

Hydrogenation Properties of Nanostructured Tungsten Carbide (WC) Catalysts in a Continuous Flow Reactor

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Tungsten monocarbide (WC) obtained via urea glass route showed a high activity as well as chemoselectivity for the continuous flow reduction of a variety of nitro groups under milder conditions, compared to previous reports. The favorable effect of the nanostructure was shown by comparison to other commercial WC species. Moreover, WC functioned as an efficient support for nickel nanoparticles, expanding its range of applicability and leading to a bimetallic Ni@WC composite characterized by high activity for the hydrogenation of cardanol, a phenolic lipid obtained from cashew nutshells.

Introduction

Attempts to use tungsten mono carbide (WC) as a catalyst are going on since Levy and Boudart elucidated the electronic structure of this material in 1973 highlighting the similarity to Pt.^[1] Considering the drawbacks associated to platinum extraction^[2] as well as its scarcity in the earth crust^{[3] [3b]} the possible replacement of Pt with WC appeared as a very promising sustainable alternative. However, early studies revealed that despite their similarity in electronic structure, the catalytic behavior of WC and Pt in heterogeneous catalysis is different. Compared to the more versatile Pt, WC was shown to perform as an active catalyst for reactions of hydrogenation and hydrogenolysis^[4], dehydrogenation^[5], reforming^[6] and even Fischer-Tropsch-like processes^[7], but activity was only observed at high reaction temperatures (150 °C to 400 °C). Indeed, at low temperatures (40 °C to 90 °C), WC showed only limited activity, with an important exception being the reduction of nitrocompounds and quinones^[8]. In this case, reactions were performed under very acidic media, suggesting a limited applicability of the method. In the last years however, the interest in WC as catalytic material returned since the need of sustainable catalysts as alternative for the traditional precious metal based systems has increased [9] [10] [11] Recent research uncovered for instance the hidden potential of nanostructured WC as a hydrodeoxygenation catalyst^[12], as well as a support for nickel particles in biorefinery.^[13] This study showed that it is possible to convert cellulose into ethylenglycol with 29 % yield using tungsten carbide catalysts at 245 °C and 60 bar of hydrogen in a batch reactor. Interestingly, the yield could be increased to 61 % using a 2 % nickel doped tungsten carbide.[14] Other groups have re-explored the alternative use of WC based systems for the chemoselective reduction of nitro compounds.

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These groups used temperatures exceeding 200 °C and high pressures (30 bar) in a batch reactor. In particular, a nickel modified tungsten carbide composite showed high conversions and high selectivity with a variety of substrates.^[15] Interestingly, cobalt modified carbides enabled the use of lower temperatures (80 °C) for nitroarene reduction.^[16] However, the toxic hydrazine was used here as the reducing agent. Surprisingly, reduction protocols based on the use of the sole WC under mild conditions are still missing. One of the possible reasons is the lack of methods to synthesize WC particles with high surface area, as well as difficulties in controlling the geometry of the active site and catalytic facets, despite the progresses of methods for the synthesis of nanoparticles with defined geometry.

In this work we show how nanostructured WC obtained by urea route (WC_{urea}) can be used for the chemoselective reduction of nitro groups under mild and environmentally friendly conditions (100 °C, 10 bar, ethanol) in the presence of hydrogen in a flow reactor. The general hydrogenation properties of tungsten carbides were investigated trying to highlight the correlation between particle size and catalytic performance. The selectivity towards nitro moieties in the presence of other functional groups is also discussed. Finally, the possibility of using this particular form of WC as a support for nickel deposition was also investigated, showing the advantages of a composite system for the more challenging hydrogenation of cardanol, as an example of biorefinery applications.

