Thermal decomposition of 4-methoxy cinnamic acid over nanoceria

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Surface Si

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Introduction

The development of effective technologies for processing lignin is one of the most relevant areas of recent decades. An effective method that can be used for the conversion of lignocellulosic raw materials is pyrolysis [1,2]. To establish the mechanisms of lignin decomposition under catalytic pyrolysis conditions, it is important to study the interaction of its macromolecule with the catalyst, as well as the study of thermal transformations of the lignin model compounds, cinnamic acids [3,4].

Therefore, we studied the complexes of 4-methoxy cinnamic acid (4MCA) with the surface of nanoceria and the pyrolysis mechanisms of the formed complexes.

Method

Nanosized cerium oxide was impregnated with an ethanol solution of 4-methoxy cinnamic acid.

The structure of the 4MCA surface layer on the oxide was investigated by FT-IR spectroscopy. Catalytic pyrolysis of 4MCA/CeO_2 was studied by Temperature programmed desorption-mass spectrometry (TPD-MS) using an MX-7304 monopole mass spectrometer (Electron, Sumy, Ukraine). The programmed linear heating of the samples was carried out at a rate of 0.17°C/s to a temperature of ~750 °C under vacuum conditions.

Results

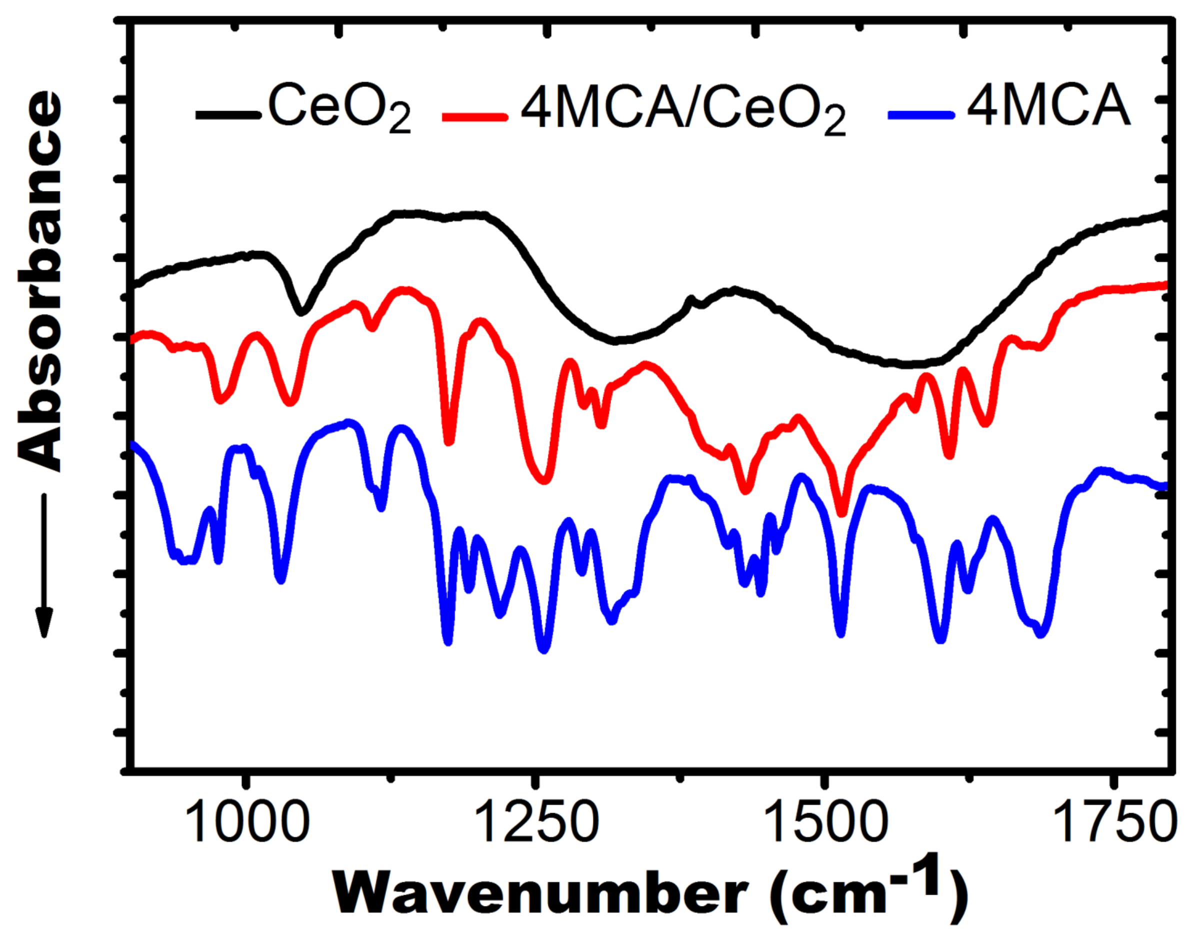

Figure 1. Fourier Transform–Infrared (FT–IR) spectra for 4MCA/CeO_2 (0.6 mmol/g) sample

