Electronic Supplementary Information

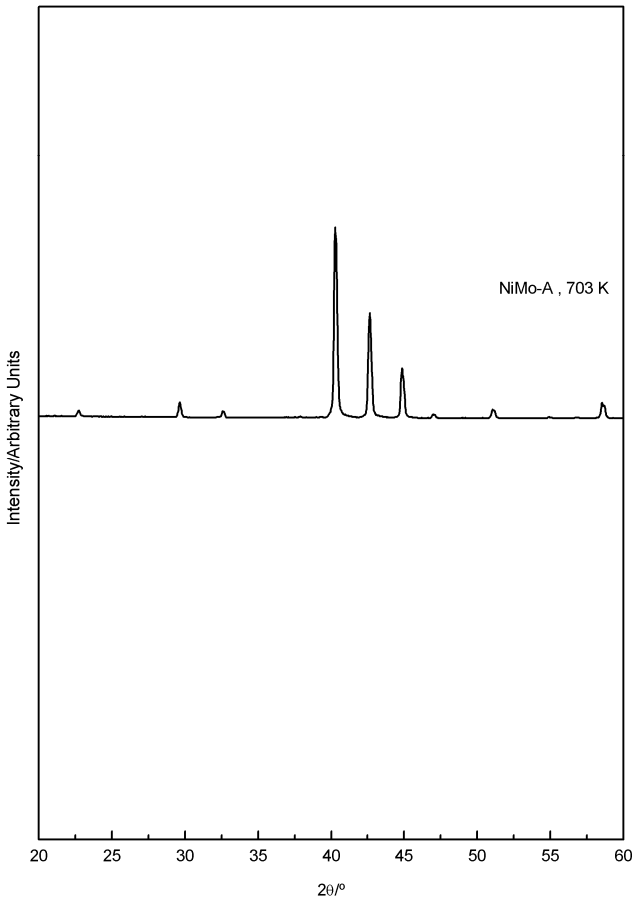

Fig. S1 XRD pattern of NiMo-A (703 K, CH_4/H_2/Ar 16/4/80 vol%).

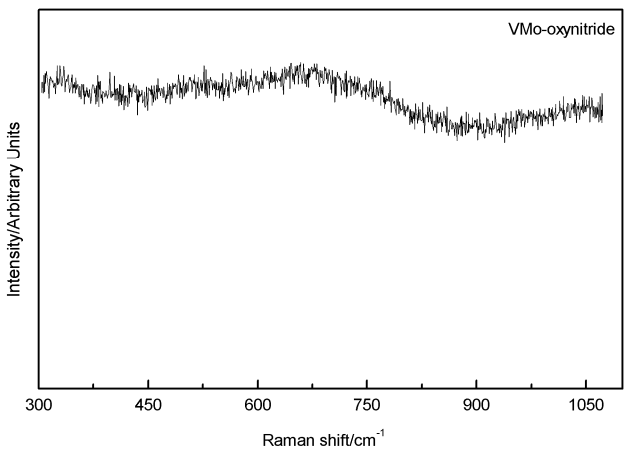

Fig. S2 LRS spectrum of VMo-oxynitride.

Results corresponding to NiMo samples obtained with CH_4/H_2/Ar 4/16/80 vol%

Table S1 Experimental preparation conditions and chemical compositions of Ni_2Mo_3N compound before and after reacting with a CH_4/H_2/Ar 4/16/80 vol% gas mixture

Sample[a]	T_f/K[b]	Analysis (%)				Stoichiometry proposed[f]
		M/Mo[c]	C[d]	N[d]	O[e]	
NiMo-A	703	-	0.17	3.33	-	-
NiMo-B	923	0.77	1.44	1.84	0.13	$Ni_2Mo_3C_{0.5}N_{0.5}$

[a] A-B point temperature in Figure 1. [b] Final temperature, t = 0 h. With NH_3, t = 2-4 h. [c] EDAX (at%). [d] Combustion analysis (wt%). [e] From TGA. [f] Stoichiometry of the bulk samples assuming the nominal M/Mo ratio. H content was < 0.1% in all samples.

