Benzylation of aromatics on ion-exchanged clays

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Abstract

The alkylation of benzene and toluene with benzyl chloride and benzyl alcohol have been investigated over a series of clays obtained by exchanging the original cations of K10 by Ti^{4+}, Fe^{3+}, Zr^{4+}, Cu^{2+}, Zn^{2+}, Ce^{3+}, Cr^{3+} and Sn^{2+} cations. The acidity of these solids has been determined by infra red spectrometry using pyridine as molecular probe. The acidity of K10 clays can be changed to a great extent by cation exchange and by the thermal treatments applied to the solids. The clays treated in air at 773 K show practically pure Lewis acidity, while those dried at 393 K possess Brønsted acidity. The rate of alkylation is roughly related to acidity when the substrate is benzyl alcohol, but not when benzyl chloride is used. In that case the catalysts containing reducible cations (Fe^{3+}, Sn^{4+}, Cu^{2+}) exhibit high activities in spite of their low number of acid sites. It is proposed that an oxido-reduction is the first step of the reaction in that case.

Keywords: Aromatics; Alkylation; Benzyl alcohol; Benzyl chloride; Exchanged clays; Lewis acidity

1. Introduction

Friedel–Crafts alkylations constitute a very important class of reactions which are of common use in organic chemistry. These reactions are usually catalyzed by Lewis acids in liquid phase [1], and the present tendency is to replace these catalysts by solid acids, which are less corrosive. The alkylation of toluene and benzene by benzyl chloride or alcohol is interesting for the preparation of substitutes of polychlorobenzenes used as dielectrics. In homogeneous phase this reaction is catalyzed by $FeCl_3$ [2]. In heterogeneous catalysis zeolites [3], sulfated zirconia [4] and clays exchanged by metallic ions [5,6] have been described. Clark et al. [7] recently reviewed the work published on clays impregnated by zinc chloride, and activated at low temperature ($T < 573$ K). K10 activated in these conditions was reported to be non-acidic, and the catalytic activity for the reaction of benzyl chloride on aromatics was then ascribed to Zn cations.

Using a dealuminated protonic zeolite (HY with a Si/Al ratio of 20) the use of Hammett relationships gave results in favour of an ionic mechanism. However the rate on zeolites is limited by diffusion because of the microporosity and no relationship could be established between the acidity of different zeolites and the catalytic properties. Using exchanged clays Laszlo and Mathy

[6] found no relation between the activity of the exchanged clays and the properties of the same chlorides used as Lewis acids in solution. Unfortunately the acid properties of these solids were not determined, and it is then impossible to be conclusive on a possible change of mechanism. Yadav et al., [4] investigated the alkylation of toluene by benzyl chloride on sulfated zirconia, which is usually considered as a very strong Lewis acid, and reported a surprisingly low activity (50% conversion in 90 min.) compared to Fe/K10.

We have recently investigated this type of samples for their acidity and catalytic properties [8–11]. The nature of the acid sites can be changed to a great extent by changing the cations exchanged into the clay and by the pretreatment. Using Diels–Alder synthesis as model reaction, results consistent with those obtained from the determination of acidities were obtained: calcination of the clay induced an increase of Lewis acidity and a parallel increase of activity. On the clays calcined at 773 K, and then converted to Lewis acids, the rate of the Diels–Alder addition of cyclopentadiene on methyl acrylate was proportional to the number of acid sites [11].

This series of catalysts was then interesting to investigate in other acid catalyzed reactions and we report here the results obtained in the alkylation of aromatics (benzene and toluene) by benzyl alcohol and benzyl chloride.

2. Experimental section

2.1. Preparation and characterization of the catalysts

2.1.1. Preparation

The K10 original sample was purchased from Süd-Chemie. The chemical composition (wt%) of this starting material (main elements) is Al_2O_3: 14.6, SiO_2: 67.6, Fe_2O_3: 2.9, MgO: 1.8, the BET surface area 229 m^2/g and the microporous volume 0.1 cm^3/g. Cation exchange was performed by gradually adding the clay to a stirred solution of the cation (Table 1) at room temperature and stirring the suspension for 24 h. After exchange, suspensions were filtered and washed with deionised water. The resulting solids were dried on a thin bed at 373 K and ground. The solids were equilibrated over saturated salt solutions in order to give reproducible water contents. Calcination was carried out in air (25–30 ml/min) with the following temperature programme: 293 K, 10 K/min → 393 K, 1 K/min → 773 K (10 h), 1 K / min → 313 K.

