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Mendeleev Commun., 2019, **29**, 669–671

Mendeleev
Communications

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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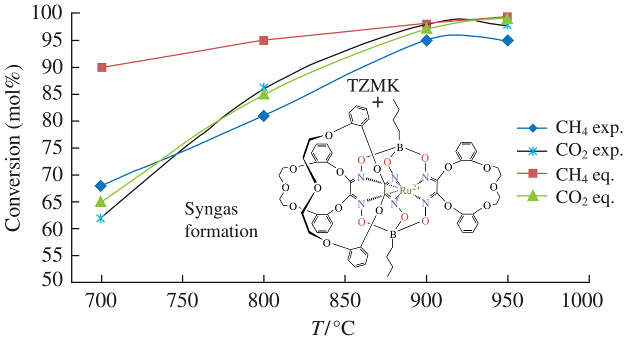
DOI: 10.1016/j.mencom.2019.11.022

The Fe, Co and Ru clathrochelates bearing terminal polar groups were immobilized as the precursors of single atom catalysts on a surface of highly porous ceramic material used as the support. The obtained materials, which were evaluated for a syngas production from CH_4 based on its partial oxidation and dry reforming reactions, did not catalyze the partial oxidation of CH_4, while that based on immobilized Ru^{II} clathrochelate served as the active and selective catalyst of dry reforming conversion of $CH_4 + CO_2$ mixture into a syngas containing the equimolar amounts of H_2 and CO.



The rational choice of catalytically active centers and supports for their immobilization and anchoring plays a key role in the overall efficiency of catalysts. Highly porous (up to 95%) silica-based ceramic materials TZMK† seem to be promising for this purpose,[1–3] since they combine a low density and a high specific surface with the presence of opened and interrelated pores sized up to hundreds of µm. These materials also possess a high thermal resistance (up to 1700 °C in some cases). Such highly porous supports have earlier been successfully applied for the preparation of catalytic materials based on mixed oxide $NdNi_{0.5}Co_{0.5}O_3$ as the catalytically active component, and they were reported to provide both the high selectivity and high yield (>90%) of syngas ($CO + H_2$) in the reactions of partial oxidation and dry reforming of methane (POM and DRM, respectively). Thus, it was reasonable to explore other TZMK-supported catalytic materials containing catalytic centers of different nature, including those based on the *d*-metal clathrochelates.[4] Indeed, these cage complexes containing the metal ion encapsulated in a three-dimensional cavity of the corresponding macropolycyclic ligand possess unusual chemical, physicochemical and physical characteristics. In particular, they were reported to serve as the electro(pre)catalysts for H_2 production from organic and aqueous solutions.[5–9] In recent years, the investigations of electrocatalytic H_2 production using the clathrochelate-modified carbon and precatalyst (*i.e.*, the precursor of catalytically active species) materials,[10,11] as well as those of the clathrochelate-modified metal oxide photocatalysts of H_2O splitting,[12] have been performed. Thus, we suggested that the TZMK-based oxide materials doped with appropriate metal clathrochelates immobilized on their surfaces, either *via* a chemical (covalent) bonding *via* or the strong physical (polar) interactions, may be employed as efficient heterogeneous catalysts for the oxidative conversion of methane into syngas. It is of practical interest, since modern industrial methods of H_2 production include the intermediate step of syngas formation.[13–18] The approaches to such manufacturing are based on a steam reforming of methane [industrial method, reaction (1)], POM (2) and DRM (3) reactions:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2,\ \Delta H^0_{298} = +206\ \text{kJ} \qquad (1)$$

$$2CH_4 + O_2 \leftrightarrow 2CO + 4H_2,\ \Delta H^0_{298} = -36\ \text{kJ} \qquad (2)$$

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2,\ \Delta H^0_{298} = +247\ \text{kJ} \qquad (3)$$

The POM and DRM reactions are considered as prospective and environmentally benign cost-effective processes for the syngas production. Reaction (2) is exothermic and, thus, a more energetically favorable for obtaining syngas with a stoichiometry of its components $H_2 : CO = 2 : 1$, which fits well for MeOH and Fischer–Tropsch syntheses. Reaction (3) looks promising due to the utilization of CO_2 and methane (*i.e.*, the most common greenhouse gases) and the opportunity to use the renewable raw material, biogas. Thus, a search for suitable catalysts of DRM and POM processes is still of current importance.