Table S2 Crystal parameters and selected bond distances for sample NiMo-B prepared with a CH_4/H_2/Ar 4/16/80 vol% gas mixture

Atom/Wyckoff site	*x*	*y*	*z*
$Ni_2Mo_3(C_xN_y)$, space group $P4_132$, a = 6.65142(3) Å			
Ni (8c)	0.18211(18)	0.18211(18)	0.18211(18)
Mo (12d)	0.79861(10)	0.04861(10)	1/8
C, N (4b)	7/8	7/8	7/8
χ^2 = 1.37, Rp = 13.0, R_{wp} = 13.0, R_B = 2.41, R_F = 2.91[a]			
Ni-Ni = 2.471(2) Å; Ni-Mo = 2.7275(10), 2.7577(16), 2.8251(10) Å, Mo-Mo = 2.7814(8), 2.8286(10) Å; Mo-C,N = 2.0873(5) Å			

[a] $R_p = \Sigma|y_i(obs)-y_i(calc)|/\Sigma y_i(obs)$, $R_{wp} = \{\Sigma w_i(y_i(obs)-y_i(calc))^2/\Sigma w_i(y_i(obs))^2\}^{1/2}$, $R_B = \Sigma|I_K(\text{`obs'})-I_K(calc)|/\Sigma I_K(\text{`obs'})$, $R_F = \Sigma|I_K(\text{`obs'})^{1/2}-I_K(calc)^{1/2}|/\Sigma I_K(\text{`obs'})^{1/2}$.

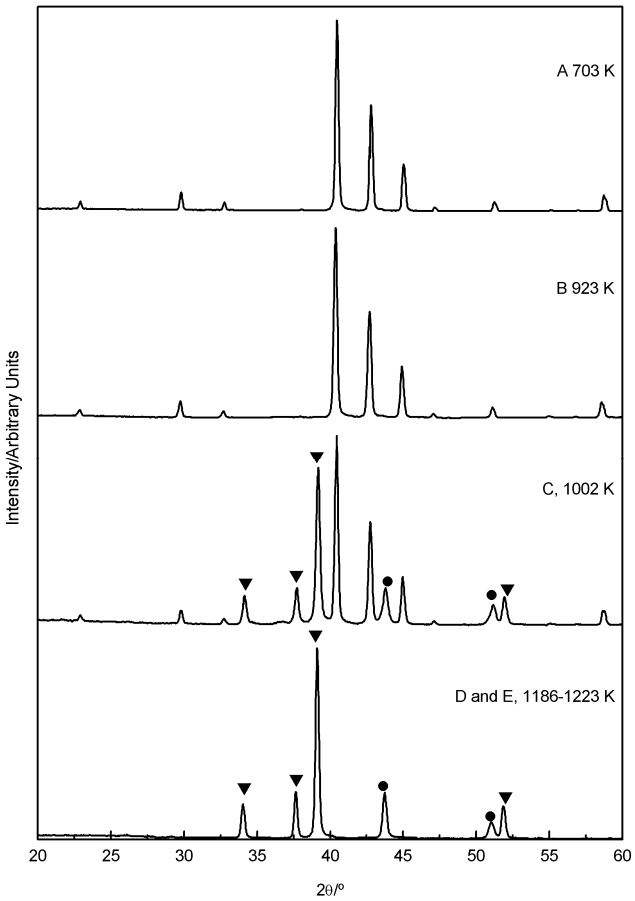

Fig. S3 X-ray diffraction patterns of the products obtained during the temperature-programmed reaction in $CH_4/H_2/Ar$ (4/16/80 vol %) stopped at different temperatures (Samples A-E) of Ni_2Mo_3N. Marked reflections correspond to: ● Ni-Mo-C solid solution, ▼ β-Mo_2C (JCPDS card Nº 35-0787).

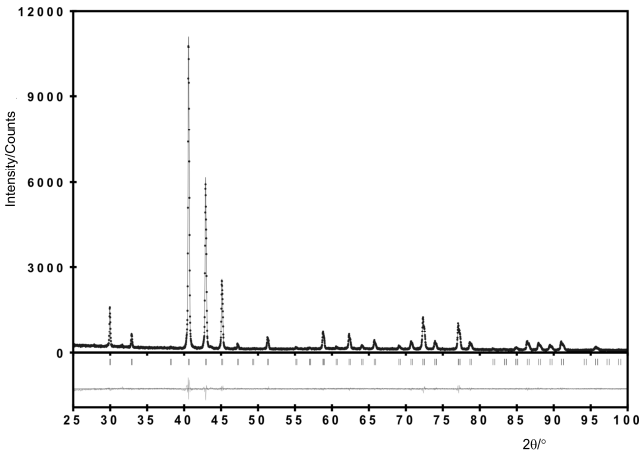

Fig. S4 Observed (dotted) and calculated (solid) X-ray diffraction profiles for sample NiMo-B prepared with a $CH_4/H_2/Ar$ 4/16/80 vol% gas mixture. Tic marks below the diffractograms represent the allowed Bragg reflections. The residual lines are located at the bottom of the figure.