Supporting Information (SI) for

Surface Properties of Hydrotalcite-Based Zn(Mg)Al Oxides and Their Catalytic Activity in Aldol Condensation of Furfural with Acetone

Lucie Smoláková[†], Karel Frolich[*†], Jaroslav Kocík[†], Oleg Kikhtyanin[‡], and Libor Čapek[†]

[†] *Department of Physical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic*

[‡] *Research Institute of Inorganic Chemistry, RENTECH-UniCRE, Chempark Litvínov, Záluží – Litvínov, 436 70, Czech Republic*

[*] Tel: +420-466037261; E-mail: karel.frolich@upce.cz

List of contents:

Figure SI 1: Adsorption isotherms of CO_2 at 34 °C on Mg_2Al, Mg_2Al (B), Zn_1Mg_1Al and Zn_2Al mixed oxides.

The measurement of adsorption isotherms was performed on homemade volumetric/manometric device equipped with capacitance pressure gauges (Pfeiffer Vacuum) connected to the calorimeter.
The curve limiting is shifted among samples according to the amount of adsorption sites. The curve shape among samples is comparable. Depicted isotherms are typical for systems where both chemisorption and physisorption occur. Near zero equilibrium pressure corresponds to the irreversible sorption of molecules, interaction energies higher than 50 kJ.mol^{-1}. With increasing equilibrium pressure the reversible sorption takes place.

Figure SI 2: FTIR spectra of the Mg_2Al, Mg_2Al (B), Zn_1Mg_1Al, and Zn_2Al mixed oxides treated at 450 °C: detail on the region of OH stretching. Spectra are translated according to y axis.

HT precursors contain large amount of water (and carbonates) in the interlayer. During the sample treating the intensity of OH stretching is decreasing due to water desorption (physisorbed and interacting with carbonates) and dehydroxylation of the sample. Relatively small amount of hydroxyls is still remaining after treatment even at 450 °C which is declared on attached spectra. These basic hydroxyls are responsible for the formation of bicarbonate species with CO_2 molecules.

Figure SI 3: FTIR spectra of the CO_2 interaction with Mg_2Al, Mg_2Al (B), Zn_1Mg_1Al and Zn_2Al mixed oxides: detail on the region of molecularly bound CO_2 (antisymmetric stretching vibration (ν_3)). Spectra obtained at 100 mbar CO_2 equilibrium pressure (gas phase and activated sample spectrum subtracted in background).

The CO_2 adsorption on mixed oxides is related besides (pseudo)carbonates also with molecularly bound molecules characterized by IR signals around 2340 cm^{-1}. Such species are formed on unsaturated cations Me^{n+}. Molecular species have low stability – they are decomposed rapidly at RT during evacuation of gas from IR cell. Such species correspond to the lowest adsorption energies, the lowest adsorption heats observed (see calorimetric curves).
Majority of Me^{n+} are engaged in basic Me^{n+}-O^{2-} pairs being responsible for relatively stable carbonate species with IR bands in region 1100 – 1800 cm^{-1}.

Figure SI 1:

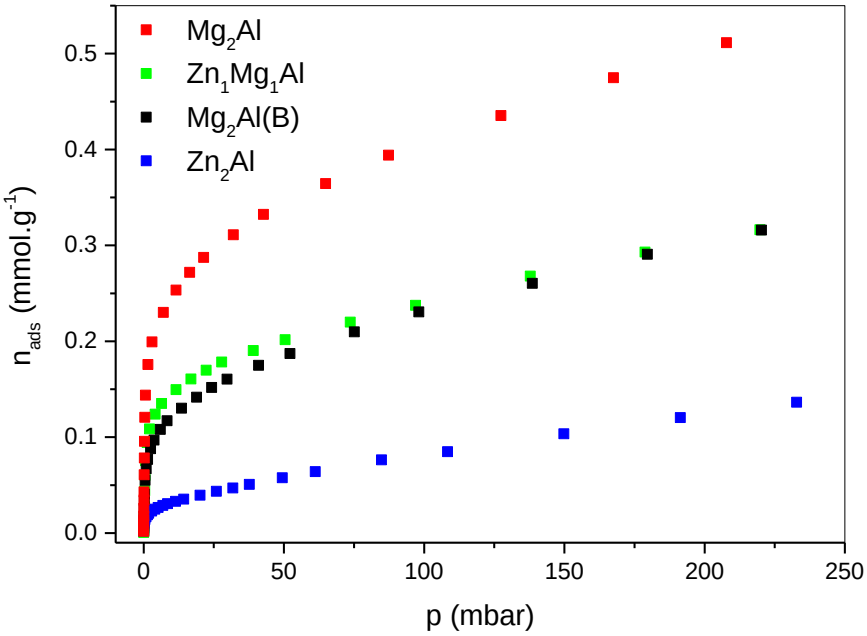


Figure SI 2:

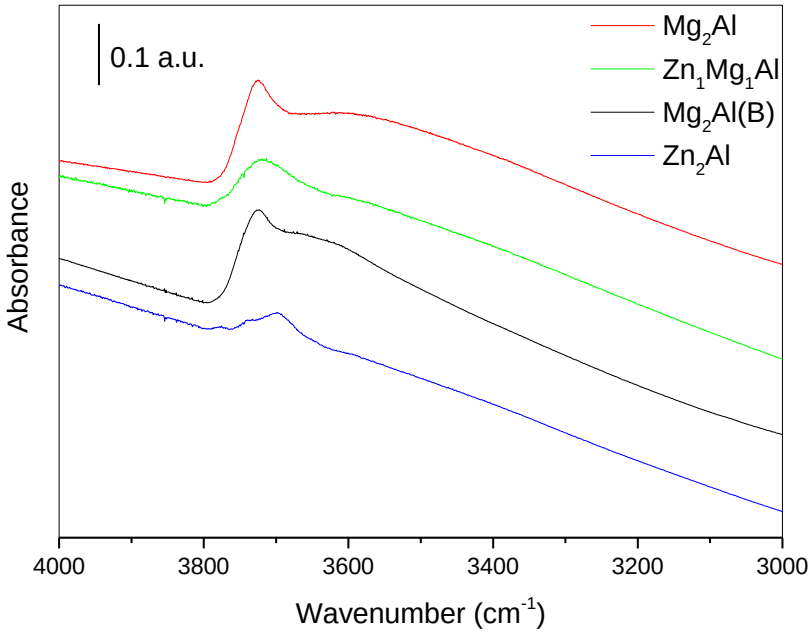
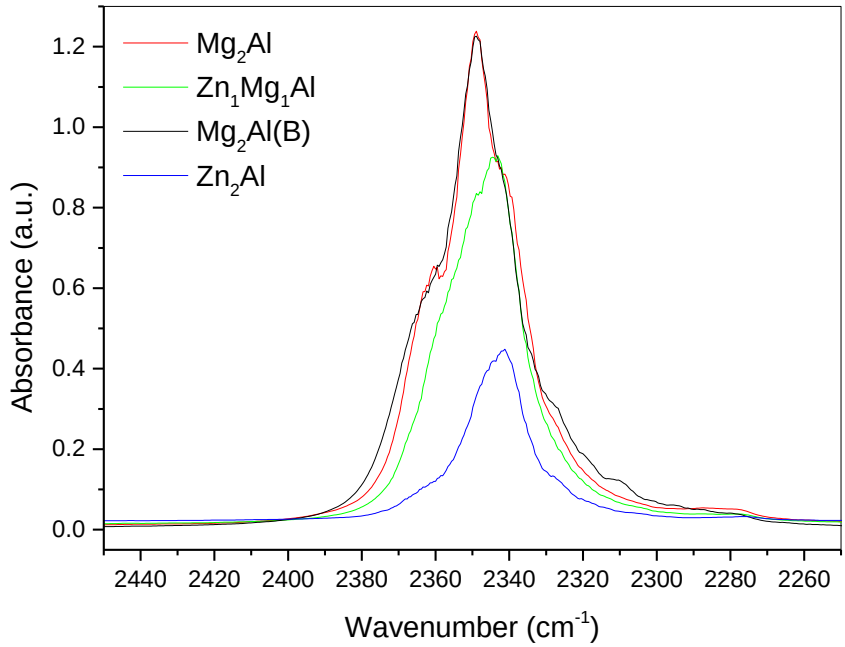


Figure SI 3:


Mg2Al
Zn1Mg1Al
Mg2Al(B)
Zn2Al
Absorbance (a.u.)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
2440
2420
2400
2380
2360
2340
2320
2300
2280
2260
Wavenumber (cm-1)