Solid acid catalysts from clays: Cumene synthesis by benzene alkylation with propene catalyzed by cation exchanged aluminum pillared clays

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Abstract

The alkylation of benzene with propene to produce cumene was carried out in batch (benzene/propene = 20/1) at $T = 353$ K and $P = 0.55$ MPa over aluminum pillared bentonite (APB) exchanged with K^+, La^{3+} and Al^{3+} cations. Both Al^{3+} and La^{3+} exchanged pillared clays were more active than APB. As expected a complete deactivation was observed for the K^+ exchanged pillared clay. The large modifications of the catalytic activity cannot be explained by the observed slight textural differences. Cation exchange appeared to strongly modify the amount and nature of the clays acid sites. The relative amount of Lewis and Brønsted acid sites was evaluated by IR spectroscopy of adsorbed pyridine and analyzing the product distribution of the catalytic 1-butene isomerization. An apparent dependence of the reactivity from the amount of strong Lewis acid centers was clearly evident while a relationship with the amount of strong Brønsted acid sites was not found.

Keywords: Alkylation; Cumene; Acidity; Exchanged pillared clays

1. Introduction

The Friedel–Crafts reaction is probably one of the more important reactions in organic chemistry. Most of the Friedel–Crafts reactions can be catalyzed by both Brønsted and Lewis acid sites [1]. Traditional Friedel–Crafts processes employ mineral acids such as HF and H_2SO_4, or Lewis acids such as $AlCl_3$ and BF_3. The use of these substances involves technological and environmental problems due to their corrosive nature and to the difficulty of recycling with consequent economic and environmental problems. The present tendency is to replace these conventional catalysts by solid acids, which are less corrosive. Zeolites [2–4] and modified clays, particularly acid treated [5,6] and pillared clays [7] can exhibit acidities close to those of traditional mineral acids solutions.

Pillared interlayered clays (PILC) are two dimensional zeolite-like materials prepared by exchanging the charge-compensating cations between the smectite clay layers with large polymeric or oligomeric hydroxy metal cations formed by hydrolysis of metal salts. Upon heat-

ing, the cation pillars form oxide clusters that permanently prop open the clay layers creating an interlayer space of molecular dimensions and a well defined pore system. Much interest and research have been directed to metal oxide pillared clays and comprehensive reviews of the voluminous literature are available [8–10]. Many papers and patents [11,12] appeared on allumina pillared montmorillonites and their possible use as acid catalysts was also investigated. Pillared clays exhibit interesting physico–chemical properties. Specific surface areas between 250 and 350 m^2/g, mean pore diameters of 7–9 Å, and the ability to adsorb hydrocarbons [13,14] define a bidimensional porous system accessible to relatively voluminous molecules. Both Brønsted and Lewis-type acidities have been reported in pillared montmorillonites [15,16]. The catalytic properties of the pillared clays are believed to be associated with the high surface area generated by pillaring and the acidity introduced by the pillars. The number and the strength of the acid sites can be changed to a great extent by exchanging cations into the pillared clays.

In this work we studied the possibility of modifying the catalytic activity for the Friedel–Crafts reaction of an aluminum pillared clay by a simple ion-exchange process. Among the Friedel–Crafts reactions the alkylation of benzene with propene to produce cumene was investigated.

2. Experimental

2.1. Materials

The clay used as starting materials was a natural Na^+-bentonite (commercial designation Detercol P1™) from Nador (Morocco) with unit cell formula $(Si_{7.46}Al_{0.53})(Al_{3.30}Fe_{0.19}Mg_{0.51})O_{20}(OH)_4$ supplied by Laviosa (Leghorn, Italy) with a C.E.C of 85 mequiv/100 (montmorillonite = 97%).

Chlorhydrol™, a commercial 5/6 basic alu-

minum chloride salt produced by Reheis was obtained as a kind gift from Eigenmann and Veronelli (Milan).

Benzene was C. Erba reagent ≥ 99.5% pure.

Propene (5 vol% in N_2) was supplied by SIAD.

The KCl, $Al(NO_3)_3 \cdot 9H_2O$ and $LaCl_3 \cdot 8H_2O$ salts were technical grade reagents from Janssen.

2.2. Synthesis of pillared and exchanged pillared clays

The aluminum pillared bentonite APB (C.E.C. = 16.0 meq/100 g) was obtained as described in a previous paper [17]. The aluminum pillared clay was ion-exchanged, after C.E.C. restoring through ammonia modification, by treatment with 0.1 N aqueous solutions of K^+, La^{3+} chlorides and Al^{3+} nitrate. The pillared clays were suspended in the salt solutions for seven days to favor the complete exchange process.

