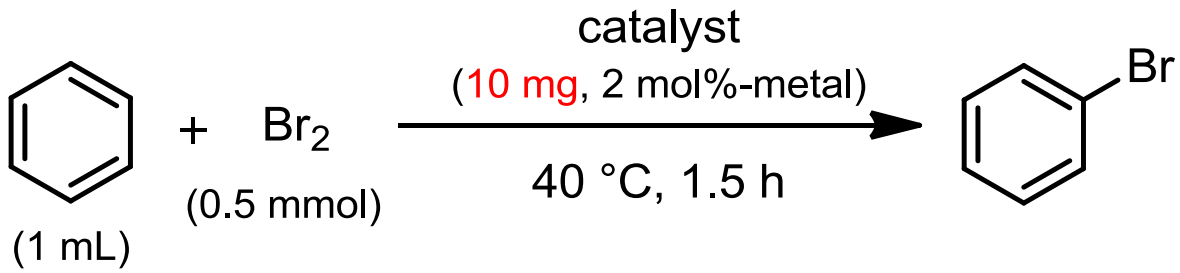
Fe-Zeolite as Catalyst for Bromination of Benzenes

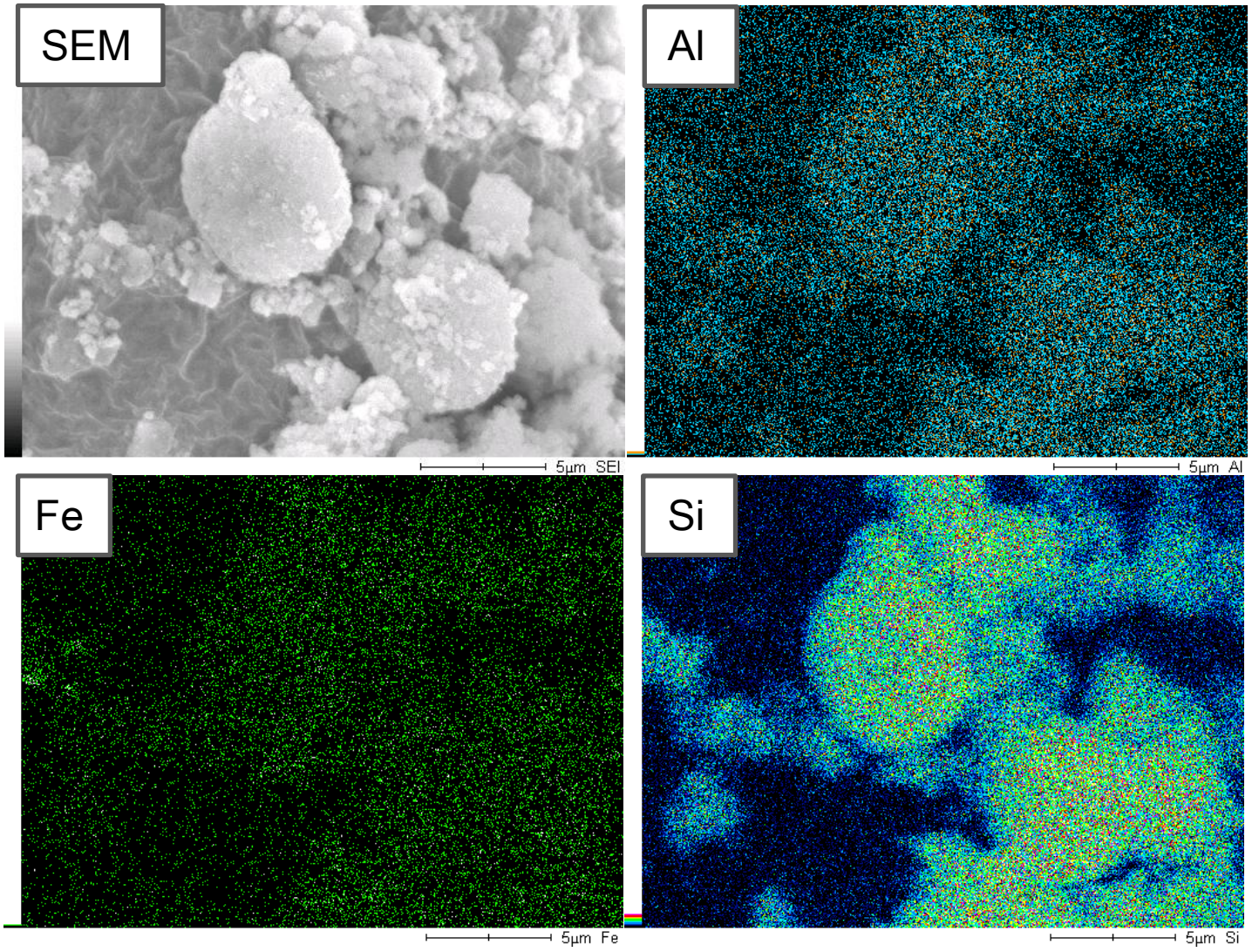


entry	catalyst[a]	Yield / %[b]
1	Fe_2O_3/zeolite	>99
2	ZnO_x/zeolite	77
