Electronic Supplementary Material (ESI) for Chemical Communications.

Supplementary Information

One-pot imine synthesis from methylarenes and anilines under air over heterogeneous Cu oxide-modified CeO_2 catalyst

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Experimental

General

The GC (Shimadzu Corporation, GC-2014)) and GCMS (Shimadzu Corporation, QP2010) analyses were carried out with a CPSil-5 capillary column (GL Sciences Inc.) using nitrogen as the carrier gas. All the chemicals for organic reactions were analytic reagents from chemical product corporations and were used without further purification.

Catalyst

CeO_2 was prepared by calcining cerium oxide HS (Daiichi Kigenso, Japan) for 3 hours under air at 873 K. The specific surface area (BET method) of CeO_2 was 84 m^2/g. The purity of CeO_2 is 99.97%. Other metal oxides were commercially available or supplied from the Catalysis Society of Japan: ZrO_2 (Daiichi Kigenso Kogyo Co. Ltd., $Zr(OH)_2$ was calcined under air at 673 K for 3 h.), MgO (Ube Industries, Ltd., MgO 500A), TiO_2 (Nippon Aerosil Co. Ltd., P-25), γ-Al_2O_3 (Nippon Aerosil Co. Ltd.), SiO_2 (Fuji Silysia Chemical Ltd., G-6 was calcined under air at 773 K for 1 h.), SiO_2-Al_2O_3 (JRC-SAL-3), Ta_2O_5 (Wako Pure Chemical Inductries Ltd.), La_2O_3 (Soekawa Chemicals), ZnO (Finex-50, Sakai Chemicals), CaO (Soekawa Chemicals), MnO_2 (Sigma-Aldrich), Nb_2O_5 (Companhia Brasileira de Metalurgia e Mineracao (CBMM), $Nb_2O_5{\cdot}nH_2O$ was calcined at 773 K 3h). Pr_6O_{11}, Dy_2O_3 and Y_2O_3 were prepared by the precipitation method. $Pr(NO_3)_3{\cdot}nH_2O$ (Pure Chemical Industries Ltd., >99.5%), $Dy(CH_3COO)_3{\cdot}4H_2O$ (Pure Chemical Industries Ltd., >99.9%), $Y(NO_3)_3{\cdot}nH_2O$ (Pure Chemical Industries Ltd., >99.9%) were used as a precursor. A precursor (25 g) was dissolved in water (100 ml) and NH_3aq (1 M) was dropped with stirring. The pH of the solution was set to 10 and resulted in a precipitate. The precipitate was filtered and washed by water, following a drying at 383 K overnight (12 h) and calcined under air at 873 K for 3 h. The specific surface area of the metal oxides summarized in Table S6.

Metal oxide-modified CeO_2 (MO_x-CeO_2, M=Cu, Hf, Co, W, Mn, Mo, Pt, Fe, Zr, Pd, Al, Nb, Ag, Ru, Ni, Pr, Sc, Re, Rh, Ga, Ir, Sn, Y, La, Zn, Nd, Au) catalysts were prepared by impregnation method, and the loading amount of metal species is typically 1 wt%. The typical procedure for CuO_x-CeO_2 with 1 wt% Cu species is shown below: CuO_x-CeO_2 catalyst was prepared by impregnating CeO_2 (Daiichi Kigenso Kogyo Co. Ltd., CeO_2-HS, calcined at 873 K and 3 h in air, 84 m_2/g) with an aqueous solution of $Cu(NO_3)_2{\cdot}3H_2O$ (FUJIFILM Wako Pure Chemical Corporation). After evaporating the solvent and drying at 383 K for 12 h, the catalyst was calcined at appropriate temperature (473-1073 K) and 3 h in air. The precursors for other metal species are $Hf(CH_3COCHCOCH_3)_4$ (FUJIFILM Wako Pure Chemical Corporation), $Co(NO_3)_2{\cdot}6H_2O$ (FUJIFILM Wako Pure Chemical Corporation), $(NH_4)_{10}W_{12}O_{41}{\cdot}5H_2O$ (FUJIFILM Wako Pure Chemical Corporation), $Mn(NO_3)_2{\cdot}6H_2O$ (FUJIFILM Wako Pure Chemical Corporation), $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (FUJIFILM Wako Pure Chemical Corporation), $[Pt(NH_3)_4](NO_3)_2$ (Sigma-

