

Heterogeneous Transesterification of *Camelina sativa* Catalysed by Potassium impregnated Mg/Al Mixed oxides to prepare Biodiesel

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Introduction

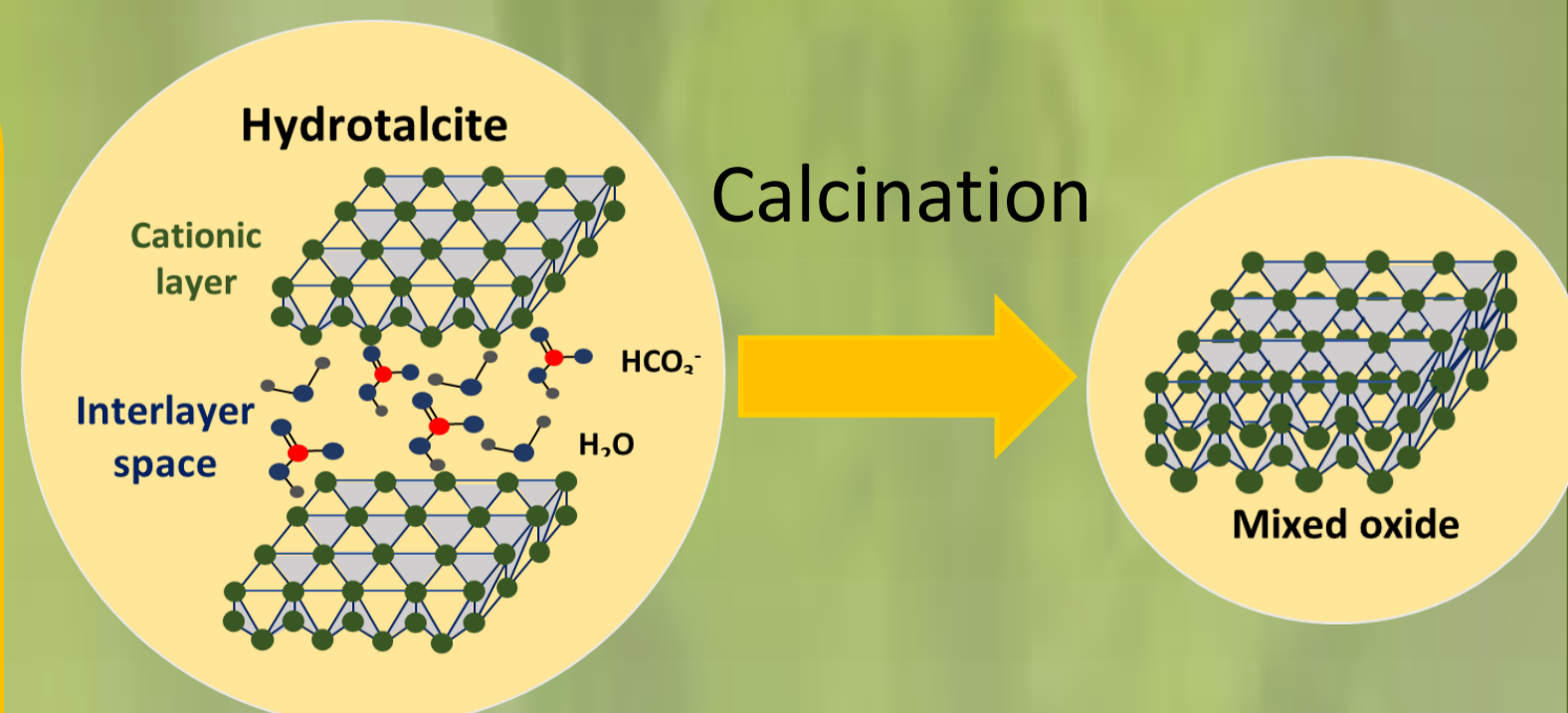
With the population increase, as well as transport and car needs, the production of a sufficient amount of good-quality fuels is a challenge. Transesterification of vegetable oils, containing triglycerides, with alcohol under basic or acid conditions produces fatty acids alkyl esters (biodiesel) and glycerol.