2.3. Restoring the C.E.C. of APB through modification with ammonium

The APB pillared clay was placed into a desiccator in the presence of a becker containing a NH_4OH solution. The system was gently evacuated and then maintained in ammonia atmosphere for 24 h. The ammonia becker was then taken away and the excess of ammonia was removed under vacuum. The ammonium clay NH_4-APB was immediately exchanged with the desired cation [18].

2.4. Surface area measurement

Adsorption/desorption experiments using N_2 were carried out at 77 K on a C. Erba Sorptomatic 1900. Prior to each measurement the samples were outgassed at 1.33×10^{-3} Pa and at 423 K for six hours. The N_2 isotherms were used to determine the specific surface areas (SA). Surface areas were obtained using the full

BET equation. The α-plot method was used to calculate the surface area of the mesopores and the micropore volume. The starting clay was used as reference material [19].

2.5. X-ray diffraction

X-ray diffraction spectra were recorded on a Philips PW 1310 diffractometer using the Cu K_α radiation. The samples were disc shaped pressed powders.

2.6. Infrared spectroscopy

IR spectral measurements were carried out in an evacuable Pyrex cell with CaF_2 windows. Pyridine adsorption experiments were performed as described by Occelli [15]. The clay samples were ground to a fine powder, pressed into self-supporting wafers and mounted in the holder of the IR cell, evacuated at 1.33 Pa, and degassed by heating at 673 K. After cooling the wafers at room temperature, pyridine was adsorbed in the samples. IR spectra were recorded after degassing the wafers under vacuum at 423 K for 2 h. Measurements were carried out also after desorption under vacuum at increasing temperatures (up to 673 K). Infrared spectra were recorded on a FT-IR Nicolet Magna-IR™ 750 in the 1700–1400 cm^{-1} region.

2.7. Catalytic 1-butene isomerization

Catalytic 1-butene isomerization tests were performed at atmospheric pressure in a tubular glass flow microreactor. Catalyst samples (250 mg) were pretreated for 2 h in air flow at 673 K. Experiments were performed at $T = 673$ K and $\tau = 2.4$ g$_{(cat)}$ g$_{(1\text{-butene})}^{-1}$ h. The 1-butene was 5% in nitrogen and the time on stream was 120 min. The unconverted 1-butene and the reaction products were analyzed on line in a gas chromatograph (HP 5890 series II) equipped with a wide-bore KCl/AlCl$_3$ column ($\phi = 0.53$ mm, $l = 25$ m) and a flame ionization detector (FID).

The amount of coke was deduced from the weight loss of the spent catalyst during burning in air in the range 363–1073 K, measured by thermogravimetry (TG).

2.8. Catalytic alkylation of benzene with propene

The alkylation of the benzene with propene was carried out at 353 K for 1 h in a 250 ml magnetically stirred autoclave. A total of 1.63 g of 5% propene/N$_2$ mixture, 5 ml of benzene and 100 mg of catalyst were used. All the catalysts were previously treated in air flow at 673 K for 2 h. The system was heated to 353 K and the pressure raised up to 0.55 MPa. After 1 h of reaction the autoclave was cooled and the products were analyzed in a gas chromatograph (HP 5890) equipped with a wide-bore FFAP column ($\phi = 0.53$ mm, $l = 25$ m) and a flame ionization detector (FID).

3. Results

3.1. Effect of the ion exchange on the pillared clay structure

The ammonium form of the aluminum pillared bentonite clay NH$_4$-APB (C.E.C. = 73.0 meq/100 g) was ion-exchanged, by treatment with aqueous solutions of K$^+$, La^{3+} chlorides and Al^{3+} nitrate. Only a slight decrease of the specific surface area and a very small modification of pore distribution were observed after ion-exchange with K, Al and La, as reported in Table 1.

Nevertheless a decrease in the intensity of the $d_{(001)}$ peak and a shift towards lower basal spacing values was observed, after cation exchange, by X-ray diffraction (Table 2).

3.2. Effect of the ion exchange on the pillared clay acidity: FT-IR study of adsorbed pyridine

The IR spectra of pyridine adsorbed on PILCs wafers, obtained after evacuation, are shown in Fig. 1.

