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New heterogeneous catalytic systems based on highly porous ceramic materials modified with immobilized *d*-metal cage complexes for H_2 production from CH_4

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Preparation of metal(II) clathrochelates 1–4.

Complexes **1–4** were obtained according to the known[S1–S3] synthetic procedures as described below.

Complex 1[S1]

A mixture of $FeCl_2{\cdot}4H_2O$ (0.065 g, 0.33 mmol), nioxime (0.15 g,1.08 mmol), and *para*-(hydroxymethyl)phenylboronic acid (0.11 g, 0.72 mmol) was dissolved/suspended in methanol (10 ml). The reaction mixture was stirred for 4 h and stored for 24 h. The formed precipitate was filtered off, washed with MeOH (15 ml total, in three portions), and dried *in air*. The product was extracted with $CHCl_3$ (15 ml). The extract was filtered, evaporated to a small volume, and precipitated with hexane. The precipitate was filtered off, washed with hexane and dried *in vacuo*. The yield: 0.19 g (82%).

Complex 2[S1]

A mixture of $CoCl_2$ (0.028 g, 0.22 mmol), nioxime (0.106 g, 0.742 mmol), and *para*-(hydroxymethyl)phenylboronic acid (0.072 g, 0.524 mmol) was dissolved/suspended in MeCN (15 ml). The reaction mixture was stirred for 4 h at 80 ºC and then for 24 h at rt. The formed precipitate was filtered off, washed with H_2O (15 ml total, in three portions), EtOH (15 ml total, in three portions), and dried *in air*. The product was extracted with CH_2Cl_2 (10 ml). The extract was filtered, evaporated to a small volume, and precipitated with hexane. The precipitate was filtered off, washed with hexane, diethyl ether, and dried *in vacuo*. The yield: 0.80 g (53%).

Complex 3[S2]

Nioxime (0.75 g, 5.3 mmol) and $CoCl_2 \cdot 6H_2O$ (0.38 g, 1.6 mmol) were dissolved/suspended in dry MeCN (20 ml) under Ar. The reaction mixture was stirred for 15 min, and a solution of *n*-butylboronic acid (0.36 g, 3.5 mmol) and triethylamine (0.44 ml) in MeCN (5 ml) was added. The reaction mixture was stirred for 5 h, and the formed light-brown precipitate was filtered off. The solid product was extracted with CH_2Cl_2, and the extract was filtered through a silica gel (mesh of 0.035–0.070 mm, 30-mm layer). The filtrate was evaporated to a small volume and precipitated with MeOH. The precipitate was filtered off, washed with MeOH, and dried *in vacuo*. Yield: 0.63 g (63%).

Complex 4[S3]

An excess of disodium bis[2-(o-oxyphenoxy)]diethyletherate was freshly prepared in dry MeOH (15 ml) *via* refluxing metallic sodium (0.28 g, 12.3 mmol), bis[2-(*o*-oxyphenoxy)]-diethyl ether (2.2 g, 7.7 mmol), and an phase-transfer catalyst $[Bu^n{}_4N]Br$ (0.77 g, 5.1 mmol) for 30 min. This disodium salt was dissolved/suspended in dry THF (50 ml), and a solution of $Ru(Cl_2Gm)_3(BBu^n)_2$ (1.2 g, 1.7 mmol) in THF (30 ml) was added dropwise to the stirred reaction mixture during 2 h at 50 °C. The solution/suspension was stirred for 30 h at 50 ºC and cooled down to rt. The reaction mixture was filtered, and the filtrate was precipitated with a three-fold volume of hexane. The precipitate was filtered off, and the filtrate was evaporated to dryness. The solid residue was washed with H_2O and then MeOH, and the product was extracted with $CHCl_3$. The chloroform extract was filtered through a Silasorb SPH-300 layer (20 mm), evaporated to dryness, and extracted with a small amount of diethyl ether. The extract was evaporated to dryness. The resulting orange residue was washed with hexane and dried *in vacuo*. Yield: 0.32 g (14%).