- For the base homogeneous catalysed transesterification, the catalyst KOH, NaOH and sodium methoxide is commonly used for biodiesel preparation. It is quite difficult to separate liquid products and homogeneous catalyst, which is easier in the case of heterogeneous transesterification. In basic homogeneous transesterification, emulsification is another complication, though the use of a solid catalyst eliminates this problem
- Mixed oxides obtained from hydrotalcites provides useful properties in heterogeneous transesterification reaction. The basic hydrotalcites are composed of Al and Mg in cationic layer and anions mostly CO_3^{2-} or HCO_3^{2-} in interlayer space. Impregnation of potassium on hydrotalcite surface could improve catalytic properties, which can cause higher yield of biodiesel from transesterification.

Materials and Methods

Camelina Sativa as an alternative oil-seed crop is flexible plant, that can grow under different climatic conditions, is not demanding on soil quality and is relatively resistant to drought.

Mixed metal oxides (MO) were obtained by calcination at 450 °C from hydrotalcites which were prepared by co-precipitation. Prepared MO were wet impregnated by potassium (KF, CH₃COOK, KNO₃)



Several techniques were used for measuring physico-chemical properties of prepared catalysts (XRD, FTIR, TPDA, TPD-CO₂, ICP, SEM)

Catalyst activity was tried in transesterification of CS oil at temperature of 140°C, 3 wt.% of catalyst to oil, Molar ratio Me/Oil 30:1, for 7 hours.

Results

Impregnation of Potassium on prepared mixed oxides should improve catalytic properties in transesterification by increasing basicity and specific surface. For potassium addition wet impregnation with different sources of K were chosen. In Table 1 types of K solutions are shown. As can be seen the highest amount of K was captured on catalyst from KF solution.

Tab.1 Composition of prepared mixed oxides

Sample	Cations	Solution for impregnation	Mg/Al (molar ratio)	Amount of K (mg/kg)
HT - KF	Mg ²⁺ , Al ³⁺	KF	2,26 : 1	1941,2
HT - KNO ₃	Mg ²⁺ , Al ³⁺	KNO ₃	2,21 : 1	221,7
HT - CH ₃ COOK	Mg ²⁺ , Al ³⁺	CH ₃ COOK	2,15 : 1	294,9

For confirmation of mixed oxides structure formations, XRD analysis was chosen. All measured records indicate amorphous structure of mixed oxides formed through calcination.