Specific surface areas were calculated from BET nitrogen isotherms determined at 77 K (Micromeritics ASAP 2000) on samples degassed at 523 K for 12 h before the experiment. Chemical analyses were obtained by plasma emission spectroscopy. At pH < 4 clays start to be dealuminated, and ion exchange must then be

Table 1
Preparation of cation exchanged clays (for 10 g of clay)

Sample	Salt	Molar concentration	Volume of solution (ml)	Metal retained (wt%)	Starting clay	Surface area (m^2/g)
H^+	HCl	1	125	–	K10	269
Fe^{3+}	$FeCl_3$	1	125	2.92	K10	239
Ti^{4+}	$TiCl_4$	0.8 [a]	125	16.2	K10 in 2.5 l H_2O [b]	318
Zr^{4+}	$ZrOCl_2$	0.1	250	4.89	K10 in 1 l H_2O [b]	268
Cu^{2+}	$CuCl_2$	1	125	1.24	K10	236
Zn^{2+}	$ZnCl_2$	1	125	1.19	K10	213
Ce^{3+}	$CeCl_3$	0.25	267	1.74	K10	227
Cr^{3+}	$Cr(NO_3)_3$	0.1 [b]	1250	5.95	K10 [b,c]	304
Sn^{2+}	$SnCl_2$	0.1	125	10.1	K10	240

[a] $TiCl_4$ added to HCl (4 ml, 6 M) under Ar atmosphere.
[b] Solution of the cation gradually added to the clay suspension.
[c] Na_2CO_3 (125 mmol) was added to a stirred solution of chromium(III) nitrate (1.25 l, 0.1 M) at room temperature and the solution was refluxed for 36 h.

performed at a higher pH. In these conditions tri and tetravalent cations have a tendency to hydrolyse in aqueous solutions, and the reactions of condensation then observed yield polycations, which are preferentially exchanged on silico-aluminates such as clays. The amount of metal retained in the exchange then increases, as is observed here for Ti, Zr, Cr and Sn clays.

2.1.2. Infrared spectroscopy

The self-supporting wafers (7 tons/cm^2), 20 mg, 2 cm^2) of clays (ion-exchanged clays) were placed in a quartz IR cell equipped with KBr windows and activated under vacuum (up to 1.2×10^{-4} Pa) at 393 K (catalysts dried) or 773 K (catalysts calcined) for 12 h. After cooling, the temperature was stabilised at 323 K and the cell was equilibrated with 260 Pa of pyridine (spectroscopic grade, dried over Linde 4 A molecular sieve and further outgassed by standard freeze–pump–thaw technique for 3 h). The cell was then evacuated to 1.2×10^{-4} Pa to remove the gaseous and weakly adsorbed pyridine. The desorption was then continued at for 2 h at 393 K. After this treatment the infrared spectra were recorded, at room temperature, with a FTIR Nicolet 320 spectrometer (resolution 2 cm^{-1}).

A quantitative determination of the two types of acidities was done by measuring the area of the absorption peaks. These values were related to the area of the structure band of the clay in the same spectral region, the position of which does not change on the different samples. The band at 1545 cm^{-1} was considered as characteristic of Brønsted acidity and the band at 1456–1448 cm^{-1} of Lewis acidity.

2.2. Reactions

Two substrates and two alkylating agents were investigated in standard conditions of reaction, using a batch reactor at a temperature of 353 K (Scheme 1).

The weight of catalyst was 100 mg, and the stoichiometries for the reaction of benzene: aromatic 10 ml (112 mmol), alkylation agent 6.25
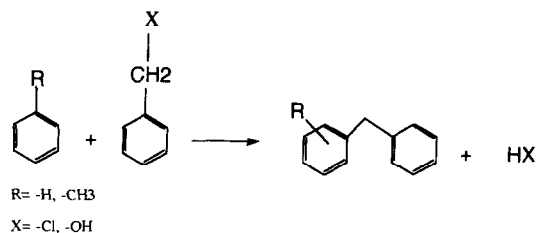
Scheme 1.

mmol, and for toluene: aromatic 10 ml (94 mmol), alkylation agent 6.25 mmol.

GC analyses were carried out in a Carlo Erba Fractovap 24 (HP 35900 AD converter, Olivetti PC 286) equipped with flame ionization detector, PEG wetted fused silica column (25 m, 0.32 mm, thickness of the stationary phase 1.2 μm), helium as carrier gas, injector temperature of 548 K, detector temperature of 548 K and the following temperature program: 333 K (2 min), 6 K/min → 423 K (30 min) → 333 K.

