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Synthesis of Early-Transition-Metal Carbide and Nitride Nanoparticles through the Urea Route and Their Use as Alkylation Catalysts

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Abstract: The use of urea as either a carbon or a nitrogen source enabled the synthesis of various early-transition-metal nitride and carbide nanoparticles (TiN, NbN, Mo₂N, W₂N, NbC_xN_{1-x}, Mo₂C and WC). The ability of these particles to promote alkylation reactions with alcohols was tested on benzyl alcohol and acetophenone at 150 °C for 20 h in xylene. Group IV and V ceramics proved to be able to cata-

lyse the formation of 1,3-diphenyl propenone, whereas group VI ceramics showed a tendency to promote the Friedel–Crafts-type reaction of benzyl alcohol on xylene (the solvent). TiN

Keywords: alkylation • C–C coupling • Friedel–Crafts reaction • heterogeneous catalysis • sustainable chemistry

featured the highest activity for the alkylation of ketones and was further tested for more difficult alkylations. Group VI ceramics were further investigated as catalysts for the Friedel– Crafts-type alkylation of aromatics with activated alcohols. Interestingly, even hexanol could be effectively used for these reactions.

Introduction

It was recognised that early-transition-metal carbides and nitrides exhibit catalytic activities that are similar to those of platinum-group metals (PGMs).^[1] Such ceramics thus attracted huge attention, especially in the fields of oil refining and petrochemistry.^[2] This interest was driven by both the relative low cost of such carbides and nitrides as compared with PGMs (because of the huge amounts of catalysts involved in petrochemical process) and their relative resistance towards poisoning by nitrogen- and sulphur-containing feedstocks. There are, therefore, numerous reports on the use of early-transition-metal carbides and nitrides as catalysts for hydroprocessing (including hydrodesulfurisation, hydrodenitrogenation and hydrodeoxygenation reac-

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tions),^[3,4] hydrogenation,^[5,6] dehydrogenation^[7] or isomerisation reactions.^[8,9]

Surprisingly, much less effort has been devoted to the use of such catalysts for fine chemical applications. To the best of our knowledge, only TiN found such applications, namely, for the selective hydrogenation of C–C multiple bonds^[10] or as a catalyst for the alkylation of ketones with alcohols (Scheme 1).^[11]



Scheme 1. Alkylation of ketones with alcohols, catalysed by mesoporous titanium nitride.

However, when the current financial crisis is over, the price of PGMs will surely increase again. This, in turn, will prompt intense efforts to substitute early-transition-metal ceramics (including oxides)^[12,13] for noble metals, even in fine chemical synthesis.

Herein, we report our efforts to promote the use of alcohols as alkylation agents (which is a typical green chemistry issue)^[14] with early-transition-metal carbide and nitride nanoparticles as catalysts. For this purpose we synthesised our nanoparticles by using the urea glass route. The use of urea as nitrogen source for synthesising bulk metal nitrides



(MN) has been known since 1995.^[15,16] In 2003, it was shown that under favourable conditions, by isolating crystalline urea complexes, MN nanoparticles could be obtained.^[17,18] The usefulness of this technique to also produce metal carbides (MCs) has only been recently demonstrated.^[19] In our approach, a metal-loaded urea glass (by its mechanical behaviour a secondary valence polymer, that is, a polymer-like structure held together by secondary valences such as hydrogen bridges and Coulumbic interactions) was formed in a first stage and thermally transferred into carbides and nitrides. No further purification steps were required before or after the heat treatment (i.e., no solid precipitations, re-crystallisation, side reactions or side products were observed). Several Group IV, V and VI metals were tested to ascertain the general validity of this method. For each chosen metal,

nitrides and/or carbides have been successfully synthesised. We then tested the activity of these particles in various alkylation reactions.