Table 1
Surface areas and porosity data of the cation exchanged PILCs

PILC	S.A. (m^2/g)	V. Micro (cm^3/g)	S. Meso (m^2/g)	Ion radius of the exchanged cation (Å)
APB	305	0.12	31	—
K-APB	268	0.11	24	1.33
La-APB	241	0.09	28	1.15
Al-APB	298	0.12	25	0.50

A general decrease of the IR bands intensity in the 1700–1400 cm^{-1} region was observed when APB was exchanged with K^+ (Fig. 1, Spectra APB and K-APB). In particular the 1545 cm^{-1} and 1620 cm^{-1} bands typical of the pyridine bonded to the Brønsted acid sites almost disappeared.

The Al^{3+} exchanged pillared clay showed a general increase of the typical bands due to both the Brønsted and Lewis of the acid sites. The spectra recorded after degassing the sample at 673 K for two hours in vacuo showed that the pyridine was still retained by the catalyst surface indicating the presence of strong acid sites.

The IR spectrum of the La-APB sample resulted substantially unchanged in comparison with that of the APB clay. A band at 1600 cm^{-1} was also detected in this sample that was not removed by thermal treatment under vacuum at 673 K. The signal can be attributed to pyridine coordination on La^{3+} cations.

3.3. Effect of the ion exchange on the pillared clay acidity: Catalytic 1-butene isomerization test

We used the 1-butene isomerization [20–22] as catalytic test reaction, to evaluate the acidity

Table 2
X-ray diffraction data of the cation exchanged PILCs

	d_{001} (Å)	Ion charge/ion radius of the exchanged cation (e^-/Å)
APB	17.8	—
K-APB	17.0	0.75
La-APB	16.7	2.61
Al-APB	16.5	6.00

of the clay samples. The distribution of the reaction products (principally *cis*- and *trans*-2-butenes, isobutene, *n*- and isobutanes, and the products of cooking) can give in fact information on the strength and the type of the acid sites.

The product distribution for 1-butene conversion is summarized in Table 3.

The reaction products can be divided into the following groups: (a) double bond isomerization products (*cis*-2-butene and *trans*-2-butene); (b) skeletal isomerization products (isobutene); (c) hydrogenated products (*n*-butane and isobutane); (d) cracking products (methane, ethane, ethylene, propane and propene); (e) surface carbon residue.

It was reported that the formation of isobutene (skeletal isomerization) needs stronger Brønsted
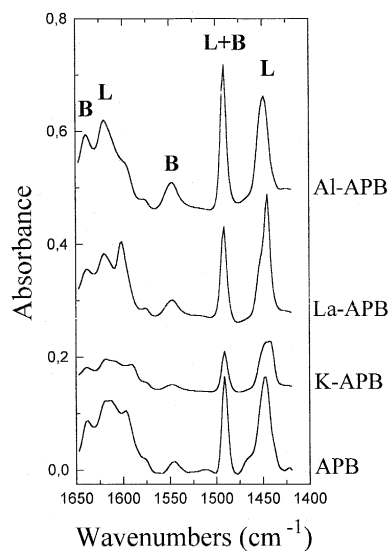

Fig. 1. IR spectra of pyridine adsorbed on the exchanged aluminum pillared clays.

Table 3
Product distribution for the 1-butene conversion (250 mg of catalyst, $T = 673$ K, $P = 0.10$ MPa, $\tau = 2.4$ $g_{(cat)}$ $g^{-1}_{(1\text{-butene})}$ h, time on stream = 2 h)

	Isobutane (%)	*n*-butane (%)	*Trans*-butene (%)	Isobutene (%)	*Cis*-butene (%)	Conv. 1-butene (%)	Coke (%)
APB	1.20	0.55	29.54	12.42	23.03	77.22	1.6
K-APB	0.00	0.00	35.41	0.53	31.51	68.89	0
Al-APB	2.51	0.91	29.98	16.85	23.10	81.19	2.9
La-APB	0.94	0.49	32.99	12.52	26.51	77.51	2.1

acid sites ($H_R < -6.63$) than those required by the geometric isomerization and the double bond migration ($0.82 > H_R > -4.04$) [23–25]. The reaction is thought to occur on Brønsted acid sites via carbenium ion intermediates by a three-step mechanism: protonation of the reactant, rearrangement of the carbenium ion formed, desorption of the products, with the rearrangement being the reaction rate limiting step [20,26]. The hydrogenated compounds *n*-butane and isobutane are usually generated by butene cracking and their presence can be explained by a cracking reaction of butene oligomeric carbenium ions or alternatively, by a direct hydrogenation of the butene isomers through hydride transfer on the corresponding monomeric carbenium ions.