3	CoO_x/zeolite	16
4	MnO_x/zeolite	30
5	CuO_x/zeolite	28
6	FeO_x/SiO_2	1
7	FeO_x/Al_2O_3	69

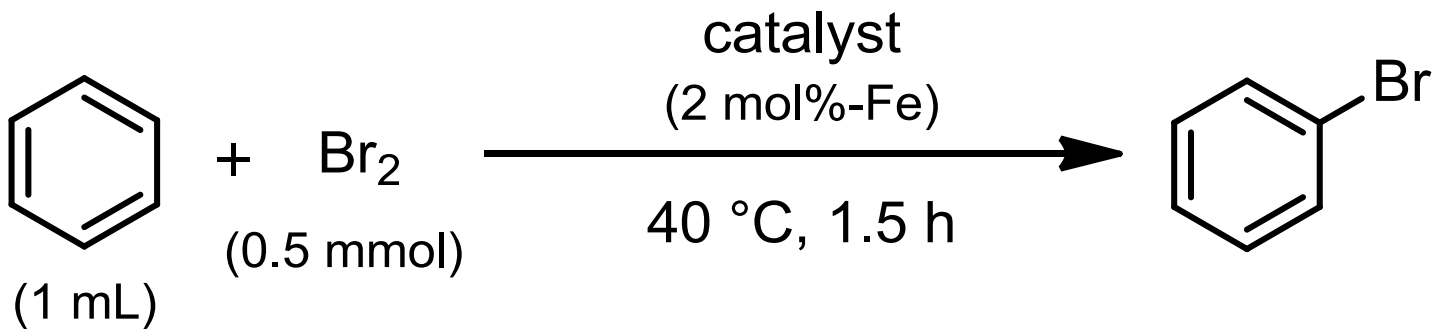
[a] 1mmol of metal was supported on 1 g of zeolite. [b] GC yield.