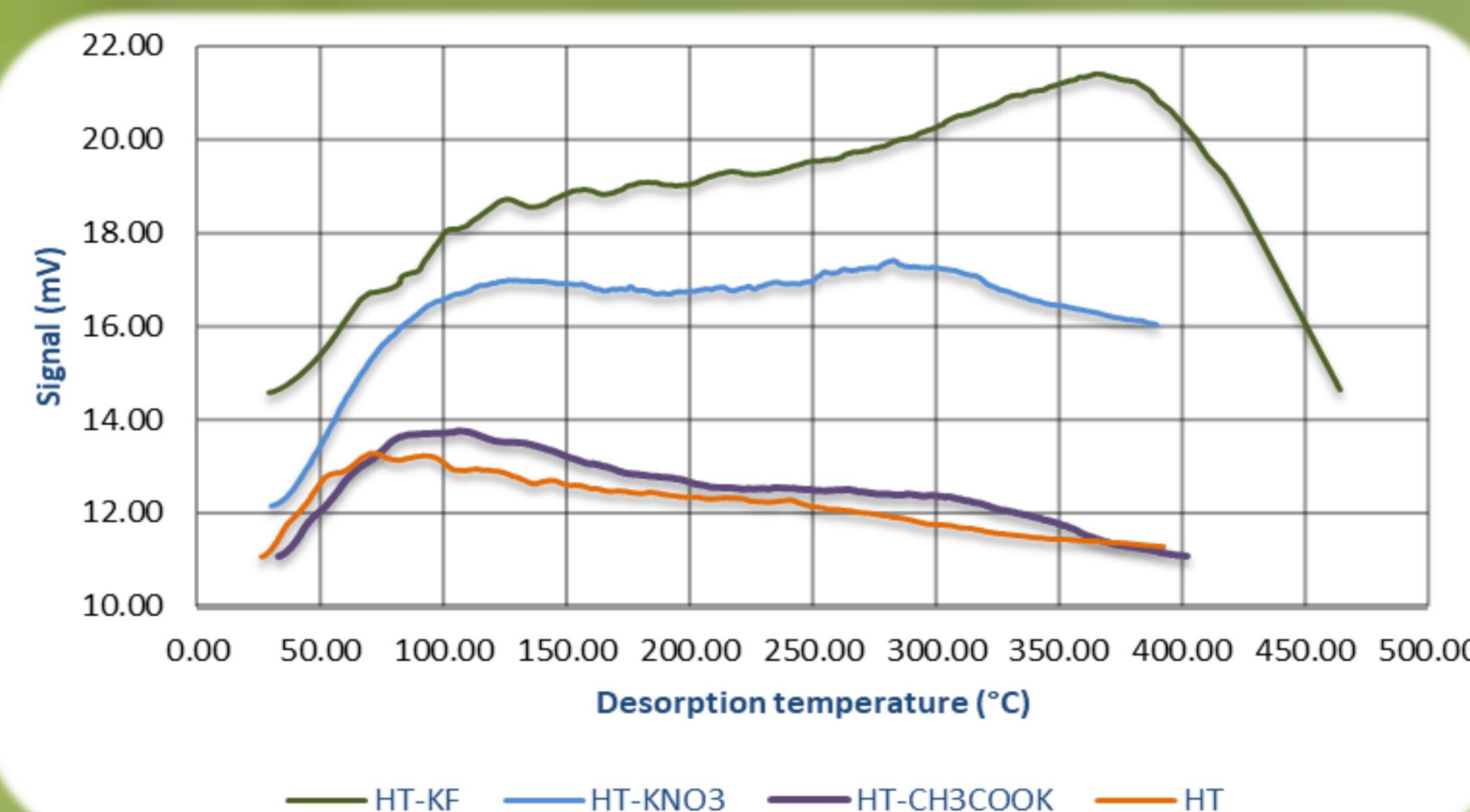


Fig. 1 Dependence of signal on desorption temperature of CO₂ from TPD-CO₂

Transesterification over mixed oxides goes by basic mechanism. Therefore, one of the most important properties of catalyst is basicity. As can be seen in Fig. 1 impregnation of K on catalyst significantly increased total basicity (Tab.2). On the other hand, acidity is rapidly increased with K impregnation, which is not desirable. In case of specific surface, important catalyst parameter, CH₃COOK impregnation increased specific surface in compare with basic HT catalyst.

Tab.2 Catalytic properties of prepared mixed oxides

Sample	S(BET) (m ² /g)	V _p (cm ³ /g)	D _p (nm)	Total basicity (mmol CO ₂ /g)	Acidity (mmol /g)
HT	252	1.04	11	0.521	0.54
HT - KF	134	0.592	16	1.376	1.0
HT - KNO ₃	237	0.689	8	0.803	1.1
HT - CH ₃ COOK	335	0.389	14	0.616	1.12

