

detected with XRD in the studied samples. Chemical analysis confirmed that the real compositions of the samples corresponded to the nominal ones. ESR investigation revealed that both isolated and clustered Cu(II) ions are present in all samples, the contribution from the latter strongly increasing with γ . Activity of LDH samples in oxidation of xylenes depended on their composition, the maximum yield approaching 20%. The presence of copper ions was essential for generating the catalytic activity. The major oxidation products were methylbenzaldehydes and dimethylphenols. With increasing concentration of copper the overall yield of the reaction increased, passed through a maximum, and then decreased. Additional experiments showed that in the absence of an organic reagent the samples decomposed the hydrogen peroxide, the activity in this process being particularly pronounced for materials with high concentration of copper, i.e. with large content of clustered copper ions. On the other hand, significant yields of xylene oxidation products appeared only in samples with appreciable contribution of isolated copper species. The pattern of activity is discussed in terms of the nature of copper centres and competition between the oxidation of the organic substrate and the decomposition of hydrogen peroxide.

LOCATION AND QUANTIFICATION OF THE STRUCTURAL IRON IN KAOLINITE: A COMBINED X- AND Q-BAND ELECTRON PARAMAGNETIC RESONANCE STUDY
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Trivalent iron is the most common impurity in kaolinites. X-band Electron Paramagnetic Resonance (EPR) spectra of natural kaolinites exhibit three superimposed signals due to paramagnetic Fe^{3+} ions located in distorted sites and a broader signal related to superparamagnetic nanocrystalline Fe oxides. Paramagnetic Fe^{3+} signals are referred to as $\text{Fe}_{(1)}$, $\text{Fe}_{(1)A}$ and $\text{Fe}_{(1)B}$. The $\text{Fe}_{(1)}$ signals correspond to Fe^{3+} substituted at Al^{3+} crystallographic sites Al1 and Al2 in the kaolinite structure whereas the $\text{Fe}_{(1)}$ signal occurs in the spectra of poorly ordered kaolinites. We present a detailed EPR investigation of kaolinites and dickites from different environments at 9 GHz (X-band) and 34 GHz (Q-band) which: (i) shows that the $\text{Fe}_{(1)}$ signal is due to the occurrence of dickite-like sequences in the structure of poorly ordered kaolinites, (ii) allows quantification of the distribution of Fe^{3+} between isolated ions and concentrated phases. Using an inversion procedure based on the calculation of X and Q-band EPR spectra, we determined the distribution of fine-structure parameters related to the stacking disorder in kaolinites. This distribution indicates that, in poorly ordered kaolinites, Fe^{3+} ions are distributed between $\text{Fe}_{(1)}$ sites and other sites with the symmetry of the dickite sites. Calculation of the X-band spectrum of kaolinites, and comparison with the EPR spectrum of an Al_2O_3 sample doped with Fe^{3+} as an external standard, allowed a quantitative assessment of site occupancies regardless the stacking order of the kaolinite.

ELECTRON OPTICAL OBSERVATIONS OF CRYSTAL GROWTH AND REACTIVITY OF NATURAL AND SYNTHETIC 1:1 LAYER SILICATES

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Due to the polar structure of their single layer, 1:1 layer silicates may nucleate a wealth of possible microstructures with different layer topologies. They may also result from solid-state phyllosilicate transformations. Electron microscopy techniques like high-resolution transmission electron microscopy (HRTEM) and field emission gun scanning electron microscopy (FEGSEM) are used here to identify and characterize such features and their admixtures in natural and synthetic samples. Flatness and/or curvature of the single layer are basic features that operate separately or combine to build-up these microstructures as platelets, tubes, cones and polygonal rolls. Curved and flat microstructures form under high and low supersaturation

conditions, respectively. Starting from gel hydrothermal ripening in the $\text{MgO-SiO}_2\text{-H}_2\text{O}$ (MSH) system yields successively conical and tubular chrysotile, polygonal serpentine (PS) and eventually flat lizardite. This suite of microstructures illustrates their decreasing metastabilities and progressive elimination of the layer curvature. From HRTEM images, crystal growth mechanisms of chrysotile tubules are found to be first the closure of "roman tiles" and then concomitantly the lateral extension of permanent steps (outside and inside the tube) for scrolls of chrysotile and PS, and thick-layer nucleation inside and outside the tube for cylindrical chrysotile and PS. Interlayer hydrogen bonding plays an essential role for stabilizing flat microstructures. This is also valid in case of strong intralayer misfit. Curvature causing partial resorption of the intralayer misfit shows up in metastable microstructures only. From their mode of storage of elastic energy rolled microstructures of 1:1 layer silicates cannot be considered as stable phases either.

