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Solid state metathesis: synthesis of metal carbides from metal oxides

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Bulk reactions of transition metal oxides (V_2O_3, $NaVO_3$, Nb_2O_5, $LiNbO_3$, Ta_2O_5, $LiTaO_3$, MoO_3, Li_2MoO_4 and Li_2WO_4) with calcium and strontium carbides at 1000 °C for 12 h produce a range of transition metal carbides (V_8C_7, NbC, TaC, Mo_2C and WC) in good yields (*ca.* 90%). The carbides were characterised by X-ray powder diffraction, scanning electron microscopy (SEM), energy dispersive analysis by X-rays (EDAX), electron probe, FTIR, microelemental analysis, transmission electron microscopy (TEM) and electron diffraction.

Introduction

Solid state metathesis (SSM) reactions are fast, self-energetic processes, which produce crystalline materials with unusual microstructure.[1] Reactions involve the exchange of reacting partners and are largely driven by the lattice energy of a co-produced salt.[2] SSM reactions have been reported to form metal pnictides,[3] chalcogenides,[4] carbides,[5] silicides[6] and borides[7] as well as ternary phases.[8] In all of these reactions metal halides have been used in conjunction with alkali and alkaline earth salts of main group anions, such as Na_2S, Li_3N and Mg_2Si (eqn. 1).[8,9] Typical exothermicities are such that a bright orange/yellow synthesis flame moves through the material (1200 °C) away from an initiation point. Often this flame is hot enough to vaporise the majority of the co-formed salt, however only thermally robust materials can be isolated from the reactions.

$$MX_n + Na_nE \rightarrow ME + nNaX \qquad (1)$$

Recently new techniques such as the addition of a diluent reagent[10] or by conducting the reaction in a liquid medium[11]—solvent phase metathesis—have proved successful in forming phases of intermediate thermal stability.

We have shown that metal carbides can be made from metathesis reactions that utilise metal halides and calcium carbide.[12] Reactions can be initiated inside sealed evacuated ampoules that are heated in a furnace or by point-source flame initiation in air. Flame initiation is somewhat remarkable in that crystalline carbide products are produced in 10 s from the reactions.[5] Notably, despite the reactions taking place in air no oxygen contamination was noted in the carbide product. This promoted us to consider the possible use of transition metal oxide starting materials in the synthesis of carbide materials by solid state metathesis. To our knowledge previous reactions that have been termed SSM have always utilised metal halides as the metal source;[8] this has the advantages of making the reactions extremely exothermic and for easy removal of the co-produced salt by trituration with water.[8] Here we report the first solid state metathesis reaction to use transition metal oxides as starting reagents.[13] The reactions are still exothermic, driven by the formation of calcium and strontium oxide. Conveniently these oxides can be removed from the product by washing in dilute acids. The systems that we have chosen to study were transition metal carbides; this is because of the widespread technological use of these materials[14] and for their robustness to acid washing conditions.

Experimental

All powders were of 99.9% purity or better except calcium carbide which was 80+% (the only commercial source of CaC_2 we could find; analysis indicated the sample was *ca.* 90% CaC_2 and 10% CaO). All chemicals were purchased from Aldrich Chemical Co. and used without further purification. Strontium carbide was prepared by heating the elements at 800 °C for 12 h in an evacuated quartz ampoule. Manipulations and weighings were carried out in a Saffron Scientific nitrogen filled glove box. Ampoules were made from quartz (0.6 cm diameter, 15 cm long, 2–3 mm walls) and were flame dried under vacuum prior to use. Dilute hydrochloric acid (5%) was used for all triturations. After treatment with acid the remaining solids were always rinsed with distilled water and dried in vacuum. X-Ray powder diffraction patterns were determined on a Siemens D5000 transmission powder diffractometer using germanium monochromated Cu $K_{\alpha 1}$ radiation ($\lambda = 0.15046$ nm). Patterns were indexed using TREOR or METRIC-LS programs. SEM/EDAX was carried out on a JEOL JSM820 microscope, equipped with a Kevex Quantum Detector Delta 4, and a Hitachi SEM S-570. Infra-red spectra were recorded on a Nicolet 205 spectrometer using KBr pressed discs. Elemental compositions were determined by the departmental service using combustion in oxygen with tin powder as a combustion aid. The TEM and electron diffraction spectra were recorded on a JEOL 1200 conventional transmission electron microscope operated at 100 keV. Electron probe measurements were made on a JEOL EMA.