Results and Discussion

WC_{urea} nanoparticles were prepared by carbothermal reduction of a tungsten-urea gel as described by Giordano et al.^[17] Such process, which is based on a combination of sol-gel chemistry and carbothermal reduction treatment, represents an interesting alternative to conventional methods for the preparation of carbides and nitrides. Urea serves as nitrogen/carbon source as well as stabilizing agent for the formation of particles, and in combination with the metal precursor affords a gel that is successively treated in a carbonization process. The composition of this gel in turn, can be modulated controlling the metal-urea ratio, resulting in the possibility of tuning the final composition of the material, including its carbon and nitrogen content. In order to get an overview of the hydrogenation properties of the obtained nanostructured tungsten carbide, the continuous reduction of several functional groups was attempted as shown in table 1. Ethanol was chosen as the solvent due to its sustainability and low toxicity. In addition, since we were interested in the catalytic behavior of WC at relatively low temperature, 100 °C was chosen as the default temperature, while pressure was set to 10 bar. Under standard conditions no conversion was observed for the reduction or hydrogenolysis of nitriles, aryl ethers, carbonyl compounds or multiple bonds, as

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Table 1: Hydrogenation screening of different substrates using WC catalysts
Conditions: 10 bar H ₂ , 100 °C, 0.1 M, ethanol. [a] WCurea; [b] 20 wt% WCurea or
Al ₂ O ₃ ; [c] 20 wt% WC _{com nano} on Al ₂ O ₃ ; [d] WC _{com} ; [e] Al ₂ O ₃ ; [f] Conversion is
calculated using GC-FID/MS data; [g] R (see SI).

Entry	Substrate	Flow Rate [ml min ⁻¹]	Conversion ^[f] [%]	Mass Specific Reaction Rate R ^[g] [s ⁻¹]
1 ^[a]	C N	0.6	0	-
2 ^[a]	$\langle \rangle$	0.6	0	-
3 ^[a]	HO	0.6	0	-
4 ^[a]		⊸ 0.6	0	-
5 ^[a]		0.6	33	-
6 ^[a]	NO ₂	0.6	>99	-
7 ^[a]	"	1.1	30	-
8 ^[b]	u	0.6	>99	66.4 10 ⁻⁵
9 ^[b]	u	0.85	27	44.0 10 ⁻⁵
10 ^[c]	"	0.6	27	5.2 10 ⁻⁵
11 ^[d]	"	0.6	0	-
12 ^[e]	u	0.6	0	-

shown in entries 1-4. However, we were pleased to observe activity for the reduction of the terminal triple bond in phenylacetylene (entry 5), with moderate conversion, as well as a full conversion of nitrobenzene to aniline (entry 6). In the latter case, the reaction went to completion under very mild conditions and the use of acids, which can be used as promoters ^[18], could be avoided unlike described in previous reports based on WC^[8]. In order to obtain gualitative structure-activity relationships, we compared WCurea to commercially available WCs for the reduction of nitrobenzene, and calculated the mass specific reaction rate R (SI). Two commercially available catalysts were selected with particle sizes in the micrometer and nanometer range respectively. Unlike the case of nanostructured tungsten carbide (WC_{urea}), which can be applied as produced showing high conversion (entry 6), the texture of WC_{com nano} (fine powder) hampers its direct utilization in the catalytic bed, resulting in elevated back pressure. In order to bypass this problem, we dispersed both WC_{com nano} and WC_{urea} on alumina as support, by wet impregnation. Due to its basic nature, alumina functions generally as a basic promoter, besides favoring the dispersion of the catalyst. The highest mass specific reaction rate (66.41 10⁻⁵ s⁻¹) for reactions at 30% conversion was achieved using WC_{urea} on Al₂O₃ (entries 8, 9). In contrast, WC_{com nano} on Al₂O₃, with nanometer sized particles, gave a much lower conversion and mass specific reaction rate R under the chosen conditions (entry 10). Finally, unsupported tungsten carbide particles with size in the micrometer range (WC_{com}, entry 11), did not show activity under the applied conditions as well as the pure Al₂O₃ powder that was used as control (entry 12). All in all, the results highlight the higher activity of WC_{urea}. Therefore, we performed the characterization of the materials in order to highlight in detail the differences in the structure that may be responsible for the enhancement in activity. Results are summarized in figure 1 and in the supporting information (pages S2 and S3).