AN X-RAY DIFFRACTION AND ABSORPTION STUDY OF THE PHASES FORMED UPON CALCINATION OF Zn-Al-Fe HYDROTALCITES

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In the present paper we report on the properties of mixed oxides obtained after calcination of hydrotalcite-like materials containing Zn(II) and Al(III) in the brucite-like layers, and hexacyanoferrate in the interlayer, as well as on other materials containing Zn(II), Al(III) and Fe(III) in the layers, but carbonate in the interlayer, with different Al/Fe ratios. Thermal decomposition of samples in air has been studied by TG-DTA. The parent hydrotalcite samples were calcined in air at 200, 400, 600 and 800°C, in order to identify the phases existing before or after each thermal effect, and after high temperature calcination. Calcination at 800 °C leads to samples with sharp PXRD peaks due to ZnO and a spinel. From a study of the precise PXRD positions of the peaks recorded, the nature of the spinel formed in our case could be concluded, taking into account the linear relationship existing between the Fe/Al ratio and the a parameter in synthetic $\text{ZnFe}_y\text{Al}_{2-y}\text{O}_4$ spinel. PXRD peaks due to ZnAl_2O_4 spinel are recorded in all samples, but slightly shifted because of partial Fe/Al substitution. On the other hand, for Fe/Al = 0.5, peaks due to ZnFe_2O_4 spinel are also recorded, and also are shifted because of the Fe/Al substitution. From the Fe/Al ratio, and upon comparison with the Fe/Al ratios from elemental chemical analysis, an approximate value for the content of each spinel has been calculated.

THERMAL EVOLUTION AND CATALYTIC ACTIVITY OF Pd/Mg/Al MIXED OXIDES OBTAINED FROM HYDROTALCITE-TYPE PRECURSOR

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Innovative palladium catalysts were prepared from a new hydrotalcite precursor (HT) containing magnesium aluminium and palladium ions (66/29/5 as atomic ratio) homogeneously dispersed in the brucite-type sheets. The insertion of palladium ions inside a crystalline precursor overcomes the problem of dishomogeneity and low stability very often found in the catalysts obtained by impregnation methods and allows a deeper investigation of the sample evolution. The thermal evolution of the HT phase and the reversibility of the Pd/PdO transformation were studied using several techniques in order to correlate the catalytic activity in the total oxidation of methane with the Pd-containing species, which seem to play a determinant role during the reaction. The X-ray diffraction data of the HT calcinated at 923K and 1173K showed an increasing amount of Pd-segregated phases. In order to clarify its thermal

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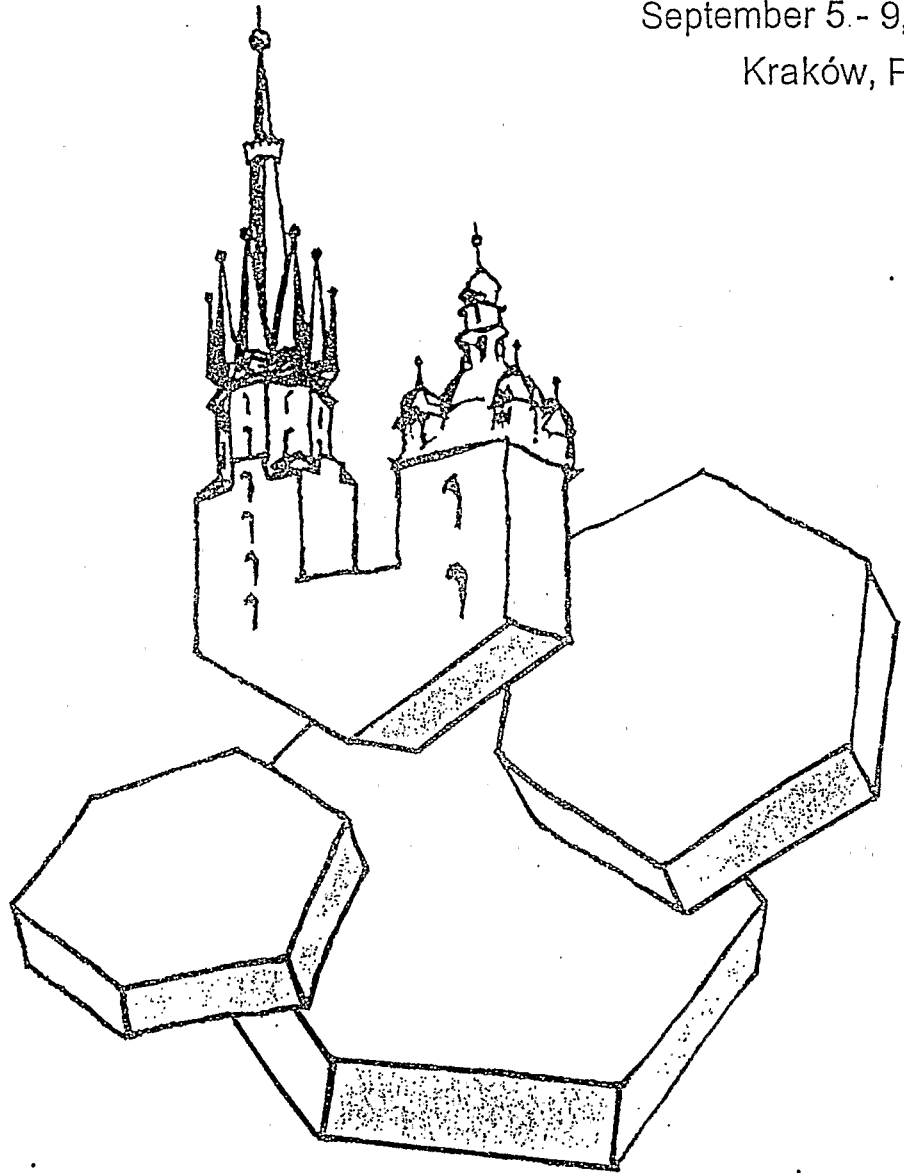
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