Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary information

Novel heterogeneous ruthenium racemization catalyst for dynamic kinetic resolution of chiral aliphatic amine

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Additional experimental information

The main experimental details can be found in the manuscript.

TEM:

TEM imaging was performed on a JEOL ARM200F equipped with a cold field emission gun and a probe aberration corrector and operated at 200 kV. Samples were prepared by taking a drop of ethanol-sample suspension and depositing it on a Lacy-carbon coated Cu grid (300 mesh, Pacific Grid Tech).

XPS:

XPS spectra were recorded on a Kratos Axis Supra X-ray Photoelectron Spectrometer employing a monochromated Al K_α (hν = 1486.7 eV) X-ray source, hybrid (magnetic/electrostatic) optics with a slot aperture, hemispherical analyser, multichannel plate and delay line detector (DLD) with a take-off angle of 90°. The analyser was operated in fixed analyser transmission (FAT) mode with survey scans taken with a pass energy of 160 eV and high resolution scans with a pass energy of 20 eV. The resulting spectra were processed using CasaXPS software. Spectra were charge referenced to aliphatic carbon at 284.8 eV. High resolution spectra were fitted using the "LA(α,m)" lineshape for symmetric peaks and the "LF(α, β, w, m)" lineshape for asymmetric peaks corresponding to a numerical convolution of Lorentzian functions (with exponents α and β for the high binding energy and low binding energy sides) with a Gaussian (width m) and inclusion of tail-damping (w) to provide finite integration limits. "U2 Tougaard" backgrounds were used for integration of peak areas. Details of these lineshape (and background) functions are available in the CasaXPS documentation online.
Ruthenium 3d and 3p spectra were analysed with reference to the comprehensive work of D. Morgan[1]. The relative separation of the Ru 3d doublet peaks was constrained to 4.17 eV, and the full-width half-maximum of the j=3/2 peak was constrained to 0.5 eV greater than the j=5/2 peak to allows for broadening of the j=3/2 state due to the Coster-Kronig effect while stabilizing peak fitting in the presence of significant carbon 1s components in the samples. Three areas per sample were measured to ensure accurate representation of sample composition.

