Supplementary Material to

Green and selective toluene oxidation–Knoevenagel-condensation domino reaction over Ce- and Bi-based CeBi mixed oxide mixtures

Gábor Varga[a,b]*, Ákos Kukovecz[c], Zoltán Kónya[c,d], Pál Sipos[b,e], István Pálinkó[a,b*]

[a] *Department of Organic Chemistry, University of Szeged, Dóm tér 8, Szeged, H-6720 Hungary*
[b] *Materials and Solution Structure Research Group and Interdisciplinary Excellence Centre, Institute of Chemistry, University of Szeged, Aradi Vértanúk tere 1, Szeged, H-6720 Hungary*
[c] *Department of Applied and Environmental Chemistry, University of Szeged, Rerrich Béla tér 1, Szeged, H-6720 Hungary*
[d] *MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, Rerrich Béla tér 1, Szeged, H-6720 Hungary*
[e] *Department of Inorganic and Analytical Chemistry, University of Szeged, Dóm tér 7, Szeged, H-6720 Hungary*

*Correspondig authors.
E-mail addresses: gabor.varga5@chem.u-szeged.hu (G. Varga), palinko@chem.u-szeged.hu (I. Pálinkó)

STable 1
Calculated cell parameters for pure oxides and solid solutions in the CeO_2–Bi_2O_3 system.

Obtained materials	a (nm)	b (nm)	c (nm)	space group
CeO_2 [4]	0.5411	equals with a	equals with a	$Fm\bar{3}m$
$Ce_{0.9}Bi_{0.1}O_{1.8}$	0.5421	equals with a	equals with a	$Fm\bar{3}m$
$Ce_{0.4}Bi_{0.6}O_{1.7}$	0.5837	0.8154	0.7504	$P2_1/c$
α–Bi_2O_3 [5]	0.5848	0.8166	0.7510	$P2_1/c$

STable 2
Conversion/TOF and selectivity results of the Knoevenagel condensation over varying amount of $Ce_{0.4}Bi_{0.6}O_{1.7}$ catalyst (benzaldehyde (1.0 eq), diethyl malonate (1.5 eq), T = 35°C, t = 180 min in ethanol).

Amount of catalyst (g)	Conversion (%)/TOF (molecules/basic sites/h)	Selectivity (%)
0.001	10/35.4	100
0.002	20/35.4	100
0.005	50/35.4	100
0.015	60/13.8	100
0.02	**80/14.4**	100
0.03	90/8.4	85

STable 3
Conversion/TOF and selectivity results of the Knoevenagel condensation over $Ce_{0.4}Bi_{0.6}O_{1.7}$ in various solvents (benzaldehyde (1.0 eq), diethyl malonate (1.5 eq); m_{cat} = 0.02 g, T = 35°C and t = 180 min).

Solvent	Conversion (%)/TOF (molecules/basic sites/h)	Selectivity (%)
chloroform	1/0.12	100
acetonitrile	–	–
ethanol	**80/14.4**	100
water	49/9.0	100
water/ethanol = 1:1	61/10.8	100

STable 4

Conversion/TOF and selectivity results of the Knoevenagel condensation over $Ce_{0.4}Bi_{0.6}O_{1.7}$ at varying reaction temperatures and time (benzaldehyde (1.0 eq) and diethyl malonate (1.5 eq); m_{cat} = 0.02 g in ethanol).

Temperature (°C)	Reaction time (min)	Conversion (%)/TOF (molecules/basic sites/h)	Selectivity (%)
25	180	53/9.0	100
35	180	80/14.4	100
35	**360**	**100/9.0**	**100**
45	180	100/15.0	83
60	120	100/19.8	74
60	60	71/28.8	76
25	360	92/8.4	100
25	1440	98/2.4	100
reflux	60	100/38.4	73

STable 5

The scope of the reaction – conversion/TOF and selectivity results of the Knoevenagel condensation between benzaldehyde derivatives (1.0 eq) and active methylene compounds (1.5 eq) over $Ce_{0.4}Bi_{0.6}O_{1.7}$; m_{cat} = 0.02 g, T = 25°C, t = 360 min, ethanol.

Aldehyde derivative	Active methylene compound	Conversion (%)/TOF (molecules/basic sites/h)	Selectivity (%)
4-chlorobenzaldehyde	diethyl malonate	93/7.8	98
4-nitrobenzaldehyde	diethyl malonate	96/8.4	94
4-hydroxybenzaldehyde	diethyl malonate	54/3.6	70
4-methylbenzaldehyde	diethyl malonate	48/3.6	78
benzaldehyde	malononitrile	96/7.8	90
benzaldehyde	malonic acid	–	–

STable 6

Scope of the reaction – conversion/TOF and selectivity results of toluene oxidation with TBHP over $Ce_{0.9}Bi_{0.1}O_{1.8}$ catalyst; m_{cat} = 0.1 g, T = 60°C, t = 1440 min, solvent-free.

Toluene derivative	Oxidising agent	Conversion (%)/TOF (molecules/basic sites/h)	Selectivity (%)
4-chlorotoluene	TBHP	1/1.2	49
4-nitrotoluene	TBHP	0.2/0.24	60
4-hydroxytoluene	TBHP	30/46.2	80
4-methyltoluene	TBHP	34/58.8	88

STable 7

Effect of the solvents – conversion/TOF and selectivity results of toluene oxidation with TBHP over $Ce_{0.9}Bi_{0.1}O_{1.8}$ catalyst; m_{cat} = 0.1 g, T = 60°C, t = 1440 min.

Solvent	Conversion (%)/TOF (molecules/basic sites/h)	Selectivity (%)
water	35/53.4	79
ethanol	–	–
water/ethanol = 1:1	12/12.6	54