Aldrich Co. LLC), $Fe(NO_3)_3 \cdot 9H_2O$ (FUJIFILM Wako Pure Chemical Corporation), $ZrO(NO_3)_2 \cdot 2H_2O$ (FUJIFILM Wako Pure Chemical Corporation), $Pd(NO_3)_2$aq (4.6 wt%, Sigma-Aldrich Co. LLC), $Al(NO_3)_3 \cdot 9H_2O$ (FUJIFILM Wako Pure Chemical Corporation), $C_4H_4NNbO_9 \cdot xH_2O$ (Sigma-Aldrich Co. LLC), $AgNO_3$ (FUJIFILM Wako Pure Chemical Corporation), $Ru(NO)(NO_3)_x(OH)_y$aq (1.5 wt%, FUJIFILM Wako Pure Chemical Corporation), $Ni(NO_3)_2 \cdot 6H_2O$ (FUJIFILM Wako Pure Chemical Corporation), $Pr(NO_3)_3 \cdot 6H_2O$ (Kanto Chemical Co., Inc.), $Sc(NO_3)_3 \cdot 5H_2O$ (FUJIFILM Wako Pure Chemical Corporation), $(NH_4)ReO_4$, $Rh(NO_3)_3$aq, $Ga(NO_3)_3 \cdot nH_2O$ (FUJIFILM Wako Pure Chemical Corporation), $Ir(NO_3)_4$aq (FURUYA METAL Co., Ltd.), $C_{10}H_{14}O_4Sn$ (FUJIFILM Wako Pure Chemical Corporation), $Y(NO_3)_3 \cdot nH_2O$ (FUJIFILM Wako Pure Chemical Corporation), $La(NO_3)_3 \cdot 6H_2O$ (FUJIFILM Wako Pure Chemical Corporation), $Zn(NO_3)_2 \cdot 6H_2O$ (FUJIFILM Wako Pure Chemical Corporation), $Nd(NO_3)_3 \cdot 6H_2O$ (FUJIFILM Wako Pure Chemical Corporation), $HAuCl_4 \cdot 4H_2O$ (FUJIFILM Wako Pure Chemical Corporation).

Imine formation from aniline and mesitylene

A typical procedure for the imine formation from aniline and mesitylene is as follows: Metal oxide catalyst (50 mg) was added to the mixture of aniline (1.0 mmol, Tokyo Chemical Industry Co., Ltd., >98%) and mesitylene (1.5 g, FUJIFILM Wako Pure Chemical Corporation, >97%) in a reaction vessel under air. The resulting mixture was vigorously stirred at 800 rpm at 393 K. After the reaction, the reaction mixture was diluted with methanol, filtrated and transferred to a vial. Details of the reaction conditions are described in each result. The products were analyzed using GC. Conversion and yield of the imine products were determined based on aniline by GC using dodecane (~0.2 g, Tokyo Chemical Industry Co., Ltd., >99%) as an internal standard. Conversion and selectivity were calculated on aniline basis. Products were also identified using standard compounds and GC-MS. The typical GC chart for the imine synthesis from mesitylene and aniline over CuO_x-CeO_2 after 24 h is shown in Figure S3.

Reusability test of CuO_x-CeO_2 is conducted as follows: the catalyst is retrieved from the reaction mixture by filtration. For each successive use, the catalyst was washed with methanol (5 ml) three times to remove the substrate and products, followed by drying in air at 383 K for 12 h. After this treatment, the obtained catalyst was tested for the next reaction.

BET, XRD, ICP-AES and TEM analyses

The surface area of metal oxides and metal oxide and CuO_x-CeO_2 catalysts was measured with BET method (N_2 adsorption) using Gemini (Micromeritics). X-ray diffraction (XRD) patterns were recorded by Rigaku MiniFlex-600 with Cu *K*α (40 kV, 40 mA) radiation. The amount of eluted metal into the reaction solution was analyzed by inductively-coupled plasma atomic emission

spectrometry (ICP-AES, Thermo Fisher Scientific iCAP 6500). The sample for the ICP was obtained by removing the CeO_2 from the reaction mixture by filtration. Scanning transmission electron microscopy (STEM) and STEM-EDX images were recorded on a JEM-ARM200F electron microscope (JEOL, Japan) at an acceleration voltage of 200 kV. The Cs-corrector CESCOR (CEOS GmbH, Germany) was used in the STEM mode.

Tables and figures

Table S1. Effect of calcination temperature of CuO_x-CeO_2 catalysts in the direct imine formation from mesitylene and aniline.

