Shape Selective Pillared Clay Catalysts for P-Xylene Production

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ABSTRACT

Catalytic alkylation of toluene with methanol was carried out over Zr- Cr- and Co- pillared clay catalysts in a catalytic flow system operated under atmospheric pressure at a temperature range of 250-450°C. The pillared clay catalysts were prepared via sonication technique. Results indicated that the pillaring of montmorilonitic clay material with polyoxy-metalic cations (Zr- Cr- and Co-) improves the texture properties and thermal stability of the obtained catalysts. The Co-PILC catalyst is the most active and selective catalyst towards p-xylene formation, i.e. Co-PILC catalyst is a shape selective for p-xylene formation.

1. Introduction

Materials based upon mineral clays are very interesting, since their physical and chemical properties can be changed and/or modified by many ways [1, 2]. Montmorillonite clay is an inexpensive and thermally unstable clay mineral which can be converted into highly porous and stable structures by pillaring process leading to optimization of its properties as sorbents or catalysts [3, 4].

Pillaring of montmorillonites clay with polyoxymetal cations enhance the solid acid catalysts properties by propping apart the clay sheets leading to increase surface area and pore volume, so exposing much of the interlayer region (intracrystal surface area) and acid sites to reactant molecules. Acidic properties of the pillared clay arise from Lewis centers, presented in the pillars and Brönsted centers, associated with the structural hydroxyl groups of the layers, so, it can change by varying the pillaring agent [5, 6], parameters and method of the pillaring processes [7].

Aromatic hydrocarbons, especially benzene, toluene and xylenes are the most important raw materials for petrochemical industries. Over the past decade, the price of toluene has lagged considerably behind benzene and xylenes, thereby providing considerable incentive for the development of a process to alkylated toluene. Alkylation of toluene with methanol is an attractive synthetic route to either xylenes or styrene and ethyl benzene [8, 9].

The product distribution is depended on whether ring alkylation, side chain alkylation or toluene disproportion is favored. Xylenes are mainly generated from ring alkylation of toluene with methanol, while styrene and ethyl benzene are the main products of side-chain alkylation (Scheme 1) [10, 11]. The ring-alkylation of toluene with methanol is a reaction well-characterized as a Brönsted acid catalytic process.

In this study, the polyoxycationic (Zr, Cr and Co) oligomeric pillaring species are prepared uniformly and rapidly by heating effect of microwaves, after that, the intercalation process occurred via ultrasonic route to obtain more

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stable intercalated materials within a few minutes at an ambient temperature. Characterization of the prepared samples was investigated by X-ray diffraction, N_2-adsorption/desorption isotherm (BET), TGA analysis and pyridine desorption (total acidity measurements).The effect of the different pillaring agent (Zr- Cr- and Co-) on the performance of the prepared PILCs towards toluene methylation and the correlation between the acidity measurements of the samples and their catalytic activity was also investigated.

2. Experimental procedure
2. 1. Catalyst preparation
Cobalt, Chromium and Zirconium polyoxycationic species were prepared using microwave radiation. 0.1M of $ZrOCl_2$, $CrCl_2$ and $CoCl_2$ solutions were brought to irradiate in a microwave at a power level of 640W for 10min.

Co-, Cr- and Zr-PILCs are prepared using ultrasonic route, 150ml of the prepared polyoxycationic solution was added dropwise to 5wt% of clay suspension. The mixture was then subjected to sonication for 30 min for enhancing the pillaring process. The obtained slurry was filtered, washed until it was chlorine free, dried and calcined at 450^oC for 4 h in purified air.

2.2. Characterization methods
Thermal gravimetric analysis (TGA) was carried out using SETARAM Labsys TG-DSC16 equipment in the temperature range of room temperature up to 1000^oC under a nitrogen flow, in order to follow the thermal stability of the prepared catalyst.

X-Ray diffraction analysis (XRD) was carried out by Shimadzu XD-1 diffractometer using Cu-target and Ni-filtered radiation, to trace the various changes in the crystalline structure and the different phases accompanied with the intercalation process. The sample powders were packed in a glass holder, and then measurements were taken of the diffraction intensity by step scanning in a 2h range between 4o and 70°.

The textural properties were determined from the N_2 adsorption–desorption isotherms measured at liquid nitrogen temperature (-196^oC) using a NOVA2000 gas sorption analyzer (Quanta chrome Corporation) system. All samples were degassed at 200^oC for 17hrs in a nitrogen atmosphere prior to adsorption to ensure a dry clean surface.