Reactions of CaC_2 and SrC_2 with transition metal oxides V_2O_3, $NaVO_3$, Nb_2O_5, $LiNbO_3$, Ta_2O_5, $LiTaO_3$, MoO_3, Li_2MoO_4 and Li_2WO_4 inside ampoules

The same reaction scale and procedure was used for all reactions exemplified below for the reaction of $LiNbO_3$ and CaC_2.

Lithium niobate, $LiNbO_3$ (0.200 g, 1.35 mmol) and calcium carbide (0.130 g, 2.00 mmol) were ground together and placed inside an ampoule that was evacuated and sealed. The ampoule was placed in a tube furnace that was brought from room temperature to 1000 °C over 1 h. At 650 °C some white residue settled at the cooler part of the ampoule whilst the solid at the hottest part of the ampoule had turned black over a 20 s period. The ampoule was annealed at 1000 °C for 12 h. After annealing the ampoule was allowed to cool to room temperature, broken

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open and the contents triturated with dilute hydrochloric acid (3×6 ml), rinsed with distilled water (3×10 ml) and then dried in vacuum. The resultant black solid was analysed using powder XRD, SEM/EDX, FTIR, TEM, electron diffraction and microanalysis.

(Microanalysis: TaC: Obs. C, 5.69; H, 0.21; N, 0.31. Calc. TaC C, 6.22, $TaC_{0.91}$ C, 5.69%; WC: Obs. C 6.67; H, 0.10; N, 0.26; Calc. WC C, 6.12%).

CAUTION: Solid state metathesis reactions are exothermic and can generate high temperatures. Reactions carried out in sealed ampoules can explode. The initiation temperatures were determined by looking along the central tube of the furnace and looking for a change in colour of the reagents. A blast proof screen and a safety mask were between the ampoule and the observer.

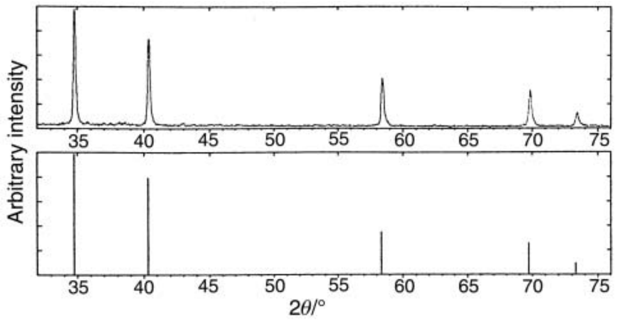

Fig. 1 Top trace: X-ray powder diffraction pattern of the triturated product from reaction of $LiNbO_3$ and SrC_2 at 1000 °C for 12 h. Bottom trace: standard stick pattern for stoichiometric NbC.

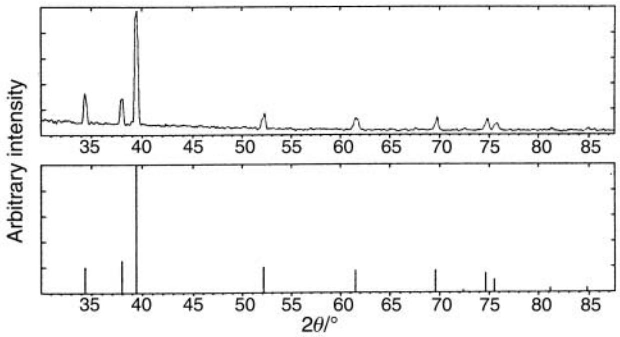

Fig. 2 Top trace: X-ray powder diffraction pattern of the triturated product from reaction of Li_2MoO_4 and CaC_2 at 1000 °C for 12 h. Bottom trace: standard stick pattern for α-Mo_2C.

