Electronic Supplementary Information

Carbon nanofibres-supported KCoMo catalysts for syngas conversion into higher alcohols

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Table S1. Description of the codes of the catalysts investigated in this study.

Catalyst	Catalyst composition		Synthesis route	Catalyst activation at ambient pressure in a 20 cm^3 min^{-1} flow of 10 vol.% H_2/He		*In situ* re-activation before reaction at 0.5 MPa in a 20 cm^3 min^{-1} flow of 10 vol.% H_2/He		Catalyst activation at 5 MPa in a 20 cm^3 min^{-1} flow of pure H_2	
	Nominal molar K/Co/Mo ratio	Nominal CoMo loading		*T*	*t*	*T*	*t*	*T*	*t*
	(-)	(wt.%)		(K)	(h)	(K)	(h)	(K)	(h)
DI-Co/MoK-673	0.1/1/1	5	Dry impregnation 1. K+Mo, 2. Co	673	4	573	3	-	-
DI-MoK/Co-673	0.1/1/1	5	Dry impregnation 1. Co, 2. K+Mo	673	4	573	3	-	-
DI-673[a]	0.1/1/1	5	Dry impregnation K+Co+Mo	673	4	573	3	-	-
BM-673	0.1/1/1	5	Ball milling K+Co+Mo	673	4	573	3	-	-
SG-673	0.1/1/1	5	Sol-gel K+Co+Mo	673	4	573	3	-	-
SG-2-673	0.1/1/1	5	Sol-gel K+Co+Mo	673	4	573	3	-	-
SG-0.5-673	0.1/1/1	5	Sol-gel K+Co+Mo	673	4	573	3	-	-
SG-no K-673	0/1/1	5	Sol-gel Co+Mo	673	4	573	3	-	-
SG-723	0.1/1/1	5	Sol-gel K+Co+Mo	723	4	573	3	-	-
SG-773	0.1/1/1	5	Sol-gel K+Co+Mo	773	4	573	3	-	-
SG-573(4)	0.1/1/1	5	Sol-gel K+Co+Mo	-	-	-	-	573	4
SG-573(18)	0.1/1/1	5	Sol-gel K+Co+Mo	-	-	-	-	573	18

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	Nominal molar K/Co/Mo ratio	Nominal CoMo loading		*T*	*t*	*T*	*t*	*T*	*t*
	(-)	(wt.%)		(K)	(h)	(K)	(h)	(K)	(h)
SG-723-573(18)	0.1/1/1	5	Sol-gel K+Co+Mo	723	4	573	3	573	18
SG-723-573(18)-sg	0.1/1/1	5	Sol-gel K+Co+Mo	723 (in CO/H_2)	4	573 (in CO/H_2)	3	573 (in CO/H_2)	18
SG-723-573(18)-CO	0.1/1/1	5	Sol-gel K+Co+Mo	723 (in CO)	4	573 (in CO)	3	573 (in CO)	18
BM-723-573(18)	0.1/1/1	5	Ball milling K+Co+Mo	723	4	573	3	573	18
KCoO-MoO_2	0.1/1/1	5	Sol-gel K+Co and K+Mo physical mixing	573[b] for KCoO 773 for $KMoO_2$	4	-	-	-	-

[a]This catalyst was coded as CNF in the comparison of supports. [b]The catalyst activation was conducted in a 20 $cm^3 min^{-1}$ flow of Ar instead of diluted H_2.

