

Direct dehydration of 1,3-butanediol into butadiene over aluminosilicate catalysts

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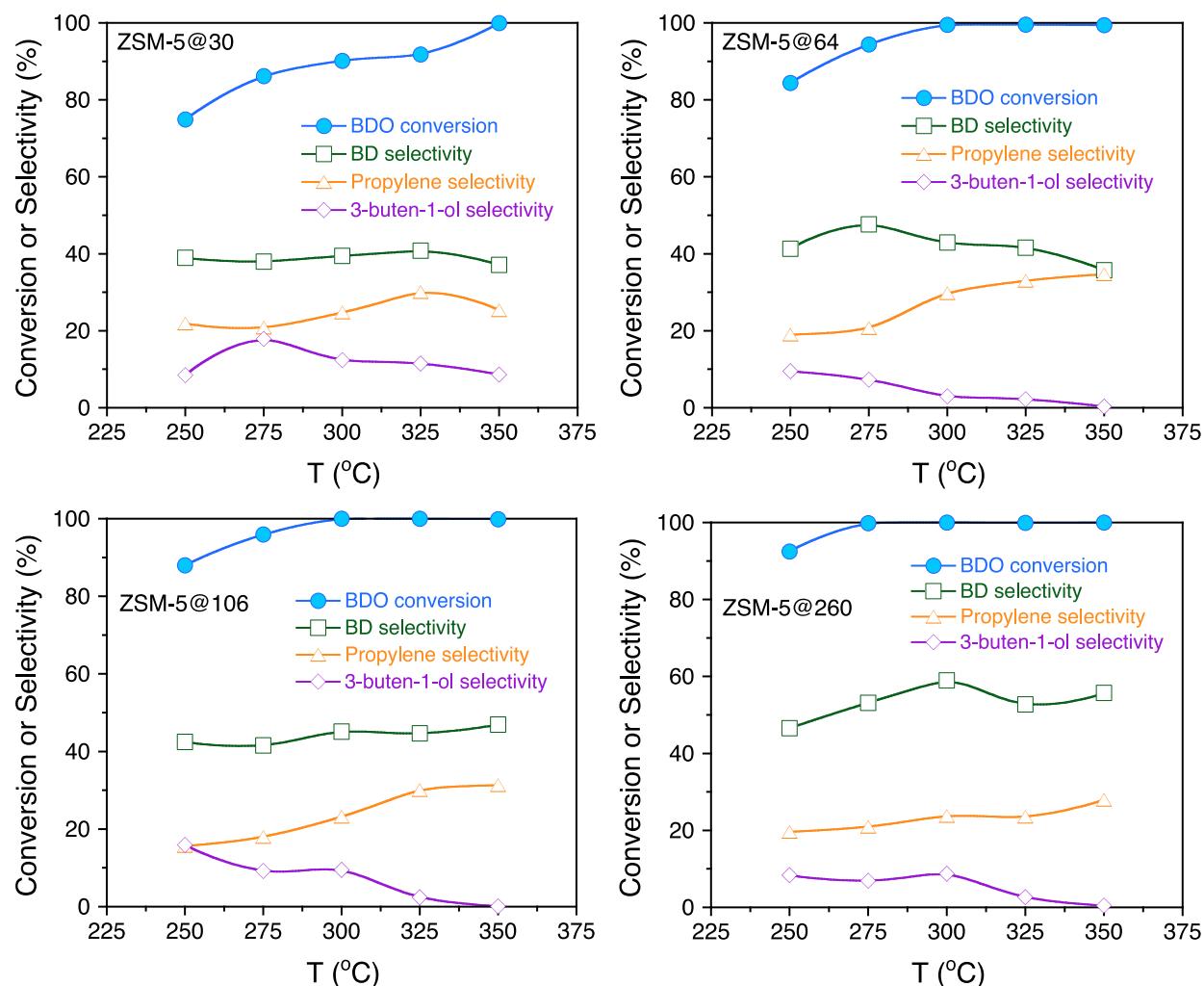
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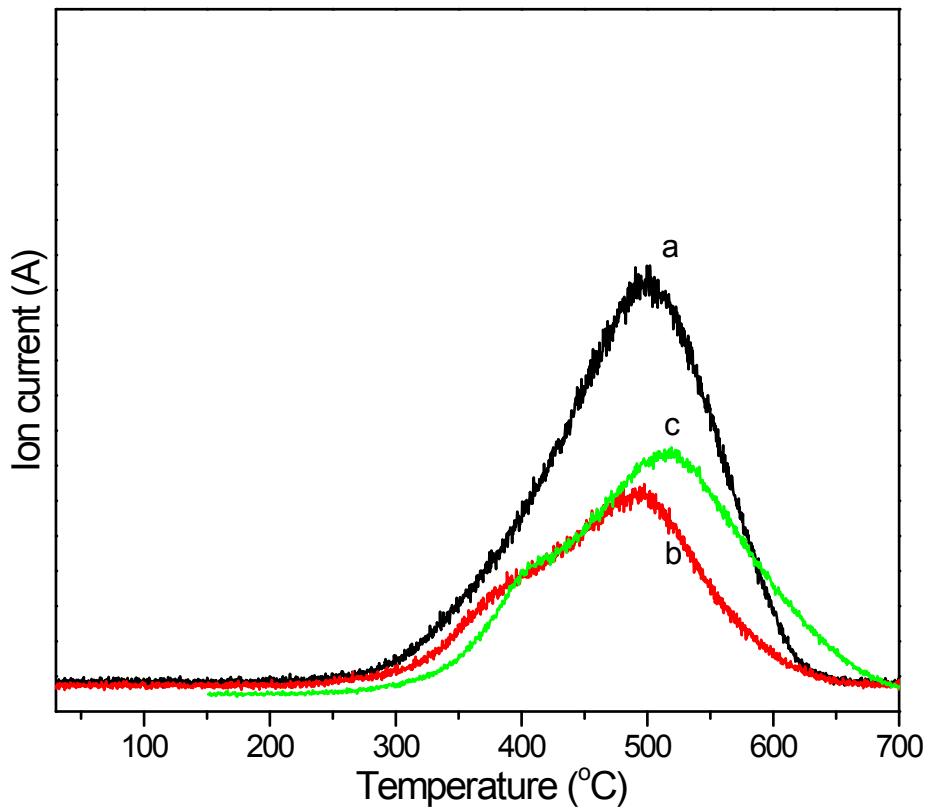