⇢ **Fe_2O_3/zeolite showed highest catalyst activity.**

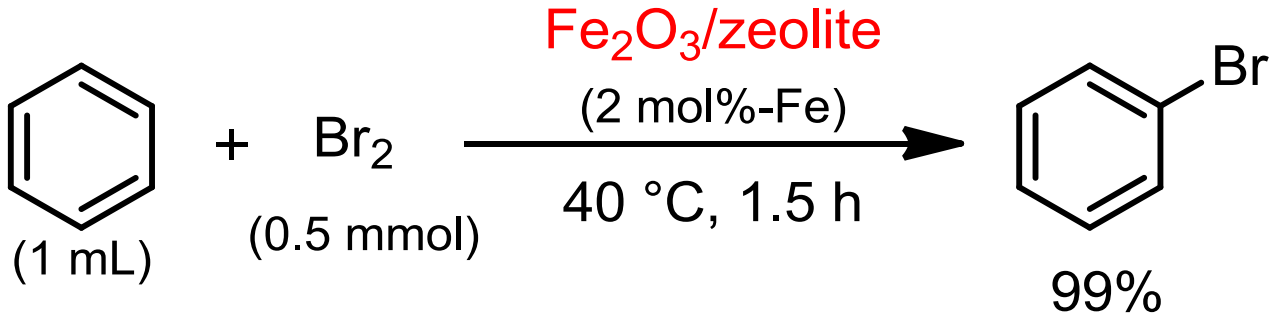
Elemental Analysis of Fe/zeolite

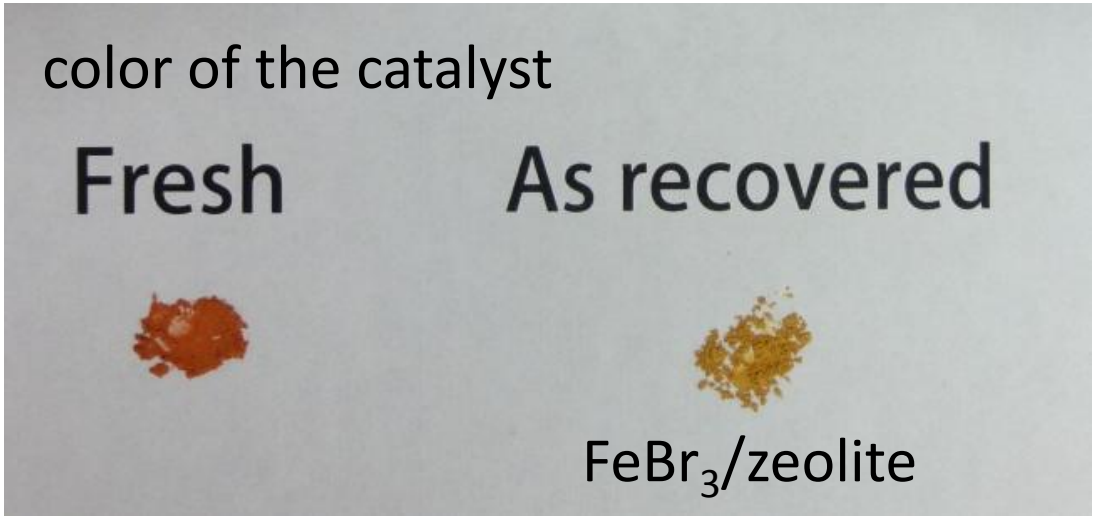