The total amount of acidity was estimated from weight loss measurements of the adsorbed pyridine using SETARAM Labsys TG-DSC16 equipment. First, platinum crucible containing 50mg of the sample was placed in a shallow porcelain plate and inserted into a glass reactor adapted to a tubular furnace. The sample was dehydrated in dried N_2 (100 ml min-1) at 120^oC for 2h, cooled to 70^oC, and then gaseous pyridine diluted in N_2 was allowed to pass through the sample for 1.5h. The temperature was held at 70^oC under N_2 for 1h to remove the physically adsorbed pyridine. After that, the samples were subjected to TGA investigation.

2. 3. Catalytic activity
Catalytic toluene methylation over the prepared pillared interlayered clay catalysts was performed in a flow system operated under atmospheric pressure, in the temperature range of 250-450^oC, with a N_2 flow rate of 40ml/min, and at toluene/methanol molar ratio = 3/1. A 0.5 g catalyst was activated at 400^oC for 2 h before being subjected to the reaction, then the reactant was fed into the reactor by means of a syringe pump (Cole palmer) at LHSV = 0.6h-1. The products and the unreacted reactant were condensed by means of a water condenser, the liquid samples were collected and subjected to gas chromatographic analysis (Perkin-Elmer GC) with hydrogen flame ionization detector.

3. Result and discussion
3.1. Characterization data
The thermal behavior of the prepared pillared interlayered clay materials (Fig. 1), represents an endothermic peak at a temperature range 25-200^oC (centered at 140^oC) accompanied by 18.5. 14.3 & 3% weight loss (TGA curve), for Co-PILC, Cr-PILC and Zr-PILC respectively, corresponds to the loss of the physically adsorbed water on the external surface.
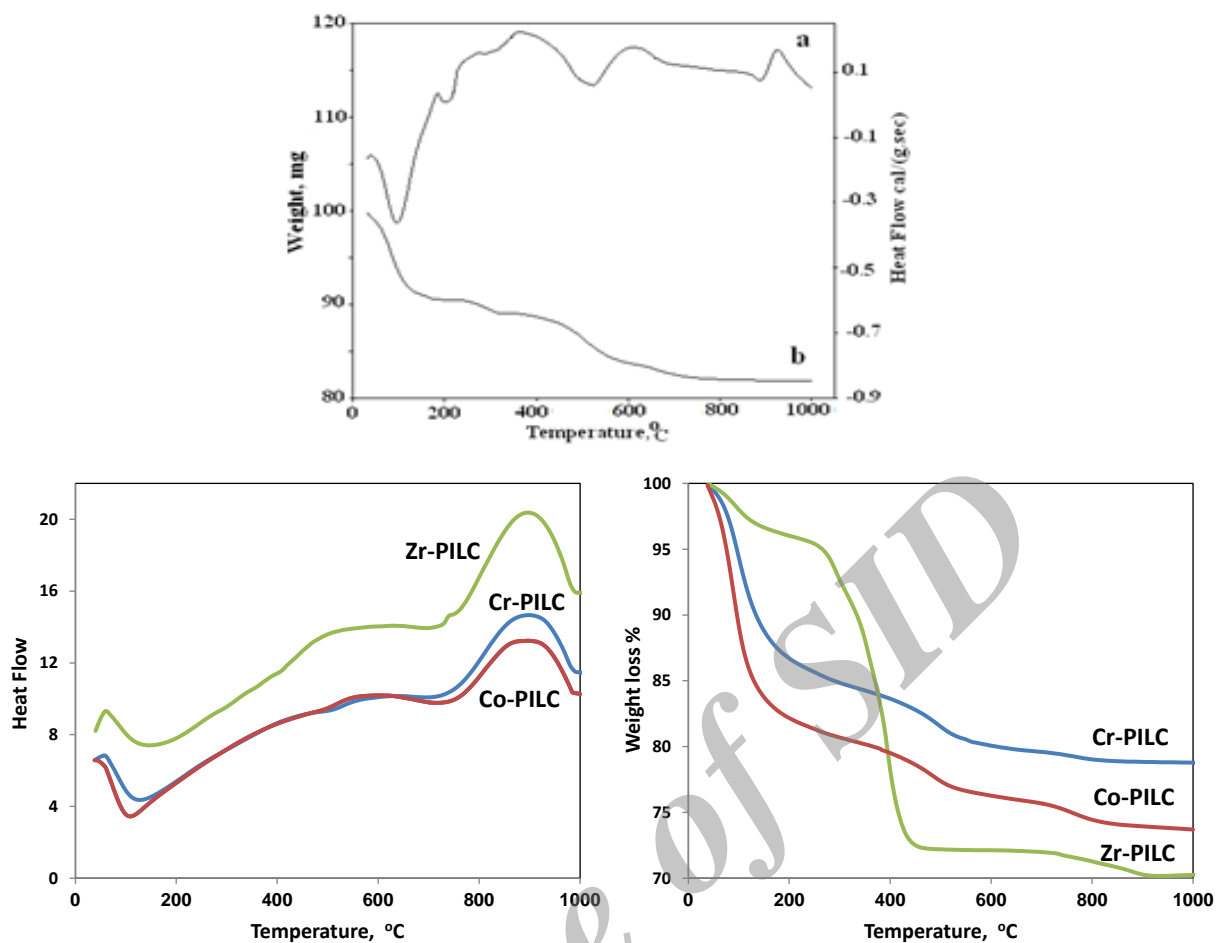
Fig. 1. Thermal behavior of parent clay (a) and the prepared pillared interlayered clay samples