Entry	Calcination *T* /K	Specific surface area /m^2 g-1	Conv. /%	Imine yield /%	Selectivity /%			
					Imine	Azobenzene	Azoxybenzene	Others
1	473	(81)	16	13	82	10	6	2
2	573	(80)	15	12	80	10	6	3
3	673	78	15	13	86	9	3	1
4	773	79	13	11	85	10	4	1
5	873	77	12	11	87	10	3	<1
6	973	75	10	8	81	13	6	<1
7	1073	58	10	9	86	11	3	<1

Reaction conditions: aniline 1 mmol, mesitylene 1.5 g, CuO_x-CeO_2 (Cu: 2 wt%) 50 mg, air, 393 K, 24 h. Conversion and selectivity are calculated on aniline basis.

Table S2. Effect of reaction temperature in the direct imine formation from mesitylene and aniline over CuO_x-CeO_2 (673 K, 3 h) catalyst

Entry	Reaction temp.	Conv. /%	Imine yield /%	Selectivity /%			
				Imine	Azobenzene	Azoxybenzene	Others
1	373	2	1	44	41	16	<1
2	383	6	5	72	20	8	<1
3	393	15	13	86	11	3	1
4	403	27	24	89	10	3	1
5	413	51	47	92	4	2	3

Reaction conditions: aniline 1 mmol, mesitylene 1.5 g, CuO_x-CeO_2 (Cu: 2 wt%, calcined at 673 K for 3 h) 50 mg, air, 24 h. Conversion and selectivity are calculated on aniline basis.

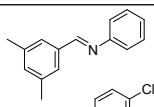
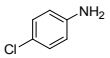
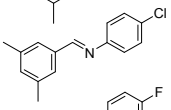
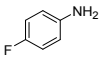
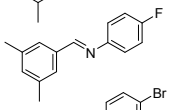
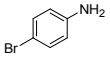
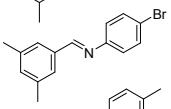
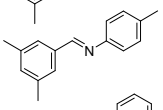
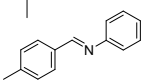
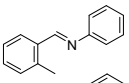
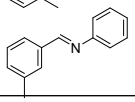
Table S3. Details of the time-course of the direct imine formation from mesitylene and aniline over CuO_x-CeO_2 catalyst (Figure 4(a)).

Reaction time	Conv.	Imine yield	Selectivity /%				Formation amount /mmol	
/h	/%	/%	Imine	Azobenzene	Azoxybenzene	Others	Imine	3,5-Dimethyl benzaldehyde
0	0	0	-	-	-	-	0	0
4	12	10	82	7	3	8	0.10	0.03
7	22	20	88	5	2	5	0.20	0.01
24	51	47	92	4	2	3	0.47	0.03
48	76	71	93	3	2	3	0.71	0.04
72	92	84	91	2	2	5	0.84	0.06
96	97	91	93	2	2	2	0.91	0.07
120	>99	93	93	3	3	2	0.93	0.09
160	>99	93	93	2	2	2	0.93	0.18

Reaction conditions: aniline 1 mmol, mesitylene 1.5 g, CuO_x-CeO_2 (Cu: 2 wt%, 673 K) 50 mg, air, 413 K.

Conversion and selectivity are calculated on aniline basis.

Table S4. Scope of aryl compounds and anilines in the direct imine formation over CuO_x-CeO_2 catalyst[a]

Entry	Aryl compound	Amine	Product	*t* /h	Conv. /%	Sel. /%
1				168	99	93
2				120	91	96
3				120	94	91
4				96	97	97
5				96	97	92
6				168	91	91
7				168	95	93
8				216	93	92

Reaction conditions: amine 1 mmol, aryl compound 1.5 g, CuO_x-CeO_2 (Cu: 2 wt%, 673 K) 50 mg, air, 413 K. [a]Conversion and selectivity are calculated on amine basis.

Table S5. Direct imine formation from mesitylene and aniline with various catalyst combinations

Entry	Catalyst	Conv. /%	**1** yield /%	Selectivity/%			
				1	Azobenzene	Azoxybenzene	Others
1	CeO_2	25	10	39	50	9	2
2	CuO_x-CeO_2	15	13	86	9	3	1
3	CeO_2+1 wt% CuO	21	10	51	33	17	1
4	CeO_2+1 wt% Cu_2O	23	12	53	29	18	1
5	Cu_2O	<1	<1	-	-	-	-
6	CuO	<1	<1	-	-	-	-

Reaction conditions: aniline 1 mmol, mesitylene 1.5 g, CuO_x-CeO_2 (Cu: 2 wt%, 673 K), CuO or Cu_2O 50 mg, air, 393 K, 24 h.

