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THE INFLUENCE OF CATION INTERCALATING INTO CLAY ON ACIDIC PROPERTIES

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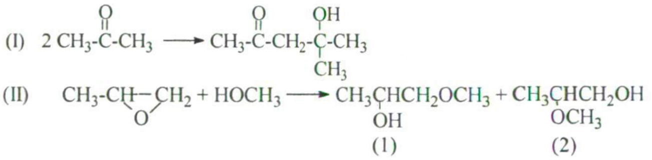
Pillared clays (PILC) are applied both as support and active phase in heterogeneous catalysis. These materials may possess acid-base character as well and in some cases they are regarded as super acidic materials. Our task was to find the correlation between the type of cation species (pillaring agent) intercalating into the interlayer space of clay and catalytic activity of PILC ($M^{n+}_{x/n}(Al_{4-x}Mg_x)(Si)_8O_{20}(OH)_4$ montmorillonite type, M = Na^+, H^+, cation of Keggin structure Al_{13}^{7+}). The nature of pillaring agent determine the surface area and pore size. X-ray and BET data show that texture characteristics depends on thermal treatment of Al_{13}^{7+}-PILC.

Acidities of PILCs (Na^+-PILC, H^+-PILC and Al_{13}^{7+}-PILC) were studied by IR spectroscopy both analysing the band due to OH-vibrations and following the adsorption of carbon oxide. Acid strength distribution of the PILC pretreated under different conditions was determined by using an indicator method. It was found that the total acidity was increased in the order: Na^+-PILC > H^+-PILC > Al_{13}^{7+}-PILC (Table 1). The number of acid sites decreases exponentially. As the pretreatment temperature of PILC is increased, the measured number of most strongly acidic sites ($H_0 = -5.6$) increases up approximately 500°C, apparently due to the elimination of water molecules previously guarding the proton.

The catalytic property was studied in the reactions such as the acetone dimerisation (I) and the reaction of propylene oxide with methanol (II):



$$\text{(I)}\quad 2\,CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_3 \longrightarrow CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}CH_2\text{-}\underset{CH_3}{\overset{OH}{C}}\text{-}CH_3$$

$$\text{(II)}\quad CH_3\text{-}\underbrace{CH-CH_2}_{O} + HOCH_3 \longrightarrow \underset{(1)}{CH_3\underset{OH}{C}HCH_2OCH_3} + \underset{(2)}{CH_3\underset{OCH_3}{C}HCH_2OH}$$

It was shown, that in both reactions catalytic activity of PILCs correlated with the amount and nature of the acidic sites and increased in the order: Na^+-PILC > H^+-PILC > Al_{13}^{7+}-PILC. In the reaction (II) the selectivity is virtually independent of the nature of the pillaring agent. Catalytic activity increased with increasing total acidity. It was established that catalytic activity depends on pretreatment procedure, namely temperature, nature and ratio pillaring agent–clay. The mechanisms of reactions (I) and (II) in the presence of PILCs was discussed. H^+-MM and Al_{13}^{7+}-MM were more efficient than H-ZSM–5 and bentonite in both reactions.

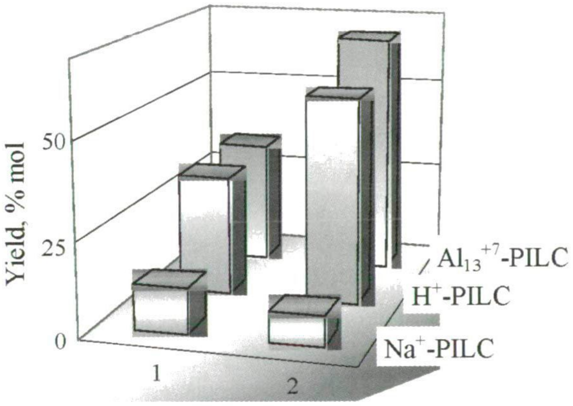


Fig. 1: The reaction propylene oxide with methanol (C_3H_7O / MeOH = 1/10 mol) in the presence of PILCs (3wt%) at 60°C for 6 hours

Acknowledgements
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Reference

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Table 1: The main characteristics of PILC

PILCs	d_{001} Å	(A) $k \cdot 10^4$ s^{-1}	Acidity, $mmol \cdot g^{-1}$ (B)	Acidity, $mmol \cdot g^{-1}$ (C) Ho = –5.6	Ho = –3.0	Ho = +3.3	Ho = +4.8
Na^+-PILC	15	2.1	0.03	0.01	0.04	0.30	0.42
H^+-PILC	15	4.7	0.04	0.10	0.20	0.28	0.41
Al_{13}^{7+}-PILC	17	9.3	0.06	0.10	0.24	0.32	0.43

(A) Reaction rate constant of acetone dimerisation reaction (50°C, catalyst 10wt%, PILCs heated at 500°C, 3 hours); (B) Total acidity measured by adsorption CO; (C) Acid strength distribution was determined by Hammet acidity titration with n-butylamine