Results

Synthesis

Solid state metathetical (SSM) reactions of binary and ternary metal oxides of Group 5, molybdenum and tungsten with Group 2 carbides lead to formation of transition metal carbides and Group 1 and 2 oxides, Table 1. The idealised equations for the formation of TaC are shown in eqn. 2 and eqn. 3. Reactions were conducted inside sealed quartz tubes. The tubes were heated inside a furnace from room temperature to 1000 °C. All reactions initiated between 480 °C (Ta_2O_5) and 650 °C ($LiTaO_3$). This was demonstrated by the passage of a synthesis wave through the reagents. The synthesis wave was not accompanied by a flash of light—typical of SSM processes[8]—but rather a distinct darkening of the product mixture from grey to black over a *ca.* 20–30 s period. Some reactions were stopped after passage of the synthesis wave and the ampoule cooled with the furnace to room temperature. X-Ray analysis of the product at this stage showed amorphous material with no trace of the initial calcium or strontium carbide. This indicates that a metathesis reaction had occurred. In the majority of cases, however, the product was not isolated after passage of the synthesis wave, rather the ampoule was allowed to reach 1000 °C and maintained at that temperature for 12 h. This annealing stage was found to be important to produce crystalline metal carbides. After cooling and work up with weak acids, single-phase metal carbides were isolated (Table 1).

$$Ta_2O_5 + 5CaC_2 \rightarrow 2TaC + 5CaO + 8C \qquad (2)$$

$$2LiTaO_3 + 5CaC_2 \rightarrow 2TaC + 5CaO + Li_2O + 8C \qquad (3)$$

Characterisation

X-Ray powder diffraction analysis of the annealed and triturated products from the SSM reactions showed only single-phase products (Fig. 1, 2). The powder patterns were indexed, this showed cubic metal carbides had formed for V_8C_7, NbC and TaC and that orthorhombic α-Mo_2C and hexagonal WC were formed. The carbides had lattice parameters which matched either fully stoichiometric or slightly substoichiometric metal carbide. Cubic metal carbides are known to tolerate a degree of non-stoichiometry,[15] Vegard's law can be readily applied to determine the extent of non-stoichiometry.[16] For example, $NbC_{1.00}$ has $a = 4.471$ Å whilst $NbC_{0.77}$ has $a = 4.432$ Å; the NbC formed from reaction of either Nb_2O_5 or $LiNbO_3$ and CaC_2 has $a = 4.462$ Å corresponding to $NbC_{0.95}$ and the NbC formed from reaction of Nb_2O_5 and SrC_2 has $a = 4.467$ Å corresponding to $NbC_{0.98}$. Reaction of V_2O_3 with CaC_2 produced substoichiometric V_8C_7 that showed superstructure lines corresponding to ordered carbon vacancies within the structure, the lattice parameters obtained from the reactions corresponded to $VC_{0.87}$ and $VC_{0.85}$, that is, close to the highest carbon content for the V_8C_7 phase ($VC_{0.87}$–$VC_{0.73}$).[15] The orthorhombic α-Mo_2C and hexagonal WC phases are known not to tolerate non-stoichiometry in the same way as the cubic carbides. Samples

Table 1 Transition metal carbides prepared from reaction of metal oxide with strontium and calcium carbides at 1000 °C for 12 h

Reactants	Products after annealing and trituration	Observed lattice parameter a_{obs}/Å +/−0.002 Å	Literature lattice parameter for fully stoichiometric product a_{lit}/Å[14,17]
$V_2O_3 + CaC_2$	V_8C_7	4.159	4.165
$NaVO_3 + CaC_2$	V_8C_7	4.161	4.165
$NaVO_3 + SrC_2$	V_8C_7	4.165	4.165
$Nb_2O_5 + CaC_2$	NbC	4.462	4.471
$Nb_2O_5 + SrC_2$	NbC	4.467	4.471
$LiNbO_3 + SrC_2$	NbC	4.462	4.471
$Ta_2O_5 + CaC_2$	TaC	4.446	4.456
$LiTaO_3 + CaC_2$	TaC	4.448	4.456
$MoO_3 + CaC_2$	Mo_2C	$a = 4.730$, $b = 6.017$, $c = 5.208$	$a = 4.732$, $b = 6.037$, $c = 5.204$
$Li_2MoO_4 + CaC_2$	Mo_2C	$a = 4.733$, $b = 6.006$, $c = 5.203$	$a = 4.732$, $b = 6.037$, $c = 5.204$
$Li_2WO_4 + CaC_2$	WC	$a = 2.901$, $c = 2.838$	$a = 2.906$, $c = 2.838$

produced in these SSM reactions matched with literature measurements.[17] Average crystallite sizes as assessed by X-ray line broadening (Scherrer equation) in all samples were of the order of 100–400 Å, ignoring possible disorder and variations in stoichiometry.[16]

The samples produced after work up in all of the reactions were black. The FT-IR spectra matched authentic samples with a broad band at *ca.* 600 cm^{-1}. Elemental microanalysis of the carbides using powdered tin as a combustion aid showed good agreement for carbon and negligible amounts of nitrogen and hydrogen.