Table S6. Specific surface area of used metal oxides

Entry	Metal oxide	Specific surface area / $m^2\ g^{-1}$
1	CeO_2	84
2	MnO_2	28
3	Pr_6O_{11}	20
4	MgO	37
5	Y_2O_3	51
6	Eu_2O_3	5.7
7	Sm_2O_3	38
8	Al_2O_3	164
9	ZnO	66
10	ZrO_2	46
11	Nb_2O_5	40
12	TiO_2	55
13	La_2O_3	28
14	CaO	12
15	SiO_2-Al_2O_3	560
16	SiO_2	432

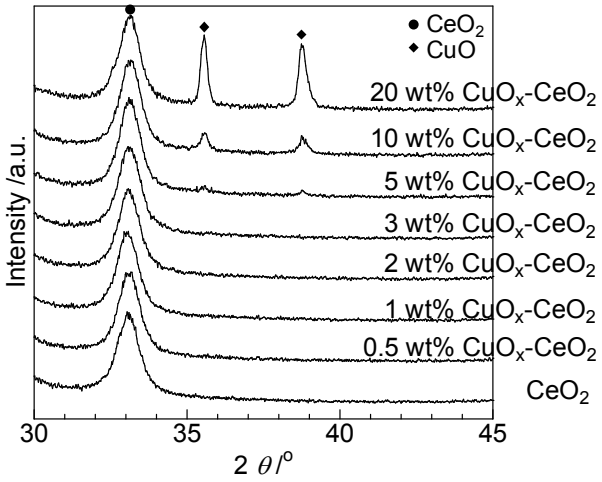


Figure S1. Expanded XRD patterns of CuO_x-CeO_2 and CeO_2 catalysts

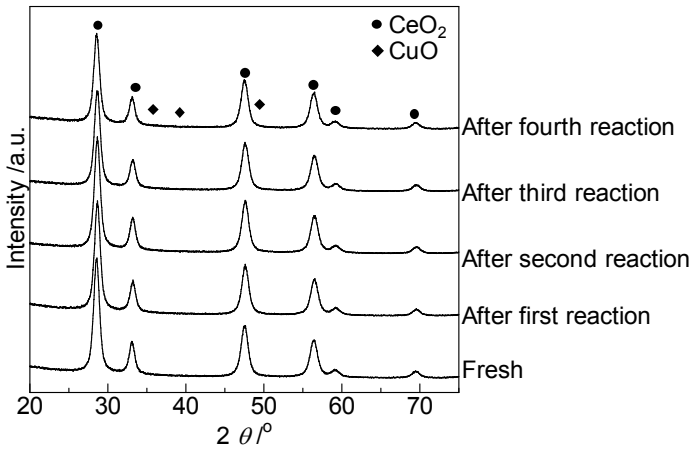
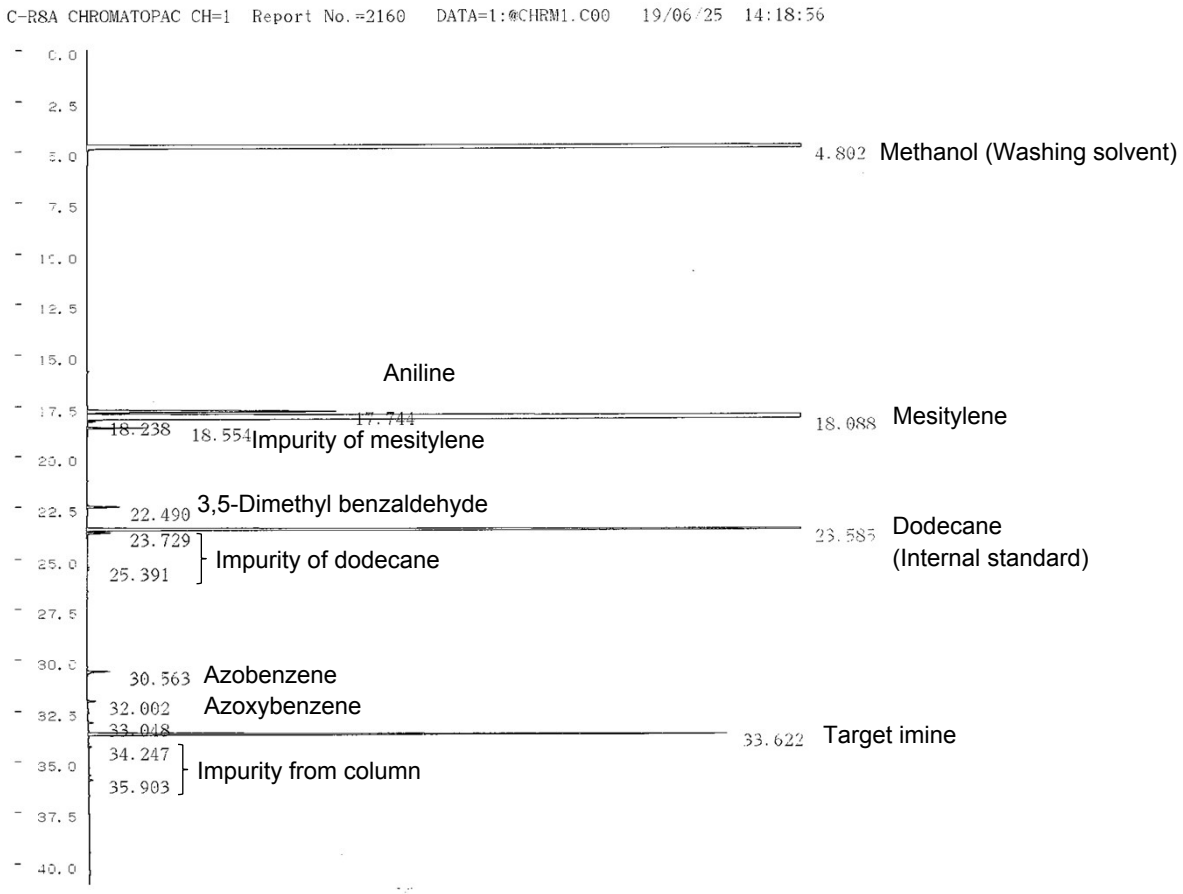