A second weight loss was observed at 230°C (for Zr-PILC sample), which is attributed to the loss of water and some hydroxyls from the oligocations pillars in the interlayer region [12]. The observed shift of this peak to a higher temperature 400°C for Co-PILC and Cr-PILC samples may be attributed to the strong solvation power of Co and Cr cations that hindered the escape of the interlamellar water in their coordination sphere and enhanced the stability of the silicates interlayer structure. Moreover, the higher weight loss observed for Zr-PILC (23.36 %) compared to Co-PILC and Cr-PILC (2.53 & 3.34 %, respectively) indicates the high crosslinking of the Zr pillars inside the lamella and the decrease in the

Brönsted acid cites (in correlation with acidity data Table 1). The weight losses 1.77, 1.52 & 0.55% for Zr- Co- & Cr-, respectively, at temperatures higher than 700 ^{o}C are associated with the DE hydroxylation of the pillars and the clay structure. In addition, an exothermic peak appeared at 950°C due to the crystallization of new oxide phases from destroying pillared clay structure [13].

X-ray diffraction pattern of the parent clay reveals the main characteristic lines for montmorillonite identified by d-spacings at 12.99, 4.53 &1.49Å [ASTM 12-0204], in addition to the smell of kaolinite and quartz together with non-clay minerals of quartz (Fig. 2).
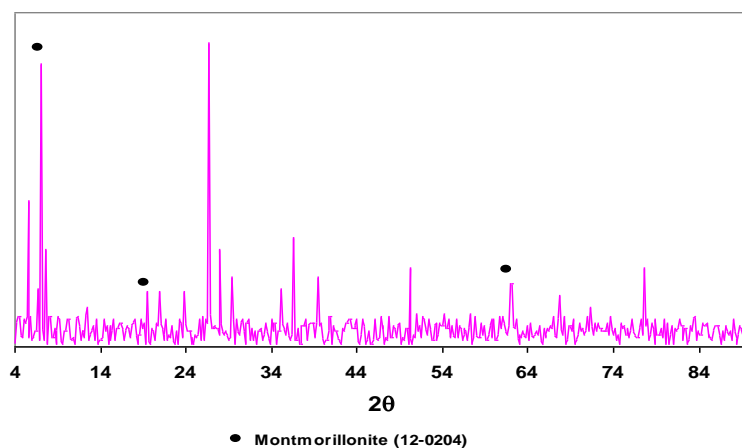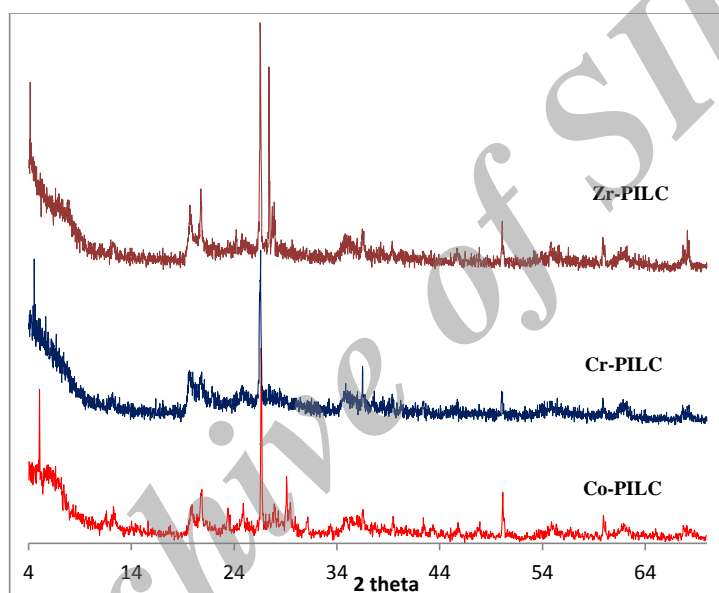
Fig. 2. XRD pattern of the parent clay

Fig. 3. XRD pattern of the prepared pillared interlayered samples

On the other hand, the XRD data for the prepared pillared interlayered clay samples established the success of sonication route for the pillaring process. The basal spacing of Co-PILC, Cr-PILC and Zr-PILC increased from 12.99Å (for the parent clay) to 17.97, 19.39 and 21.27 Å, respectively, indicating the inclusion of the pillars probing penetrates the interlayer structure and results in an observed expansion in the interlamellar distance (Fig. 3). Accordingly, the expansion of the interlamellar distance was found to be dependent on the

atomic radius of the pillaring agent (Co (125), Cr (129) and Zr (160 pm)), concurrently, the Zr-pillar is the most efficient one in propping apart the clay layers.

