorophenol can be accelerated as a result of the co-action of hydrogen and phenol. Indeed, the pretreatment of a catalyst precursor with hydrogen at 30 °C in an aqueous solution of phenol (75 mg dm^{-3}) for 1 h produced an active catalyst: the reaction rate of HDC was high [see Figure 2(*a*) for Pd/Al_2O_3]. A similar treatment of the phenol-free suspensions of the catalysts in water with hydrogen did not lead to their reduction, as followed from the absence of a color change and an extremely low rate of 4-chlorophenol conversion.

The catalysts reduced by hydrogen in an aqueous phenol solution at 30 °C for 1 h (0.05 g samples) were compared in the hydrodebromination of 4-bromophenol at a concentration of 150 mg dm^{-3} [Figure 2(*f*)]. The Pd-containing catalysts were

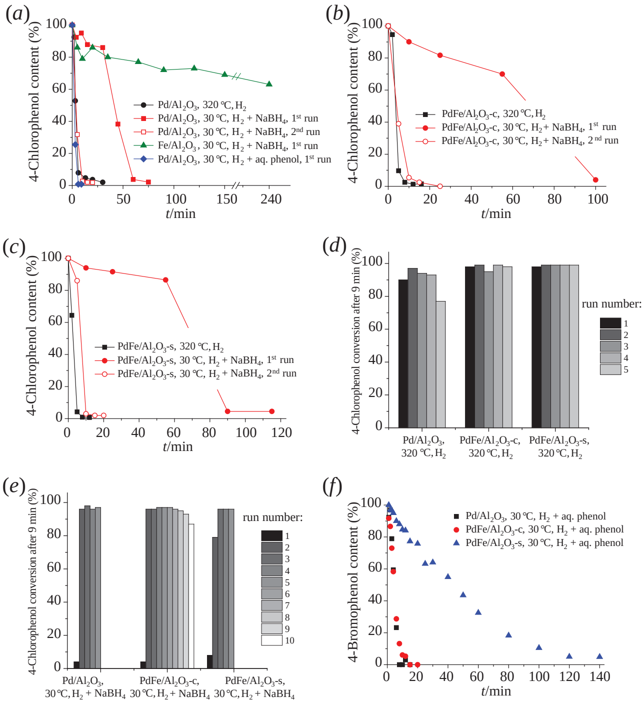

Figure 2 HDC of 4-chlorophenol (30 °C, 15 ml, $C_{4\text{-ClPh}}$ = 75 mg dm^{-3}) over 0.1 g of catalyst after severe (H_2, 320 °C, 2 h) or mild (30 °C, 1 h, H_2 + $NaBH_4$ or H_2 + aq. phenol) reduction: (*a*) Pd/Al_2O_3, (*b*) $PdFe/Al_2O_3$-s, (*c*) $PdFe/Al_2O_3$-c; 4-chlorophenol conversion after 9 min in consecutive runs on catalysts after (*d*) severe (H_2, 320 °C, 2 h) and (*e*) mild reduction (H_2 + $NaBH_4$, 30 °C, 1 h); and (*f*) hydrodebromination of 4-bromophenol (30 °C, 15 ml, $C_{4\text{-BrPh}}$ = 150 mg dm^{-3}) over 0.05 g of catalyst reduced under mild conditions (H_2, 30 °C, 1 h, aqueous phenol solution).

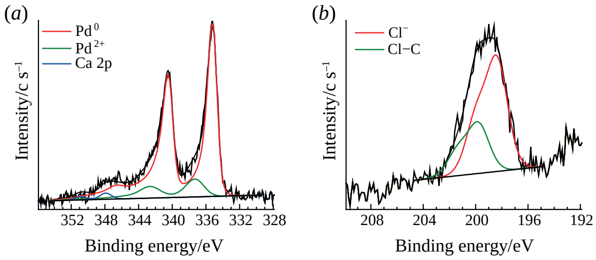

Figure 3 (*a*) Pd3d and (*b*) Cl2p XPS spectra of used Pd/Al_2O_3 catalyst tested in three consecutive cycles of 4-ClPh HDC. Peaks attributed to each species are combined into synthetic components.

active in this reaction, and phenol was the main product. PdFe/Al_2O_3-c and Pd/Al_2O_3 showed similar activities, while PdFe/Al_2O_3-s was significantly less efficient.

