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Mechanochemical Reactions in Cu/ZnO Catalysts Induced by Mechanical Milling

Hessel L. Castricum,^{*,‡} Hans Bakker,[‡] Bart van der Linden,[‡] and Eduard K. Poels[‡]

Van der Waals-Zeeman Instituut, Faculty of Science, Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands, and Department of Chemical Engineering, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

Preparation of Cu/ZnO catalysts is discussed in which mechanochemical reactions are involved. These reactions include oxidation of copper and copper oxides during milling in the presence of oxygen, reduction under vacuum, and formation of carbonates in CO₂. Oxidation and reduction are promoted by the presence of ZnO. Formation of Cu₂O-like intermediates is suggested in oxidic mixtures, which are not observed when milling occurs without ZnO. This effect may be partly due to defect formation. The various resulting copper species reduce at different temperatures in H₂ atmosphere and this gives an indication for the intimacy of the Cu-Zn interaction. When milling is carried out in the presence of CO₂, mixed carbonates are formed. Intimate mixtures of Cu and Zn are thus obtained, exhibiting high surface areas after reduction that can be explained by evolved porosity. A linear relation between Cu₀ surface area and activity for methanol synthesis at 2 bar is observed. Irreversible deactivation is explained by over-reduction and sintering. Both Cu₀ specific surfaces and BET surfaces (determined after reduction in hydrogen) are substantially increased for all milled Cu/ZnO samples, but especially for samples that undergo mechanochemical reactions. This method thus allows investigation of mixed oxide catalyst precursors and provides an interesting alternative for the preparation of promoted heterogeneous catalysts.

TABLE 1: Analytical data of unmilled and milled Cu, Cu₂O and CuO samples.

Sample	Milling	Relative	Mean	% CuO	% CuO	$T_{\text{Max. reduction}}$
	conditions	crystalline	particle size	reduced	reduced	(TGA)
		fraction [a.u.]	[μm]	(TGA)	(TPR)	[K]
Cu	unmilled	46	11.7	5.4	-	402
Cu	synth. air	25	9.3	99.6	-	408
Cu	CO ₂	27	-	1.2	-	368
Cu ₂ O	unmilled	44	8.5	50.1	-	515
Cu ₂ O	vacuum	36	-	52.2	-	408
Cu ₂ O	synth. air	24	-	108.3	-	406
Cu ₂ O	CO ₂	39	11.6	49.9	-	397
CuO	unmilled	48	16.2	101.2	100	414
CuO	vacuum	27	10.7	95.4	85	404
CuO	synth. air	15	10.0	103.6	-	410
CuO	CO ₂	6.6	13.6	97.2	98	407

TABLE 2: Cu⁰ and BET surface areas after H₂ reduction of unmilled and milled Cu, Cu₂O and CuO samples.

Cu ⁰ surface area (N ₂ O) [m ² /g]	Unmilled	Vacuum	Synth. Air	CO ₂
Cu	0.6	-	2.1	0.5
Cu ₂ O	0.4	2.1	1.9	0.4
CuO	2.2	15.4	19.2	10.0
BET surface area (N ₂) [m ² /g]				
CuO	4.9	28	31	17

TABLE 3: Analytical data of unmilled and milled ZnO samples.

Milling conditions	Relative crystalline fraction [a.u.]	Mean particle size [μm]	BET surf. area [m ² /g]	% metallic contamination
Unmilled	56	15.0	3.0	0.05
Vacuum	34	11.6	4.2	1.2
synth.air	37	13.0	6.0	0.5
CO ₂	35	10.5	8.4	0.1

TABLE 4: Analytical data of Cu, Cu₂O or CuO, and ZnO containing samples milled under vacuum or in synthetic air. (For * see text.)

Sample	Milling conditions	Relative crystalline fraction [a.u.]	% reduced CuO (TGA)	% reduced CuO (TPR)	$T_{\text{Max. Reduction}}$ (TGA) [K]	Average $T_{\text{Reduction}}$ (TPR) [K]
Cu/ZnO	synth. air	18	104.9	107	432	484
Cu ₂ O/ZnO	vacuum	28	43.7	45	383	435
Cu ₂ O/ZnO	synth. air	21	94.4	98	414*, 442	480
CuO/ZnO	vacuum	24	91.0	93	412*	459
CuO/ZnO	synth. air	28	105.7	103	409*	443

TABLE 5: Analytical data of Cu, Cu₂O or CuO, and ZnO containing samples milled in the presence of CO₂.

Sample	Milling conditions	% CO ₃ ²⁻	Average $T_{\text{Decomp.}}$ CO ₃ ²⁻ [K]	$\Delta H_{\text{Decomp.}}$ [kJ/mol CO ₃ ²⁻]	% CuO (DSC/ TGA)	% CuO (TPR)	Average $T_{\text{reduction}}$ (TPR) [K]
Cu/ZnO	CO ₂	26.8	612	335	6	5	402
Cu/ZnO	s.a.+CO ₂	20.8	676	528	63	68	421
Cu ₂ O/ZnO	CO ₂	31.4	610	345	36	34	405
Cu ₂ O/ZnO	s.a.+CO ₂	33.4	743	622	88	94	429
CuO/ZnO	CO ₂	44.4	732	577	86	81	423
CuO/ZnO	s.a.+CO ₂	33.6	709	613	92	99	427

TABLE 6: Cu⁰ and BET surface areas after H₂ reduction of samples in which Cu and Zn precursors were milled separately and subsequently physically mixed (‘+’) and milled together (‘/’).