As it is known, the pillared bentonitic clay has a high permanent porosity that was obtained by separating the clay sheets by a molecular prop or pillaring agent. Thus, the high surface area and porosity of the pillared clay samples (Table 1 & Fig. 4) are related to incorporation of Co, Cr and Zr pillars into the interlamellar space.

Table 1. The texture properties of the prepared samples

	Total acidity µmol/g	surface area m²/g	external surface area m²/g	micropore surface area m²/g	total pore volume cc/g	micropore volume cc/g	pore radius Å
Parent clay	216.12	43.1	40.6	3.5	0.78	0.056	37.00
Zr-PILC	706.07	205.3	134.7	70.6	0.21	0.0007	17.92
Cr-PILC	10047	141.9	106.1	35.8	0.19	0.007	18.15
Co-PILC	14853	133.2	84.6	48.7	0.11	0.001	18.02
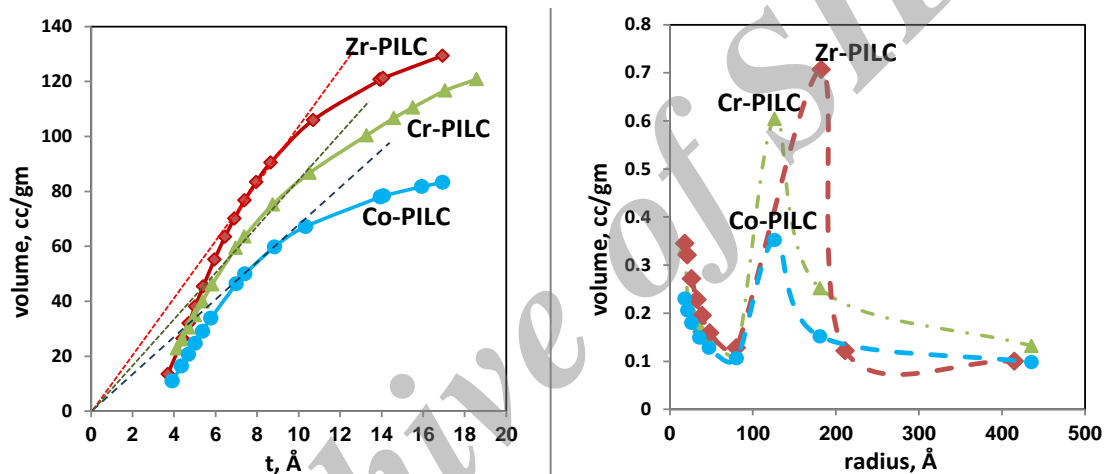
Fig. 4. BJH pore size distribution and v-t plot of the prepared samples

The adsorption-desorption isotherms of the prepared pillared clay samples are related to type IV according to Brunauer, Deming, Deming, Teller (BDDT) classification, indicating a well-developed mesoporous structure that includes micropores as improved by v-t plot (Fig. 4). The samples isotherm exhibit H3 type hysteresis loop according to IUPAC classification. This type indicates the presence of slit shaped pores or plate like particles with space between the parallel plates [14]. The decrease of pore volume is most probably due to the occupation of the pores by the pillars species that gives rise to decrease of pore radius (Fig. 4).