Visual representation Ru-species leaching from Ru(III)/Y catalyst

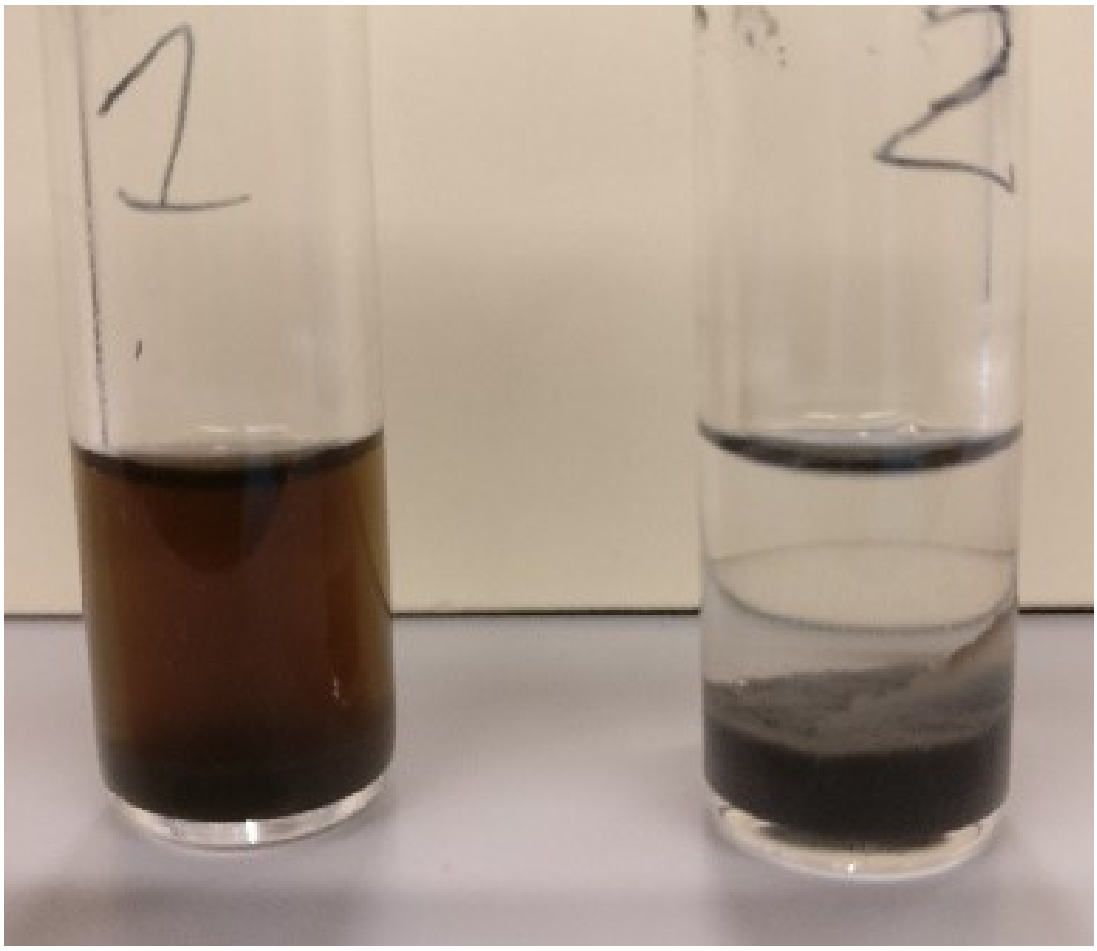
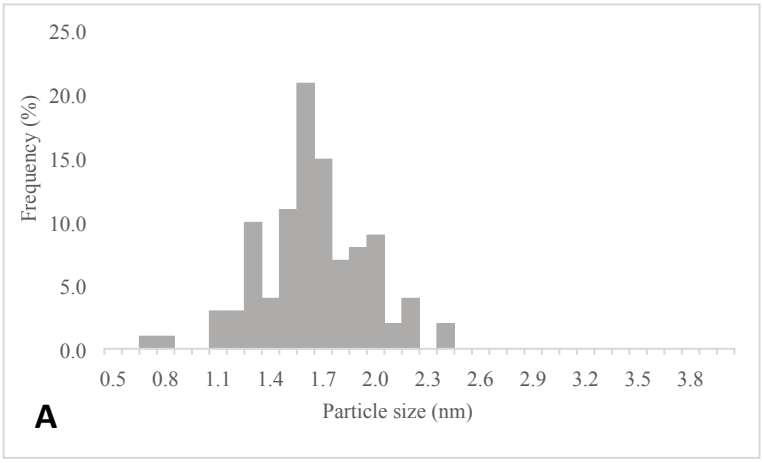
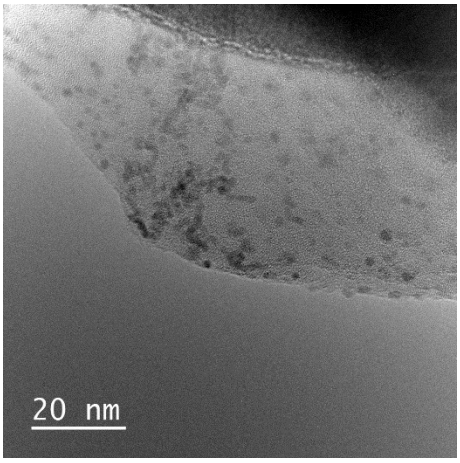
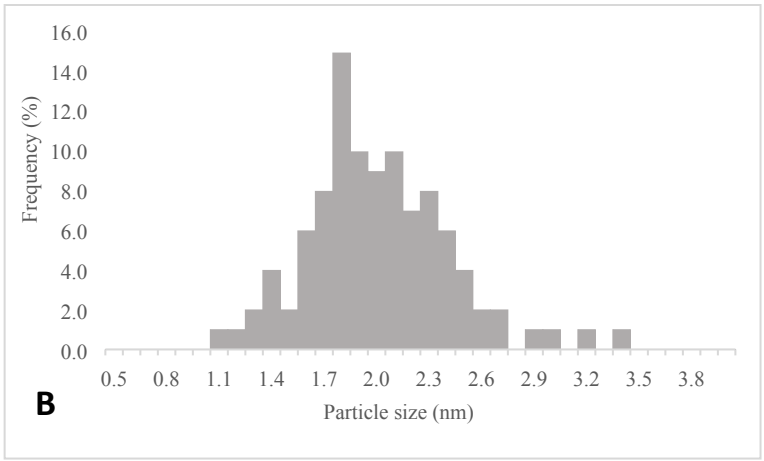