Results and Discussion

Synthesis and characterisation of the carbide and nitride nanoparticles: As previously mentioned, urea has already been used as either a carbon or a nitrogen source to synthesise early-transition-metal ceramic nanoparticles. This easy and relatively soft method nicely complements other recently described methods such as the use of cyanamide to convert oxide nanoparticles into the corresponding nitrides^[20] or the use of porous carbon nitride (mpg-C₃N₄) as both a nitrogen source and a nanoreactor for the conversion of metallic salts into nitride nanoparticles^[21] and mixed nitride nanoparticles.^[22] The use of this enhanced urea method enabled us to synthesise (with high yields) well-defined nanoparticles of the following compounds: TiN, NbN, Mo₂N, W_2N , NbC_xN_{1-x} , Mo_2C and WC. As previously reported, a given metallic precursor tends to yield nitrides at relatively low urea to metal ratios, whereas carbides can be obtained at higher urea to precursor ratios.^[19] Elemental analysis and X-ray diffraction (by using the ICDD PDF-4+ database) were used to ascertain the chemical nature of the particles that we obtained by using the urea route.

Figure 1 displays some examples of X-ray diffraction patterns (WAXS) and transmission electron microscopy (TEM) pictures of the obtained particles. The absence of crystalline side products as well as the crystallinity of the sample is supported by the WAXS patterns. The size of the crystallites were estimated by Scherrer's equation and are in agreement with the sizes obtained by the TEM investigation. These micrographs show well-defined, spherically shaped nanoparticles with a relatively low polydispersity and the results are summarised in Table 1.





Figure 1. WAXS diffraction patterns (top, experimental = — and calculated =-----), and corresponding TEM micrographs (bottom) of a) TiN (scale bar 100 nm), b) NbC(N) (scale bar 200 nm) and c) Mo₂C (scale bar 100 nm) nanoparticles.

Table 1. Some typical features of the synthesised nanoparticles.

					-		
Material	Urea/ metal precursor molar ratio	Nitrogen and carbon content [mass%] N C		Mean di- ameter of the parti- cles [nm] ^[a]	Crystallite size ^[b]	Average surface area $[m^2g^{-1}]^{[c]}$	
TiN	5	14.3	6.4	10-20	10	≈ 200	
Mo ₂ N	1	7.21	0.07	20-40	20	12	
W_2N	1	3.58	0.16	2-10	3	64	
NbN	3	11.4	0.4	15-20	15	23	
NbC_xN_{1-x}	10	5.4	7.3	10-15	8	140	
Mo ₂ C	5	1.57	4.60	15-30	25	10	
WC	7	1.69	4.90	3–6	3.7	84	

[a] As determined by TEM. [b] As determined on the X-Ray diffractograms by using the Debye–Sherrer equation. [c] As determined by nitrogen adsorption/desorption by using the Brunauer–Emmett–Teller equation.

Note that for niobium, even at higher urea contents, no pure carbide phase could be obtained. The WAXS patterns of the corresponding sample showed a single cubic phase and no secondary product (Figure 1b). This result was also confirmed by TEM (Figure 1b) and scanning electron microscopy (SEM, data not shown) investigations. The WAXS peak positions are placed between the ones expected for a pure NbN phase and the ones expected for a pure NbC compound. In addition, elemental analysis revealed a comparable amount of nitrogen and carbon. Because NbC and NbN feature the same crystal structure, the formation of a mixed carbonitride in the form of a solid solution is not a surprise. In that respect, the intermediate peak positions in the XRD pattern correlates well with the comparable amounts of C and N in the elemental analysis and fits quite well with Vegard's law. A similar but less pronounced tendency to form solid solutions can also be seen for our TiN, Mo₂C and WC.

Initial screening of the catalytic properties of the synthesised particles: To screen the catalytic properties of these particles in the activation of alcohols, we heated an equimolar mixture of benzyl alcohol and acetophenone in xylene to 150 °C for 20 h. Indeed, we recently found the corresponding (typically noble-metal catalysed)^[23] alkylation to be effectively promoted by mesoporous TiN.^[11] In addition, such a test proved very useful to determine which kind of reactions can be promoted by each type of particle. As well as the expected aklylation of ketones, we anticipated that other reactions could be observed such as the oxidation of benzyl alcohol, the formation of dibenzyl ether or the Friedel–Crafts-type alkylation of the solvent (xylene). Table 2 gives quantitative data about these experiments.