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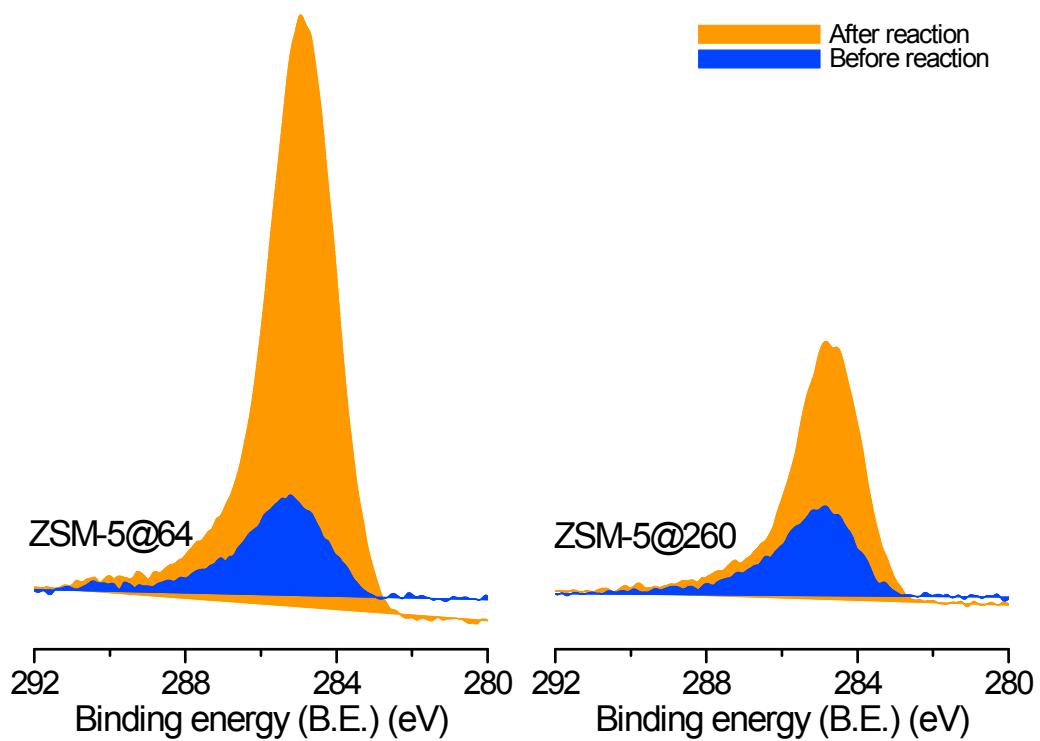


Figure S3. C1s spectra of the spent ZSM-5@64 and ZSM-5@260 catalysts after 8 h reaction. Reaction conditions as in Figure S1.