Table S2. Performance data for the catalysts investigated in this study.[a]

Catalyst	$STY_{HA[ROH]}$ ($mmol_{HA[ROH]}\ g_{CoMo}^{-1}\ h^{-1}$)	X_{CO}[e] (%)	S_{MeOH}[e] (%)	S_{HA}[e] (%)	S_{HC}[e] (%)	S_{CO2}[e] (%)
Al_2O_3	3.7 [6.8]	5.1 (0.43)	5 (0.4)	6 (0.6)	84 (1.2)	5 (0.4)
SiO_2	0.1 [0.4]	0.2 (0.02)	13 (1.6)	3 (0.5)	38 (2.6)	46 (4.5)
MgO	0.1 [0.3]	0.2 (0.01)	9 (0.7)	5 (0.1)	61 (0.6)	25 (1.2)
AC	0	0	0	0	0	0
CB	1.4 [5.4]	1.6 (0.06)	21 (0.5)	7 (0.3)	62 (1.3)	11 (2.0)
DI-Co/MoK-673	7.0 [9.6]	5.3 (0.07)	4 (0.5)	11 (0.8)	70 (2.3)	15 (2.5)
DI-MoK/Co-673	0.2 [1.0]	1.2 (0.04)	8 (0.2)	2 (0.3)	84 (1.0)	5 (0.1)
DI-673	8.0 [12.0]	3.7 (0.08)	9 (0.3)	18 (1.4)	53 (1.3)	20 (0.2)
BM-673	1.5 [2.9]	1.6 (0.10)	7 (0.7)	8 (0.6)	53 (1.0)	32 (0.9)
SG-673	9.7 [16.6]	7.9 (0.08)	7 (0.1)	11 (0.1)	68 (0.4)	14 (0.4)
SG-2-673	9.6 [14.4]	10.2 (0.80)	4 (0.2)	8 (0.1)	79 (0.4)	9 (0.4)
SG-0.5-673	3.9 [5.8]	2.0 (0.17)	8 (0.7)	16 (0.1)	37 (1.8)	39 (1.2)
SG-no K-673	13.5 [28.7]	7.0 (0.57)	18 (1.6)	16 (1.9)	52 (3.3)	14 (0.8)
SG-723	14.1 [22.1]	4.7 (0.03)	14 (0.2)	25 (0.5)	31 (0.6)	30 (0.3)
SG-723-bis[b]	13.8 [22.9]	5.0 (0.05)	15 (0.1)	23 (0.4)	30 (1.1)	32 (1.5)
SG-773	14.3 [22.8]	4.4 (0.08)	16 (0.1)	27 (0.1)	23 (0.7)	34 (0.5)
SG-573(4)	11.1 [18.7]	4.2 (0.20)	15 (0.3)	22 (0.4)	36 (0.9)	27 (1.1)
SG-573(18)	22.4 [38.0]	8.1 (0.24)	16 (0.8)	23 (0.8)	30 (0.5)	31 (1.4)
SG-723-573(18)	37.6 [56.4]	14.2 (0.33)	11 (0.7)	22 (0.6)	20 (1.4)	48 (0.4)
SG-723-573(18)-bis[b]	36.7 [55.0]	12.7 (0.19)	12 (0.3)	24 (0.5)	20 (0.3)	45 (0.4)
SG-723-573(18)-sg	6.9 [10.8]	2.8 (0.18)	12 (0.6)	20 (1.3)	36 (1.5)	32 (0.4)
SG-723-573(18)-CO	1.0 [1.9]	0.6 (0.03)	13 (0.4)	15 (1.0)	44 (1.1)	28 (0.7)
BM-723-573(18)	0.3 [1.1]	0.2 (0.02)	33 (0.3)	11 (0.1)	43 (0.4)	14 (0.7)
KCoO-MoO_2	3.4 [4.3]	0.8 (0.03)	9 (0.2)	33 (0.3)	29 (0.5)	29 (0.7)
CoMoK-MWCNT[c]	23 [24]	33	3	52	10	35
KCoMo/AC[d]	7 [9]	47	6	17	32	45

[a]Reaction conditions: $P = 5$ MPa, $T = 543$ K, molar $H_2/CO = 2$ and $WHSV = 4000\ cm^3\ g_{cat}^{-1}\ h^{-1}$. [b]bis: testing of newly prepared SG-723 and SG-723-573(18). [c]Reference catalyst, data retrieved from ref. 16 in the main manuscript. [d]Reference catalyst, data retrieved from ref. 15 in the main manuscript. [e]Standard deviation in brackets.