As can be seen, Group IV and V ceramics (nitrides as well as carbides, Table 2; entries 1–3 and 6) show a strong tendency to promote the desired alkylation reaction to yield 1,3-diphenyl-1-propanone. Titanium nitride proved to be the most effective catalyst with almost 90% yield. Interestingly, the TiN nanoparticles synthesised through the urea route proved to be more active than those produced through the C_3N_4 route, although their surface area was lower. This can be related to their relatively lower amount of residual carbon.^[11] Molybdenum nitride was not very active and yielded a complex reaction mixture, whereas W_2N , WC and Mo_2C were very active and very selective towards the Friedel–Crafts alkylation of xylene, the solvent.

Investigation of the activity of urea TiN: In our initial study on the catalytic activity of mesoporous TiO_2 and TiN (prepared by converting porous TiO_2 into the nitride by using C_3N_4 as both a nitrogen source and a scaffold to prevent the collapse of the porous structure),^[11] we noticed that the porous oxide yielded mainly saturated alkylation compounds, whereas the porous nitride yielded mainly unsaturated compounds and was less active and less versatile (i.e., only very active alcohols could be converted). The first feature was attributed to differing reaction mechanisms relying on strong differences in electronic and acidic/basic properties of both catalysts. The lower activity of mesoporous TiN was attributed to the passivating action of large amounts of residual carbon on the surface of our nitride. The urea-synthesised TiN used here appeared to be much more active

Catalyst	Conv. [%] ^[a]	Yield [%] ^[b]							
		O							
1	TiN	95	_	-	5	94			
2	TiN ^[c]	70	-	_	_	100			
3	NbN	90	-	_	17	83			
4	Mo ₂ N	30	20	64	14	-			
5	W_2N	100	_	94	_	6			
6	NbC(N)	15	_	_	37	63			
7	Mo ₂ C	94	_	88	11	-			
8	WC	100	-	80	20	-			

Table 2. Detailed analysis of the reaction mixtures obtained from benzyl alcohol and acetophenone at 150 °C after 20 h in the presence of various ceramic nanoparticles.

[a] Conv.=conversion; amount of products formed as compared with the initial amount of benzyl alcohol as determined by GC-FID. [b] Amount of the compound relative to the other detected products as determined by GC-FID. [c] Synthesised by the mpg– C_3N_4 method as a reference.^[21]

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than the C_3N_4 TiN, which is consistent with the fact that they feature much less residual carbon. It was, therefore, relatively straightforward to test our TiN nanoparticles with other (less reactive alcohols). For simplicity, we focussed on acetophenone as the ketone. Indeed, it has been previously shown that the choice of the ketone had only a minor effect on the speed of the reactions. We, therefore, submitted various mixtures of acetophenone and alcohols to the action of our TiN nanoparticles at 150 °C for 24 h in xylene. Table 3 summarises the obtained results.

Table 3. Alkylation of acetophenone with various alcohols catalysed by urea TiN nanoparticles. $^{\left[a\right] }$

Alcohol	Conv. [%] ^[b]	Product	Yield [%] ^[c]
benzyl alcohol	100		93
4-methylbenzyl	55		65
alcohol	55		35
4-methoxybenzyl	87	MeO OH ON	83 le
			12
cinnamyl alcohol	65		10
			90
1-phenyl ethanol	0	-	_

[a] Reaction conditions: The catalyst (25 mg) was added to the alcohol (1 mmol) and acetophenone (1 mmol) in xylene (2 mL). The solutions were stirred and heated at 150 °C for 24 h. [b] Conv.=conversion; amount of formed products as compared with the initial amount of alcohol as determined by GC-FID. [c] Amount of the compounds relative to the other detected products as determined by GC-FID.

As can been seen, only *p*-methylbenzyl alcohol formed the expected alkylation product with high selectivity. *p*-Methoxybenzyl alcohol formed the Guerbet condensation product as previously seen. Less active alcohols such as 1-phenyl ethanol did not react. Hence, we can conclude that the TiN particles obtained by the urea route are indeed more reactive than the one produced trough the C_3N_4 route (we obtained higher yields than in our previous study in less than half of the reaction time), but they were not more versatile (the product distributions were roughly the same and no new substrate could be used).