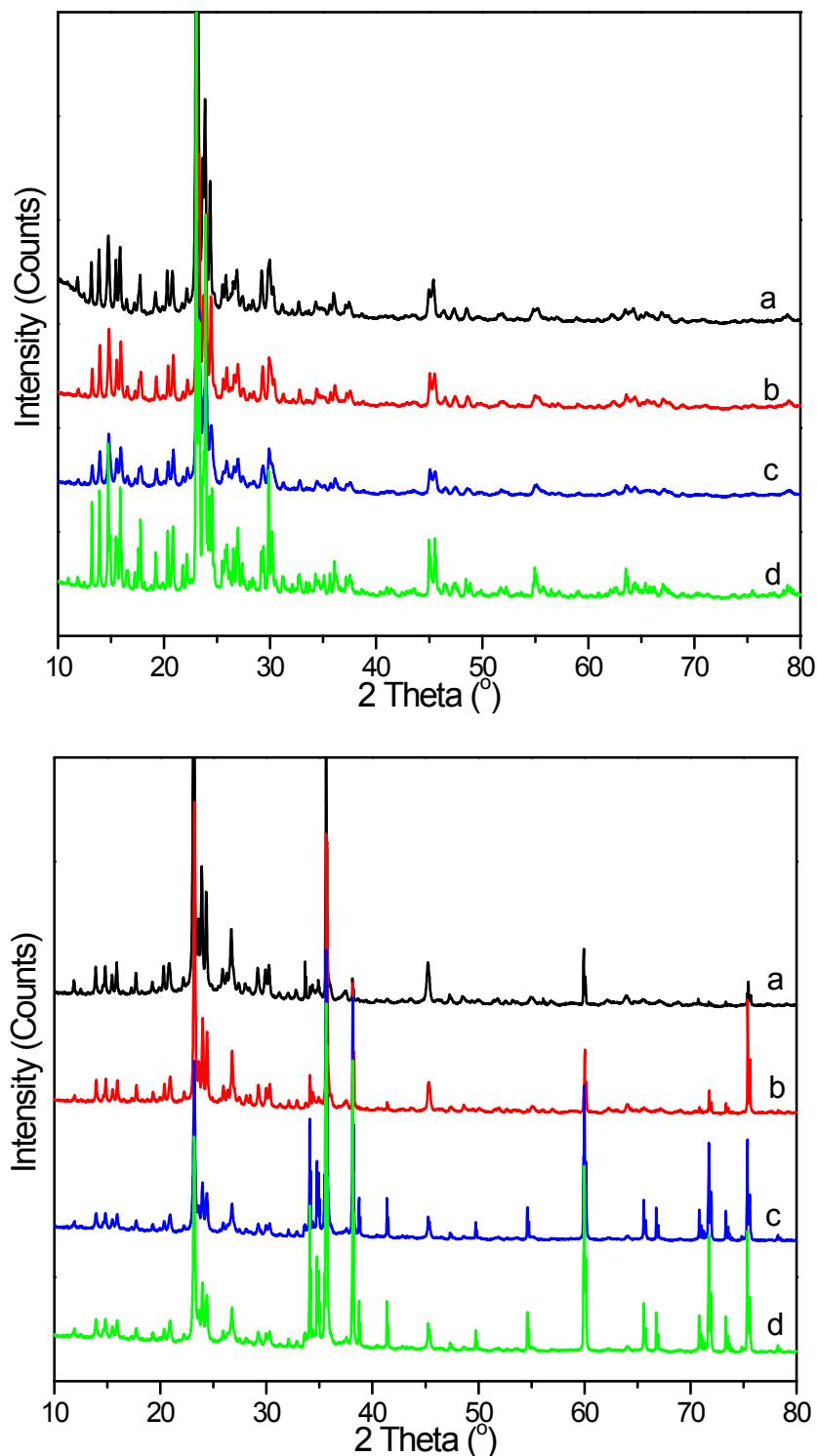


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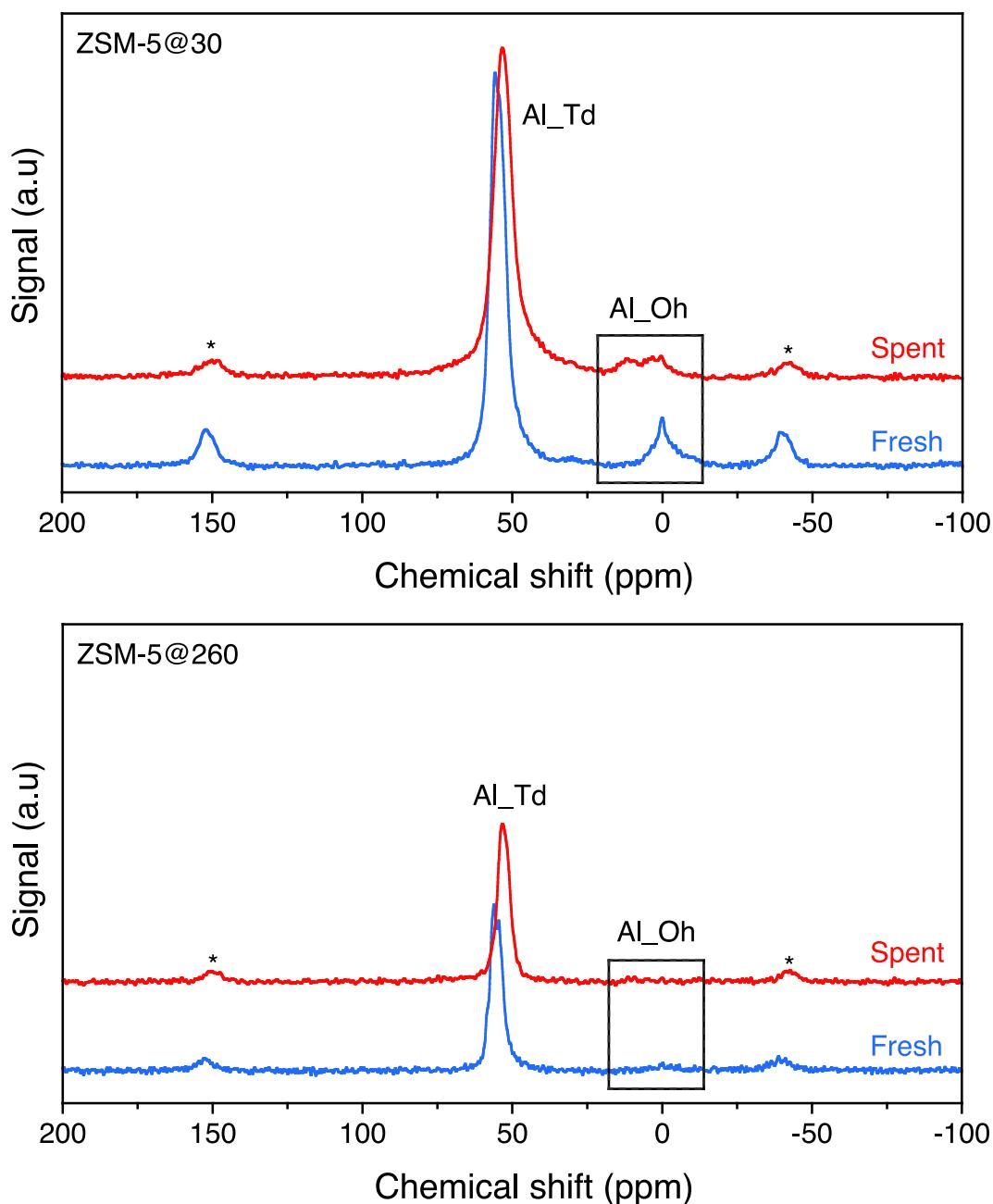


Figure S5. ^{27}Al -NMR MAS spectra on the fresh and spent ZSM5@64 and ZSM5@280 catalysts. The asterisks indicate spinning sidebands. Reaction conditions as in Figure S1.