In the present work aimed at the POM and DRM transformations of CH_4 into the hydrogen-containing gaseous products, we have employed the catalytic materials, which were prepared *via* the immobilization of appropriate Fe^{II} and Co^{II} cage complexes **1** and **2** bearing the terminal reactive (polar) groups at

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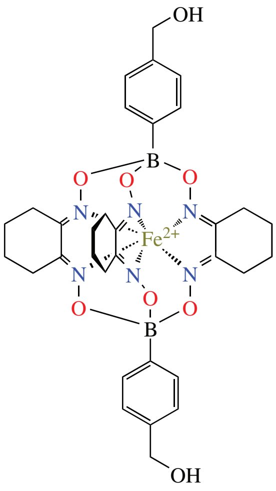
† TZMK is a brand name of the materials, which were designed and prepared at the All-Russian Scientific Research Institute of Aviation Materials.



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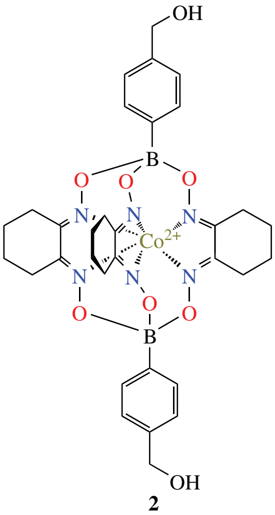

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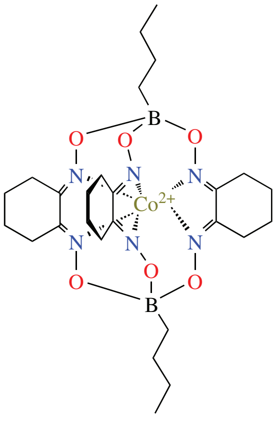

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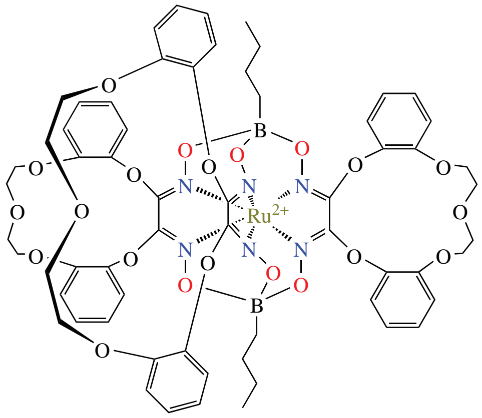
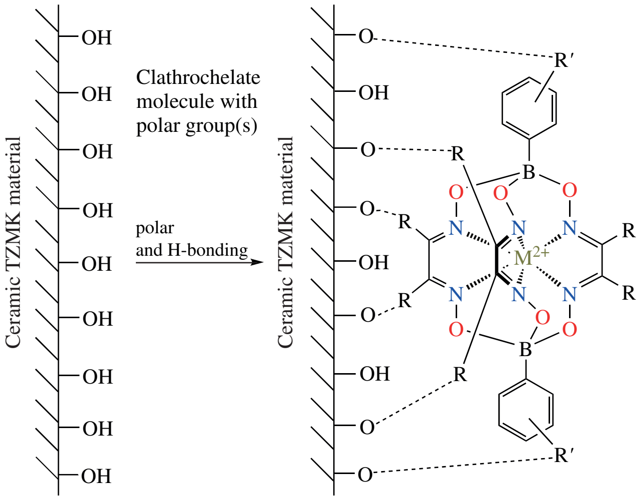


4

their apical substituents (Figure S1, see Online Supplementary Materials) and also of their Ru-containing analog **4** containg the polar ribbed substituents on the surface of TZMK used as a support (Figure 1).