As shown in Table 3 the Al-APB pillared clay was more active in the skeletal isomerization, that needs stronger Brønsted acid sites (isobutene and isobutane formation), than the APB pillared clay. The Al-APB sample produced more *n*-butane and isobutane. Coke formation was also investigated. The Al-APB sample was found to produce 2.9 wt% of coke, whereas the APB pillared clay contained 1.6 wt% of carbonaceous compounds. The increased amount of carbonaceous products on the catalyst could be connected to a higher number of Lewis acid sites which are responsible for the formation of the carbocation that initiates the coke formation [27–30].

The product distribution for the reaction catalyzed by La-APB is very close to that of the unexchanged clay. The only interesting variation is the higher amount of cooking products found on this catalyst. Carbonaceous product

were 1.6 wt% on the APB and 2.1 wt% on the La-APB.

The well known noxious effect of the K^+ ions which poisoned almost all the stronger Brønsted acid sites responsible for skeletal isomerization was confirmed.

Moreover the total absence of *n*-butane, isobutane and of coke indicated that also the Lewis acid sites, responsible for the formation of these products, were poisoned.

3.4. Effect of the ion exchange on the pillared clay catalytic activity: The catalytic alkylation of the benzene with propene to produce cumene

The alkylation of the benzene with propene was carried out at 353 K for 1 h in a stirred batch reactor. The high ratio benzene/propene $= 20/1$ and the relatively low temperature were chosen to favor the mono-alkylated product and to avoid the formation of poly-alkylated products and of *n*-propylbenzene [2]. A 100% selectivity in cumene was obtained on all the tested samples. Propene polymerization products were never detected.

A normalized reaction time τ is defined as: $\tau = W \cdot F^{-1} \cdot t$, where W is the catalyst weight (g), F is the amount of benzene–olefin mixture (g), and t is the reaction time (min).

The data relative to the conversion of the propene on APB and cation exchanged APBs are reported in Table 4.

The Al^{3+} and La^{3+} exchanged samples resulted very active, the former being the best catalyst.

The catalytic activity of all the samples was checked also at 383 K ($P = 0.81$ MPa) and after

Table 4
Propene conversion in the cumene synthesis by benzene alkylation with propene on the cation exchanged aluminum PILCs (100 mg of catalyst, $T = 353$ K, $P = 0.55$ MPa, $\tau = 1.3$ min)

	Propene conversion (%)
APB	13
K-APB	0
Al-APB	22
La-APB	18

1 h the conversion of propene was complete when APB, Al-APB and La-APB were used.

4. Discussion

The catalytic alkylation of benzene with propene is an electrophilic substitution on the aromatic ring. Alkylation reactions catalyzed by acidic zeolites are commonly considered to proceed via a carbenium-ion mechanism. Alkylation of benzene with an olefin may be catalyzed by both Lewis and Brønsted acid sites. Quantum chemical studies showed that ethylene interacts with the Lewis sites of a decationized zeolite to give a π-complex more stable than that formed on a Brønsted site where only physisorption of ethylene takes place [31]. Occelli et al. [32] showed that catalysts with open microporosity and high Lewis acidity such as pillared bentonites and amorphous aluminosilicates could interact with propene to form a stable π-complex. Transfer of π-electrons of the chemisorbed olefin to the empty orbitals of the Lewis sites (L) to form a σ-complex leads to the formation of a positive charge on the propene molecule. The carbocation can then attack the benzene molecule to give the alkylation products (Scheme 1).

Reactivity and spectroscopic data confirmed that the chemical properties of the surface of the APB pillared bentonite were strongly modified by exchange of the residual interlayer cations with K^+, La^{3+} and Al^{3+} cations. On the other hand the clay structure appeared only slightly affected by the exchange process. The slight progressive decrease of the basal spacing of the clays sheets with the increasing values of the charge/ion radius ratio of the exchanged cations can be attributed to the pillared clay layers deformation caused by the stronger electrostatic cation–layer interaction (Table 2). The slight decrease of the specific surface area values (Table 1) is attributable to the filling of the interlamellar space by the bulkier cations. Nevertheless cation exchange appeared to modify mainly the number and strength of the acid sites of the clay catalysts.