Fig. S1 Setup for HA synthesis comprising a liquid injection system (green), a reactor, a hot trap (red) and an online GC (purple).

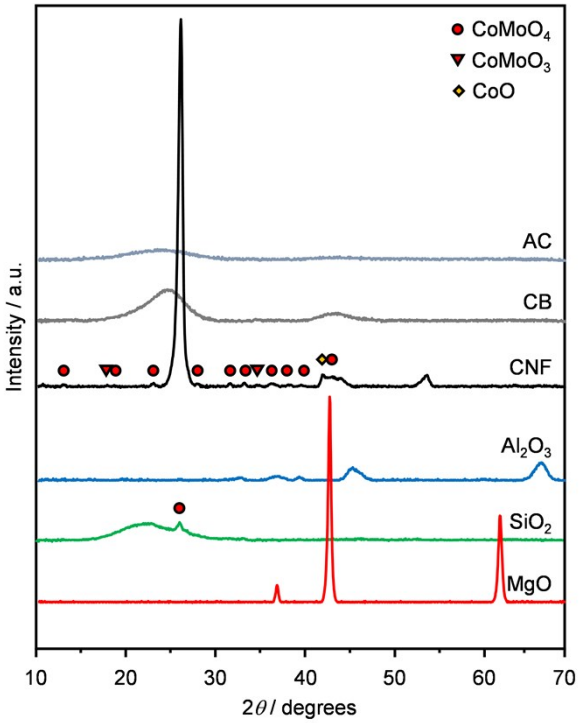

Fig. S2 XRD patterns of KCoMo catalysts supported on different carriers and reduced under the standard conditions. The reflections of the supports are not marked.

