

## CoMoS/K catalysts for higher alcohols synthesis from syngas prepared by mechanochemical activation of Molybdenite

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### 1. Synthesis

50 g of Molybdenite ( $\text{MoS}_2$ , Aldrich) is loaded in a 0.4 L mill jar (Roalox Alumina-Fortified Grinding jar, U.S Stoneware) filled 2/3 of the volume with 6.5 mm  $\times$  6.5 mm size of cylindrical alumina grinding media (US Stoneware) with a mass of 825g. The mill jar is placed in a roller equipped with a ¼ horsepower motor (operational range 20-300 RPM) and the ball milling process is conducted with 200 rpm of rolling speed for different durations (24h, 48h, 72h, 1, 2, 3 and 4 weeks).

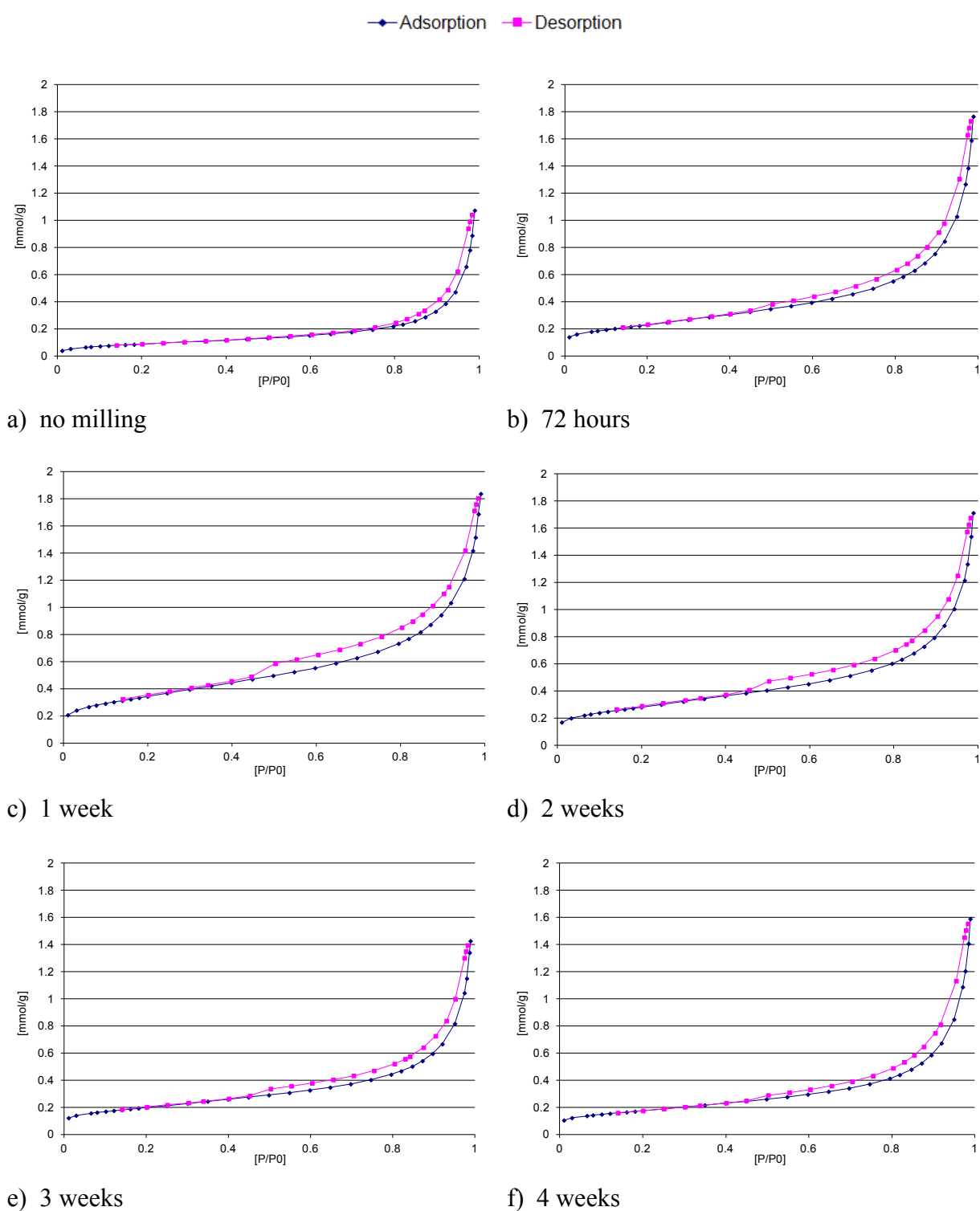
Cobalt sulfide is prepared by co-precipitating 24 ml of 1.17 M aqueous solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.495 mg Co/mg) with 11 ml of 20% aqueous solution of  $(\text{NH}_4)_2\text{S}$ . The precipitate is filtered using a vacuum pump and Whatman Grade 3 (6  $\mu\text{m}$ ) qualitative filter paper, dried at 50°C for 4 hours and calcined at 500°C under  $\text{N}_2$  flow (200 ml/min) and heating rate of 2.5°C/min in a muffle furnace equipped with an enclosed stainless steel compartment. Ball-milled  $\text{MoS}_2$ , cobalt sulfide and  $\text{K}_2\text{CO}_3$  are mixed in a mortar with pestle to obtain  $\text{Mo/Co} = 2$  (mol/mol).  $\text{K}_2\text{CO}_3$  amounts to 10 wt% based on the final catalyst weight. The finished catalysts are potassium promoted cobalt molybdenum sulfides.