The nitrogen adsorption porosimetry for the commercial tungsten carbide WC_{com} did not show measurable surface area, which is possibly lower than the detection limit. The adsorption measurement of WC_{com nano} resulted in an area of 6.8 m² g⁻¹, whereas the surface of WC_{urea} is 70.5 $m^2\ g^{\text{-1}}.$ The difference in surface area can also be appreciated by scanning electron microscopy. In particular, WCurea (A, B) features a clustered structure characterized by rough surface. Such roughness decreases going to WC_{com nano} (C, D) and the bulkier WC_{com} (E, F) in agreement with the BET data. Besides morphology and surface area differences, the composition of the three tungsten carbides can additionally influence their catalytic activity. X-rays diffraction (SI, Figure S3) was used to confirm the common identity of the crystalline phases of all samples.^[19] The commercial catalysts are highly crystalline and present the typical pattern of WC, however feature relatively high crystallite sizes (> 20 nm) and are generally conglomerated, as confirmed by SEM. Such materials showed no/low activity during catalytic tests (Table 1, entries 10, 11). In turn, WC_{urea} features much broader peaks, characteristic of a more amorphous structure, and very small crystallite size (3.5±0.5 nm), showing also the highest catalytic activity (entry 8). Noteworthy, the diffractogram of WCurea is characterized by the presence of residual W2C species. CHN combustion elemental analysis was used to further assess the composition of the different samples, which fall in the range of the expected values for WC. However, WCurea features higher nitrogen content, which could be incorporated in the form of N-doped metal carbide as reported previously.^[19] Such species, in combination with the residual W2C could additionally contribute to the superior activity of WC_{urea}. However the in depth elucidation of their possible catalytic role will be the subject of an independent contribution.

At this stage, we continued our investigation on the selective reduction of nitrobenzene derivatives. Because the amine-group itself plays a major role in many organic syntheses, the importance to have a catalyst working under mild and non-toxic conditions for the hydrogenation of nitro functionalities in a continuous flow reactor is of great interest. Due to the low activity showed for the reduction of other functional groups, we speculated that the WC_{urea} could serve as an efficient chemoselective catalyst. To further test this hypothesis different nitro compounds containing additional functional groups were tested as illustrated in table 2.

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Figure 1: SEM micrographs of nanostructured WC_{urea} (A, B), nanosized commercial tungsten carbide WC_{com nano} (C, D) and micrometer sized commercial WC_{con} (E, F) with the respective data on surface area, particle size and crystallite size (SI).

Table 2: Activity of nanostructured tungsten carbide catalyst WC_{urea} for the reduction of different nitro-groups. Conditions: 1.6 g WC_{urea}, 0.6 mL min⁻¹, 100 °C, 10 bar H₂; ethanol; WHSV 17.7 h⁻¹. [a] reactions were monitored using GC-MS, [b] conversion and selectivity were calculated using GC-FID and cyclohexan as the internal standard.

Entry	Substrates	Products ^[a]	Concentration [M]	Conversion (Selectivity) ^[b] [%]
1	OH NO2	NH2	0.005	99 (100)
2	он		0.05	100 (100)
3	NO2	NH2	0.1	100 (100)
4	O,N O	HN	0.05	99 (100)
5	NO ₇	NH ₀	0.05	98 (73)
6	COOH NO2		0.05	100 (80)
7	N ⁱ o O		0.05	100 (100)
8	NO2	~~~~~ ^N	• 0 .1	39 (75)
9	CH-SPH	NH2	0.05	100 (87)
10		NH2	0.05	82 (100)

Going from the simple nitrobenzene to substituted nitro aromatic compounds, the catalyst conserved its activity. Increasing the electron density on the aromatic ring with electron donating groups had only a limited effect on the reaction as indicated by the reduction of 2-nitrophenethylalcohol (table 2, entry 1), a nitrated lignin monomer model (entry 2)^[20] or 3-nitrostyrene (entry 3). In a similar way, slightly deactivated substrates like nitro-acetophenones (entry 4) could be efficiently converted. Noteworthy, reduction of the nitrofunctionality could be performed in a chemoselective way both in the presence of olefin or carbonyl groups (entries 3, 4).

In the case of p-nitroaniline (entry 5) the already present amino functionality does not affect the activity of the catalyst, resulting in the formation of the di-anilin in 98% conversion and a selectivity of 73%.