3. Results

3.1. Characterization of acidities

The ion-exchanged clays show different acidities depending on the nature of the cation introduced into the clay and the temperature of pretreatment. After drying at 393 K the general tendency observed by adsorption of pyridine is that cation exchange increases Lewis acidity, at the expense of Brønsted acidity (Fig. 1).

After calcination at 773 K Brønsted acidity is nearly suppressed and the clays are then converted to rather pure Lewis acids. The simultaneous decrease of the intensities of the IR bands of pyridinium ions and of pyridine coordinated to Lewis sites however suggests a lower number of sites. Apparently some reaction occurs between the cations and the support, for instance formation of silicates, which decreases the number of sites accessible to pyridine. The position of the IR band is shifted by at most 2–3 cm^{-1}, then the strength of the Lewis sites is practically unchanged by calcination. It can be remarked that pyridine bands are retained after evacuation at 573 K and cannot
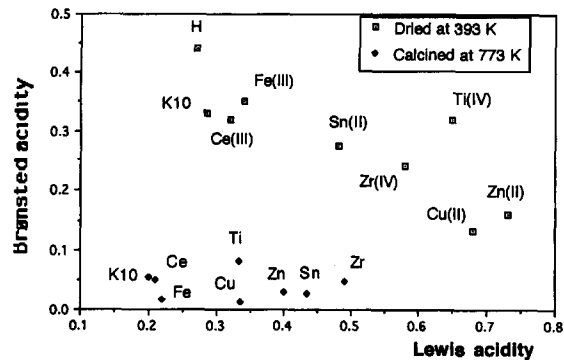
Fig. 1. Acid properties of the exchanged clays either dried at 393 K or calcined at 773 K.
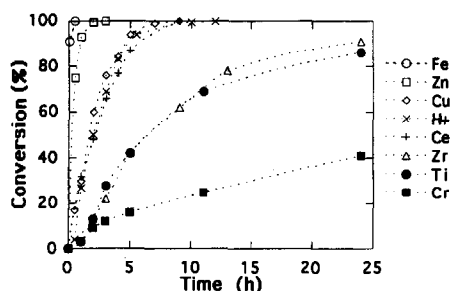

Fig. 2. Alkylation of benzene by benzyl chloride on ion-exchanged K10 catalyst dried at 393 K.

be ascribed to hydrogen bonded species, even on K10.

3.2. Alkylation of benzene

The results obtained in the reactions of benzyl chloride are illustrated in Fig. 2. A complete conversion of the alkylating agent can be observed in a few hours. The selectivity to monoalkylation is 100%, which can be ascribed to the high ratio benzene/alkylating agent used here.

3.3. Alkylation of toluene

3.3.1. Reaction of benzyl chloride

As expected from the literature [1] the alkylation of toluene is faster than that of benzene. Yields of 100% can be reached in less than 3 h with many catalysts when benzyl chloride is used as reactant. With Fe/K10 the reaction is so fast that it is even limited by intraparticle mass transfer.

Calcination decreases dramatically the catalytic activity of these clay catalysts for the alkylation by benzyl alcohol (Table 2), but has no simple effect on the alkylation by benzyl chloride. In that case catalytic activity is depressed by calcination in the case of Zr, Ce, Cr, H, Zn, but increased in the case of Sn/K10 and unchanged for Cu and Fe exchanged samples. It can be supposed that due to the high Sn content of the solid, well dispersed SnO_2 is formed upon calcination. A more detailed investigation was performed on K10 on the influence of calcination. The results depicted in Fig. 3 show a gradual decrease of activity with the temperature of calcination. On catalysts calcined at 473 K, the conversion as a function of time shows a sigmoidal curve which reflects the activating effect of the water produced in the reaction. These

Table 2

Initial rates of reaction ($\times 10^4$ mol/g·h) for the alkylation of toluene by benzyl alcohol (BzOH) and benzyl chloride (BzCl) on cation exchanged clays either dried or calcined

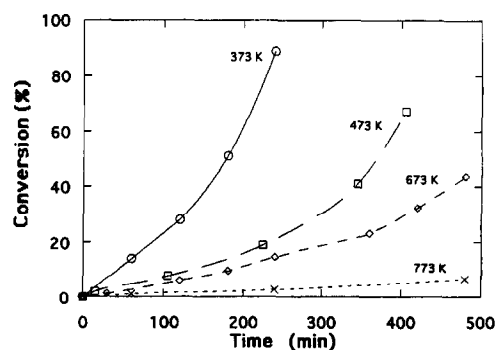| Catalyst	Reagent/temperature of treatment			
	Dried at 393 K		Calcined at 773 K	
	BzCl	BzOH	BzCl	BzOH
Zn	1025	21	206	8
Sn	420	221	1110	9
Cu	525	50	440	2
Zr	120	88	15	19
Ce	60	34	15	37
Fe	2400	47	1250	1
Cr	83	58	27	–
H	776	73	10	–
K10	104	120	14	0.2

Fig. 3. Alkylation of toluene by benzyl alcohol; effect of the temperature of treatment of a K10 catalyst.