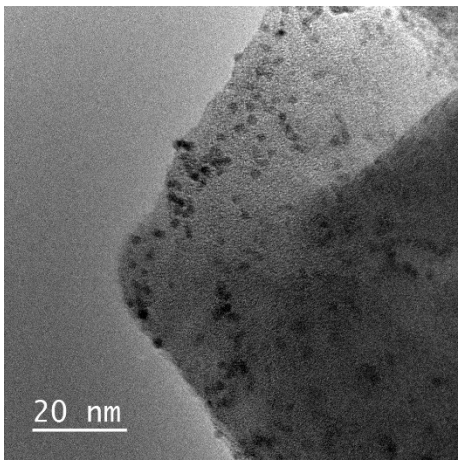
Figure 1: Visual representation of reaction media after racemization reaction: without addition of LiOH (left) and with LiOH (5.0 equivalets to substrate)(right).

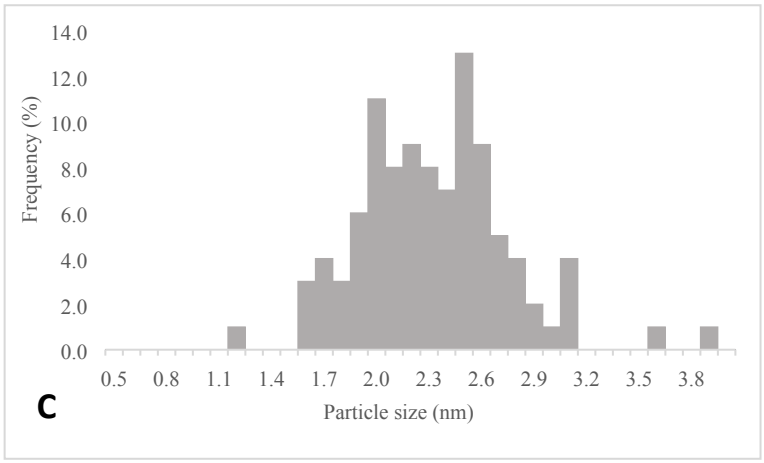
Particle size distributions determined from TEM images

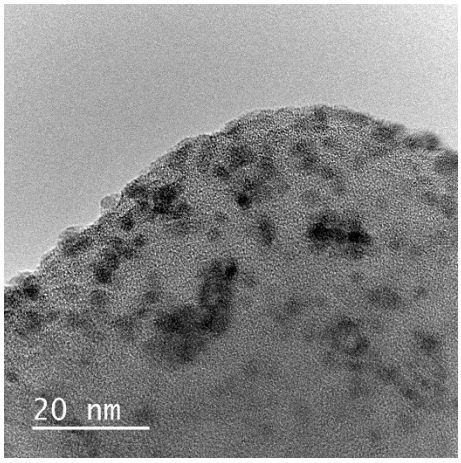










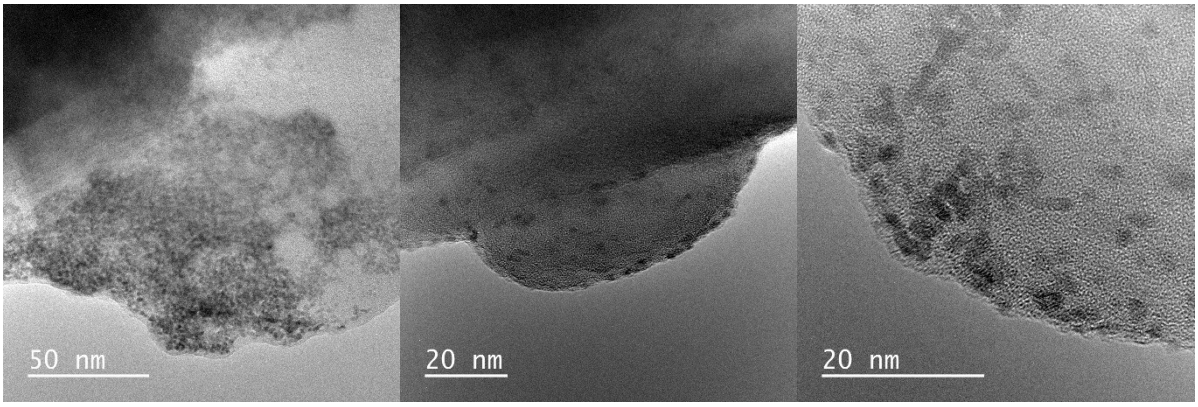


Sample	Mean (nm)	Median (nm)	Std dev (nm)
A	1.60	1.58	0.30
B	1.96	1.90	0.40
C	2.28	2.26	0.42