SEM/EDAX analysis of the metal carbides formed from the SSM reaction showed that the pre-washed material contained free carbon and calcium or strontium oxide. Trituration with dilute acid and water proved to be effective in removing the coformed calcium and strontium oxide. It was also effective in removing some free carbon due to density considerations; the carbide product sank in dilute acids whilst the trace of free carbon in the product floated. EDAX analysis of the triturated product gave the expected elemental ratios for carbon and transition metal over a number of surface spots. Electron-probe line-scan analyses were consistent with the EDAX results. Notably no calcium, strontium, free carbon or oxygen could be detected in the triturated products by either electron probe or EDAX. SEM analysis revealed that the triturated products consisted of particles of typical dimension 20 μm with rough and sharp surfaces, suggesting agglomeration of smaller particles with dimensions on the scale of 1000 Å, Fig. 3, 4.

TEM analyses have been performed on the niobium carbide prepared using lithium niobate and strontium carbide, and tantalum carbide prepared using lithium tantalate and calcium carbide. Tantalum carbide had agglomerates of average size 4000 Å with the crystals varying in size from 200–1200 Å, Fig. 5. The cubic *a*-parameter was found from electron diffraction to be 4.435 Å ($TaC_{0.77-0.99}$ = 4.410–4.456 Å[15]) corresponding to $TaC_{0.86}$. This compares to $TaC_{0.94}$ from XRD analysis. The niobium carbide sample had larger agglomerates that were composed of a mesh of small crystals of average size between 200 and 500 Å, Fig. 6. The cubic *a*-parameter was found from electron diffraction to be 4.458 Å ($NbC_{0.77-0.99}$ = 4.432–4.471 Å[15]) corresponding to $NbC_{0.92}$, in good agreement with the parameter derived from the XRD study.[15] The TEM analysis showed that both samples were fairly homogenous with no obvious secondary impurity phase. Electron diffraction patterns for both samples showed ring patterns corresponding to polycrystalline grains with the crystallites randomly orientated.

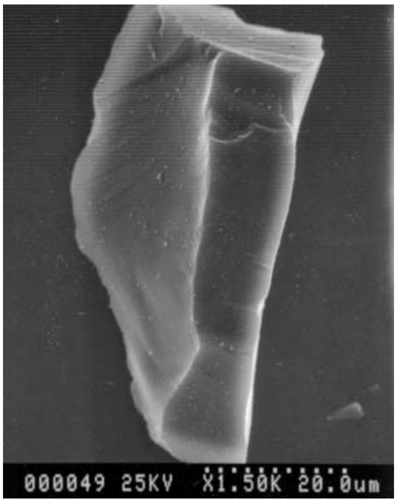

Fig. 3 SEM micrograph of triturated cubic tantalum carbide TaC, prepared using tantalum(v) oxide and calcium carbide at 1000 °C for 12 h.

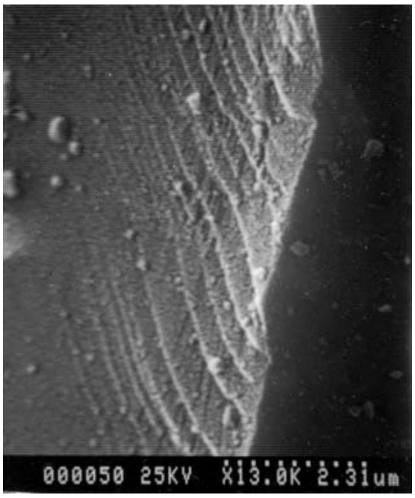

Fig. 4 SEM micrograph of triturated cubic tantalum carbide TaC, prepared using tantalum(v) oxide and calcium carbide at 1000 °C for 12 h.

Discussion

Solid state metathetical reactions of transition metal oxides and ternary metal oxides with calcium and strontium carbide form transition metal carbide and coformed oxide. The reaction is largely driven by the difference in ΔH_f of the coformed oxide—CaO −634 kJ mol^{-1}—and the starting carbide—CaC_2

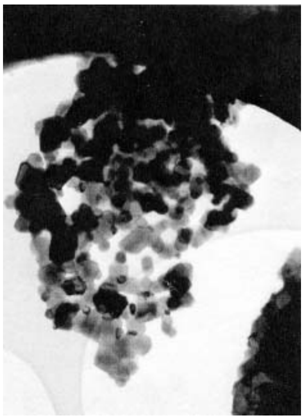

Fig. 5 TEM micrograph of triturated cubic tantalum carbide TaC, prepared using lithium tantalate and calcium carbide at 1000 °C for 12 h.