Investigation of the Friedel–Crafts reactions catalysed by Mo₂C and WC: In a recent study on the use of tin dioxide

nanoparticles as catalysts for the activation of alcohols, we showed that chlorine atoms present at the surface of the particles played a predominant role in controlling the activity of the particles.^[24] Indeed, we observed that the alcohols were converted, in a first step, into the corresponding chlorides at the surface of the particles and further reacted with other alcohols to yield ethers or Friedel–Crafts alkylation products, when an aromatic compound was used as the solvent (Scheme 2).



Scheme 2. Proposed chlorine-borrowing mechanism for the activation of alcohols with SnO₂ nanoparticles.

Therefore, we suspected that Mo₂C, W₂N and WC could promote the observed Friedel-Crafts-type alkylation of xylene with benzyl alcohol in a similar way. And, indeed, traces of benzyl chloride could be detected by GC-MS in the initial reaction mixtures. In addition, the presence of chlorine at the surface of the synthesised carbide nanoparticles could be shown by energy dispersive X-ray spectrometry (EDX). However, EDX showed that the TiN nanoparticles that were synthesised through the urea route also featured chlorine atoms at their surface. These observations do not allow us to account for the very different reactivity of TiN and W₂N nanoparticles, for example. Neverheless, we decided to test the activity of Mo₂C, WC and W₂N nanoparticles in the Friedel-Crafts-type alkylation of benzene, toluene and anisole with various alcohols at 150°C for 40 h. Table 4 displays some of the obtained results.

Most alcohols performed poorly when benzene was used as the aromatic compound (which is in strong contrast with what we observed with SnO₂ nanoparticles), we have thus only reported the results with anisole and toluene in Table 4. As could be expected, activated alcohols (such as benzyl alcohol, 4-methylbenzyl alcohol and cinnamyl alcohol) performed very well with anisole and toluene, yielding between 80 and 100% of the corresponding alkylation products (even in relatively short reaction times: 40 h compared with the 120 h required with our SnO₂ catalyst).^[24] With less active alcohols (hexanol and cyclohexanol), no substitution could be observed on toluene, but interestingly, anisole still performed very well. In the particular case of W2N nanoparticles 100% of conversion could be obtained for any alcohol as long as anisole was the solvent. Also note that no particular trend was observed regarding the regioselectivity of the

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Table 4. Friedel–Crafts reactions of various alcohols with benzene, toluene and anisole catalysed by Mo_2C , WC and W_2N nanoparticles prepared by the urea route.^[a]

	Mo ₂ C					W	/C			W ₂ N			
	Anisole		Toluene Anisole		ole	Toluene		Anisole		Toluene			
	Conv. [%] ^[b]	$p/o^{[c]}$	Conv. [%]	p/o	Conv. [%]	p/o	Conv. [%]	p/o	Conv. [%]	p/o	Conv. [%]	p/o	
benzyl alcohol	95	1/1	70	1/1	100	1/1	82	1/1	100	1/1	95	4/3	
4-methylbenzyl alcohol	100	3/2	100	3/2	95	3/2	91	3/2	100	3/2	75	4/3	
cinnamyl alcohol	91	4/1	0	-	80	4/1	0	-	100	4/1	0	-	
hexanol	95	4/1	0	_	95	4/1	0	-	100	4/1	0	_	
cyclohexanol	45	1/1	0	-	52	1/1	0	-	100	1/1	0	-	

[a] In a typical reaction the catalyst (25 mg), alcohol (100 mg) and aromatic compound (5 mL) were heated to 150 °C for 40 h. [b] Conv. = conversion; the conversions were determined by GC-FID with mesitylene as a reference and correspond to the molar ratio between the obtained alkylation product and the initial amount of alcohol. [c] p/o Corresponds to the molar ratio between *para*- and *ortho*-substituted alkylation products.

reaction (which is rather poor), but that each alcohol/aromatic pair yielded similar *para*- to *ortho*- ratios regardless of the catalyst. This suggests that the reaction mechanisms involved are roughly the same and that the difference between these catalysts is only marginal.