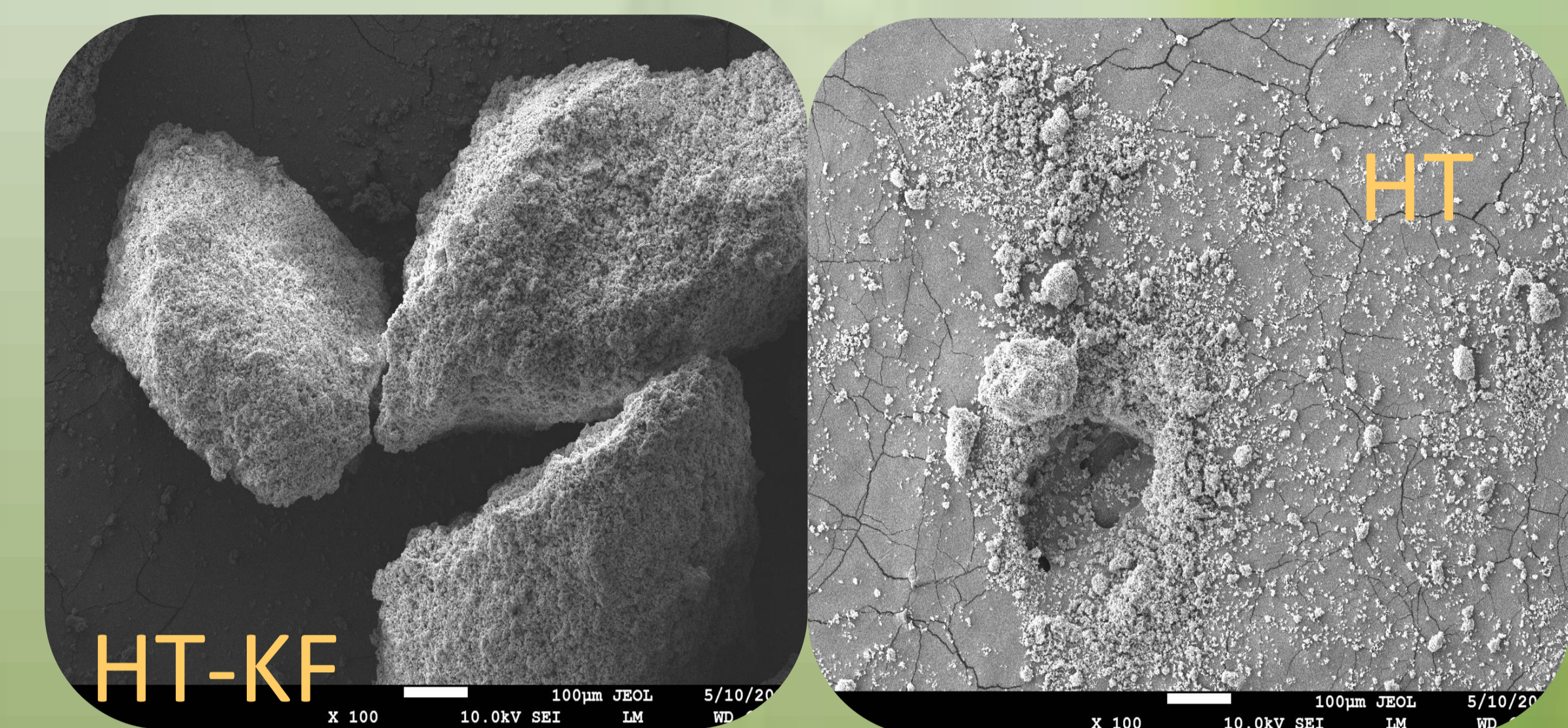


Fig. 2 SEM scans of HT-KF in compare with HT sample

For detail surface comparison SEM scans were obtained. As can be seen in Fig.2 catalyst with impregnated K shown significantly bigger particles on surface. Bigger particles should prevent entry into active sites and thus decrease catalyst activity.

