Cryptomelane modified with transition metal ions in the reaction of ozone decomposition

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Introduction

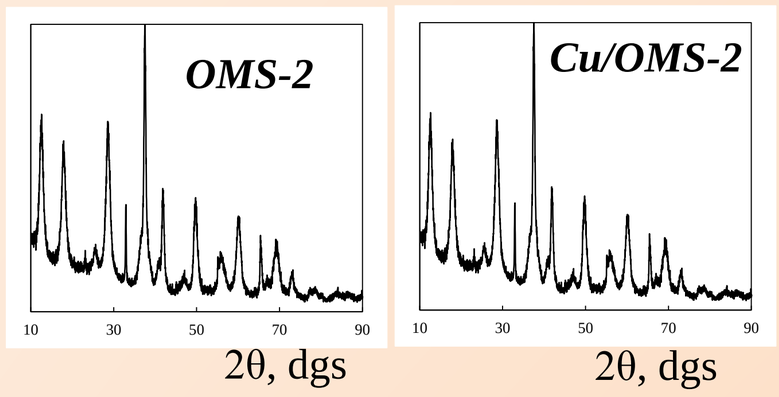
The catalytic activity increase of cryptomelan (α-MnO_2) or octahedral molecular sieve (OMS-2) in many redox reactions occurs due to the transition metal ions injection. Catalysts M/OMS-2 can be obtained by various methods: impregnation, hydrothermal, solid-phase or reflux-method. Single studies have shown that transition metal ions can enhance or inhibit the catalytic properties of cryptomelane in the ozone decomposition reaction. The ozone decomposition kinetics significantly depends on the ratio [M]/[O_3]. The constancy of this ratio for doped M/OMS-2 samples is achieved by obtaining samples impregnation.

The aim of this work is to study the effect of the Cu (II), Co (II), Fe (III) ions content in M/OMS-2 samples obtained by impregnation the cryptomelane samples were synthesized methods reflux (OMS-2 (Ref)) and melting together (OMS-2 (MS)), on the kinetics of ozone decomposition.

Characterization

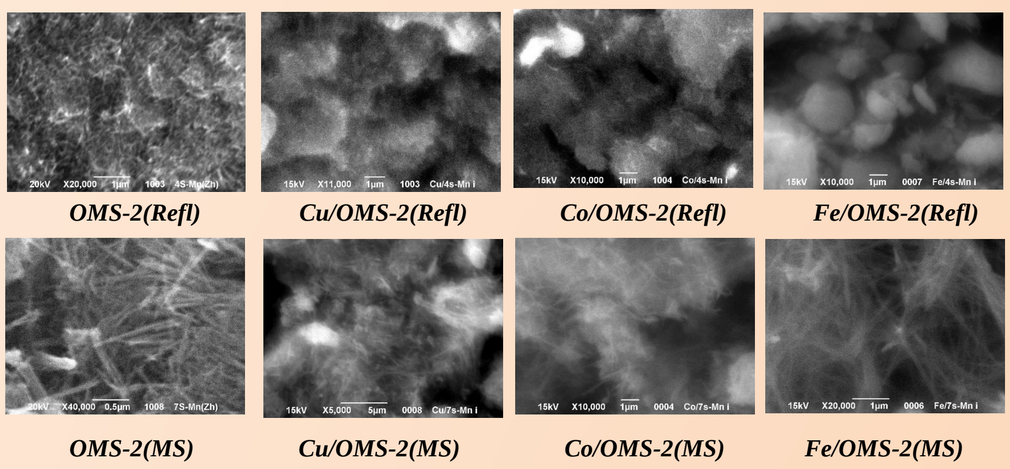
XRD analysis

It is shown that all samples are homogeneous – they contain only the cryptomelane phase. Doped metal ions do not form oxide phases and do not change the parameters of the cryptomelane crystal lattice.



SEM characterization

The original OMS-2 samples show the typical morphology of cryptomelan – these are shapeless fluffy formations composed of nanofibers. Copper (II) and cobalt (II) ions practically do not affect the morphology of cryptomelane, and for Fe/OMS-2 (Refl), denser formations of a globular shape are formed.