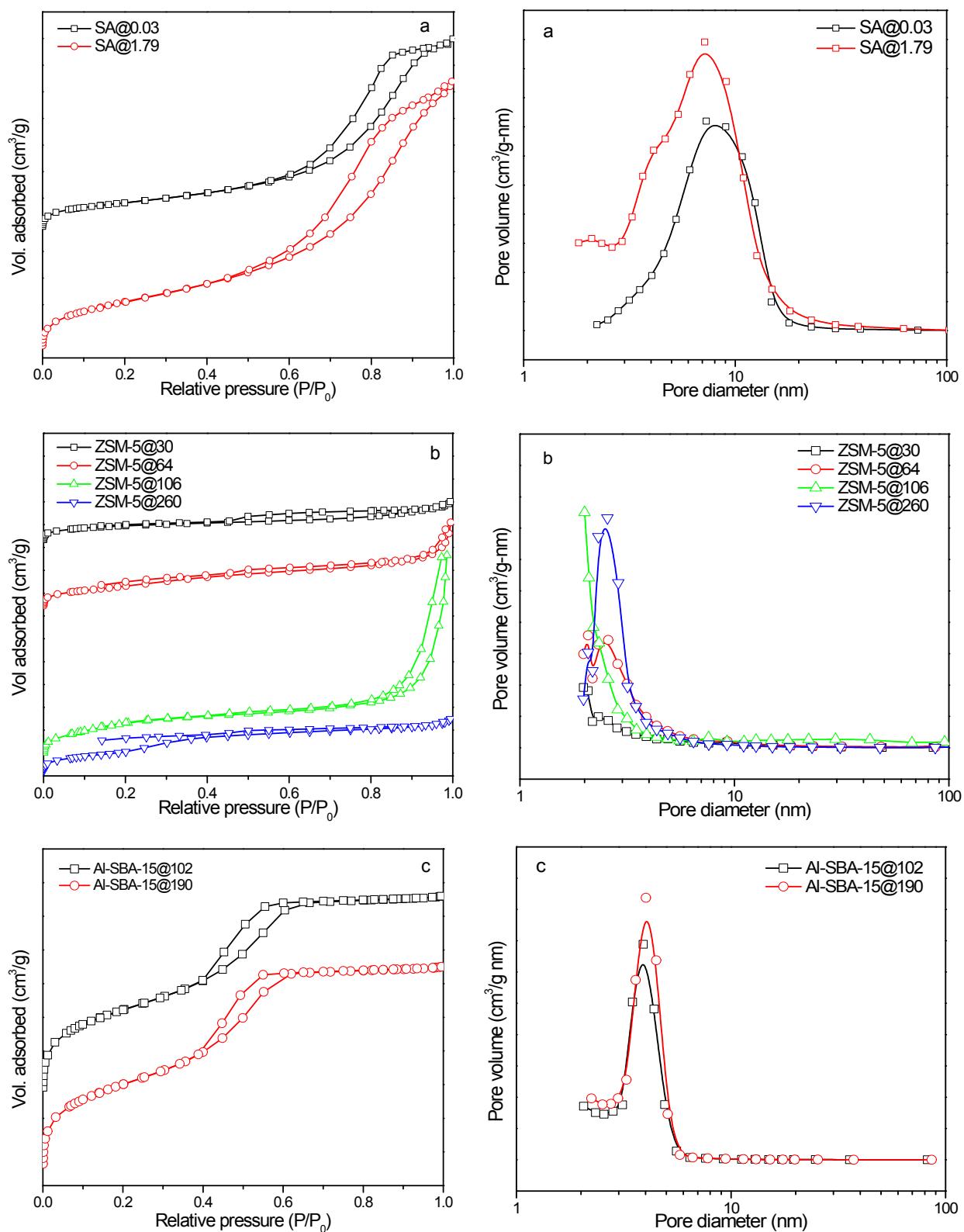


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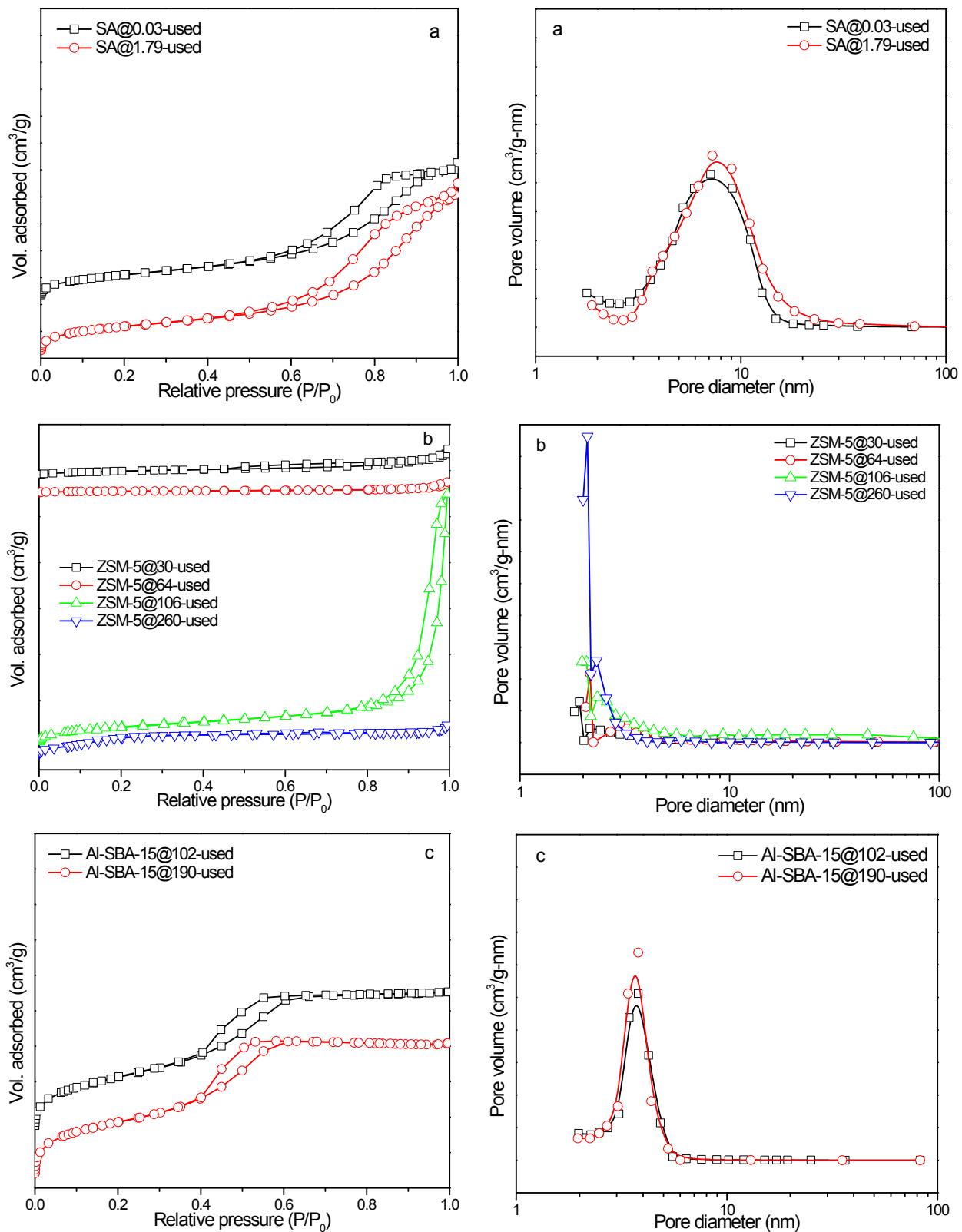