Figure S2. XRD patters of CuO_x-CeO_2 (Cu: 2 wt%, 673 K) catalysts before and after reaction.

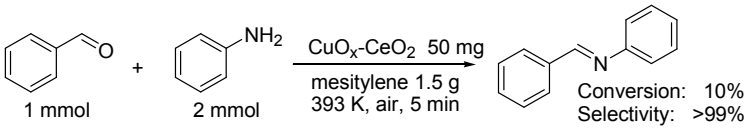


** CALCULATION REPORT **

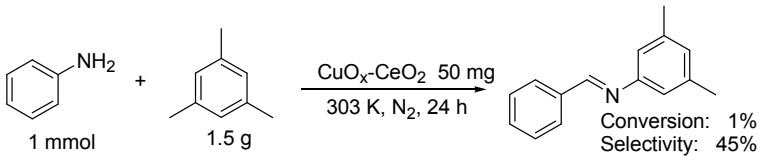
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	4.802	5907173	844355	S		72.4737	
	7	17.744	57375	11189	V		0.7039	
	8	18.088	1856249	248073	V		22.7739	
	9	18.238	969	391	V		0.0119	
	11	18.554	6633	2651	SV		0.0814	
	17	22.49	4249	1452	V		0.0521	
	22	23.585	203769	61949	V		2.5	
	23	23.729	3354	1076	SV		0.0411	
	30	25.391	312	106	V		0.0038	
	43	30.563	3562	1006	V		0.0437	
	45	32.002	1131	366			0.0139	
	50	33.048	822	239	V		0.0101	
	52	33.622	103983	28630	V		1.2757	
	56	34.247	504	134			0.0062	
	61	35.903	702	198			0.0086	
		TOTAL	8150781	1201813			100	

Figure S3. GC chart of the reaction mixture with CuO_x-CeO_2 (Cu: 2 wt%, 673 K) catalyst after 24 h.

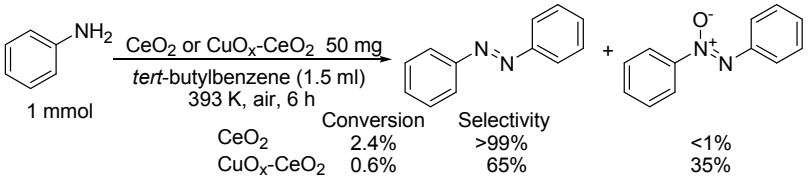
Reaction conditions: aniline 1 mmol, mesitylene 1.5 g, CuO_x-CeO_2 (Cu: 2 wt%, 673 K) 50 mg, air, 413 K, 24 h.



Scheme S1. Imine formation from benzaldehyde and aniline over CuO_x-CeO_2 catalyst (Cu: 2 wt%, 673 K)



Scheme S2. Imine formation from mesitylene and aniline under N_2 with CuO_x-CeO_2 (Cu: 2 wt%, 673 K) catalyst



Scheme S3. Coupling reaction of aniline over CeO_2 and CuO_x-CeO_2 (Cu: 2 wt%, 673 K) catalysts.