3. 2. Catalytic activity

Toluene methylation reaction is an acid catalyzed reaction, therefore, the acid sites provided by PILC catalysts are necessary for carbonium ion formation. The metal pillar assists the stabilization of the carbonium ion that is formed on the acid sites by decreasing the rate of the backward decomposition to reform methanol and toluene. So, in this study, the effect of metal pillars and reaction temperatures on toluene alkylation with methanol was carried out over Zr- Cr- & Co-PILC catalysts, at 25°C intervals within the temperature range of 250-450°C and at toluene: methanol molar ratio=3:1.
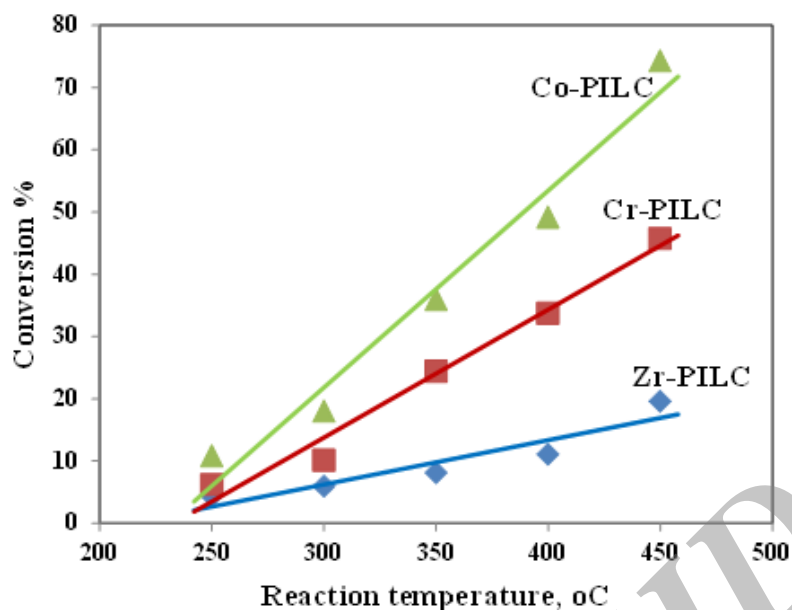
Fig. 5. The relation between reaction temperature and the total conversion over the prepared catalysts
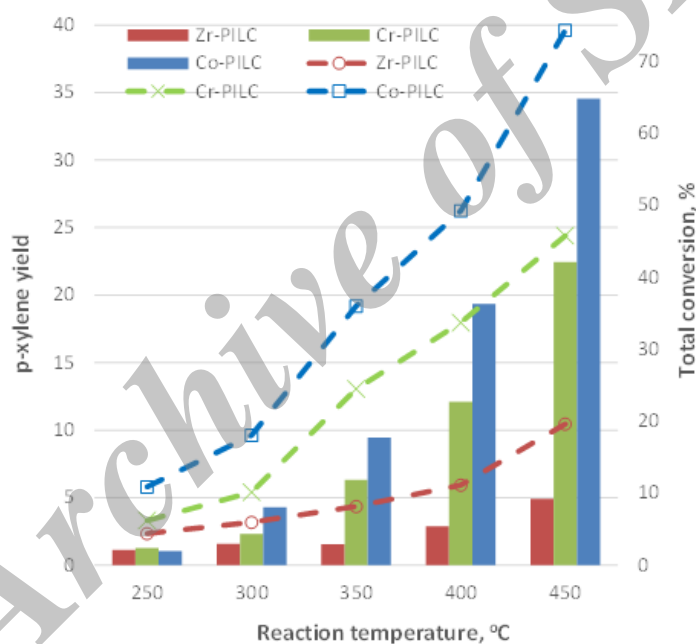

Fig. 6. The relation between total conversion (dotted line) and the yield of p-xylene (bars) at different reaction temperature over the prepared catalysts

The data presented in Fig. 5 clarified that the toluene conversion increased as the reaction temperature increased up to 450°C and the activity of the prepared pillared clay catalysts increases in the following order: Co-PILC > Cr-PILC > Zr-PILC in parallel with the order of acidity (Table 1). The reaction products are mainly composed of ethyl benzene, ethyl toluene, methyl benzene, o&m-xylenes and p-xylene (Table 2). The xylenes are the major products, whereas p-xylene exhibits the higher yield of the converted products (Fig. 6).