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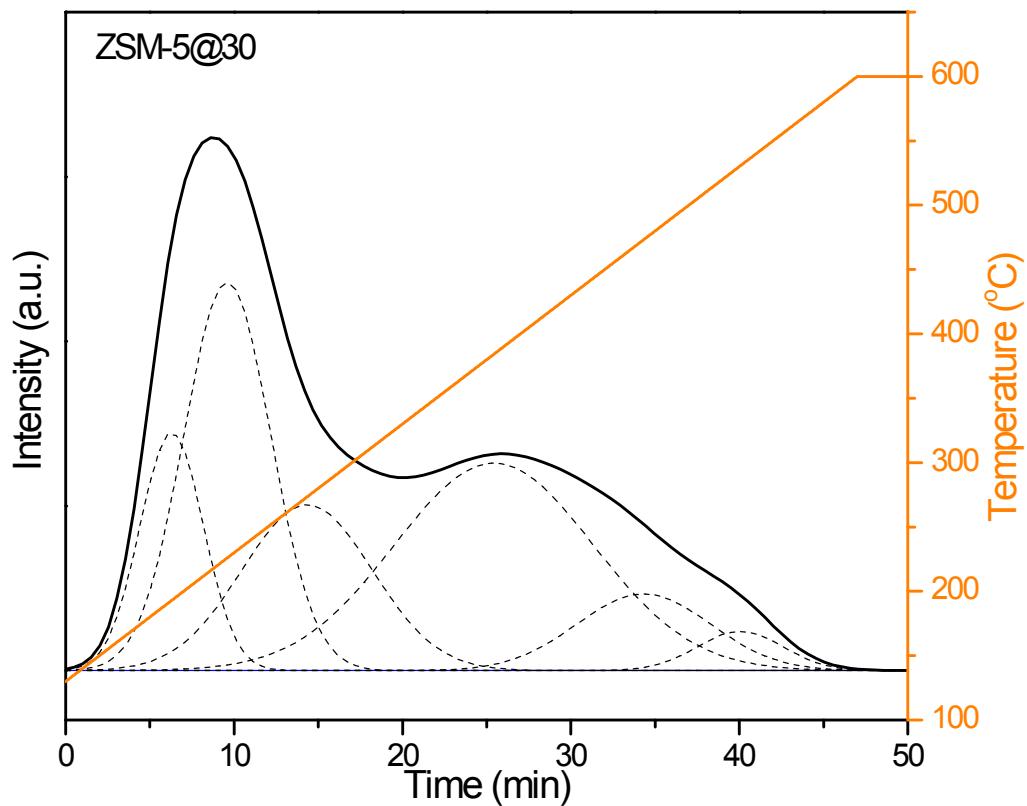


Figure S8. Example of deconvoluted NH_3 -TPD spectrum for the fresh ZSM-5@30.