2-nitro-phenylacetic acid (entry 6) afforded oxindole with high yield and a selectivity of 80% via tandem nitro reductioncyclization. The latter product is an important platform chemical for the synthesis of drugs that have been recently suggested in cancer treatment.^[21] Reaction of nitro-cinnamaldehyde (entry 7), which is prepared by nitration of cinnamaldehyde isolated by steam distillation and extraction from cinnamon^[22], resulted in high conversion and selective formation of quinoline.

This substance is a basic platform chemical employed in the production of dyes or herbicides and represents an interesting chemical feedstock. A representative aliphatic nitro compound was also tested. In particular, conversion of 1-nitrohexane (entry 8) afforded hexylamine in a moderate 39 % yield.

The reaction of nitro compounds is assumed to proceed according to two possible paths as described for Pd/C by Baron et al. $^{[\!23]}$

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Figure 2: XRD pattern of tungsten mono carbide WC_{urea} before and after reaction; tungsten monocarbide(\blacklozenge), tungsten semicarbide (\blacklozenge); long term study of nanostructured tungsten carbide over 50 hours continuously on stream. Conditions: 1.6 g WC_{urea}; 0.1 M nitrobenzene; 0.6 mL min⁻¹; 60 °C; 10 bar H₂; WHSV 17.7 h⁻¹; et al.

Such mechanism is accepted also in the case of tungsten carbide^[15], and implies the adsorption of hydrogen at the catalyst surface followed by adsorption of the nitro moiety, which is deoxygenated to yield nitrosobenzene. Thus, possible accepted intermediates are phenylhydroxylamine (entry 9), e.g. in the case of the so called "direct route", or azobenzene (entry 10) if the reaction follows the condensation route. Both chemicals were tested under standard conditions. Phenylhydroxylamine is completely converted into aniline with 87% selectivity. However, the conversion of azobenzene is lower (82%). These preliminary results seem to suggest that the reduction of nitro functionalities can follow both pathways at the surface of tungsten carbide, although direct route seems to be kinetically preferred. Additional experiments will be required in the future in order to assess the mechanism in detail.

The stability of the catalyst as well as the resistance to poisoning is one of the main criteria for a long lasting catalytic material. Therefore we performed time on stream experiments by monitoring the reduction of nitrobenzene at 70 % conversion over 50 h, which showed a significant stability (figure 2). Accordingly, XRD analysis of the catalyst before and after the reaction showed almost no alteration of the active phase.

The results discussed above, showed that WC obtained by urea route can be regarded as an efficient chemoselective catalyst for nitro reduction, at relatively low temperature. On the other side, other groups have shown that in general the reactivity of WC can be expanded by deposition of a second metal^[24].



Figure 3: Cardanol hydrogenation using 10 wt% Ni@WC_{urea} catalyst Optimized conditions: 5.68 g Ni@WC_{urea}, 0.05 g ml⁻¹ cardanol, 0.6 mL min⁻¹, 200 °C, 30 bar H₂, WHSV 5 h⁻¹, ethanol.

In order to show that the WC_{urea}, obtainable in a very simple manner, serves as an excellent candidate for the preparation of hybrid systems, we prepared 10 wt% Ni@WC_{urea} by impregnation of WC_{urea} with nickel nitrate in the presence of citric acid, followed by pyrolysis (for characterization see SI). Nickel is not only an excellent candidate for hydrogenation reactions, it is as well a non-noble metal, relatively abundant and cheap. Citric acid is a mild and common agent for the reduction and the stabilization of metal nanoparticles in solution.^[25]

The reduction and full saturation of cardanol was studied in order to evaluate the reactivity of the new composite. Cardanol. one of the main components of cashew nutshell liquid (CNSL), is a phenolic lipid containing a C-15 carbon chain. Such non-polar tail features three unsaturations at position 8, 11, 14. The fully saturated derivative of cardanol is an interesting building block^[26] ^[27], however, due to steric hindrance the double bonds are not easily accessible, making the hydrogenation process relatively challenging. Preliminary tests under mild conditions (100 °C) resulted in the reduction of double bonds, albeit with limited conversion, according to HPLC analysis. Therefore, the hydrogenation was investigated at higher temperatures, using the bimetallic Ni@WC catalyst in a partially customized reactor that expands the operating temperature and residence time ranges (see SI) and was optimized at 200 °C with 30 bar of hydrogen leading to full conversion as shown in figure 3 (see also SI). Noteworthy, during control experiments with WCurea, saturation of the double bonds was not taking place (data not shown), and only 10 wt% Ni@WCurea was able to convert the molecules to the fully saturated substance, according to HPLC-MS analysis (see SI).