In the alkylation of toluene by methanol, the following reaction products paths were detected: xylene isomers (XY), as primary products, trimethylbenzene isomers (TMB),
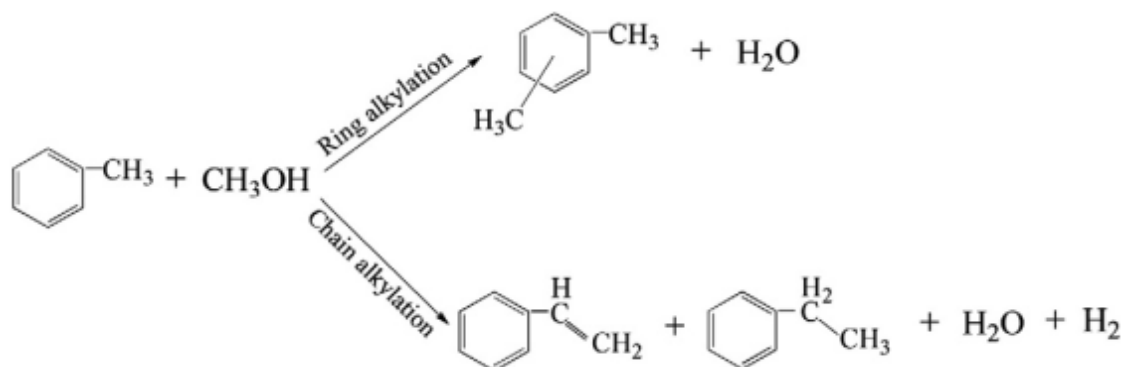
Scheme. 1. The two paths of the toluene alkylation with methanol
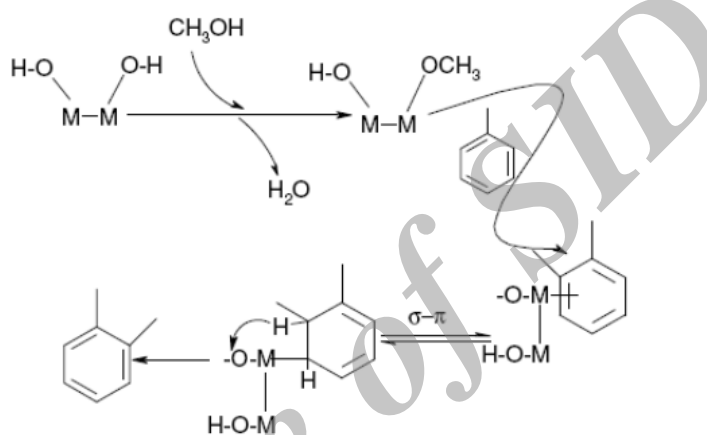
Scheme. 2. Ring alkylation mechanism over the prepared pillared clay catalysts

which provides from a second alkylation of the xylenes initially formed. On the other hand, ethyl benzene (ETB) was also produced by side-chain alkylation of toluene (Scheme 1), and ethyl toluene, produced probably due to the possible ring ethylating of toluene by ethylene provided from an intermolecular dehydration of methanol [15].

At high reaction temperature, all catalysts are selective to ring alkylation of toluene; xylenes were the major reaction products. While at lower reaction temperature, Cr-PILC and Co-PILC are more selective toward side-chain alkylation reaction (Table 2). An increase in the reaction temperature was accompanied by an increase in xylene selectivity (SXY), appearance of tri-methyl benzene and decrease in ethyl benzene and ethyl toluene. The absence of benzene as product even at the highest temperatures means that the disproportionation of toluene is negligible. The reaction of toluene
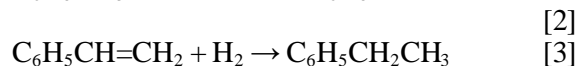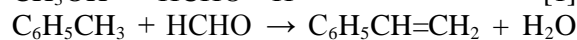
methylation is explained according to ring alkylation and side chain alkylation mechanisms:

In ring alkylation mechanism: the reactants are adsorbed on the BrÖnsted acid sites bridging hydroxyl, methanol strongly adsorbs on the catalyst acidic site before it reacts with the toluene which is weakly interact with the solid acids (Eley–Rideal type mechanism) [16]. Methanol is directly attached to the acidic proton sites on the clay via its oxygen atom and the CH3 group is immediately chemisorbed to the oxygen of the hydroxyl group [17], then the methyl group is attached to toluene forms π-complex with the layer metals. After π –σ conversion, a proton of toluene is given back to clay to form a new bridging hydroxyl group, and the xylenes and water are produced via the adsorption-desorption process.

On the other hand, the side chain alkylation mechanism [18] requires the complete absence

of Brönsted acid sites, since these would catalyze ring alkylation at a much higher rate [11]. In this mechanism, the role of the catalyst is twofold. First, it promotes the dehydrogenation of methanol to formaldehyde (step (1)). In step (2), styrene is formed from toluene and formaldehyde. This reaction may be enhanced through polarization of the methyl group of toluene by the catalyst which leads to a carbanion structure. In step (3), styrene is hydrogenated to ethylbenzene with the generated H in step (1).

$$CH_3OH \rightarrow HCHO + H \qquad [1]$$
$$C_6H_5CH_3 + HCHO \rightarrow C_6H_5CH=CH_2 + H_2O \qquad [2]$$
$$C_6H_5CH=CH_2 + H_2 \rightarrow C_6H_5CH_2CH_3 \qquad [3]$$

Table 2. Effect of reaction temperature on the catalytic activity of toluene methylation) as represent in the attached file