The reduction of Pd^{2+} in catalysts with hydrogen in phenol-containing solutions (75 mg dm^{-3}) at 30 °C was studied by XPS. After the treatment for 1 h, the liquids were decanted, and the remaining catalysts were dried in an H_2 atmosphere at < 50 °C. The unreduced catalyst precursors and those reduced *in situ* with hydrogen in a catalyst cell of the spectrometer (Ar + 5% H_2, 1 atm, 320 °C, 2 h) were also analyzed by XPS (see Table 1 and Online Supplementary Materials, SM-5, Tables S1–S3, Figures S1, S2). The unreduced catalyst precursors contained only Pd^{2+} species. The *in situ* treatment with H_2 reduced Pd completely (in PdFe/Al_2O_3-c and Pd/Al_2O_3) or almost completely (95% Pd in PdFe/Al_2O_3-s). Under mild reduction conditions, a maximum degree of reduction was 48% in PdFe/Al_2O_3-c or no more than 19% in PdFe/Al_2O_3-s and Pd/Al_2O_3. Apparently, such a small amount of reduced Pd was sufficient to provide a high degree of the substrate conversion, which was evident from the high activity of Pd/Al_2O_3 in hydrodebromination of 4-bromophenol [Figure 2(*d*)] comparable to that of the PdFe/Al_2O_3-c catalyst with a high portion of Pd^0 species.

The binding energy of $Pd3d_{5/2}$ components in the XPS spectra of *in situ* reduced bimetallic catalysts (about 335.7 eV) is slightly higher than that of bulk Pd metal (335.1 eV) (Table S3 in Online Supplementary Materials). This binding energy shift can reflect the difference in particle size, the location of Pd in the bulk and on the surface, and the Pd–Fe interaction up to the formation of PdFe alloy.[16] The binding energies of $Pd3d_{5/2}$ components in the catalysts reduced with hydrogen in a phenol solution are close to that of bulk palladium metal.

The Fe2p XPS spectra of the unreduced catalysts show a small contribution from Fe^{2+} species along with the main signal of Fe^{3+}. The mild treatment did not significantly affect the Fe^{2+}/Fe^{3+} ratio in the catalysts, while the reduction at 320 °C increased the contribution of Fe^{2+}, which is consistent with the TPR-H_2 data. Fe^0 species were not observed in the XPS spectra of the Fe-containing catalysts even after the *in situ* treatment with H_2 at 500 °C for 2 h. Therefore, the reduced catalysts should be specified as Pd/FeO_x/Al_2O_3. However, because the atomic Pd content of the bimetallic catalysts is significantly lower than the Fe content, a small fraction of Fe^0 undetectable by XPS may exist in the reduced catalysts forming a Pd–Fe alloy. At the same time, the formation of Pd−Fe−O bonds on the surface of bimetallic catalysts seems more likely.

Table 1 Mole fractions of Pd and Fe species on the surfaces of unreduced catalysts and catalysts reduced under mild and severe conditions.

Catalyst	Reduction conditions[a]	ν (Pd) (%)		ν (Fe) (%)		
		Pd^0	Pd^{2+}	Fe^0	Fe^{2+}	Fe^{3+}
Fe/Al_2O_3	No reduction	–	–	0	0	100
	320 °C	–	–	0	3	97
FePd/Al_2O_3-c	No reduction	0	100	0	11	89
	320 °C	100	0	0	37	63
	30 °C	48	52	0	14	86
FePd/Al_2O_3-s	No reduction	0	100	0	26	74
	320 °C	97	3	0	47	53
	30 °C	18	82	0	23	77
Pd/Al_2O_3	No reduction	0	100	–	–	–
	320 °C	97	3	–	–	–
	30 °C	84	16	–	–	–

[a] 320 °C, reduction in a flow of H_2 for 2 h with passivation after cooling; 30 °C, reduction in aqueous phenol solution (75 mg dm^{-3}) for 1 h.