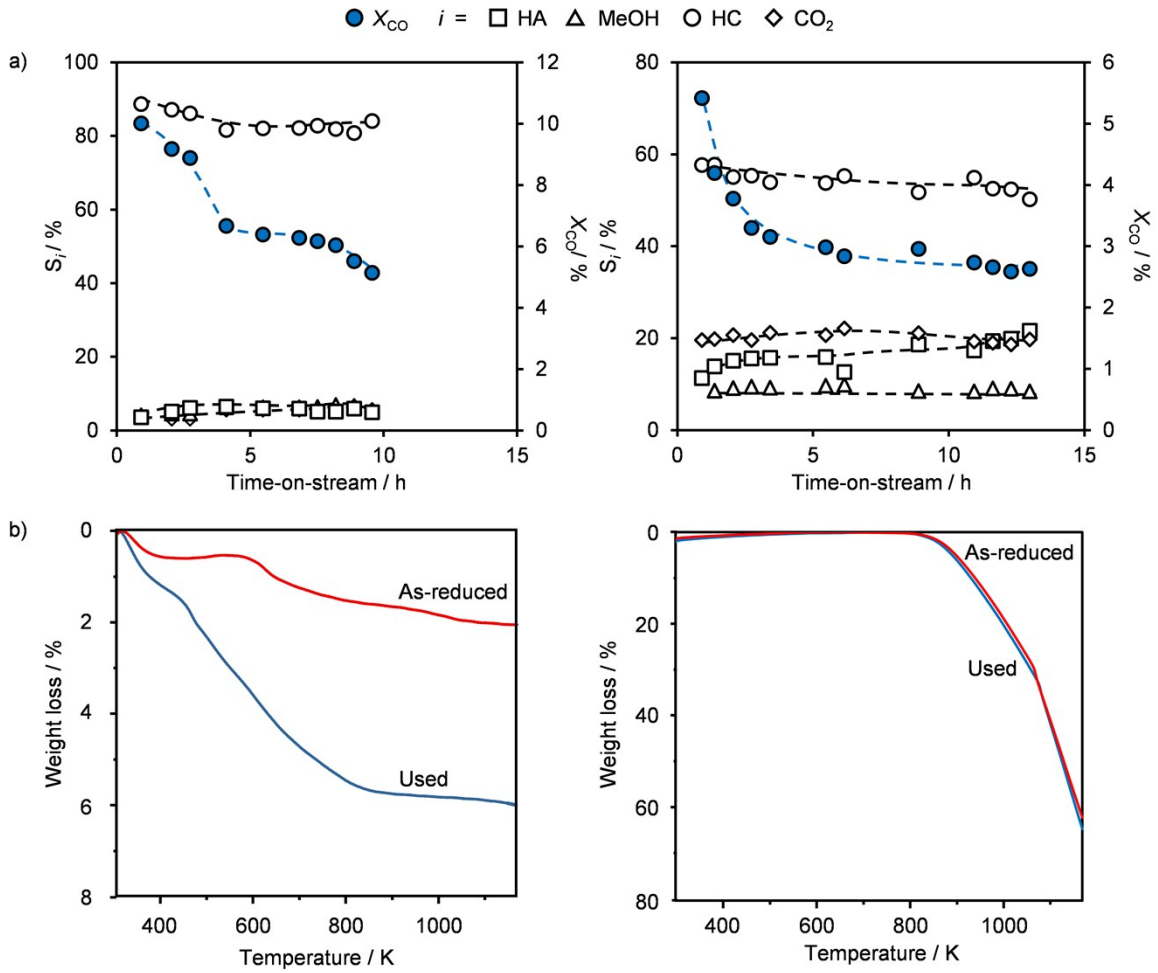

Fig. S3 (a) Temporal evolution of the CO conversion and products selectivity and (b) TGA curves for KCoMo catalysts supported on Al_2O_3 (left) and CNF (right).

