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Controlled synthesis of Co_3O_4 spinel with $Co(acac)_3$ as precursor

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Table S1: List of solvents and temperature range used for Co_3O_4 preparation

Precursor	Temperature (°C)	Preparation techniques	Solvents	Reference
$Co(acac)_2$	230-440	PSE-CVD	EtOH	[1]
$Co(acac)_2$	490-560	MOCVD	EtOH/chloroform	[2]
$Co_2(CO)_8$	600, 650	PE-CVD	1-Hexene	[3]
$Co(hfac)_2 \cdot 2H_2O \cdot$tetraglyme	65-180	MOCVD	CH_2Cl_2	[4]
$Co(tmhd)_2$	350-500	CVD	-	[5]
	350-540	MOCVD	Monoglyme	[6]
$CoCl_2$	300	Spray pyrolysis	Distilled water	[7-9]
$Co(CH_3CO_2)_2 \cdot 4H_2O$	600	Sol-gel	2-Methoxyethanol	[10]
$Co(NO_3)_2$	400-480	Spray pyrolysis	-	[11]
$Co(acac)_3$	360-540	MOCVD	Toluene	[12]

Note: PSE-CVD: pulsed spray chemical vapor deposition
MOCVD: metal organic vapor deposition
PE-CVD: pulsed evaporation
acac: acetylacetonate (2, 4-pentanedionate)
hfac: hexafluoroacetylacetonate (1,1,1,5,5,5-Hexafluoro-2,4-pentanedione)
tmhd: tetramethylheptanedionate (2,2 6,6-tetramethyl-3,5-heptanedionate)

Table S2: Experimental conditions for the preparation of Co_3O_4

Precursor	$Co(acac)_3$
Solvent	EtOH; toluene or THF
Concentration of precursor	5 mM
Frequency and opening time	4 Hz, ~2 ms
Evaporation temperature	220 °C
Vaporizer temperature	240 °C
Substrate temperature range	350 °C; 400 °C; 450 °C and 500 °C
System pressure (mbar)	20
N_2 (SLM)	0.16
O_2 (SLM)	0.5
Substrates	Glass, silicon, planar or mesh of stainless steel

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Table S3: Physical properties of the solvents

Physicals properties	Ethanol	Toluene	THF
Boiling point (°C) [a]	78.35	110.65	68.85
Density (g ml^{-1}) [b]	0.790	0.866	0.880
Vapor pressure (bar, at 220 °C)	46.57 [a]	10.53 [a]	27.36 [c]
$\Delta_{vap}H°$ (kJ/mol) [a]	42 ± 2	37 ± 3	32.16
Dipole moment (D, 20 °C) [b]	1.69	0.31	1.75
Hydrogen bonding [b]	19.4	2.0	8.0

Note: [a] data is from NIST chemistry webbook;[13] [b] data is from Koenhen and Smolders;[14] [c] vapor pressure of THF is from Dortmund data bank.[15]

Table S4: Comparison with other results

Catalyst	Weight (mg)	Gas composition	Flow rate (ml min^{-1})	T_{90} [a] (°C)	GHSV [b] (ml g^{-1} h^{-1})	Reference
Co_3O_4 thin film	12	1% CO/ 10% O_2 /89% Ar	15	350	75000	This work
Co_3O_4 bulk	50	1% CO/ 8% O_2 in He	37	350	44400	16
CeO_2	100	2% CO/ 2% O_2 in N_2	100	374	60000	17
Al_2O_3	100	2% CO/ 2% O_2 in N_2	100	394	60000	
$CeAlO_3$	100	2% CO/ 2% O_2 in N_2	100	465	60000	
$Pt/H_2SO_4/ZrO_2$	50	3.5% CO/ 4% O_2 in N_2	100	290	120000	18
Co_3O_4 thin film	12	1% C_3H_6/10% O_2 /89% Ar	15	380	75000	This work
Co_3O_4 thin film	12	2% C_3H_6/ 20%O_2 /78% Ar	15	385	75000	19
Au/A_2O_3	200	1.5% C_3H_6/ 4% O_2 in He	75	410	22500	20
Ag/Al_2O_3	50	3% C_3H_6/ 10% O_2 in N_2	10	420	12000	21
$La_{1.7}Sr_{0.3}CuO_4S_{0.2}$	200	0.1% C_3H_6/ 5% O_2/ in He	100	500	30000	22

Note: [a] T_{90} refers to the temperature at which 90% of the fuel is converted; [b] GHSV is gas hourly space velocity.