Fe is homogeneously distributed like as Al and Si



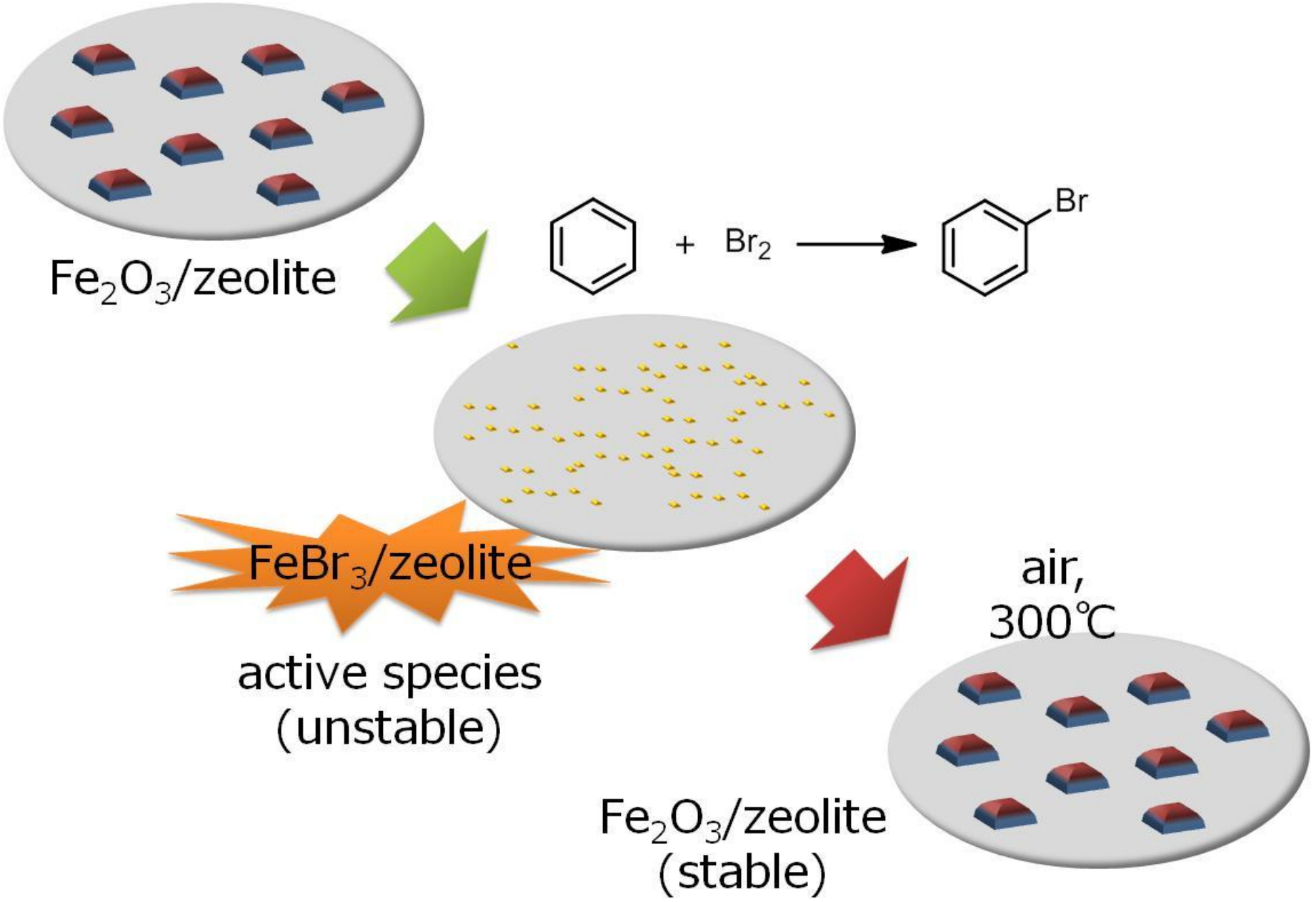
entry	catalyst[a]	Yield / %[b]
1	Fe_2O_3/zeolite	>99
2	Fe_2O_3	1
3	zeolite	36
4	$FeBr_3$	94
5	$FeBr_3 \cdot 6H_2O$	7