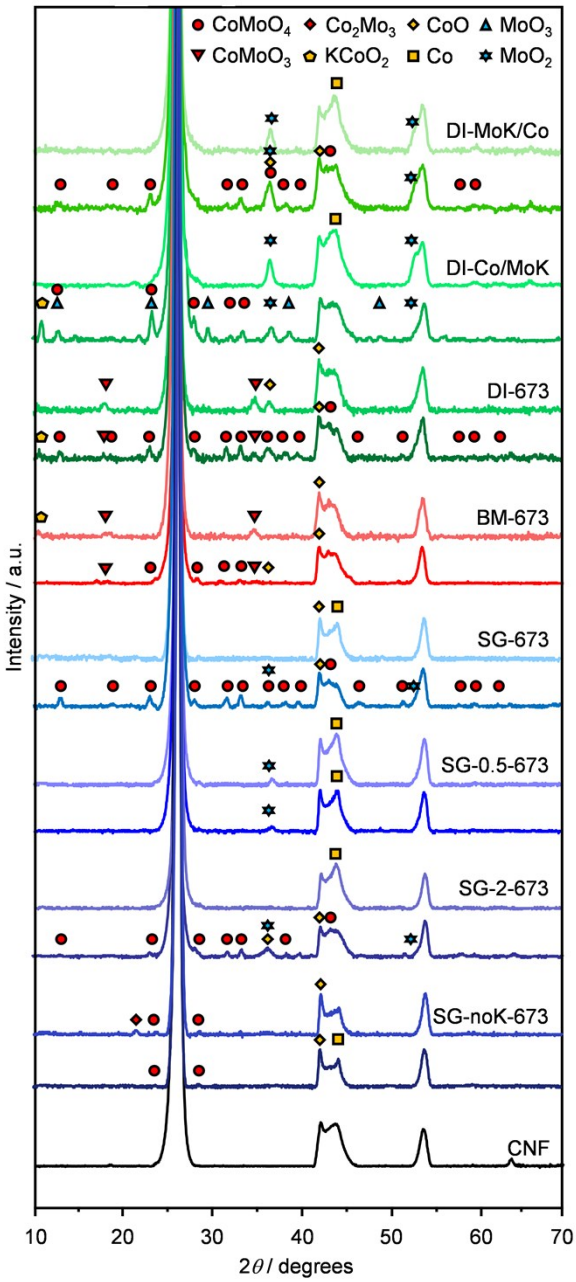

Fig. S4 (a) XRD patterns of CNF-supported KCoMo catalysts prepared by different synthesis routes and by the SG method with variable Co/Mo ratio or without K and reduced under the standard conditions prior to (dark colour) and after (pale colour) use in the reaction. The pattern of the CNF is shown at the bottom of the figure as a reference.

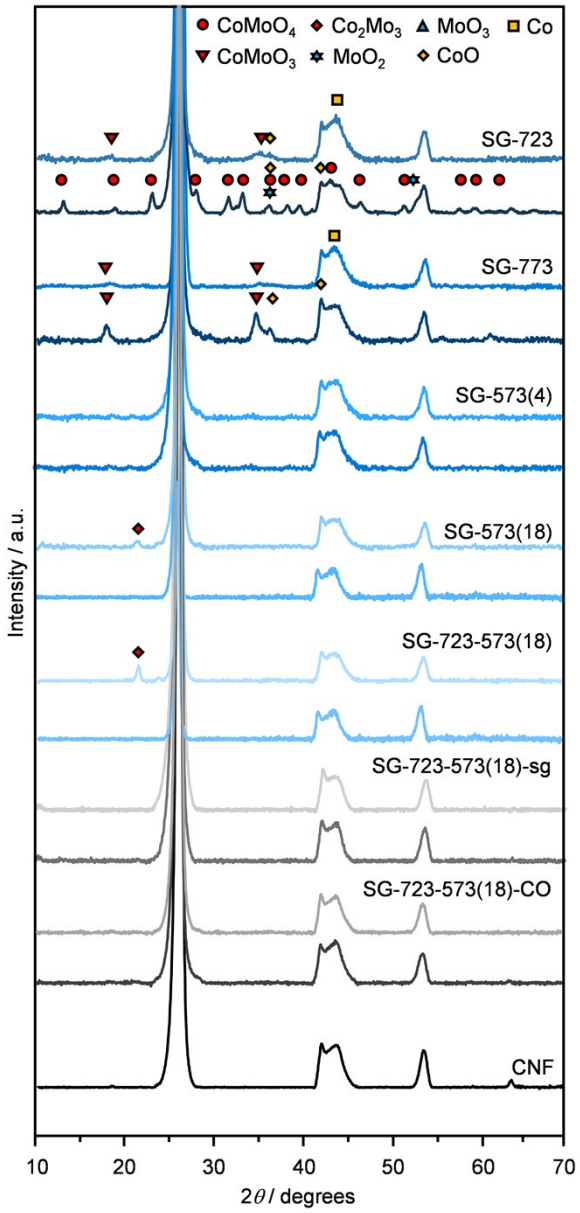

Fig. S5 XRD patterns of CNF-supported KCoMo catalysts prepared by the SG method and reduced in one or two steps at variable temperature and pressure, in H_2, CO or syngas (molar $H_2/CO = 2$), for a distinct time prior to (dark colour) and after (pale colour) use in the reaction. The pattern of the CNF is shown at the bottom of the figure as a reference.