Immobilization of the metal(II) clathrochelates on TZMK

The immobilization on the surface of this support of the Fe^{II}, Ru^{II} and Co^{II} clathrochelates shown in Scheme 1, which are intensively colored in the visible range due to their absorption maxima varied from 450 to 500 nm, was performed by the dissolution of weighed amount (~0.050 g) of the corresponding clathrochelate in CH_2Cl_2 (~3 ml), and a weighed amount of TZMK (~0.200 g) was immersed in the obtained dichloromethane solution. This allowed transporting such a cage compound in all pores of the highly porous ceramic material TZMK and immobilizing the particular metal complex on the surface of all its pores. The obtained clathrochelate-containing materials were dried *in air* to obtain a strongly physisorbed clathrochelate monolayer on the TZMK surface and repeatedly washed with a small volume (~3 ml) of CH_2Cl_2 to remove any non-physisorbed cage complex. This process can be easily controlled by a naked eye due to an intensive coloration of these complexes in the visible range (see above).

The molecule of known[S5] Co^{II} clathrochelate $CoNx_3(BBu^n)_2$ do not contain the polar groups causing its strong physisorption and therefore, this complex was used as a control.

Testing of the catalytic materials

The catalytic experiments were performed using a single-pass plug-flow setup including a tubular quartz reactor. The reactor was equipped with a pocket for a thermocouple placed axially at the center of the reactor. All the tests were carried out using 0.2 g of a given catalyst (the particles sized of 1–2 mm), which were placed on a quartz wool support. Free space of the reactor was packed with quartz pieces. Catalytic tests were performed at atmospheric pressure using $CH_4/O_2 = 2$ or $CH_4/CO_2 = 1$ mixtures at the flowing rate of 15 L g^{-1} h^{-1} without any dilution with inert gases. The catalytic materials were heated at a particular temperature for 1 h, whereas the used temperature ranges are shown in Tables S1 and S2. The initial gas mixture and outlet gaseous products were analyzed using gas chromatography.[S4,S5]

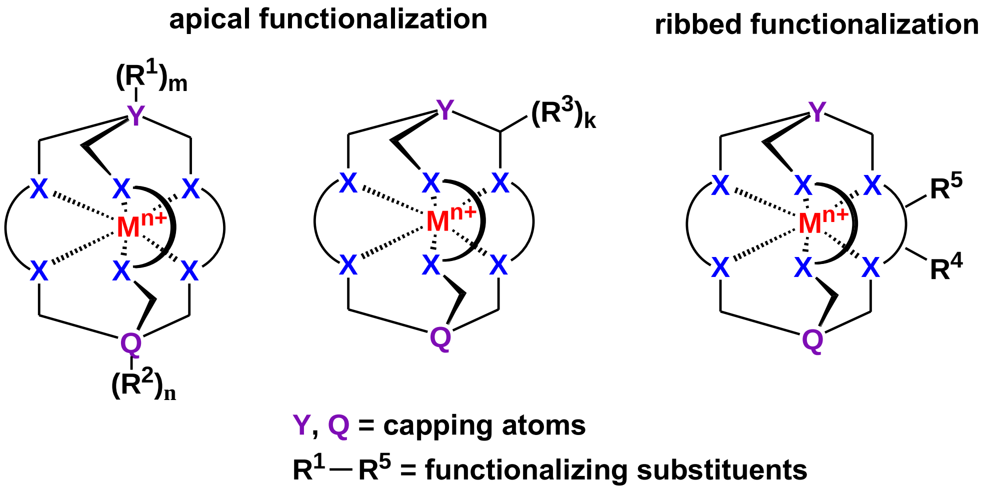
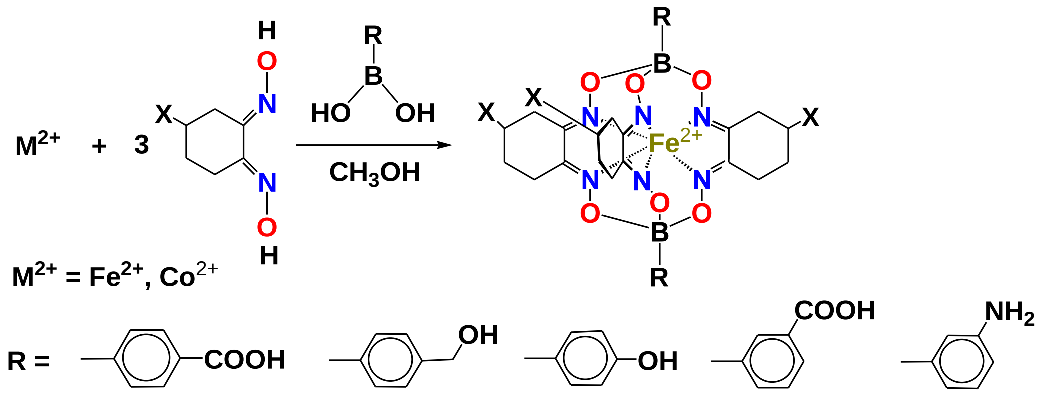
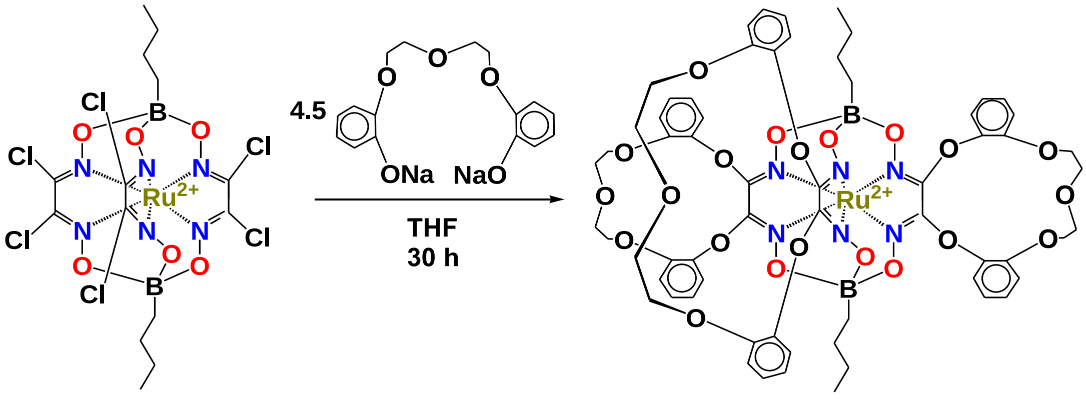