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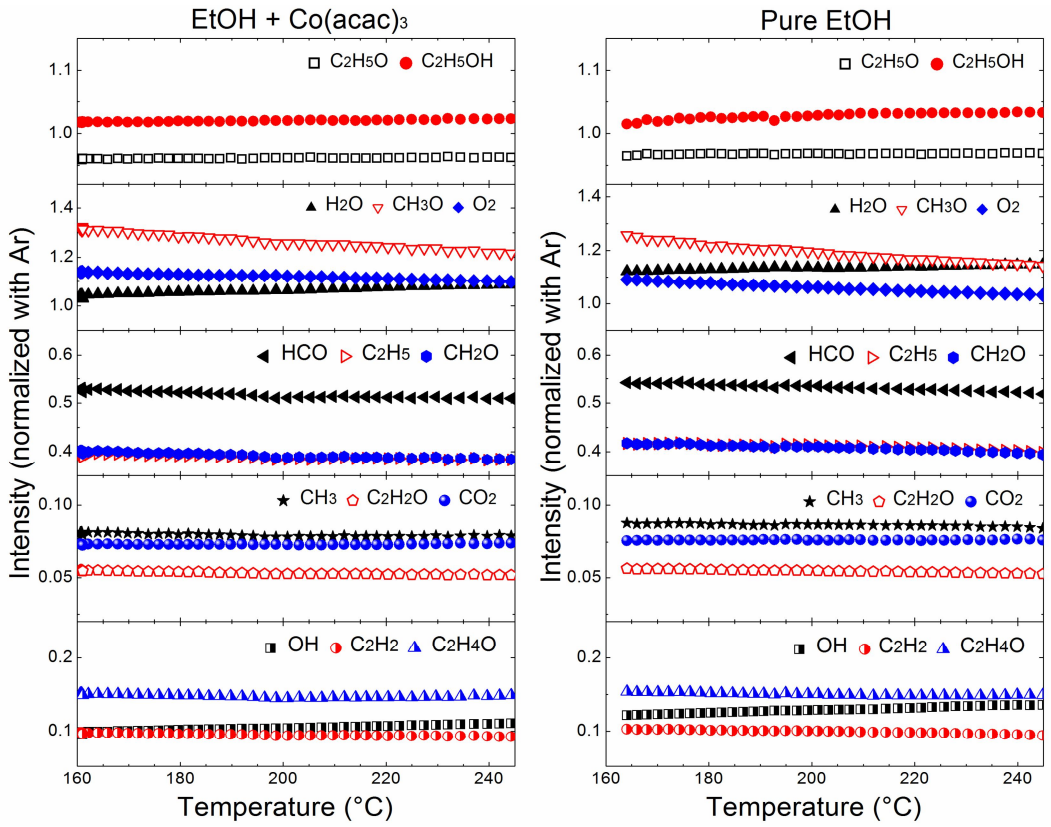

Fig. S1 Gas phase evolution of EtOH with and without $Co(acac)_3$.

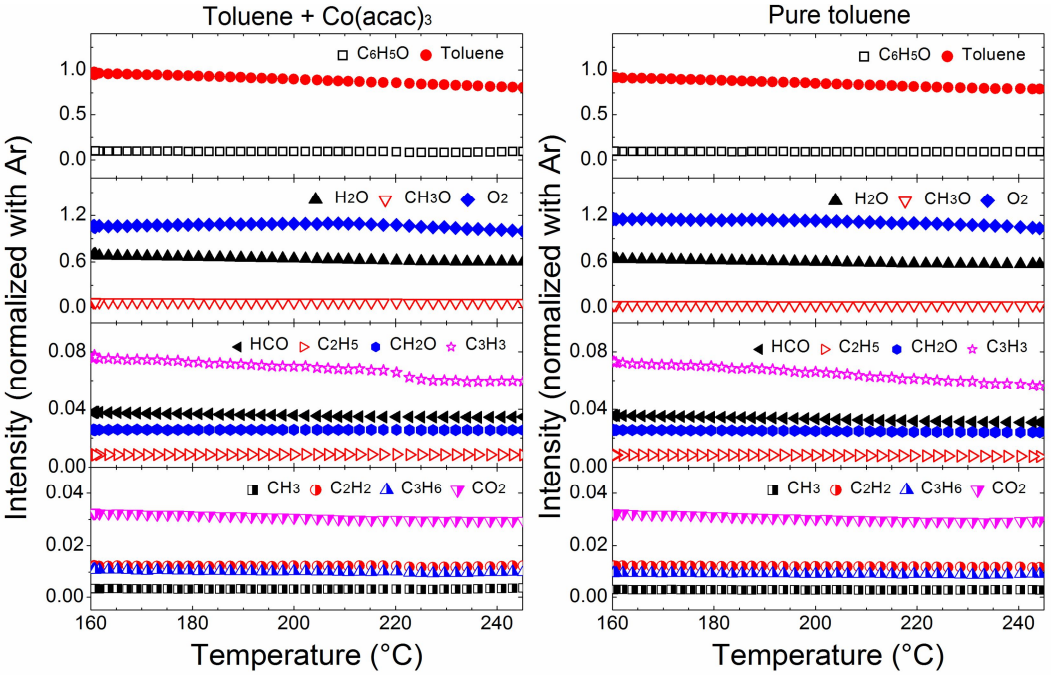

Fig. S2 Gas phase evolution of toluene with and without $Co(acac)_3$.