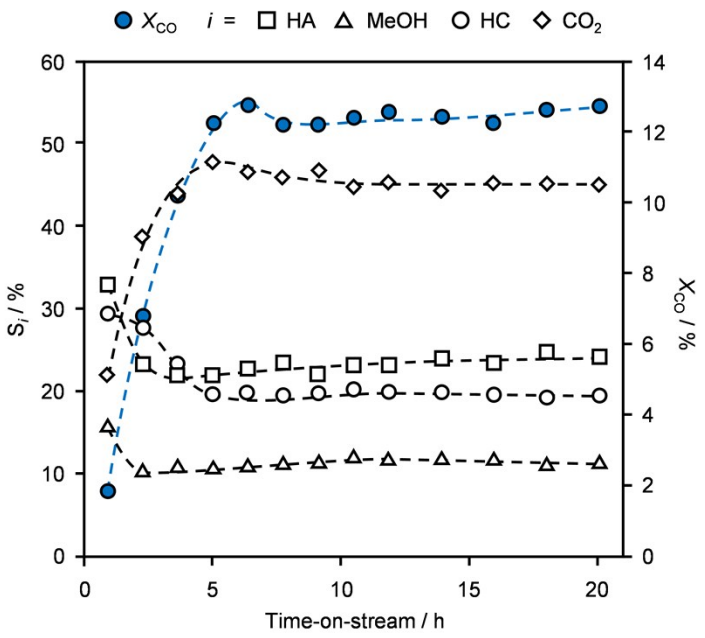

Fig. S6 Temporal evolution of the CO conversion and products selectivity over SG-723-573(18).

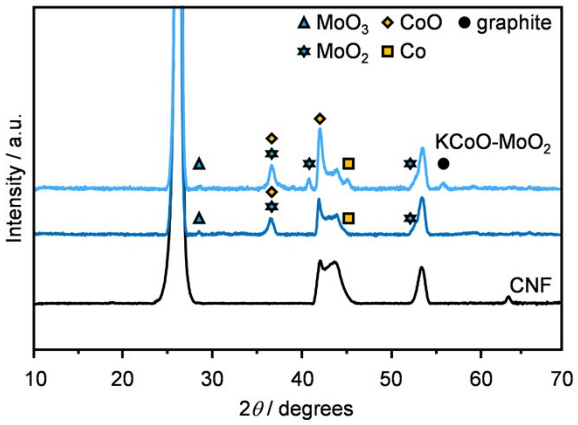

Fig. S7 XRD patterns of KCoO-MoO_2 prior to (dark colour) and after (pale colour) use in the reaction. The pattern of the CNF is shown at the bottom of the figure as a reference.

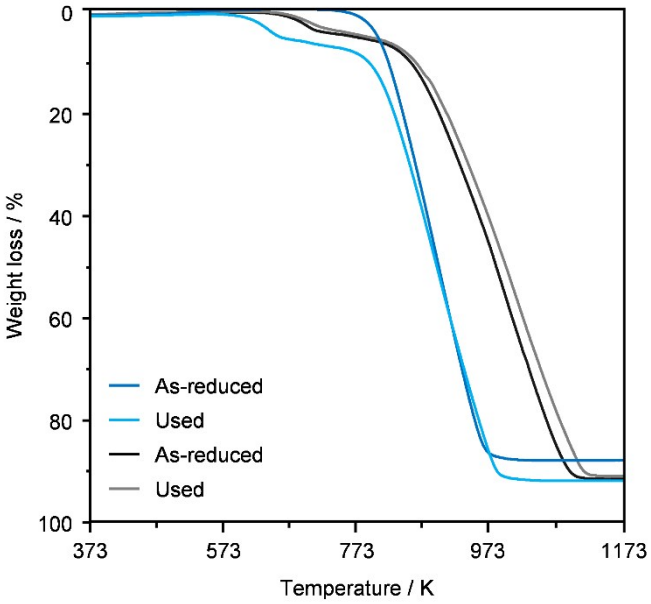

Fig. S8 TGA curves of SG-723-573(18) (blue) and SG-723-573(18)-CO (grey) in as-reduced and used forms.