The advantages of thus obtained catalytic materials include (i) an opportunity either to use complexes of the abundant 3*d*-metals instead of platinum group and rare metals and their compounds as the catalytically active components or to substantially decrease a consumption of the latter non-abundant metals by forming the adsorbed monolayers of their designed clathrochelate complexes, thus giving the so-called ‘single atom (single site) catalysts’ and (ii) high adsorptive capacities of the above highly porous ceramic materials, which allow one to substantially increase a surface concentration of the catalytic centers. Therefore, they can be considered as the prospective highly efficient catalytic materials (in particular, those for H_2 production *via* the POM and DRM processes).

The boron-capped macrobicyclic Fe^{II} and Co^{II} tris-dioximates bearing the terminal polar (reactive) OH, COOH and NH_2 groups at their apical fragments and the tris-crown ether Ru^{II} clathrochelate **4** (Schemes S2 and S3) were obtained according to the known synthetic procedures.[4] The iron, cobalt and ruthenium complexes **1**, **2** and **4** known as forming the strong supramolecular interactions with a surface of ceramic materials were immobilized[‡] on a highly porous (95%, the pore sizes up to 200 μm) and a durable TZMK material (Figure 2)[§] containing silica fibers 1–10 μm in diameter and up to 200 μm in length. This material possessing a density of 0.25 g cm^{-3} and a specific surface of ~0.12 m^2 g^{-1} is thermally stable up to 1250 °C. Cobalt(II) clathrochelate **3**, whose molecule does not contain the above mentioned functionalizing substituents, was used as the control.



R = polar ribbed substituent
(R,R) = polar ribbed cyclic fragment
R′ = apical polar group
M^{2+} = Fe^{2+}, Co^{2+}, Ru^{2+}

Figure 1 Immobilization of the metal(II) clathrochelates on TZMK surface.

A series of the obtained TZMK-based catalytic materials were tested in both the POM and DRM reactions (Tables S1 and S2). The immobilization of clathrochelates **1** and **2** did not practically affected the proceeding of the POM reaction (Table S1), and non-catalytic thermochemical processes were observed in all the cases.[14] As a result, the yields of CO and H_2 did not exceed 23%, while the formation of significant amounts of side products such as H_2O, CO_2 and hydrocarbons (mainly ethylene), which were the products of CH_4 condensation reactions, as well as of carbon depositions, was observed. Unexpectedly, the Ru-containing TZMK-based catalyst incorporating immobilized complex **4** exhibited a lowest catalytic activity in this POM process, giving syngas as the target product in its lowest yield in the temperature range of 700–900 °C (see Table S1).

More exciting results were obtained in the case of the DRM reaction (Table S2 and Figure 3). The catalytic material based on immobilized Co^{II} complex **3** gave practically no CO, while a formation of the substantial (up to 19%) amounts of gaseous products of a CH_4 condensation, such as ethylene (up to 9%), propylene, and butanes (up to 10%) was detected by the

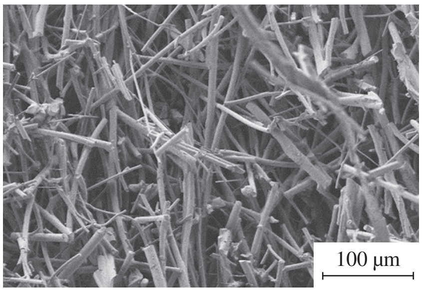


Figure 2 SEM image of TZMK surface.

[‡] See Online Supplementary Materials for the detailed experimental procedures.

[§] SEM images were obtained using a Carl Zeiss NVision 40 instrument equipped with a secondary electron detector at the accelerating voltage of 7 kV.