OMS-2(Refl) *Cu/OMS-2(Refl)* *Co/OMS-2(Refl)* *Fe/OMS-2(Refl)*

OMS-2(MS) *Cu/OMS-2(MS)* *Co/OMS-2(MS)* *Fe/OMS-2(MS)*

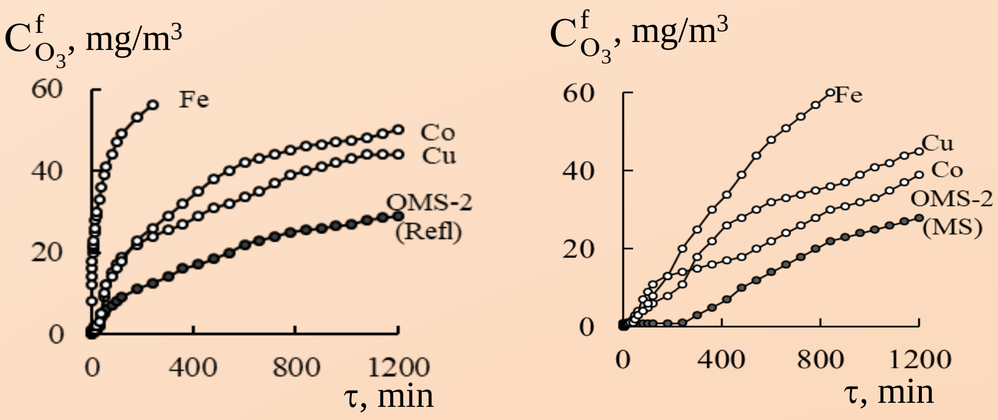
FT-IR spectroscopy

The results of IR spectra identification of OMS-2 and M/OMS-2 samples (M = Cu^{2+}, Co^{2+}, Fe^{3+})

Sample	ν_{OH}	δ_{H2O}	ν_{Mn-O}	ν_{Mn-OH}
OMS-2	3428	1641	716, 668, 527, 468, 429 пл.	1052
Cu/OMS-2	3420	1635	721, 598 пл., 530, 475, 427 пл	1044
Co/OMS-2	3420	1635	720, 529, 475, 428 пл	1046
Fe/OMS-2	3369	1629	708, 591 пл., 527, 470	1043

Catalytic properties

The figure shows examples of testing samples of M/OMS-2(Refl) (*a*) and M/OMS-2(MS) (*b*) in the decomposition reaction of ozone at its initial concentration of 100 mg/m³ compared to the original samples of cryptomelane. Under selected conditions, metal ions inhibit the catalytic properties of cryptomelane.

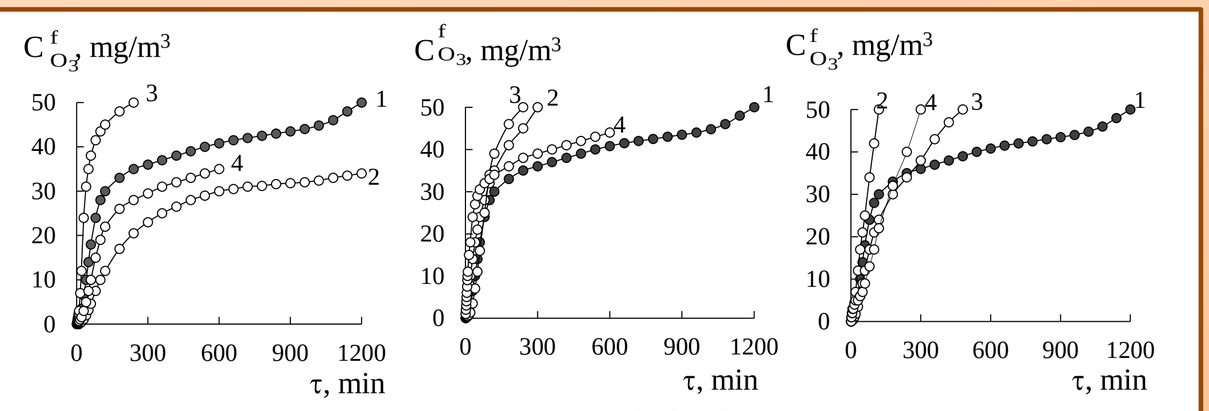


M/OMS-2(Refl) **M/OMS-2(MS)**

ω(Cu) = 0,64 %; ω(Co) = 1,45%; ω(Fe) = 9,16 %)

Refl: OMS-2 > CuOMS-2> Co/OMS-2 >> Fe/OMS-2
MS: OMS-2> Co/OMS-2> Cu/OMS-2 > Fe/OMS-2

A correct comparison of the obtained results can only be done if the content of metal ions is the same.



ω_M = 0,64 % **ω_M = 1.45 %** **ω_M = 9.66 %**

The time dependences of $C^f_{O_3}$ for ozone decomposition by samples OMS-2 (***1***), Cu/OMS-2 (***2***), Co/OMS-2 (***3***) and Fe/OMS-2 (***4***) with different metal content.

The influence of metal ions on the ozone decomposition kinetics is determined by their nature and content. For low-percentage M/OMS-2 samples (ω_M = 0.64 mass.%), copper (II) and iron (III) ions have an accelerating effect, while cobalt (II) ions have an inhibitory effect. All ions have an inhibitory effect, although the order within each series changes, with an increase the metal ions content of (1.45 and 9.66 mass.%) in the composition of M/OMS-2.