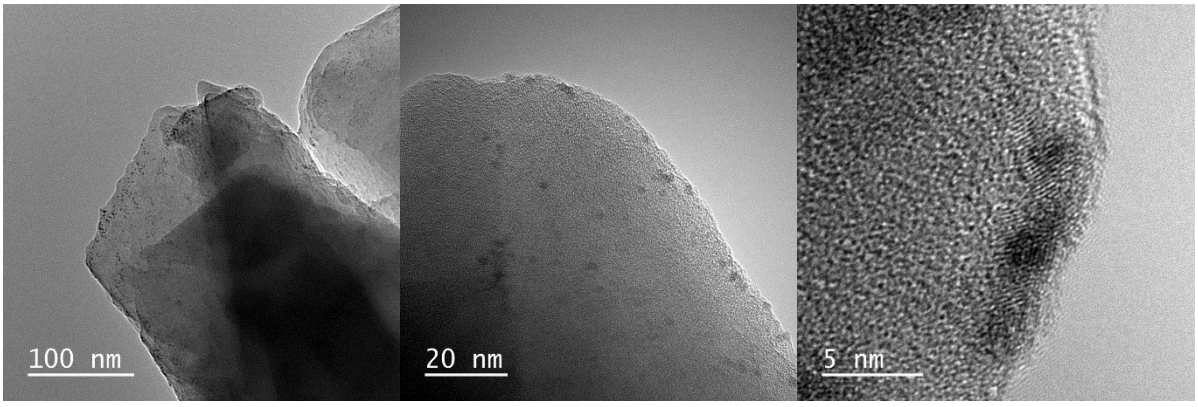
Figure 2: Particle size distribution of Ru(III)/Y catalyst before reaction (A), after reaction (B) and after reaction with addition of LiOH (C). Table depicts the mean, median and standard deviation (std dev) for each distribution.

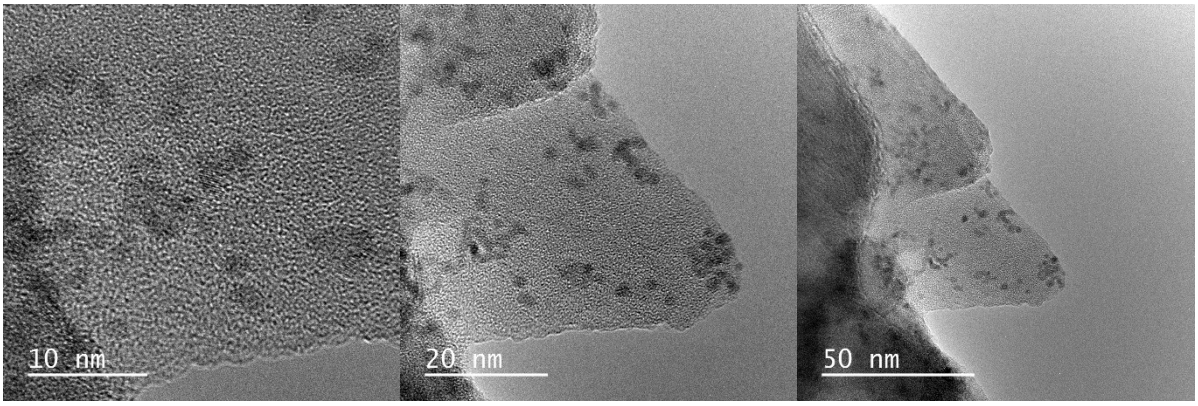
Additional TEM images

Fresh Ru(III)/Y catalyst:

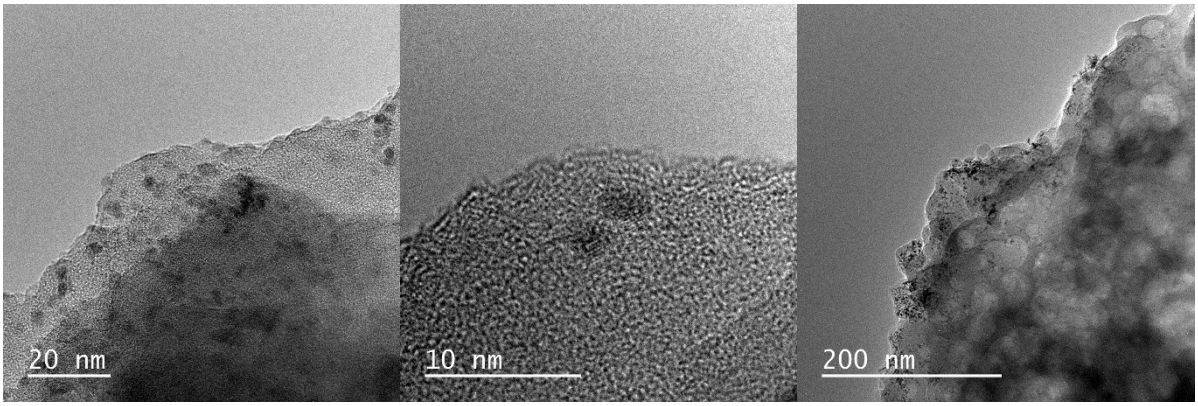


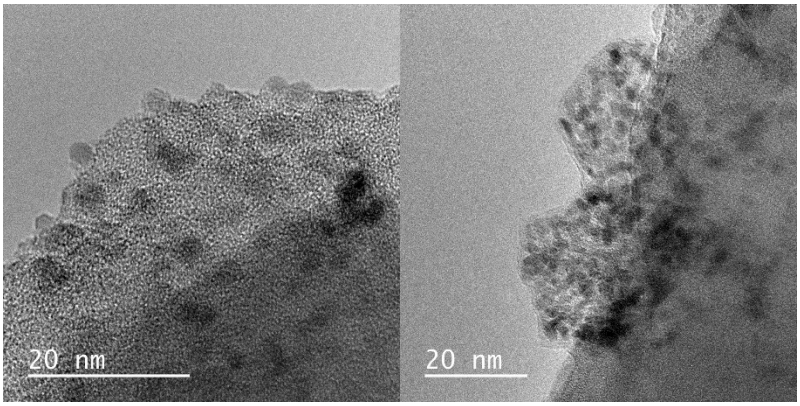
Ru(III)/Y catalyst after racemization reaction:





Ru(III)/Y catalyst after racemization reaction with addition of LiOH:





X-ray diffraction

PXRD measurements were performed in high throughput on a Malvern PANalytical Empyrian diffractometer with a PIXcel3D solid state detector using a Cu anode (45 kV, 40 mA) in transmission geometry.