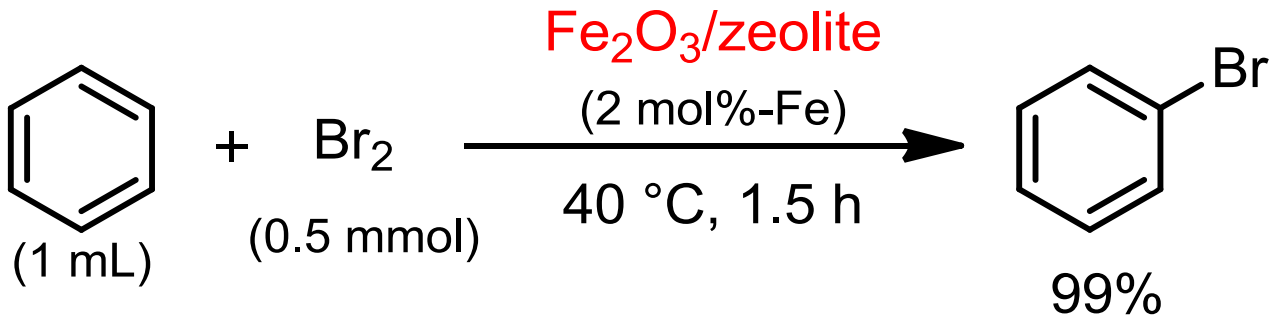


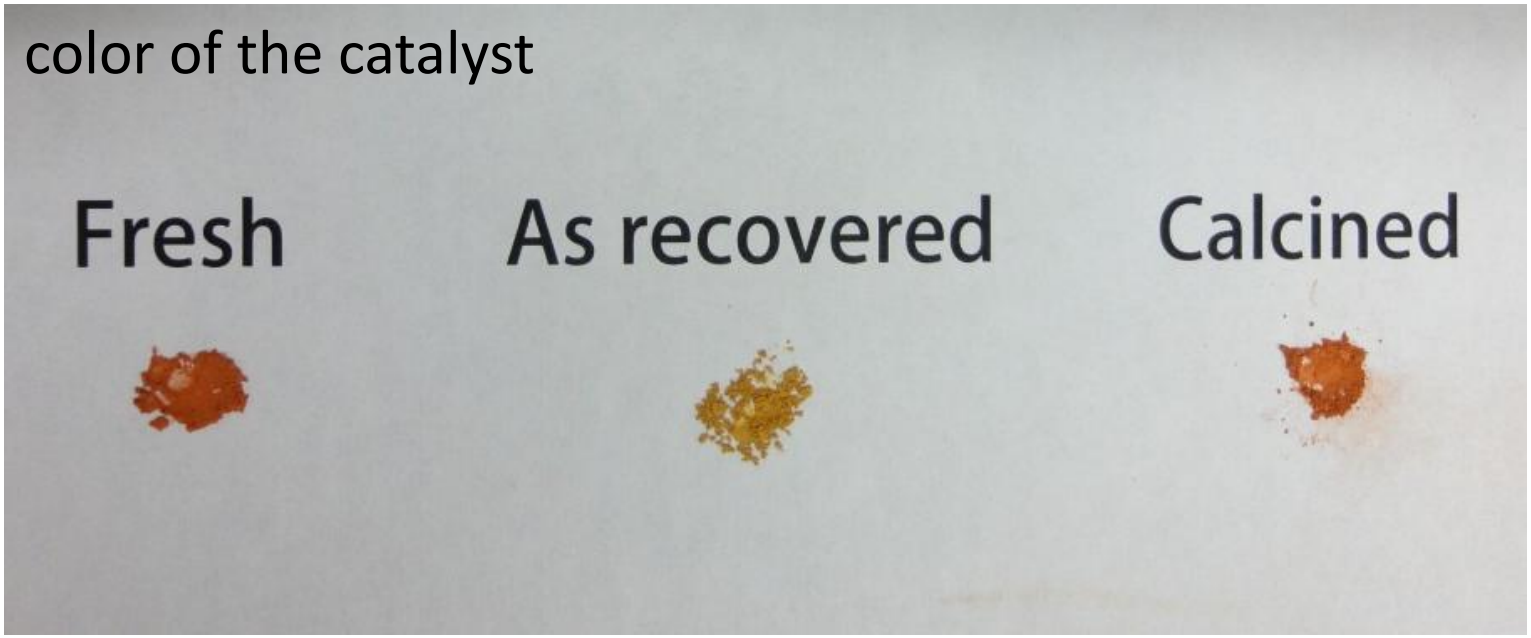
deactivated in air
impossible to reuse

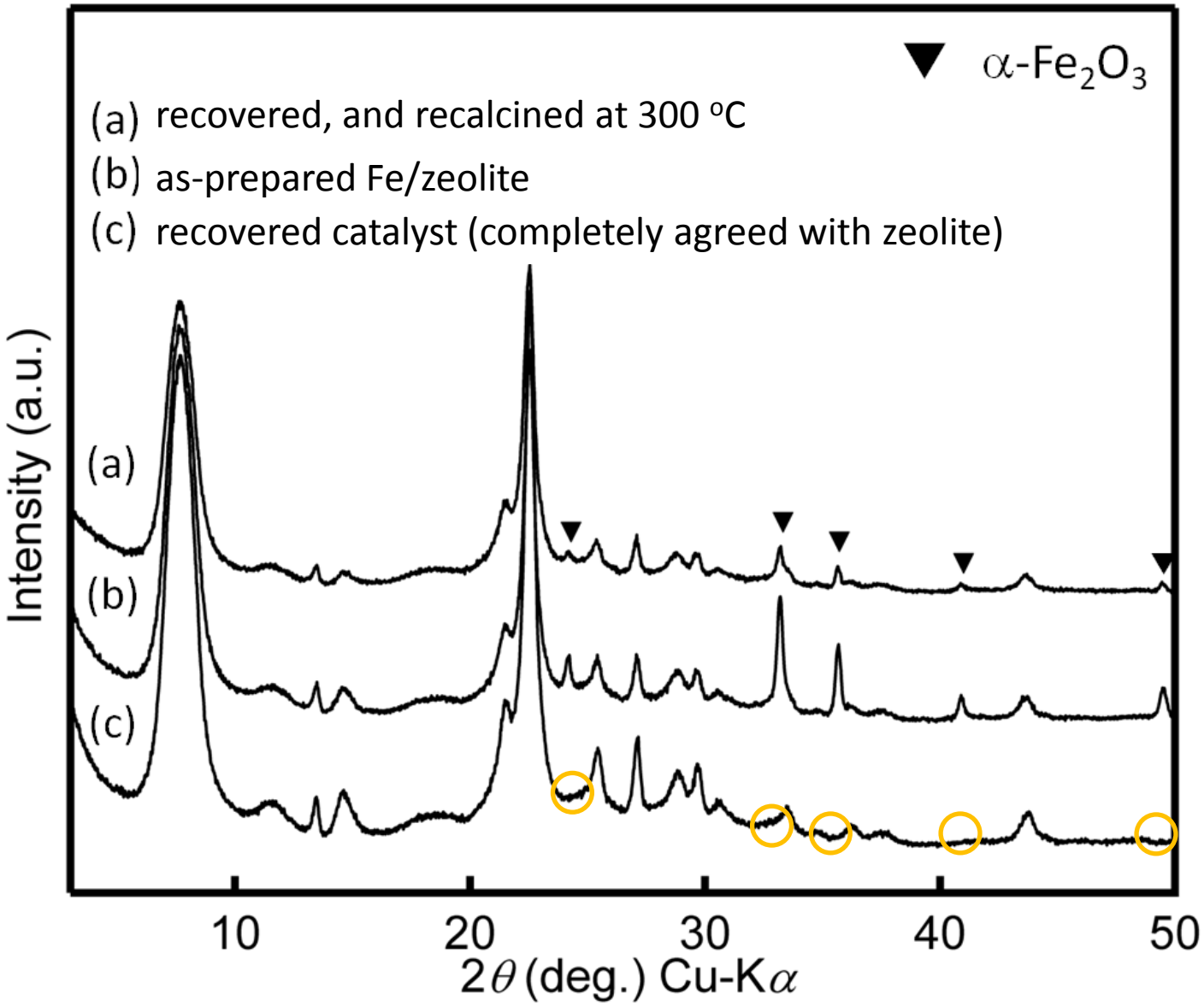
$FeBr_3 \cdot 6H_2O$ formation

