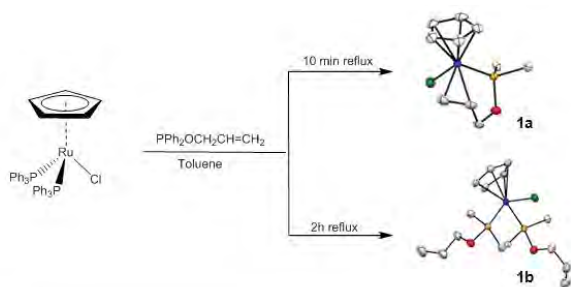


MS36-P04

Organoruthenium complexes containing allylphosphite ligand

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The reaction of the ruthenium(II) complexes $[\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{H}_5$ or $\eta^5\text{-C}_9\text{H}_7$) with an excess of allyldiphenylphosphite leads to the neutral complexes $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{k}^3(\text{P}, \text{C}, \text{C})\text{-PPh}_2\text{OCH}_2\text{CH}=\text{CH}_2)]$ (**1a**), $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}(\text{k}^1(\text{P})\text{-PPh}_2\text{OCH}_2\text{CH}=\text{CH}_2)_2]$ (**1b**) and $[\text{Ru}(\eta^5\text{-C}_9\text{H}_7)\text{Cl}(\text{k}^1(\text{P})\text{-PPh}_2\text{OCH}_2\text{CH}=\text{CH}_2)_2]$ (**2a**). The molecular structure of the new ruthenium complexes **1a**, **1b** and **2a** have been determined by X-Ray diffraction. In the complex **1a** the phosphite ligand is bonded to the ruthenium through the phosphorous and the C-C double bond. On the other hand in compounds **1b** and **2a** the ligand is bonded to the metal centre only through the phosphorous atom.

Figure: Synthesis and structure of complexes **1a** and **1b**.

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Keywords: Allylphosphite, ruthenium,

MS36-P05

In situ XRD and EXAFS/XANES study of $x\text{CuO}\text{-}y\text{Al}_2\text{O}_3\text{-}z\text{Fe}_2\text{O}_3$ catalyst in reaction of CO oxidationOlga Bulavchenko¹, Zahar Vinokurov¹, Andrey Saraev¹, Vasily Kaichev¹, Alexander Fedorov¹, Anna Tsapina¹¹. Borekov Institute of Catalysis SB RAS, Novosibirsk State University, Novosibirsk, Russiaemail: isizy@catalysis.ru

The Fe-based catalysts have been the subject of intense research in recent decades since wide application in various fields, such as water-gas shift reactions, Fisher-Tropsch synthesis, CO and hydrocarbons oxidation, ammonia synthesis. We are interesting in Fe-based system as effective catalysts for CO oxidation of gasification products of solid fuels in fluidized bed. CO is known to be the main product of gasification of dry fuels (coal, fuel oil, firewood).

One of the ways to stabilize catalyst from sintering, increase surface area and catalytic activity is using various promoters. At the same time, the introduction of different promoters affects the performance of the catalyst, i.e. shifts the temperatures of phase transformations and forms new mixed compounds. These effects strongly depends on the nature and amount of the incorporated metal cation.

We studied the influence of the nature and amount of promoter (Al and Cu cations) in Fe-O catalysts on the structural, textural, redox and catalytic properties of $x\text{CuO}\text{-}y\text{Al}_2\text{O}_3\text{-}z\text{Fe}_2\text{O}_3$ samples in CO oxidation. In this work, we use in situ techniques (XRD and XANES/EXAFS) to study the behavior of catalysts and model systems under reduction in CO. Copper and aluminum can enter into iron oxide during the preparation stage, or during reduction with the formation of a solid solutions based on spinel or hematite structures [1].

Catalytic testing in the CO oxidation revealed the difference in catalytic properties for different modifiers. Catalysts contain Fe_2O_3 , addition of Al atoms leads to a decrease of the oxide crystal size and copper contributes the formation of spinel structure. According to TPR- H_2 , Cu addition leads to improvement of reducibility of catalysts and decrease the temperatures of phase transformation.

Usually, reduction of iron oxide involves several steps including the formation of the intermediate oxides such as magnetite and wustite. The reduction of Fe_2O_3 to metallic Fe can be a two-step $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$ or three-step $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ mechanisms (depending the temperature and $\text{H}_2\text{O}/\text{H}_2$ ratio) and affected the formation of metastable wustite.

Our in situ study shown that, introduction of aluminum in Fe_2O_3 leads to slowing down the reduction of Fe_2O_3 to Fe_3O_4 and the appearance of reaction products (FeO and Fe) at higher temperatures. The formation of the intermediate solid solution of $\text{Fe}_{3-x}\text{Al}_x\text{O}_4$ and the formation in the reaction products of aluminum-containing spinel-type phases FeAl_2O_4 and $\text{Fe}_{3-x}\text{Al}_x\text{O}_4$ are also observed. The introduction of Cu has an effect on the acceleration of the stage. $\text{FeO} \rightarrow \text{Fe}$, and has little effect on the reduction of $\text{Fe}_3\text{O}_4 \rightarrow \text{FeO} / \text{Fe}$.

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Keywords: *in situ* XRD, spinel, catalyst

MS36-P06

Supramolecular dimer of sandwich triple-decker phthalocyaninates studied by single-crystal x-ray diffraction analysis

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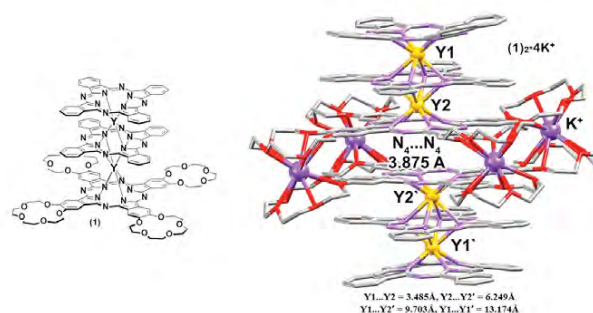
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Lanthanide phthalocyaninates with paramagnetic REE(III) ions reveal single-molecular magnetic (SMM) behaviour [1, 2]. The magnetic properties of usual double- or triple-decker sandwich complexes can be tuned by increasing the number of decks. Earlier in our group it was shown that triple-decker phthalocyaninates (1) with one terminal crown-substituted deck is capable for dimerization in solution in the presence of potassium ions [3]. In the present work we proved the formation of such sextuple-decker sandwich complex in solid state by single crystal XRD. The yttrium complex was chosen as diamagnetic reference for later investigations.

The solvates $(1)_2 \cdot (KBPh_4)_4 \cdot 4(CH_3CN) \cdot 7(CHCl_3)$ were obtained by slow diffusion of $KBPh_4$ in CH_3CN into the solution of (1) in $CHCl_3$ at 25 °C. The structural characteristics of the dimer suggest the possibility of the magnetic-dipolar f-f interaction between the ions at M1 and M2 sites, as well as additional weaker coupling between ions at M2 and M2' sites, which can be later observed in the case of isostructural complexes with Tb(III) and Dy(III).

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Keywords: Lanthanide phthalocyaninate, supramolecular dimer, single-crystal XRD