K^+ cation is a well known poison for many silica–alumina acid catalysts [33,34] and its noxious effect also on pillared clays was confirmed by spectroscopic and reactivity data (Tables 3 and 4). A general decrease of the bands intensity in the 1650–1400 cm^{-1} region and in particular of the bands at 1640 and 1545 cm^{-1}, characteristic of the pyridinium ions (Brønsted acidity) was in fact observed (Fig. 1). Also the bands at 1620 cm^{-1} and 1450 cm^{-1}, characteristic of the pyridine coordinated to Lewis acid sites, were less intense.

The exchange with an Al^{3+} cation caused an increase of both iso and carbonaceous products in the 1-butene conversion. This behavior can be correlated to a higher number of both strong Brønsted acid sites, which are responsible of the skeletal isomerization, and of Lewis acid sites which are responsible of the formation of the carbocation that initiates the coke formation. The IR spectra of adsorbed pyridine on Al^{3+} exchanged PILCs showed a general increase of the typical bands due to both the Brønsted and Lewis acid sites. The pyridine is still retained
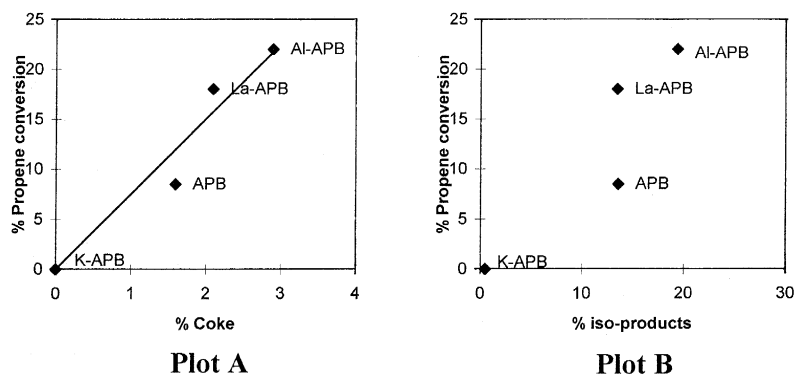

Scheme 1.

Plot A   **Plot B**
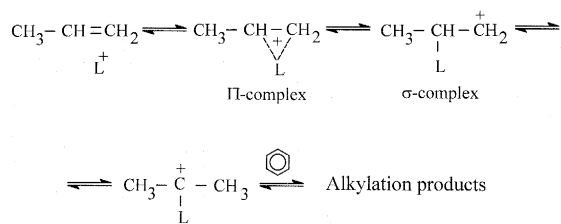
Fig. 2. Propene conversion versus % coke (A) and versus % isobutene + isobutane (B) formed in the 1-butene test reaction (100 mg of catalyst, benzene/propene = 20/1, τ = 1.3, T = 353 K, P = 0.55 MPa).

after degassing at 673 K for two hours in vacuo indicating that the acid sites of this catalyst are strong. As found for other Al^{3+} ion exchanged aluminosilicates [6,35–37] the increase of the number and of the strength of the acid sites is a consequence of the exchange process by Al^{3+} cations which have an high polarizing effect.

Exchange with rare earths cations is known to have a positive effect on activity and stability of zeolites and clays [37–40]. Nevertheless the exchange with La^{3+} on the APB pillared clay caused only a slight increase of the number of the Lewis acid sites while the number of the strong Brønsted acid sites appeared to remain almost constant. The higher acidity of the Al-APB respect to the La-APB is probably due to Al^{3+} higher charge/ion radius ratio [37] (Table 2).

An attempt to correlate the activity in the benzene alkylation with the acid properties of various cation exchanged PILCs was made plotting the propene conversion values versus the percentage of coke (promoted by strong Lewis acids) (Fig. 2(A)) and of skeletal isomers (promoted by strong Brønsted acids) (Fig. 2(B)) formed during the 1-butene conversion.

The trend of (A) strongly suggested an apparent dependence of the catalytic activity from the amount of strong Lewis acid centers while a clear relationship with the amount of strong Brønsted acid sites (B) was not found. Nevertheless it is well known that in the Friedel–Crafts

alkylation, especially with olefins, a Lewis acid catalyst catalyzes the reaction only if a small amount of proton-donating co-catalyst is present [1,41,42]. Therefore cation exchanged pillared clays where both strong Lewis acid and Brønsted sites are present can be very interesting catalyst for benzene alkylation with propene.

Acknowledgements

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