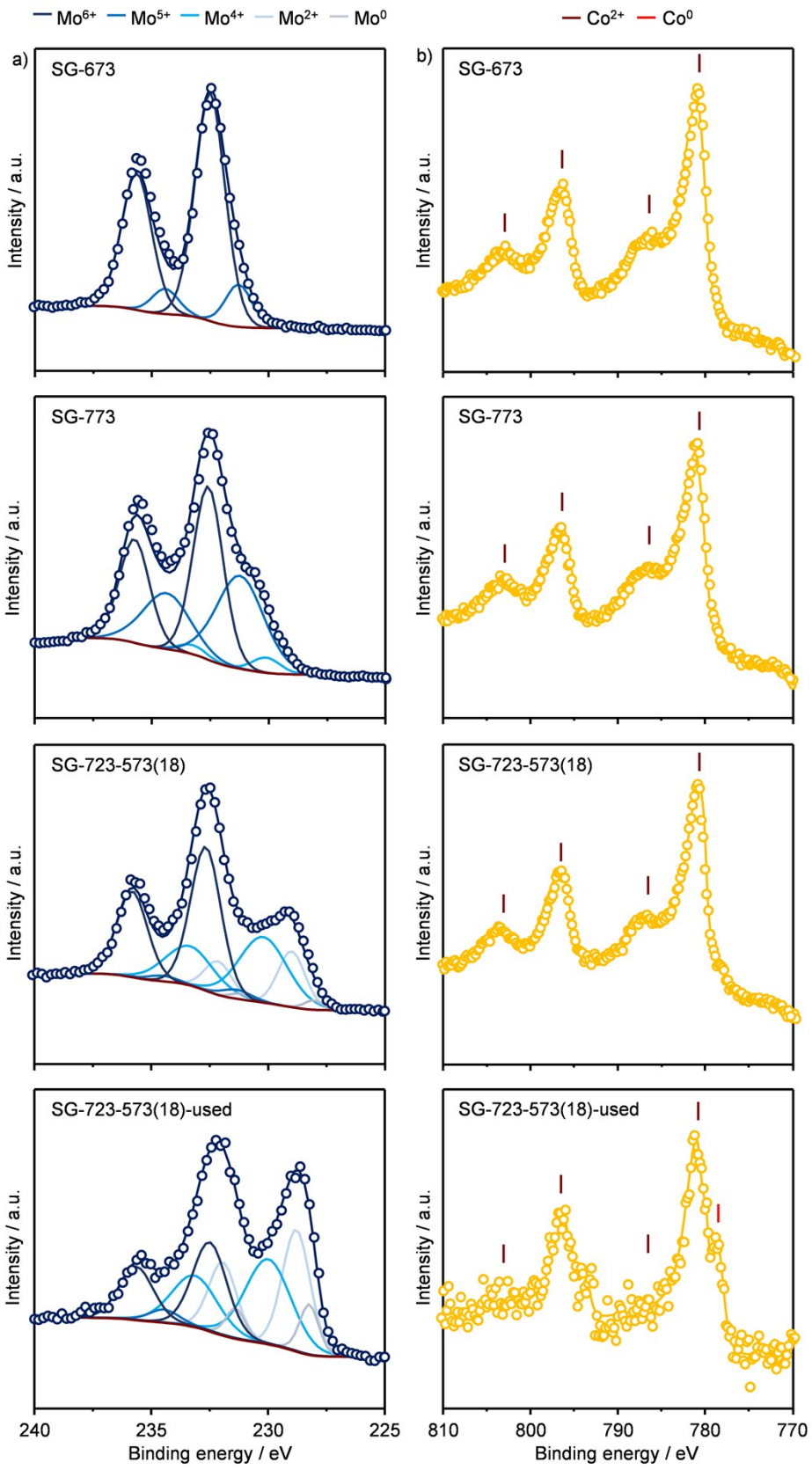

Fig. S9 (a) Mo3*d* and (b) Co2*p* XPS core-level spectra of KCoMo/CNF catalysts reduced in one or two steps at variable temperature and pressure for a distinct time in as-reduced and used forms.