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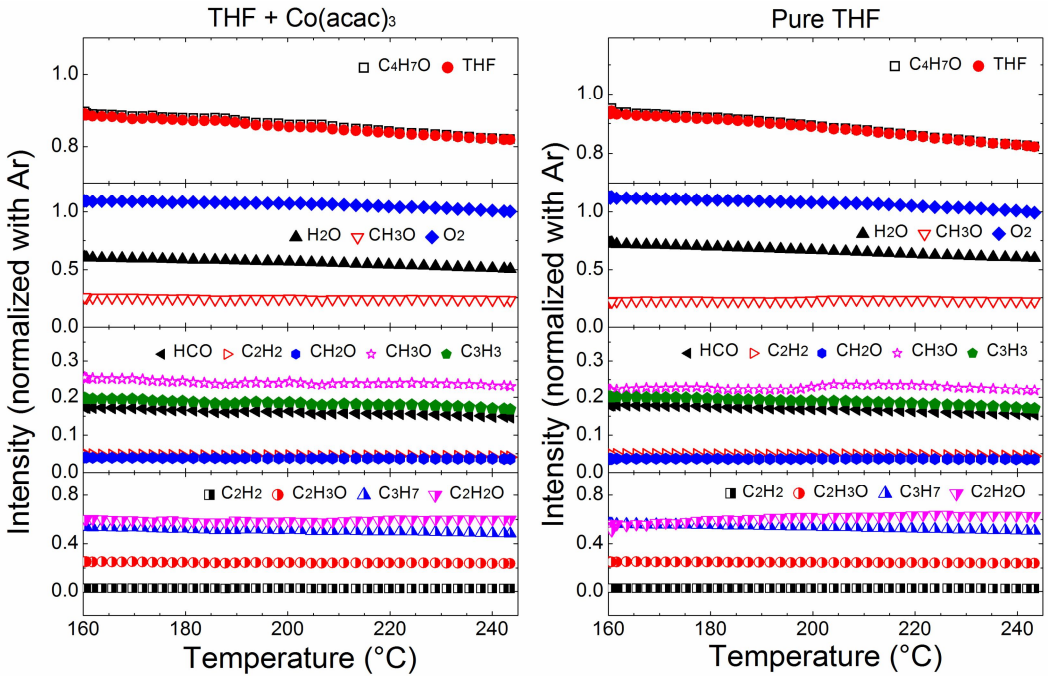

Fig. S3 Gas phase evolution of THF with and without $Co(acac)_3$.

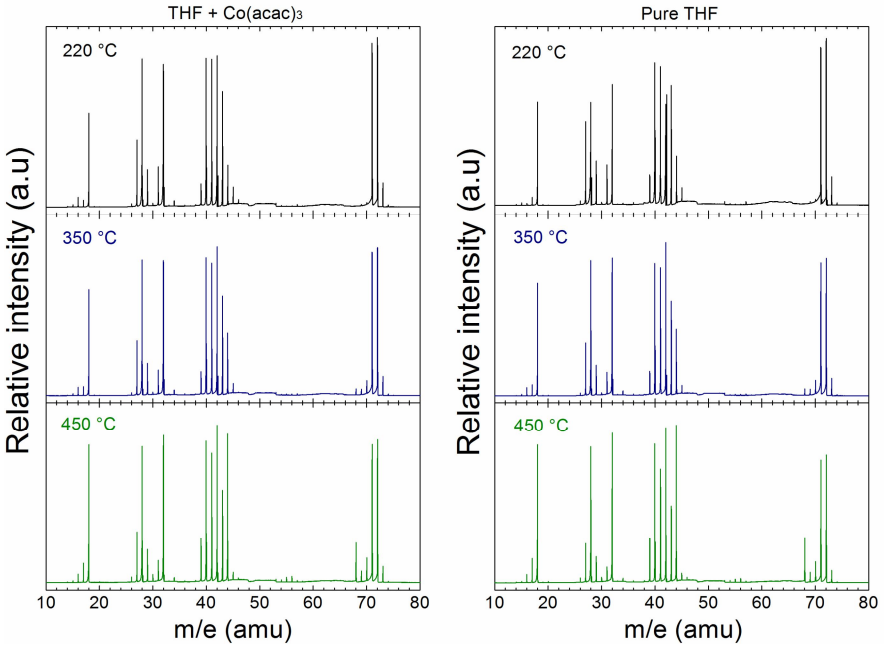

Fig. S4 Gas phase evolution of THF at 220, 350 and 450 °C with and without $Co(acac)_3$.

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Notes to the figures: Electron impact with an energy of 25 eV was used as the ionization source to perform the experimental investigation. In addition to the fragments generated by the high electron energy, some products, such as C_2H_2 in Fig. S1 and CH_3O in Fig. S3 become detectable. At high temperatures (THF as an example, see Fig. S4), pyrolysis as well as oxidation of the solvent are observed by giving more water (m/e = 18), carbon dioxide (m/e = 44), furan (m/e = 68) and other products, which reveals the occurrence of the gas phase reaction. This is also the case for ethanol and toluene (not shown here). These may affect the kinetics of film growth and morphology.

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