Catalyst	Zr-PILC					Cr-PILC					Co-PILC				
Temperature ^{o}C	250	300	350	400	450	250	300	350	400	450	250	300	350	400	450
total conversion	4.37	5.94	8.14	11.10	19.59	6.20	10.11	24.46	33.70	45.76	10.86	18.02	35.98	49.21	74.30
Yield															
ethylene	0.14	0.12	0.36	0.10	0.00	0.34	0.96	2.68	2.09	1.00	1.10	2.08	6.33	2.44	1.05
Benzene	0.00	0.00	0.00	0.01	0.05	0.00	0.00	0.00	0.02	0.05	0.00	0.00	0.00	0.09	0.08
Ethyl benzene	0.33	0.48	1.03	2.01	3.62	2.92	3.24	5.85	6.85	6.98	5.92	5.75	7.25	9.27	10.21
ethyl toluene	0.86	1.07	1.13	1.01	0.96	1.11	2.16	3.99	3.52	1.52	2.24	3.86	5.57	4.54	4.02
Tri methyl benzene	0.11	0.11	0.13	0.33	0.42	0.12	0.23	0.76	1.42	2.44	0.25	0.38	2.06	2.18	4.13
m & o-Xylene	1.83	2.59	3.96	4.78	9.65	0.46	1.23	4.85	7.68	11.33	0.32	1.65	5.33	11.33	20.25
p-Xylene	1.10	1.58	1.53	2.86	4.89	1.26	2.30	6.33	12.11	22.44	1.03	4.30	9.44	19.36	34.55
Selectivity															
ethylene	3.20	2.02	4.37	0.92	0.01	5.42	9.49	10.96	6.21	2.19	10.13	11.54	17.59	4.96	1.42
Benzene	0.00	0.00	0.00	0.10	0.28	0.00	0.00	0.00	0.07	0.12	0.00	0.00	0.00	0.17	0.11
Ethyl benzene	7.55	8.08	12.68	18.08	18.48	47.00	31.99	23.92	20.33	15.25	54.49	31.92	20.15	18.84	13.74
ethyl toluene	19.68	17.94	13.88	9.12	4.88	17.88	21.34	16.30	10.45	3.32	20.62	21.42	15.48	9.23	5.41
Tri methyl benzene	2.52	1.85	1.60	2.97	2.14	1.98	2.27	3.11	4.21	5.33	2.34	2.11	5.73	4.43	5.56
m & o-Xylene	41.88	43.60	48.65	43.05	49.25	7.41	12.16	19.83	22.79	24.75	2.95	9.15	14.81	23.03	27.26
p-Xylene	25.17	26.51	18.82	25.76	24.96	20.31	22.74	25.88	35.94	49.04	9.48	23.86	26.24	39.34	46.50
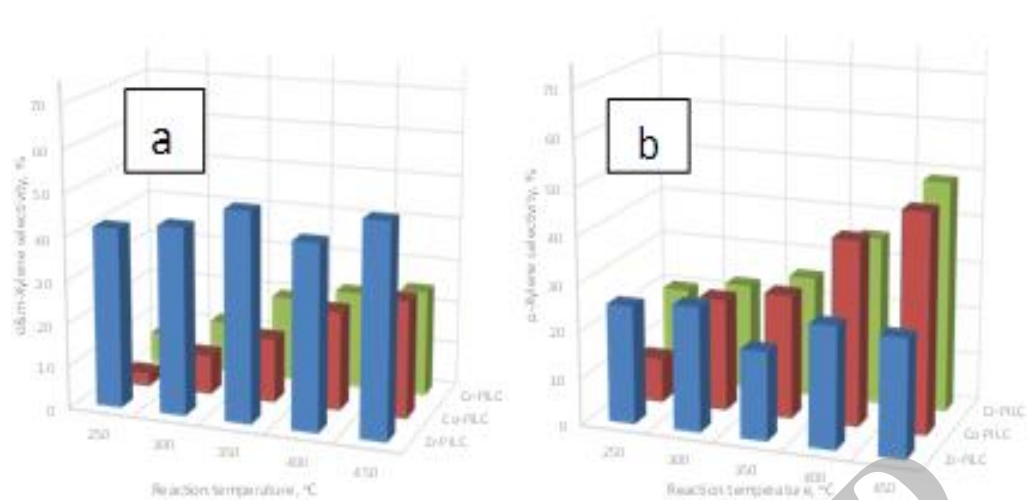
Fig .7. The selectivity of the pillared clay catalysts towards xylenes isomers formation at different reaction temperature
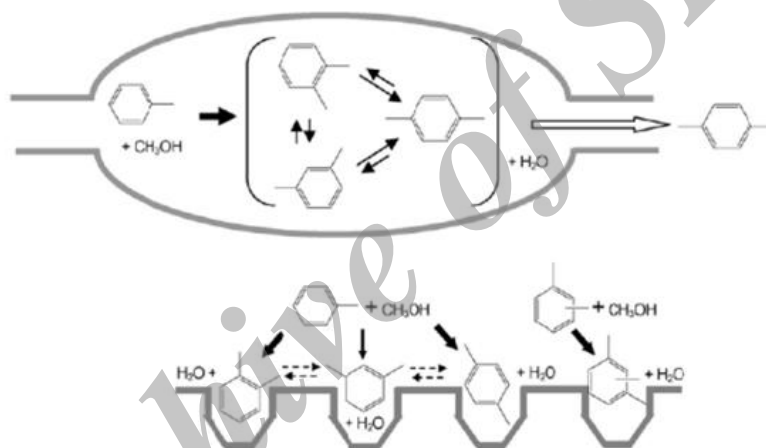
Scheme. 3. Possible scheme of shape selective alkylation of toluene with methanol on PILCs