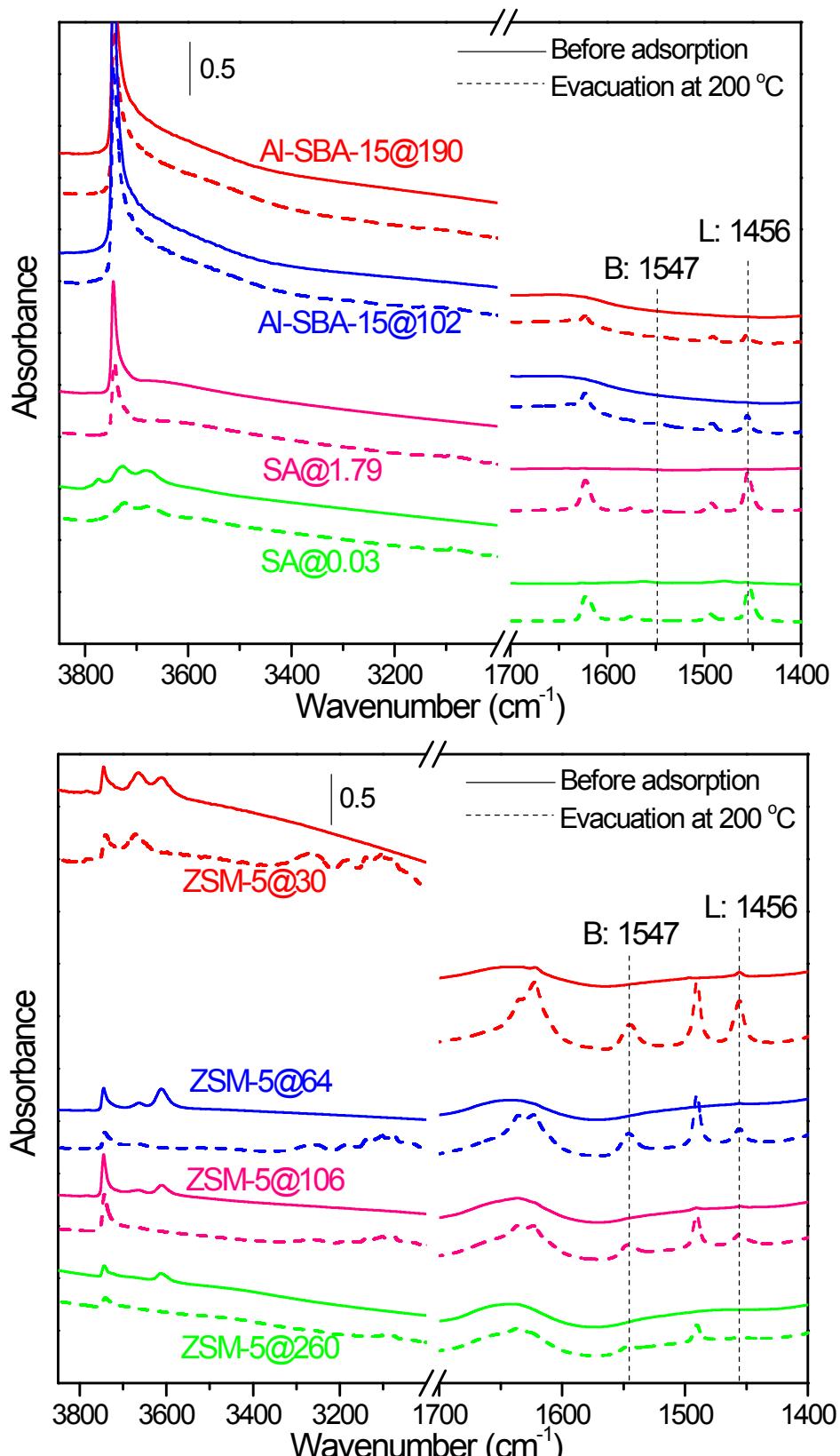


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TABLESTable S1. SiO₂/Al₂O₃ molar ratios of the different aluminosilicates measured by XRF