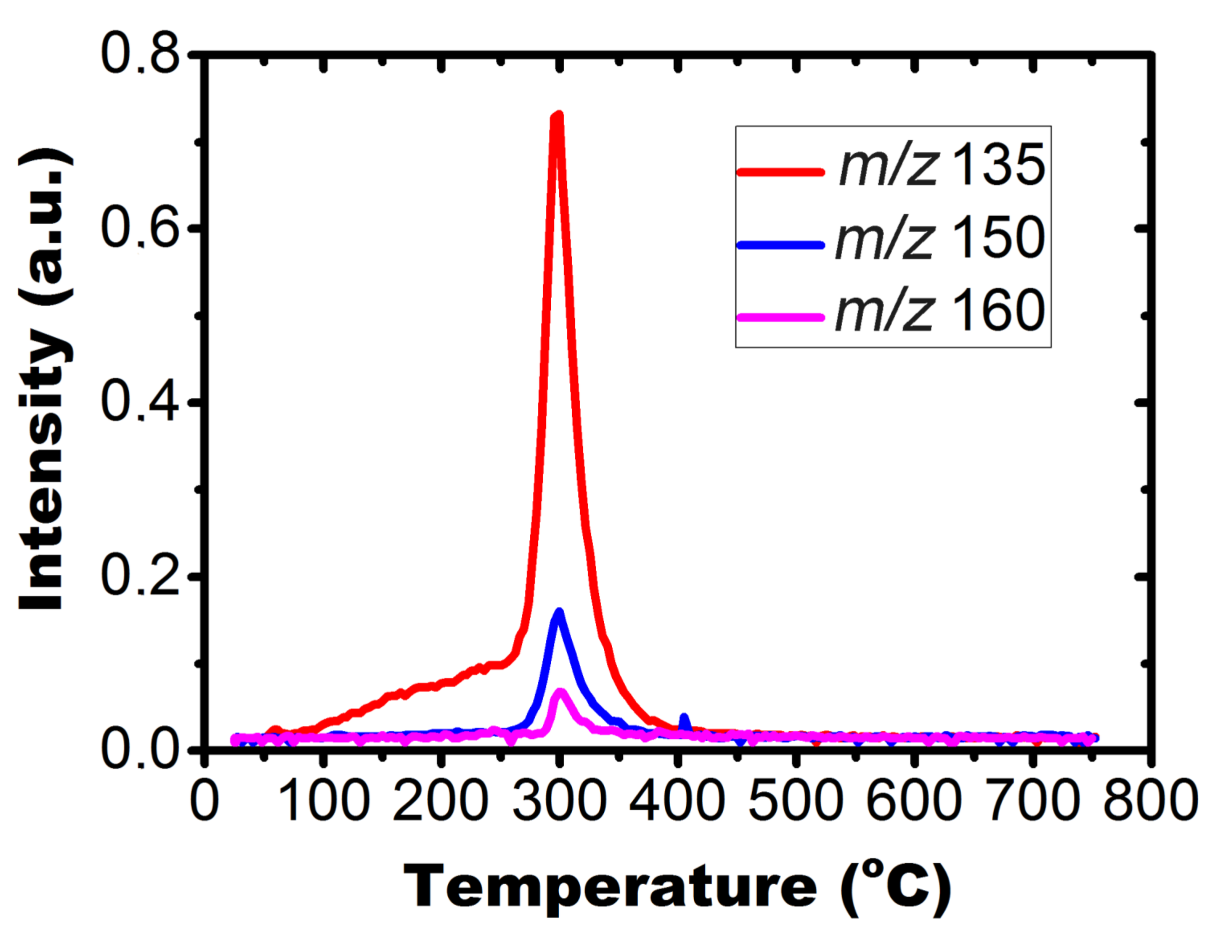

Figure 2. Temperature programmed desorption (TPD) curves for ions with *m/z* 135, 150 and 160 obtained by decomposition of 4MCA/CeO_2 (0.6 mmol/g) sample

Fourier Transform–Infrared Spectroscopy. For 4MCA/CeO_2 samples, absorptions about 1398, 1495 and 1537 cm^{-1} (Figure1) correspond to vibrations of the COO^- group. The FTIR data indicate that 4MCA forms carboxylate complexes. It was found that carboxylate complexes of 4MCA on the CeO_2 surface can have bidentate chelate and bridge structures. In addition, the spectra revealed signs of interaction of the methoxyl group with nanoceria.

Thermal transformations of 4MCA/CeO_2. Decomposition of carboxylate complexes takes place in the temperature range of 100–400°C confirmed by TPD peaks for molecular and fragment ions of pyrolysis products with *m/z* 107, 135, 150, 160 (Figure 2). The processes of decarbonylation, decarboxylation, and dehydration accompanied it. Decomposition products that may correspond to the destruction of complexes formed with the participation of methoxyl groups (*m/z* 31, 164, and *m/z* 148) were recorded above 250°C.

Conclusion

- It was established that 4MCA can interact with CeO_2, both through the carboxyl group and the methoxyl group, due to which a wide range of products is formed during the pyrolysis process.
- The obtained results may be useful for understanding the mechanisms of pyrolysis of lignin using nanoceria.

References

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Acknowledgments

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