Table 2 Textural properties and metal contents (AAS and XPS) of unreduced catalysts.

Sample	S_{BET}/ m^2 g^{-1}	V_{pore}/ cm^3 g^{-1}	d_{pore}/ nm	AAS metal content (wt%)		XPS metal content (at%)	
				Fe	Pd	Fe	Pd
Fe/Al_2O_3	150	0.39	8.2	9.29	0.00	11.4	0.00
Pd/Al_2O_3	170	0.48	9.2	0.00	0.90	–	0.04
PdFe/Al_2O_3-c	150	0.40	8.2	9.25	0.80	5.0	0.14
PdFe/Al_2O_3-s	150	0.39	8.4	8.25	0.84	3.0	0.05
Al_2O_3	190	0.46	7.6	–	–	–	–

The metal contents of the catalysts determined by AAS (Table 2) are close to the calculated values (1 wt% Pd and 10 wt% Fe). The textural parameters (specific surface area, pore size, and pore volume) are similar for all the catalysts. Slight differences between the Pd/Al_2O_3 and Fe-containing catalysts can be explained by a high iron loading in the latter.

According to the XRD data (Figure S3, Online Supplementary Materials), Pd particles in the catalysts reduced at 320 °C were finely dispersed because the XRD profiles of these catalysts show only alumina reflections (γ-Al_2O_3, PDF card #00-029-0063). The XRD profile of PdFe/Al_2O_3-s additionally contained broad reflections due to different Fe^{2+} and Fe^{3+} oxides.

The high dispersity of Pd particles was also confirmed by TEM–EDX analysis, which revealed Pd particle-size distributions with a maximum at 6–8 nm and similar localizations of Pd and Fe in the bimetallic catalysts (Figure S4, Online Supplementary Materials). The Pd particle-size distribution in PdFe/Al_2O_3-c was slightly broader (to 14 nm) than that in the two other Pd-containing catalysts (to 10 nm).

According to the XPS data, the PdFe/Al_2O_3-c catalyst had the highest surface Pd content. This catalyst also contained more iron on the surface than PdFe/Al_2O_3-s and showed a higher activity in 4-bromophenol conversion and a slightly higher rate of 4-chlrophenol conversion during an induction period of the first run after mild reduction (H_2 + $NaBH_4$, 30 °C, 1 h).

Therefore, differences in the Pd particle sizes, palladium contents, and morphologies of the Pd-containing catalysts were insignificant, but the reducibility of metals depended on catalyst compositions and synthesis techniques. Iron was more reducible in the bimetallic catalysts than in the monometallic one, and Pd showed better reducibility in the bimetallic PdFe/Al_2O_3-c catalyst.

Phenol probably affected the surface properties of the catalysts under conditions of mild reduction with hydrogen in aqueous solution. An IR-spectroscopic study of similar catalysts supported on ZrO_2–SiO_2[15] showed that such a treatment stimulated fast conversion of Pd^+ into Pd^0. The reducibility of base metal (Mn, Ni, and Cu) oxides under the action of cyclohexanol was described previously.[17,18]

We found that the reduction of Pd in the alumina-supported catalysts before the hydrodehalogenation of 4-chlorophenol and 4-bromophenol can be performed under mild conditions (H_2 at 30 °C in aqueous phenol solution). The activity of the reduced catalysts was similar to that after the reduction with hydrogen at 320 °C. In both cases, the catalysts showed high stability in 4-chlorophenol conversion during at least five runs. PdFe/Al_2O_3-c with a higher Pd content on the surface demonstrated higher activity and Pd reducibility under both mild and severe conditions.

The difference between the two bimetallic catalysts was most pronounced in the transformation of 4-bromophenol. FePd/Al_2O_3-c was as efficient as Pd/Al_2O_3, while FePd/Al_2O_3-s showed poor activity despite similar Pd^0 contents and particle sizes in the bimetallic catalysts.