Catalyst	Theoretical molar ratio SiO ₂ /Al ₂ O ₃	Percentage (mol.%) Al	Percentage (mol.%) Si	Actual ratio SiO ₂ /Al ₂ O ₃
SA@0.03	0.02	98.42	1.58	0.03
SA@1.79	1.13	52.76	47.24	1.79
ZSM-5@30	23	6.29	93.71	30
ZSM-5@64	50	3.01	96.99	64
ZSM-5@106	90	1.85	98.15	106
ZSM-5@260	280	0.76	99.24	260
Al-SBA-15@102	100	1.93	98.07	102
Al-SBA-15@190	200	1.04	98.94	190

Table S2. BD yield ratios as a function of temperature for 1,3-BDO dehydration over aluminosilicate catalysts*

Catalyst	250 °C	275 °C	300 °C	325 °C	350 °C
SA@0.03	9.0	14	5.4	4.2	6.5
SA@1.79	29	27	33	23	16
ZSM-5@30	29	33	36	37	37
ZSM-5@64	35	45	43	41	36
ZSM-5@106	37	40	45	45	47
ZSM-5@260	43	53	60	53	56
Al-SBA-15@102	57	-	53	-	-
Al-SBA-15@190	57	-	52	-	-

* Reaction conditions: ambient pressure, time on stream, 8 h; catalyst loading, 200 mg; liquid flowrate, 2.8 mL/h; carrier gas flowrate, 60 mL(STP)/min.

Table S3. BD/propylene selectivity ratios as a function of temperature for 1,3-BDO dehydration over aluminosilicate catalysts*

Catalyst	250 °C	275 °C	300 °C	325 °C	350 °C
SA@0.03	0.42	0.27	0.09	0.10	0.14
SA@1.79	1.89	1.08	0.94	0.63	0.62
ZSM-5@30	1.78	1.82	1.59	1.36	1.46
ZSM-5@64	2.17	2.30	1.44	1.26	1.03
ZSM-5@106	2.71	2.31	1.95	1.48	1.50
ZSM-5@260	2.37	2.53	2.48	2.24	1.99
Al-SBA-15@102	2.41	-	1.34	-	-
Al-SBA-15@190	2.42	-	1.30	-	-

* **Reaction conditions:** ambient pressure, time on stream, 8 h; catalyst loading, 200 mg; liquid flowrate, 2.8 mL/h; carrier gas flowrate, 60 mL(STP)/min.

Table S4. Sum of selectivities as a function of temperature for 1,3-BDO dehydration over aluminosilicate catalysts*

Catalyst	250 °C	275 °C	300 °C	325 °C	350 °C
SA@0.03	49	80	81	49	65
SA@1.79	74	66	72	63	45
ZSM-5@30	72	77	81	86	75
ZSM-5@64	73	80	81	81	74
ZSM-5@106	81	79	91	89	87
ZSM-5@260	76	81	92	83	84
Al-SBA-15@102	88	-	97	-	-
Al-SBA-15@190	86	-	97	-	-

* **Reaction conditions:** ambient pressure, time on stream, 8 h; catalyst loading, 200 mg; liquid flowrate, 2.8 mL/h; carrier gas flowrate, 60 mL(STP)/min.

Table S5. Catalytic performance of aluminosilicate catalysts for 1,3-BDO dehydration at 250 °C.

Catalyst	1,3-BDO conversion (%)	Selectivity (%) ^a			BD productivity (g _{BD} .g _{cat} ⁻¹ .h ⁻¹)	Carbon balance (-)
		3B1ol	propylene	BD		
SA@0.03	77	6.8	34	14	0.76	0.74
SA@1.79	88	14	17	33	2.4	0.84
ZSM-5@30	75	8.6	22	39	2.5	0.79
ZSM-5@64	85	9.4	19	42	2.9	0.83
ZSM-5@106	88	12	16	43	3.2	0.77
ZSM-5@260	92	8.3	20	47	3.6	0.81
Al-SBA-15@102	100	4.9	24	57	4.8	0.88
Al-SBA-15@190	100	6.0	23	57	4.8	0.88

Reaction conditions: T, 250°C; ambient pressure, time on stream, 8 h; catalyst loading, 200 mg; liquid flowrate, 2.8 mL/h; carrier gas flowrate, 60 mL(STP)/min.

^a Additional minor products detected (selectivity <5%): methyl ethyl ketone, methyl vinyl ketone, 2-butanol, 1-butanol and 3-buten-2-ol.