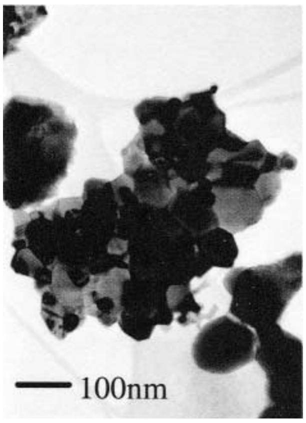

Fig. 6 TEM micrograph of triturated cubic niobium carbide NbC, prepared using lithium niobate and strontium carbide at 1000 °C for 12 h.

-59.4 kJ mol^{-1}.[18] The reactions were slow, with the grey reagent mixtures transforming to black solids over 20–30 seconds at temperatures between 450 °C and 650 °C. Notably no thermal flash or propagation wave was seen. The lack of starting materials in the X-ray pattern as well as the EDAX results indicate that the reactions occur with passage of the "dark synthesis wave", however crystalline carbide products could only be obtained after annealing for at least 6 h at 1000 °C. In conventional SSM reactions, metal halides are used as starting materials and the reactions typically proceed in 2–3 s by a yellow-orange thermal flash. Crystalline products are produced without recourse to annealing.[4–12] These conventional SSM reactions can often be initiated at a point source using filament initiation. None of the reactions of transition metal oxides with CaC_2 or SrC_2 propagated on initiation with a filament or even a point source flame (1200 °C). Reaction did occur at the tip of the filament but failed to propagate through the solid.

Ease of SSM reaction propagation through a solid flame has been empirically correlated with the reaction exothermicity and the melting point of the co-produced salt.[17] If the reaction is sufficiently exorthemic to melt the co-produced salt then the reaction propagates through the solid as the salt acts as a mediator to enable successive layers to react. In the case of metal halide reactions the coformed salt, LiCl or NaCl, melts at 605 and 801 °C respectively,[19] a sufficiently low temperature for the reaction exothermicity to overcome and promote the passage of a thermal flash. In the reactions studied here to form metal carbides from oxide starting materials, the analogous coformed salts are calcium and strontium oxides, these melt at temperatures greater than 2400 °C in excess of what can be achieved from the typical reaction exothermicities (300–450 kJ mol^{-1}).

The phases of metal carbide formed in the SSM reactions of metal oxides were close to stoichiometric. Lattice parameters obtained by X-ray and electron diffraction were largely in agreement with the formation of slightly carbon deficient products $MC_{0.95-0.86}$. This compares very closely to the analogous formation of metal carbides from reaction of transition metal halide and calcium carbide.[12,13] In the latter case reactions initiated at a point source and propagated with a thermal flash. One difference noted between the metal halide and oxide SSM reactions was that in the case of molybdenum carbide formation α-Mo_2C (orthorhombic) was formed from oxide SSM and β-Mo_2C (rhombohedral) from the chloride SSM process. This phase difference can be readily explained as α-Mo_2C is the more thermodynamically stable form and was found in the oxide reaction that was annealed at 900–1000 °C for 12 h; β-Mo_2C is a kinetic phase that was formed in the fast (2–3 s) propagative chloride SSM reaction. It should be noted that the most stable thermodynamic phase of carbide was formed in each of the oxide SSM routes.

We have attempted to extend the oxide metathesis route to Group 4 oxide starting materials. This has been largely unsuccessful forming for example $CaTiO_3$ from reaction of Li_2TiO_3 and CaC_2.

Conclusion

Solid state metathesis reactions are not restricted to the use of transition metal halides as the metal source; metal oxides in certain circumstances can be used. Reactions of a range of metal oxides and lithium/sodium transition metal oxides with calcium and strontium carbide offer a facile route to a range of transition metal carbides. The reactions do not support a solid flame synthesis wave like conventional metathesis reactions, but do support the passage of a dark wave in which transformation of reactants to products occurs. Acquisition of crystalline materials from the SSM reaction using oxide precursors required annealing at 1000 °C for at least 6 h and always formed the most thermodynamically stable transition metal carbide.

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