In conclusion, the mild reduction of Pd and Fe in the catalyst with hydrogen and phenol at room temperature produced highly active and stable mono- and bimetallic catalysts for the hydrodehalogenation of 4-chlorophenol and 4-bromophenol in a batch reactor. Catalysts remain stable during 5–10 runs without regeneration, which opens the way for use in flow reactor. The co-impregnation of an alumina support with Pd and Fe salts provided higher Pd reducibility under mild conditions.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.03.032.

References

1 F. Shakerian, J. Zhao and S.-P. Li, *Chemosphere*, 2020, **239**, 124716.

2 J. Nieto-Sandoval, E. Gomez-Herrero, M. Munoz, Z. M. de Pedro and J. A. Casas, *Appl. Catal., B*, 2021, **293**, 120235.

3 K. Pěnčíková, L. Svržková, S. Strapáčová, J. Neča, I. Bartoňková, Z. Dvořák, M. Hýžďalová, J. Pivnička, L. Pálková, H.-J. Lehmler, X. Li, J. Vondráček and M. Machala, *Environ. Pollut.*, 2018, **237**, 473.

4 Q. Zhang, J. Wang, J. Zhu, J. Liu, J. Zhang and M. Zhao, *Environ. Int.*, 2016, **94**, 43.

5 W.-L. Chen, Y. S. Ling, D. J. H. Lee, X.-Q. Lin, Z.-Y. Chen and H.-T. Liao, *Chemosphere*, 2020, **242**, 125268.

6 E. Lokteva, E. Golubina, V. Likholobov and V. Lunin, in *Chemistry Beyond Chlorine*, eds. P. Tundo, L.-N. He, E. Lokteva and C. Mota, Springer, Cham, 2016, pp. 559–584.

7 B. Zawadzki, E. Kowalewski, M. Asztemborska, K. Matus, S. Casale, S. Dzwigaj and A. Śrębowata, *Catal. Commun.*, 2020, **145**, 106113.

8 J. Xiong, L. Tian and R. Cheng, *J. Hazard. Mater.*, 2021, **416**, 125913.

9 J. Xiong, Y. Ma, W. Yang and L. Zhong, *J. Hazard. Mater.*, 2018, **355**, 89.

10 X. Ma, S. Liu, Y. Liu, X. Li, Q. Li, G. Gu and C. Xia, *Chemosphere*, 2020, **242**, 125202.

11 I. A. Witońska, M. J. Walock, M. Binczarski, M. Lesiak, A. V. Stanishevsky and S. Karski, *J. Mol. Catal. A: Chem.*, 2014, **393**, 248.

12 E. V. Golubina, E. S. Lokteva, V. V. Lunin, N. S. Telegina, A. Y. Stakheev and P. Tundo, *Appl. Catal., A*, 2006, **302**, 32.

13 J. G. Mahy, L. Tasseroul, O. Tromme, B. Lavigne and S. D. Lambert, *J. Environ. Chem. Eng.*, 2019, **7**, 103014.

14 D. A. Ryaboshapka, E. S. Lokteva, E. V. Golubina, A. N. Kharlanov, K. I. Maslakov, A. O. Kamaev, A. V. Shumyantsev, I. A. Lipatova and E. I. Shkol'nikov, *Kinet. Catal.*, 2021, **62**, 127 (*Kinet. Katal*., 2021, **62**, 55).

15 E. S. Lokteva, V. V. Shishova, N. N. Tolkachev, A. N. Kharlanov, K. I. Maslakov, A. O. Kamaev, I. Y. Kaplin, I. N. Savina and E. V. Golubina, *Molecules*, 2021, **26**, 141.

16 M. P. Felicissimo, O. N. Martyanov, T. Risse and H.-J. Freund, *Surf. Sci.*, 2007, **601**, 2105.

17 A. S. Pavitt, E. J. Bylaska and P. G. Tratnyek, *Environ. Sci.: Processes Impacts*, 2017, **19**, 339.

18 W. Tanwongwan, A. Eiad-ua, W. Kraithong, N. Viriya-Empikul, K. Suttisintong, A. Klamchuen, P. Kasamechonchung, P. Khemthong, K. Faungnawakij and S. Kuboon, *Appl. Catal., A*, 2019, **579**, 91.

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