Conclusions

In conclusion we have shown how nanostructured tungsten carbide, obtained via urea route, can be used as a high efficient and chemoselective catalyst for the reduction of nitroarenes. The method relies on the use of a continuous flow hydrogenation reactor and affords the reduction of a variety of substrates under relatively mild reaction conditions, improving the performance of this class of catalysts with respect to previous reports. We could also show that reactivity is highly influenced by the nanostructure of WC and in general particles in the nanometer range outrun the performance of micrometer sized commercial WC. In order to demonstrate the versatility of WC_{urea} we also showed its use as support for nickel

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nanoparticles. The obtained hybrid system is characterized by high activity for the reduction of multiple bonds in cardanol, a bio oil obtained from cashew nutshell liquids, confirming the potential of this class of materials as catalysts for biorefinery. Future studies will focus on in depth studies on composites based on WC_{urea}.

Experimental Section

Synthesis of WC_{urea}

WC_{urea} nanoparticles were prepared by carbothermal reduction of a tungsten-urea gel as described earlier by Giordano et al.^[17]

Synthesis of 10 wt% Ni@WCurea

Nickel nitrate hexahydrate (0.5 g, $1.72 \ 10^{-3}$ mol) dissolved in 5 mL water was combined to a solution of citric acid (1.74 g, 9.06 10^{-3} mol) dissolved in 5 mL water. The molar ratio between citric acid and nickel was 5:1. The resulting solution was added to WC_{urea} (1 g) dispersed into 20 mL of water. The suspension was stirred over night at 70 °C to partially evaporate the solvent and the resulting slurry was pyrolized in a nitrogen oven at 400 °C for 3 hours.

Reactor set-up (H-CUBE Pro[™])

Hydrogenation reactions were carried out using the flow reactor system H-Cube Pro^{TM} , equipped with a liquid as well as hydrogen feed. The schematic diagram in the supporting information shows all built-in parts as well as the optional bypass used for the hydrogenation of cashew nutshell oil. The dissolved substrate is pumped by an external HPLC pump (0.6 mL min⁻¹) while pressure in the reactor (10-30 bars) is built up via an internal back pressure regulator. The internally produced hydrogen is pressurized and mixed with the eluent before the catalytic bed. The latter is constituted by a cartridge of 70 mm in length and 3 mm in diameter.

GC-MS and GC-FID analysis

Qualitative analysis of the hydrogenation reactions was performed using an Agilent Technologies 5975 gas chromatograph equipped with a capillary column (HP-5MS, 30 m, 0.25 mm, 0.25 micron) and a MS detector. The used program started with an isothermal temperature of 50 °C for 2 min that was raised to 300 °C with a rate of 30 °C min⁻¹. For the qualitative analysis the MS library NIST 08 was used.

Quantitative analysis was performed using the same GC system on a second channel equipped with a flame ionization detector (FID). A second column of the same type (HP-5MS, 30 m, 0.25 mm, 0.25 micron) was used, applying the same heating ramp described for the qualitative analysis. Cyclohexane was used as an internal standard. The areas under the peaks were analyzed by software integration (MSD ChemStation). Conversion and selectivity for each reaction were calculated according to known standard equations.

HPLC-ESI analysis

HPLC – ESI analysis was performed on a Thermo Scientific Dionex Ultimate 3000 equipped with a Velos Pro Mass detector and a UV detector. A Hypersil gold column with 5 μ m particle size was employed as the stationary phase, which was eluted isocratically with a mixture of acetonitrile (80 %), water (19 %) and acetic acid (1 %). Data acquisition was performed over 45 min intervals.

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Keywords: Tungsten carbide• catalysis • selectivity • flow reactor • hydrogenation • cardanol

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