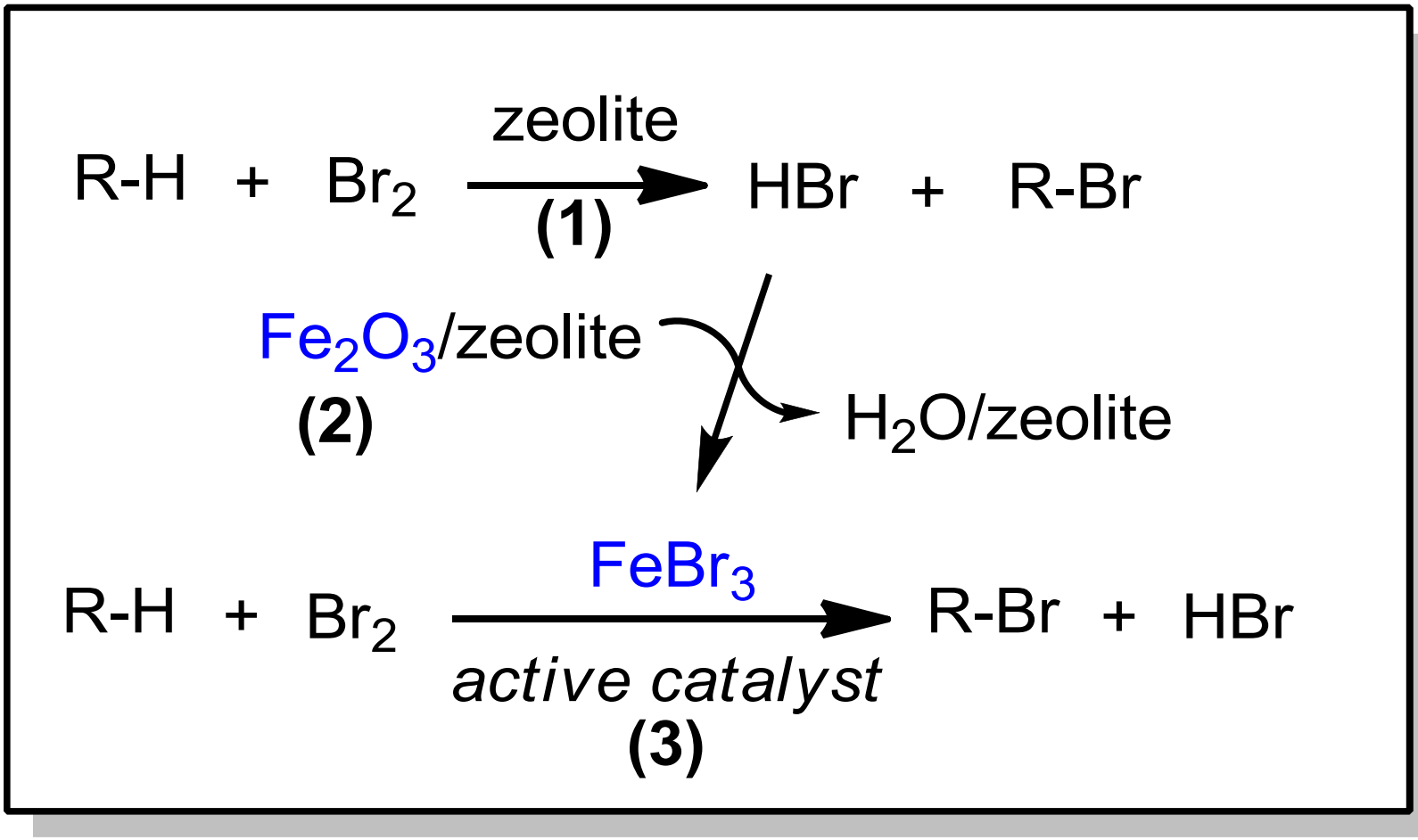

Fe2O3/zeolite
+ Br2
Br
FeBr3/zeolite
active species
(unstable)
air,
300℃
Fe2O3/zeolite
(stable)

Catalyst Recycling





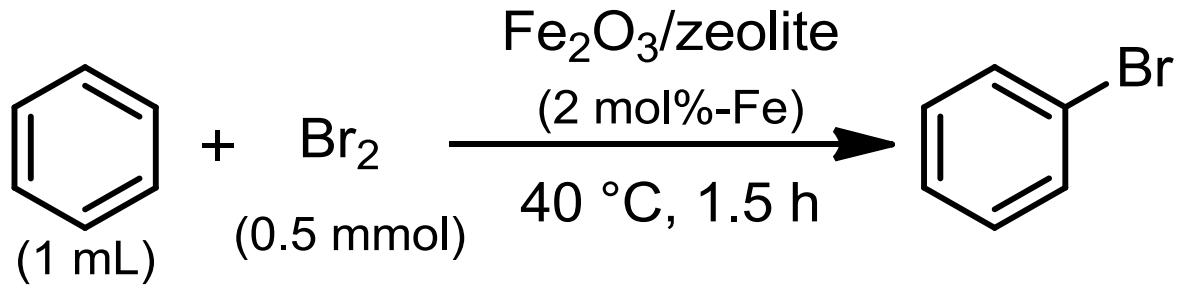

▼ α-Fe2O3
(a) recovered, and recalcined at 300 °C
(b) as-prepared Fe/zeolite
(c) recovered catalyst (completely agreed with zeolite)
Intensity (a.u.)
(a)
(b)
(c)
10
20
30
40
50
2θ (deg.) Cu-Kα