GC analysis performed similarly to the reported procedures.[19] In contrast to the POM process, the corresponding Ru-containing material demonstrated a high catalytic activity and selectivity in DRM, thus giving syngas in the relatively high yields. In the case of an equimolar mixture CH_4 and CO_2 at 900 °C, this catalyst based on immobilized complex **4** gave ~82% molar yield of CO (based on the total amount of CH_4 and CO_2). Reducing the reaction temperature to 700 °C caused a decrease in the conversion degree: the yields of H_2 and CO were 40 and 52%, respectively. The following increase in the temperature up to 800 °C allowed us to elevate the yields of H_2 and CO up to 60–71% and 79%, respectively. A further increase in the temperature of catalytic layer up to 900 °C resulted in higher yields of CO and H_2 up to 95%, while at 950 °C, their yields were somewhat lower (88–91%). Experimental values of the CO_2 conversion (see Figure 3) were in a good agreement with thermodynamically calculated data.[20] On the other hand, the CH_4 conversion at lower temperatures was lower than the corresponding equilibrium values. It is known[20] that a high CH_4 conversion at lower temperatures may be caused by a CH_4 decomposition, thus being not a result of DRM.

The reported materials of this type exhibited a lost of its catalytic activity upon a contact with atmospheric O_2, which can be explained by an oxidation of the reduced Ru-containing catalytically active species. It has to be noted that such an oxidation might also be a reason of the observed catalytic inactivity in the O_2-containing POM process.

Finally, metal(II) clathrochelates **1–4** are only the precursors (precatalysts) of single atom catalysts, where each of their catalytically active single sites is included in a matrix of its former encapsulating ligand that underwent a thermal decomposition under the reaction conditions used. On the other hand, the choice of thus designed ligands maintained an efficient immobilization of their cage complexes on the surface of all the fibers of the selected TZMK support and allowed us to increase a surface concentration of the catalytically active centers and, therefore, the catalytic activity of ceramic materials modified with these clathrochelates.

In conclusion, the immobilization of Ru clathrochelate **4** as the precatalyst on the surface of highly porous ceramic material TZMK used as the support makes it possible to obtain the active and selective catalytic material for the conversion of $CH_4 + CO_2$ mixture into syngas containing the equimolar amounts of H_2 and CO.

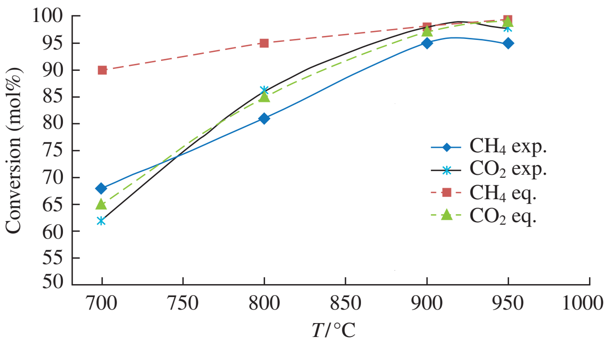


Figure 3 Proceeding of the DRM process in the presence of the catalyst based on Ru^{II} clathrochelate **4**: the experimental (shown in solid line) and equilibrium (shown in dashed line) CH_4 and CO_2 conversions at various temperatures.

This work was supported by the Russian Science Foundation (grant no. 17-13-01468) in part of the catalytic experiments, the Ministry of Science and Higher Education of the Russian Federation (within the framework of the State Task 'Leading researchers to a permanent position', project no. 4.6718.2017/6.7, profile no. 1422) in part of the GC studies. The synthesis of cage complexes was supported by the Russian Foundation for Basic Research (grant nos. 18-29-23007, 18-03-00675, and 17-03-00587). The evaluation of physical properties and spectral characterizations were supported by the State Assignment to N. S. Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences and by the program of the Presidium of the Russian Academy of Sciences (program no. 14, 'Physical chemistry of adsorption phenomena and actinide nanoparticles').

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2019.11.022.

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Received: 26th April 2019; Com. 19/5902