Table 3

Ortho–para selectivities for the alkylation of toluene by benzyl chloride (BzCl) and benzyl alcohol (BzOH) on cation exchanged clays, treated in different conditions

Catalyst	Treatment (K)	Reagent	Reaction conditions		Isomer distribution (%)	
			Temperature (K)	Time (min)	ortho	para
Cu	473	BzCl	353	420	49.5	50.5
Cu	573	BzCl	353	420	49.0	51.0
Cu	773	BzCl	353	60	47.0	53.0
Cu	773	BzCl	353	120	48.8	51.2
Cu	773	BzCl	353	180	49.0	51.0
Cu	773	BzCl	353	360	50.2	49.8
Zr	393	BzCl	368	360	46.3	53.7
Zr	393	BzCl	353	360	45.0	55.0
Zr	393	BzCl	335	360	39.2	60.8
Ce	773	BzOH	353	480	51.5	48.5
Sn	773	BzOH	353	435	50.5	49.5
Sn	773	BzCl	353	380	49.0	51.0
Cr	773	BzCl	353	480	49.7	50.3
Cu	773	BzCl	353	360	50.2	49.8
Sn	393	BzCl	353	210	49.6	50.4
Fe	393	BzCl	353	210	50.3	49.7
Zr	393	BzCl	353	270	47.3	52.7
Sn	393	BzOH	353	300	47.3	52.7
Cu	393	BzOH	353	330	45.2	54.8
Fe	393	BzOH	353	435	48.9	51.1

two observations are consistent with a proton catalyzed reaction.

The reaction yields only *ortho* and *para* isomers, which are expected for a cationic mechanism. The changes of *ortho/para* selectivity have been determined in function of time in the case of the Cu/K10 catalyst: a slight decrease of *para* selectivity is observed as a function of time, from 53 to 49.8% (Table 3) shows that isomerization of the products is negligible in these conditions. Greater variation is noticed with the reaction temperature as observed in the case of Zr/K10: the *para* selectivity decreases from 60.8 to 53.7% when the reaction temperature increases, and

approaches at 368 K the *ortho/para* ratio previously reported for zeolites (in liquid phase) at a reaction temperature of 383 K [3], or for FeCl$_3$ in homogeneous phase [2]. In comparable conditions of reaction, the selectivity is little affected by the change of catalyst.

The reaction of benzyl chloride with toluene was measured at three different temperatures on the Zr clay dried at 393 K, and an activation energy of 124 kJ/mol was determined. On a dealuminated Y zeolite an activation energy of 81.5 kJ/mol was obtained [3]. The higher value obtained here agrees with the assumption that the rate is not controlled by diffusion on this clay sample.

Table 4

Comparison of the activities, for the alkylation of toluene by benzyl chloride, of the present catalysts with those reported in the literature

Catalyst	Reaction temperature (K)	Tol/BzCl	Half reaction time (min)	Final conversion (%)	Selectivity to monoalkane	Reference
HY20	383	5	112	82	94.2	[3]
ZrO$_2$–SO$_4$	353	10	90		100	[4]
Fe/K10	353	15	10	100	100	this work
Zn/K10	353	15	20	100	100	this work

3.3.2. Reaction of benzyl alcohol

The initial rates of reaction are reported in Table 2 for the reactions catalyzed by ion exchanged clays treated in different conditions. On the catalysts dried at 393 K the *ortho/para* ratio is slightly lower with benzyl alcohol than with benzyl chloride (see Table 3). With benzyl alcohol as alkylating agent the *ortho/para* ratio is higher with the samples calcined at 773 K.

The results obtained on these exchanged clays can be compared to those reported in the literature for zeolites [3] or sulfated zirconia [4] (Table 4). Exchanged clays appear then as more active than zeolites or sulfated zirconia, and it is interesting to investigate the origin of this high activity.