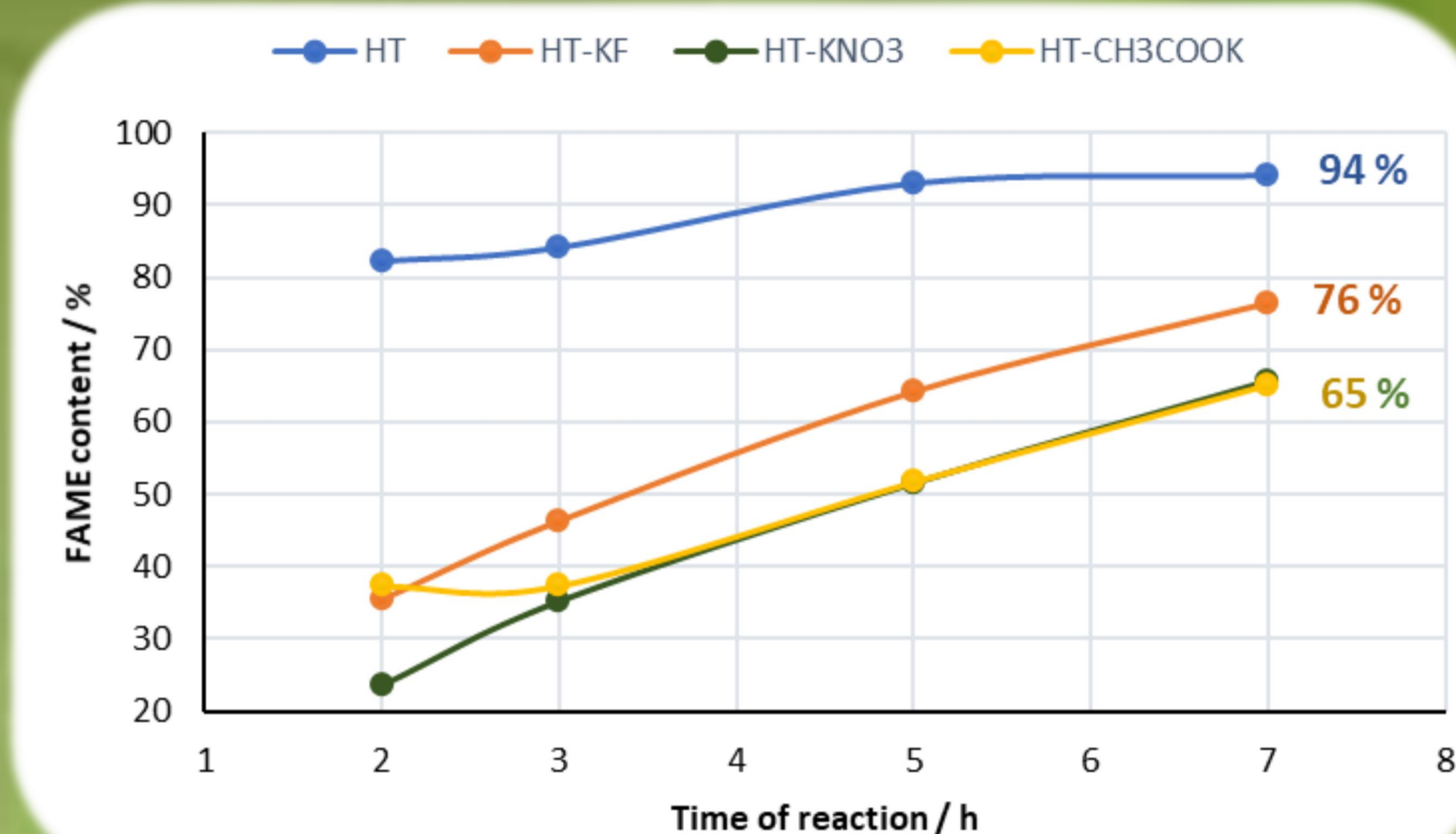


Fig. 3 Dependence of FAME content on reaction time

As can be seen (Fig.3) catalyst activity of basic catalyst and impregnated is different. Basic HT catalyst reached after 7 hours of reaction content of FAME 94 %, while impregnated samples reached lower than 80 %. Impregnation of K significantly decreased catalyst activity in transesterification.

Conclusion

- Basic Mg/Al hydrotalcite was prepared by co-precipitation
- Three different mixed oxides were treated by impregnation by potassium with different solutions (KNO₃, CH₃COOK, KF)
- Non-impregnated catalyst (HT) reached higher content of FAME (94%) after 7 hours of reaction than impregnated samples.
- Results shown that impregnation of Potassium improved properties of mixed oxides such basicity, specific surface or pore volume but decreased catalytic activity.
- With higher acidity, decreased content of FAME in product.
- Higher amount of Potassium, higher content of FAME.

Acknowledgement

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