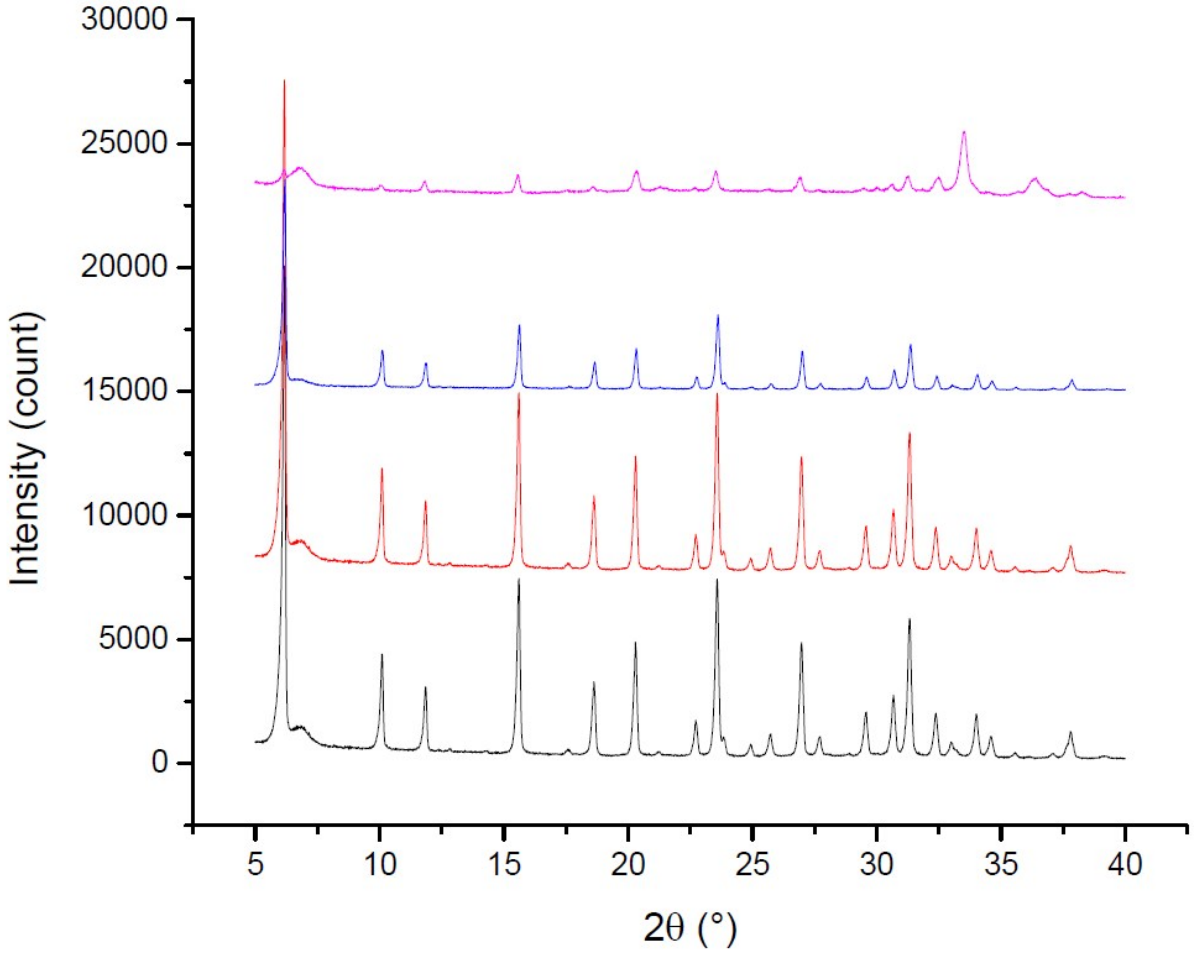


Figure 3: XRD spectra of zeolite Y (CBV-100; black), Ru(III)/Y (red), Ru(III)/Y after reaction (blue) and Ru(III)/Y after reaction with addition of LiOH (purple). Spectrum of Ru(III)/Y after reaction with LiOH still contained high amounts of LiOH, which reduces the effectiveness of the measurement.