### 2. Characterization

All different ball-milled  $\text{MoS}_2$  are characterized by XRD using Scintag X1 with  $\text{Cu K}\alpha = 1.5406$  and 2°/min of scan rate. The mean crystallite size is calculated based on Scherrer equation.

The  $\text{N}_2$  sorption measurements are performed using TriStar II 3020 instrument equipped with a SmartPrep 065, both from Micromeritics. The samples are pretreated under nitrogen at 200°C for 2h using a heating ramp rate of 10°C/min. The TriStar is designed to measure surface area, pore volume and pore distributions.

$\text{N}_2$  adsorption-desorption isotherms are shown in Figure S1. All plots show the Type III isotherm.



**Figure S1.** N<sub>2</sub> Adsorption-desorption isotherms of ball milled samples.

For the SEM measurements, the samples are mounted through a carbon pad onto aluminum SEM stubs. Cross-sectional samples are coated with 10 nm of Cr prior to analysis. The SEM imaging is performed using the FEI 30 XL-FEG SEM.

The HR-TEM (high resolution transmission electron microscopy) are performed using a HRTEM JEOL JEM-2200FS equipped with:

Schottky type field emission gun (FEG)

imaging system aberration corrector (Cs-corrector) from CEOS GmbH

slow scan CCD camera US 1000 Gatan Co, 2048x2048 pixels

HR-TEM mode: point resolution = information limit (at Cs < 5  $\mu\text{m}$ ) = 0.13 nm

The TEM analyses are performed at Gent University, Department of Materials Sciences.

### 3. Catalytic Testing

The catalysts are tested in a high-pressure parallel fixed bed reactor. The quartz reactors are loaded with 250  $\mu\text{l}$  of catalyst and tested with syngas ( $\text{H}_2/\text{CO}$  molar ratio of 1) at 1500 psi, 290-340  $^\circ\text{C}$  at 3000  $\text{h}^{-1}$  GHSV. Table 1 presents the different products distribution at different reaction conditions. For all conditions and catalysts the carbon balances are close to 100%.

*Table 1. Selectivities (%) to products given at different reaction temperatures. Selectivities to HC (all hydrocarbons, both saturated and unsaturated up to  $\text{C}_6$ ), methane, methanol, ethanol and propanol are  $\text{CO}_2$ -free. Overall  $\text{CO}_2$  selectivity is also presented.*

Ball mill Time	T. $^\circ\text{C}$	C. Conv.	$\text{CO}_2$ sel	HC sel.	$\text{CH}_4$ sel	$\text{CH}_3\text{OH}$ sel	$\text{C}_2\text{H}_5\text{OH}$ sel	$\text{C}_3\text{H}_7\text{OH}$ sel
No ball milling	330	1.7	20.7	3.1	3.1	52.0	27.1	6.3
	340	2.2	21.8	4.5	4.5	45.1	27.0	6.8
72 hours milling	290	3.0	16.2	2.8	2.8	63.5	24.3	1.7
	330	14.5	21.5	7.7	7.2	40.2	35.0	4.7
	340	18.5	24.8	10.8	9.9	32.6	35.5	6.7
1 week milling	290	4.5	14.2	2.5	2.5	63.8	28.7	1.1
	330	19.1	21.5	8.0	7.4	39.7	37.5	4.4
	340	23.9	25.1	11.5	10.5	30.9	39.1	6.8
2 weeks milling	290	4.6	13.0	2.4	2.4	68.4	22.4	1.0
	330	19.7	22.1	8.6	7.7	41.1	38.7	4.7
	340	23.7	25.6	11.5	10.4	31.9	40.6	7.0
3 weeks milling	290	5.2	11.5	2.1	2.1	69.1	24.7	0.9
	330	22.0	21.7	8.4	7.5	39.4	41.6	4.6
	340	26.4	25.4	11.7	10.4	30.0	41.0	7.4
4 weeks milling	290	5.5	14.3	4.9	3.7	63.4	25.4	2.6
	330	22.2	24.2	12.1	8.3	35.7	36.6	9.0
	340	26.0	27.3	16.0	10.3	27.3	35.0	13.8

For comparison we add the catalytic performance of KCoMoS prepared with a conventional

coprecipitation using a more expensive Mo precursor like: ammoniumtetrathiomolybdate.<sup>1</sup>

*Table 2. Selectivities (%) to products given at different reaction temperatures for KCoMoS prepared by coprecipitation. Selectivities to HC (all hydrocarbons, both saturated and unsaturated up to C<sub>6</sub>), methane, methanol, ethanol and propanol are CO<sub>2</sub>-free. Overall CO<sub>2</sub> selectivity is also presented.*

<b>T. °C</b>	<b>C. Conv.</b>	<b>CO<sub>2</sub> sel</b>	<b>HC sel.</b>	<b>CH<sub>4</sub> sel</b>	<b>CH<sub>3</sub>OH sel</b>	<b>C<sub>2</sub>H<sub>5</sub>OH sel</b>	<b>C<sub>3</sub>H<sub>7</sub>OH sel</b>
330	30.4	32.0	23.6	12.9	20.4	31.9	13.9
340	35.9	35.5	32.3	15.7	15.3	24.9	14.0

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<sup>1</sup> D. L.S. Nieskens, D. Ferrari, Y. Liu and R. Kolonko Jr., Catal. commun., 2011, **14**, 111