4. Discussion

The determination of the acid properties of the clays show great differences in protonic acidities between the samples dried at 393 and 773 K. The samples calcined at 773 K are converted to rather pure Lewis acids, and the number of sites varies in a certain range, as evidenced from the intensities of the IR bands of pyridine.

Calcination of the sample has also a strong influence on the activity when benzyl alcohol is used as alkylating agent, and in this case a rough correlation can be observed between the initial rates and the intensities of the IR bands of pyridinium ions (Fig. 4). This observation then agrees with the hypothesis of alkylation catalyzed by pro-
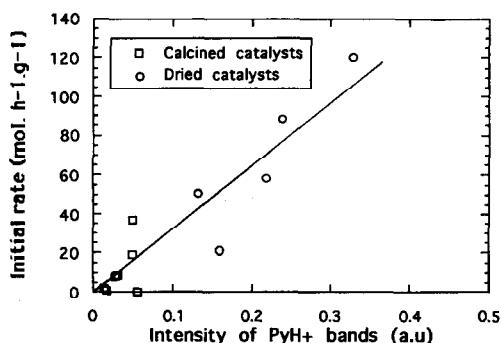

Fig. 4. Correlation between the initial rates of alkylation of toluene by benzyl alcohol and the intensities of the infrared bands of pyridinium ions for catalysts pretreated at 393 or 773 K.

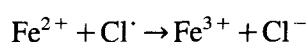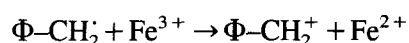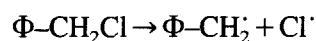tons, as would be expected for a Friedel–Crafts ionic mechanism.

When benzyl chloride is used as alkylating agent a quite different behaviour is noticed: in that case calcination does not systematically decrease the catalytic activity: indeed it can even be increased as in the case of Sn/K10. No correlation can then be found between activity and acidity, and the use of reducible cations such as Fe^{3+}, Cu^{2+} or Sn^{4+} induces a very high activity which is not commensurate to the acidity.

It must be pointed out that K10 itself contains iron, in an amount corresponding to 2.9% Fe_2O_3. Since Fe^{3+} ions are so active in this reaction, it can be assumed that part of the activity, for the alkylation by benzyl chloride, of the clays exchanged by the other cations can be due to these Fe^{3+} ions. The presence of Fe^{3+} in the clay thus most probably shades the activity of the other cations.

Laszlo and Mathy [6] first compared the activities of several clays exchanged by metallic cations for the alkylation of benzyl alcohol, benzyl chloride and cyclohexene. In these experiments the Fe and Cu clays showed normal activities, when compared to the other samples, for cyclohexene and benzyl alcohol, but were much more active than the other samples for benzyl chloride. This abnormal activity of Fe^{3+}/K10 or Cu^{2+}/K10 is then not an artefact. The low acidity of these samples after calcination is hardly consistent with such high activity for a pure ionic mechanism. It is interesting to notice that this behaviour was not observed, on the same series of solids, when studying Diels–Alder cycloaddition of methyl acrylate on cyclopentadiene, which is a reaction catalyzed by Lewis acids. In that case a linear correlation was observed between activity and number of acid sites [11].

These results therefore suggest that the slow step of the reaction is different when using benzyl chloride, and that some particular mechanism occurs in the case of reducible cations. Indeed ESR experiments showed that Fe in the clay can be reduced at room temperature and can produce radicals by interaction with anisole [8]. It is well

known that Friedel Crafts reactions proceed through carbocations [1] and that radicals are powerful reductants, which should readily be oxidized to cations in presence of reducible metallic ions such as Fe^{3+}, Sn^{4+} or Cu^{2+}. The high activity observed with these reducible cations could then be ascribed to a different *initiation* of the reaction, for instance homolytic rupture of the carbon–chlorine bond followed by the oxidation of the radical:

$$\Phi\text{–}CH_2Cl \rightarrow \Phi\text{–}CH_2^{\cdot} + Cl^{\cdot}$$

$$\Phi\text{–}CH_2^{\cdot} + Fe^{3+} \rightarrow \Phi\text{–}CH_2^{+} + Fe^{2+}$$

$$Fe^{2+} + Cl^{\cdot} \rightarrow Fe^{3+} + Cl^{-}$$

In conclusion, clays exchanged by different metallic cations show remarkable activities for the alkylation of aromatics. When the alkylating agent is benzyl alcohol the mechanism is probably purely ionic, but the particular behaviour of the clays exchanged by reducible cations with benzyl chloride suggests that a radical step can also be operative in that case.

Acknowledgements

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