Cu ⁰ area	Unmilled	Vacuum	Synth. Air	CO ₂	s.a.+CO ₂
Cu + ZnO	0.2	<0.1	0.5	0.2	-
Cu/ZnO		0.4	7.2	17	31
Cu ₂ O + ZnO	0.1	0.5	0.5	0.1	-
Cu ₂ O/ZnO		6.4	8.8	36	44
CuO + ZnO	0.6	3.9	4.8	2.5	-
CuO/ZnO		11.1	11.3	42	37
BET area					
CuO + ZnO	3.5	10.2	12.3	18.3	-
CuO/ZnO		29	24	69	59

TABLE 7: Methanol synthesis rate and Turnover Frequencies (TOF) for a CO/H₂ mixture (1:2) at 2 bar and a flow of 7.5 ml/min. (*: equilibrium conversion is reached at the applied conditions)

Sample	Milling conditions	Rate (523 K) [nmol/s]	TOF (523 K) [10 ⁻⁶ molec./ (Cu ⁰ site-s)]	TOF (498 K)	TOF (473 K)
Cu/ZnO	s.a.	3.1	76	-	-
Cu/ZnO	CO ₂	4.1	46	46	25
Cu/ZnO	s.a.+CO ₂	5.4*	33*	45	33
Cu ₂ O/ZnO	vacuum	2.0	54	41	31
Cu ₂ O/ZnO	s.a.	2.8	56	-	-
Cu ₂ O/ZnO	CO ₂	5.3*	29*	40	25
Cu ₂ O/ZnO	s.a.+CO ₂	5.9*	27*	38	30
CuO/ZnO	vacuum	2.9	45	-	-
CuO/ZnO	s.a.	5.2	82	-	-
CuO/ZnO	s.a.+CO ₂	5.7*	32*	46	35
Average			60	43	30

Figure 1. XRD patterns of Cu: (a) as-received, (b) milled in synthetic air and (c) in CO₂.

Figure 2. XRD patterns of Cu₂O: (a) as-received, (b) milled under vacuum, (c) in synthetic air and (d) in CO₂.

Figure 3. XRD patterns of CuO: (a) as-received, (b) milled under vacuum, (c) in synthetic air and (d) in CO₂.

Figure 4. XRD patterns of milled (a) Cu/ZnO/s.a., (b) Cu₂O/ZnO/vac, (c) Cu₂O/ZnO/s.a., (d) CuO/ZnO/vac and (e) CuO/ZnO/s.a. The patterns are plotted on a logarithmic scale. ZnO peaks are represented by ♦.

Figure 5. TE Micrograph of Cu₂O/ZnO milled in synthetic air.

Figure 6. TPR H₂-consumption patterns of (a) Cu/ZnO/s.a., (b) Cu₂O/ZnO/vac, (c) Cu₂O/ZnO/s.a., (d) CuO/ZnO/vac and (e) CuO/ZnO/s.a.

Figure 7. TGA reduction profiles of (a) unmilled Cu/ZnO, (b) Cu/ZnO/s.a., (c) unmilled Cu₂O/ZnO, (d) Cu₂O/ZnO/vac, (e) Cu₂O/ZnO/s.a., (f) unmilled CuO/ZnO, (g) CuO/ZnO/vac and (h) CuO/ZnO/s.a.

Figure 8. XRD patterns of milled (a) Cu/ZnO/CO₂, (b) Cu/ZnO/s.a.+CO₂, (c) Cu₂O/ZnO/CO₂, (d) Cu₂O/ZnO/s.a.+CO₂, (e) CuO/ZnO/CO₂ and (f) CuO/ZnO/s.a.+CO₂. The patterns are plotted on a logarithmic scale. ZnO peaks are represented by ♦.

Figure 9. DSC traces showing decomposition of: (a) Cu/ZnO/CO₂, (b) Cu/ZnO/s.a+CO₂, (c) Cu₂O/ZnO/CO₂, (d) Cu₂O/ZnO/s.a.+CO₂, (e) CuO/ZnO/CO₂ and (f) CuO/ZnO/s.a.+CO₂.

Figure 10. TE Micrograph of Cu₂O/ZnO milled in synthetic air + CO₂.

Figure 11. TPR H₂-consumption patterns of (a) Cu/ZnO/CO₂, (b) Cu/ZnO/s.a+CO₂, (c) Cu₂O/ZnO/CO₂, (d) Cu₂O/ZnO/s.a.+CO₂, (e) CuO/ZnO/CO₂ and (f) CuO/ZnO/s.a.+CO₂.

Figure 12. TE Micrograph of Cu₂O/ZnO milled in synthetic air + CO₂, after reduction in H₂.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12