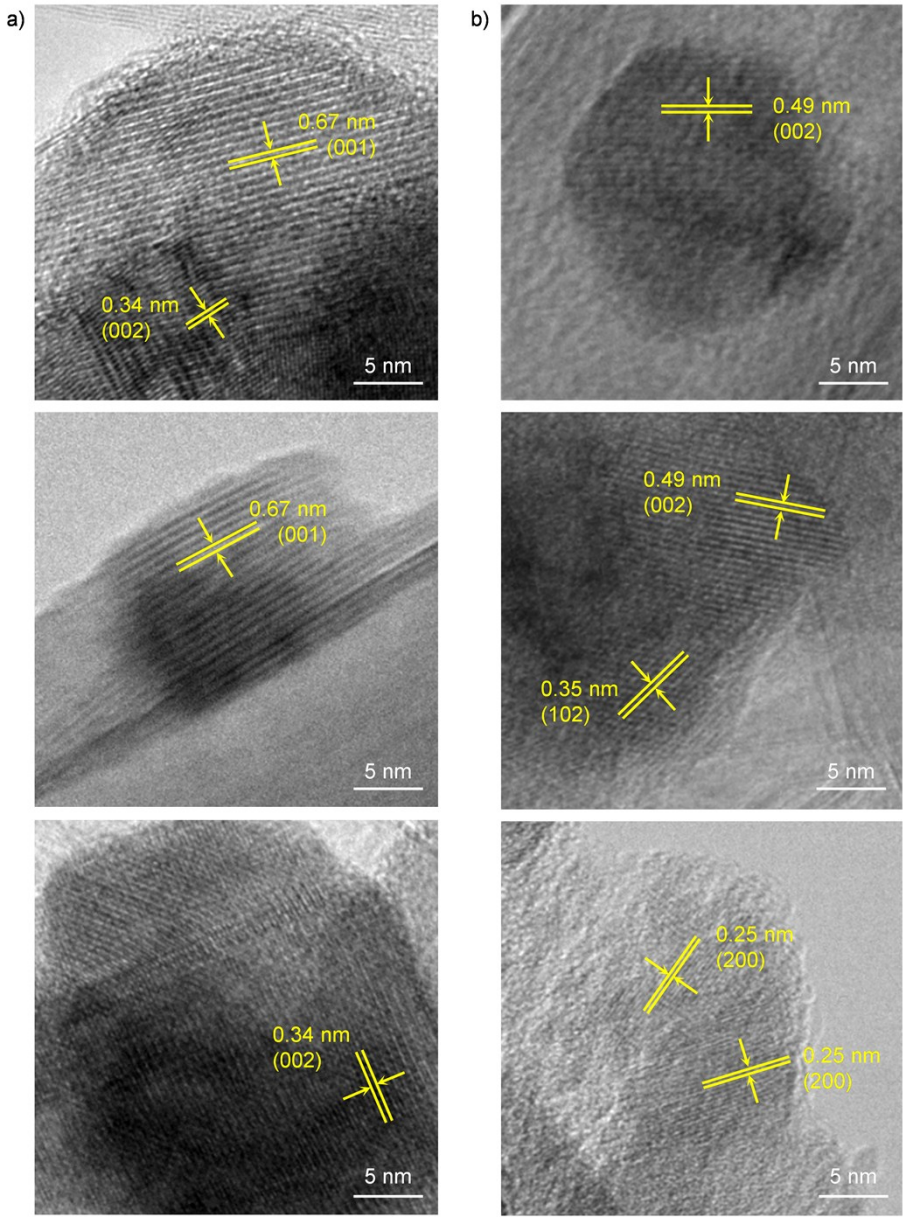

Fig. S10 HRTEM micrographs of (a) SG-673 and (b) SG-773, highlighting the *d* values associated with the observable fringes and their attribution to facets of crystalline phases.