Conclusion

In this contribution we have shown that a broad variety of early-transition-metal carbides and nitrides obtained under relatively soft conditions were able to promote the use of alcohols as alkylating agents. In particular, it has been shown that depending on the metal used, high selectivity could be achieved for the alkylation of ketones in one direction or the alkylation of aromatics in the other. Also note that in this study nanoparticles were employed because they were easy to produce through the urea route and also because they naturally feature relatively high surface areas. Nevertheless, we do think that carbides and nitrides produced through other synthetic routes should feature similar catalytic properties, which in turn should promote a renewed interest for their use as catalysts for the fine chemical industry.

Experimental Section

Methods and materials: GC-MS injections were carried out by using an Agilent autosampler 7683B. Gas-phase chromatography was performed on an Agilent GC 6890N equipped with a HP-5MS phenyl methyl siloxane capillary column (5%, 30 m×250 μ m×0.25 μ m). The routine analysis method used was a splitless injection and the classical oven program was 1 min at 50°C then a ramp from 50 to 300°C at 20°Cmin⁻¹, followed by a 5 min final plateau at 300 °C. The GC column was coupled to an Agilent 5975 mass spectrometer equipped with an electron ionisation source and a quadrupole. XRD measurements were performed on a D8 diffractometer from Bruker instruments (Cu_{Ka} radiation, $\lambda = 0.154$ nm) equipped with a scintillation counter. An Enraf-Nonius PDS-120 powder diffractometer in reflection mode, equipped with an FR-590 generator as the source of $\text{Cu}_{K\alpha}$ radiation was also used. For the gas adsorption measurements, all of the samples were degassed at 150 °C for 20 h before the measurements were taken. Nitrogen sorption experiments were done with a Quantachrome Autosorb-1 or Quadrasorb at liquid nitrogen temperature, and data analysis were performed by Quantachrome software. The elemental analysis was carried out for carbon, hydrogen and nitrogen by using a Vario EL Elementar. The TEM images were taken by using a Zeiss EM 912 Ω operated at an acceleration voltage of 120 kV. Samples were ground and then suspended in ethanol. One drop of this suspension was placed on a 400 mesh carbon-coated copper grid and left in air to dry. To prevent agglomeration of the nanoparticles, the copper grid was placed on filter paper. SEM was performed on a LEO 1550 Gemini instrument. The samples were loaded on carbon coated stubs and coated by sputtering an Au/Pd alloy prior to imaging.

Synthesis of the nanoparticles: A concentrated solution of the metal precursor in ethanol was prepared (usually 1 g of metal precursor in 2 g of ethanol). In particular, we used TiCl₄, MoCl₅, WCl₄, NbCl₅, TiN, Mo₂N and Mo₂C, W₂N and WC, NbN and NbC(N). The metal chloride reacted, partly vigorously, with the alcohol to release major parts of the chlorine as HCl and forming the corresponding metal orthoesters. In every case, a clear solution was obtained. Then, a varying amount of solid urea was added to the alcoholic solution to give the wanted urea/metal precursor molar ratio (see Table 1) and was stirred until the urea was completely dissolved (dissolution time depended on the ratio but was usually is less than 1 h) to form a gel phase. The use of an ultrasonic bath or heating was not necessary to obtain homogeneity. The gels were placed in an oven and treated under a flow of N₂ at 800 °C for 3 h (plus 4 h to reach the final temperature).

Catalytic tests: Because our aim was to access cheap and easy to handle catalysts, the obtained powders were neither stored nor handled under inert gas. The chemicals were used as received and the solvents were not further purified. As preliminary tests, the activities of our catalysts were tested in C–C bond coupling reactions between acetophenone and benzyl alcohol. In a typical reaction, the metal carbide or nitride (25 mg) were placed in a SCHOTT screw-capped glass tube (160 mm length, about 10 mm inside diameter). Benzyl alcohol (1 mmol) and acetophenone (1 mmol) in xylene (2 mL) were then added and the solution was heated to $150\,^{\circ}$ C for 48 h. The products were analysed and quantified by GC–MS.

Alkylation reactions: In a typical reaction, the catalyst (25 mg) was placed in a SCHOTT screw-capped glass tube (160 mm length, about 10 mm inside diameter). The desired amount of the pure ketone, or alternatively, a solution of ketone and aldehyde in xylene (2 mL) was added. The tube was closed and heated to 150 °C for 20 h. The products were analysed and quantified by GC–MS.

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