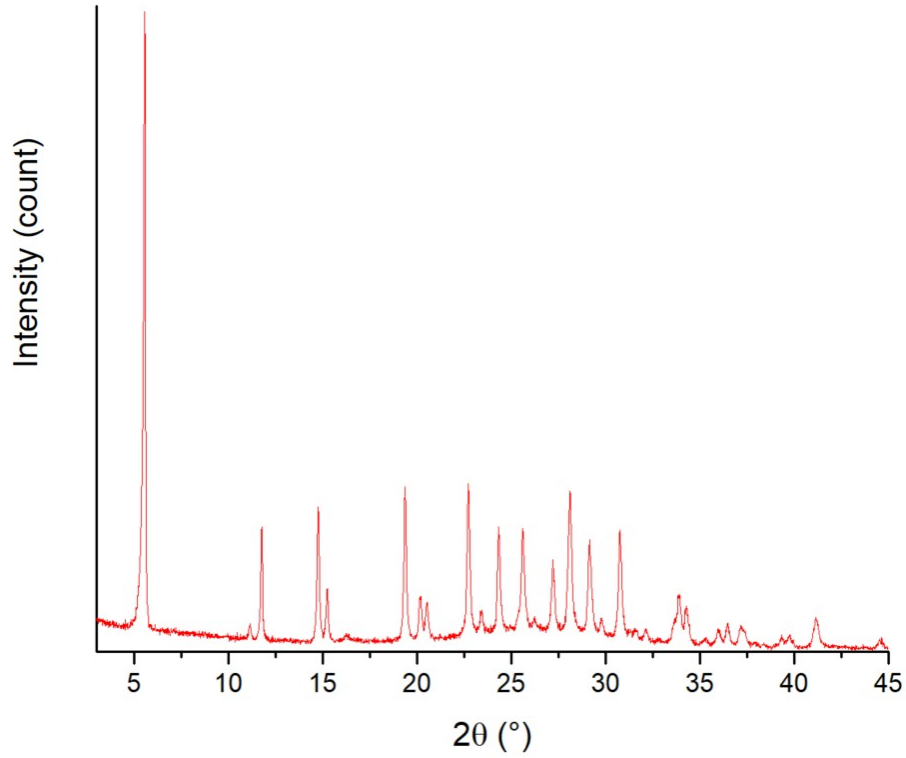


Figure 4: XRD spectrum of synthesized LTL zeolite

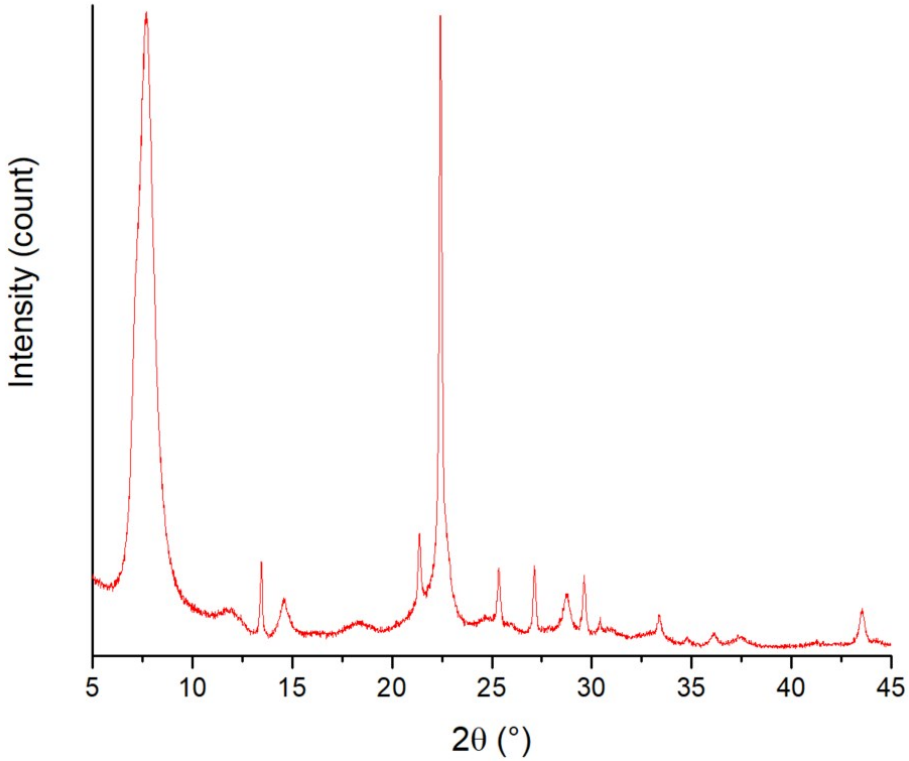


Figure 5: XRD spectrum of synthesized template-free zeolite Beta.

ICP data of zeolite supported ruthenium catalysts.

Catalyst		Before reaction			After reaction	
Support	SAR (in oxides)	Ru	Na	K	Na	K
ZSM-5	40-48	0.86	1.33	0.04	1.21	0.04
MCM-22	28	0.93	0.54	0.03	0.52	0.03
Beta	65	0.91	0.74	0.04	0.69	0.03
Beta	25	0.87	2.01	0.03	1.97	0.03
Beta	9.2	0.94	4.20	0.05	4.07	0.04
Mordenite	6.5	0.85	5.61	1.13	5.43	1.06
Zeolite L	6	1.12	0.39	9.47	0.37	9.29
Y	60	0.90	1.26	0.05	1.22	0.04
Y	30	0.89	4.32	0.05	4.31	0.05
Y	5.1	0.95	6.53	0.05	6.49	0.04
Y (2.0 wt% Ru)	5.1	1.87	6.32	0.05	6.30	0.05
Y (Cs^+)	5.1	0.89	1.86	0.05	1.81	0.05

Table 1: ICP data of Ru(III)/zeolite racemization catalysts before and after reaction. Data in weight percentages.

References

1 D. J. Morgan, *Surf. Interface Anal.*, 2015, **47**, 1072–1079.