From data in Fig. 7, it is clear that the prepared pillared interlayered clay catalysts, Cr-PILC & Co-PILC is highly selective to p-xylene (Fig. 7a) formation, while, Zr-PILC is more selective towards o&m-xylenes (Fig. 7b), this may be related to the shape selectivity that originating from the interlayer distance of the prepared catalysts. For Cr-PILC and Co-PILC the interlayer distance (19.4 and 17.47Å) is very comparable to the molecular dimension of p-xylene than Zr-PILC (21.3 Å) as confirmed by the XRD data. Moreover, the increase in the selectivity to xylene with the increase in the reaction temperature can be attributed to the conversion of Lewis acid sites into Bronsted acid sites due to the water molecules that were generated during the alkylation reaction.

Accordingly, the prepared pillared catalysts are highly selective for the ring alkylation of toluene at all reaction temperatures, and p-xylene is the most selective reaction product, which reaches ~50% of the converted products at reaction temperature of 450°C upon using Co- and Cr-PILC catalysts. The process of pillaring exposes adds acidic sites and enhances layer distance and porosity, which allows shape selective catalysis to produce p-xylenes (histogram in Fig. 7).

3. 3. Time on stream (TOS)

To study the stability of the prepared catalysts towards toluene methylation, the reaction was continuously carried out at reaction temperature of 400°C for 10h over the prepared catalysts (Fig. 8). From data, the activity of the catalysts slightly decreases with the increase in the time on stream (TOS) from 1 to 10h (~ 8%). Therefore, it can be said that the suppression of deactivation may be due to the homogenous distribution and the fine dispersion of pillars during the sonication technique.

The stability toward deactivation is slightly different from one PILC catalyst to another, in parallel with the little differences in the interlayer distance and also in the surface area measurements (Table 3). These results reveal that no collapse or sintering of the structure may be occurred during the alkylation reaction even at the high reaction temperature.

4. Conclusion

From the above results it can be conclude that:

1. The pillaring clay has strong acid sites which stabilize the formation of carbonium ions that accelerate the formation of xylene isomers during the toluene methylation

2. Para-xylene is diffused moderately fast, while the ortho and Meta isomers take more time and further convert to the para-isomer before leaving the interlayered distance structure (channel structure)

3. The sonication treatment reduces the needed pillaring time to incorporate the poly oxycations species into the clay lamellar structure to short time (30 min), that get pillared clay catalysts similar to those previously prepared with prolonged synthesis times [19].

4. oxycations species into the clay lamellar structure to short time (30 min), that get pillared clay catalysts similar to those previously prepared with prolonged synthesis times [19].
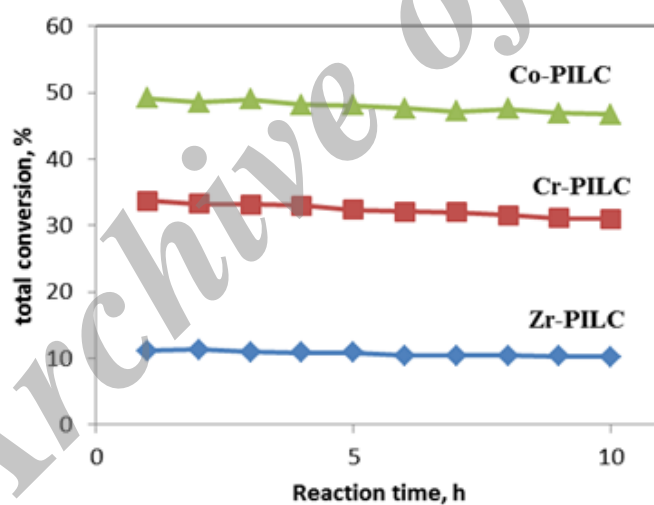
Fig. 8. The relation between the reaction time and the activity of the used catalysts at constant reaction temperature

Table 3. D-spacing and surface area of the used catalysts

	d-spacing	surface area m^2/g
Zr-PILC	20.74	198.76
Cr-PILC	19.02	129.9
Co-PILC	16.97	123.8

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