Figure S1 Functionalization of cage metal complexes.



X = H, CH_3
(R', R') = cyclohexane, 4-methylcyclohexane

Scheme S1 Synthesis of the metal(II) clathrochelates with terminal apical polar groups.



Ru(CwGm)$_3$(B*n*-C$_4$H$_9$)$_2$

Scheme S2 Synthesis of the tris-crown ether Ru^{II} clathrochelate

Table S1 Results of the POM process in the presence of the clathrochelate-containing TZMK-based catalytic materials at different temperatures.

T/°C	CH_4 conversion (%)	Yield (%)			
		CO	H_2	CO_2	C_{2+}
TZMK					
900	37	20	15	8	9
920	40	21	17	10	9
950	45	22	19	12	11
900	40	21	15	10	9
850	38	19	12	11	8
TZMK + $Ru(CwGm)_3(BBu^n)_2$					
700	15	0	1	12	3
750	27	1	3	18	8
850	23	1	5	19	4
900	23	2	7	20	1
TZMK + $FeNx_3(B(\textit{para}\text{-}C_6H_4CH_2OH))_2$					
900	39	21	15	10	8
920	40	22	19	9	9
950	43	22	20	11	10
900	40	21	15	10	9
850	36	20	12	9	7
TZMK + $CoNx_3(B(\textit{para}\text{-}C_6H_4CH_2OH))_2$					
900	39	21	16	13	5
920	40	22	17	13	5
950	46	23	23	17	6
900	38	21	15	12	5
850	37	19	13	13	5

Table S2 Results of DRM process in the presence of the clathrochelate-containing TZMK-based catalytic materials at different temperatures.

T/°C	CH_4 conversion (%)	CO_2 conversion (%)	Yield (%)		
			CO	H_2	C_{2+}
TZMK					
900	10	11	1	5	7
920	11	12	0	6	8
950	14	13	1	9	10
900	7	9	0	4	7
850	3	4	0	1	1
TZMK + $CoNx_3(BBu^n)_2$					
900	12	13	1	6	11
920	13	13	0	7	19
950	24	15	2	16	16
900	9	12	0	5	11
850	5	6	0	1	2
TZMK + $Ru(CwGm)_3(BBu^n)_2$					
900	85	91	82	82	0
700	68	62	40	52	0
800	81	86	71	79	0
900	95	98	95	95	0
950	95	98	91	91	0

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