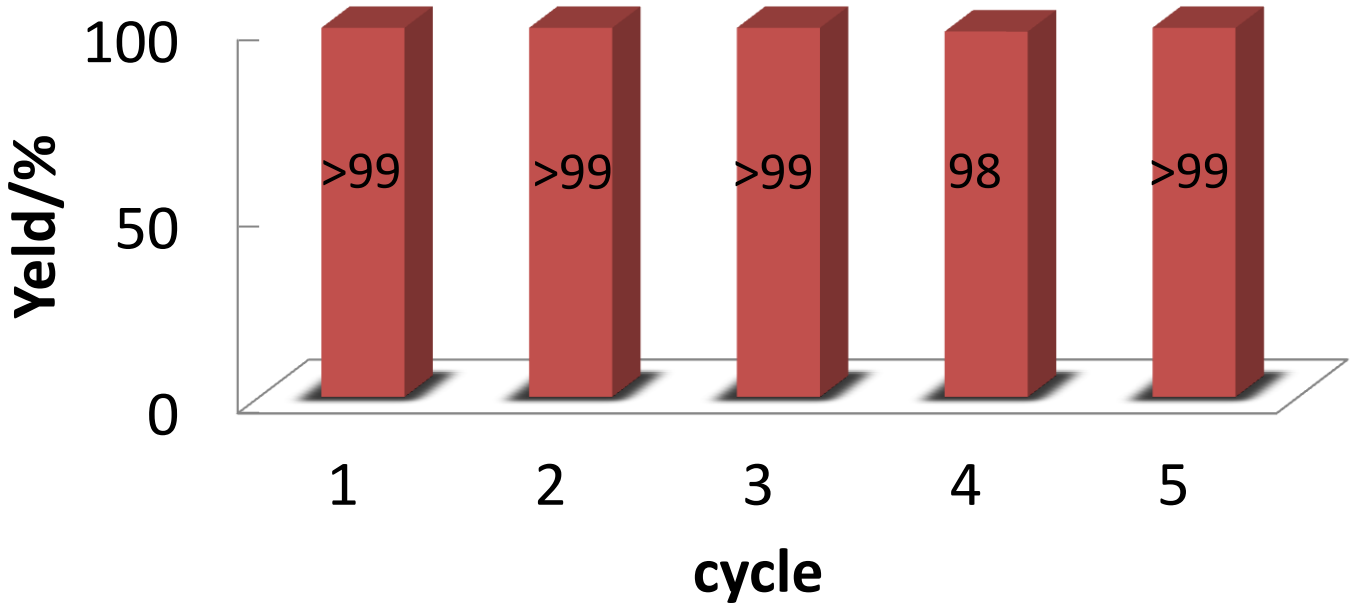


1) zeolite-catalyzed bromination and HBr formation

2) formation of $FeBr_3$ and adsorption of H_2O

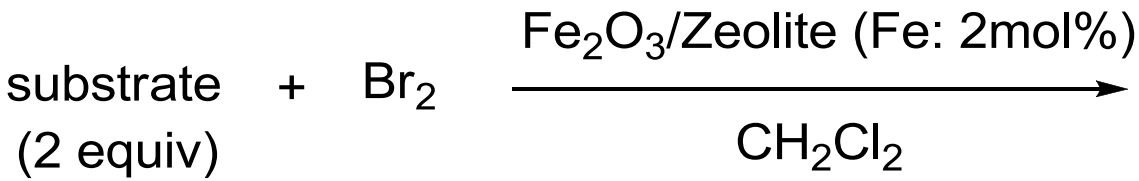
3) $FeBr_3$-catalyzed bromination





- **After the reaction, solvent and product were removed by evaporation and heated at 300 °C for 1 h.**
- **The catalytic activity did not decrease after the 5th cycle.**

Scope of Substrates



1	**2**	40 °C, 2 h	**2'** 51%	**2"** 38%
2	**3**	80 °C, 2 h	**3'** trace	
3	**4**	40 °C, 2 h	**4'** 97%	**4"** 1%
4	**5**	40 °C, 2 h	**5'** 85%	**5"** 7%
5	**6**	40 °C, 2 h	**6'** 86%	**6"** 8%
6	**7**	40 °C, 2 h	**7'** 73%	**7"** 17%
7	**8**	85 °C, 2 h	**8'** 59%	**8"** 11%
8	**9**	85 °C, 2 h	**9'** 71%	**9"** 14%
9	**10**	85 °C, 2 h	**10'** 66%	**10"** 10%
10	**11**	85 °C,2 h	**11'** >99%	
11	**12**	85 °C, 2 h	**12'** >99%	

Nishina, *et al.* Green. Chem. **2012**, 14, 2380