Thermal activation of a clayzic catalyst useful for Friedel–Crafts reactions: HCl evolved with creation of active sites in different thermal treatments to $ZnCl_2$/Mont-K10

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Received 10 December 2001; accepted 28 February 2002

Thermal activation of clayzic catalyst has been thoroughly investigated by calcining anhydrous $ZnCl_2$ impregnated on Mont-K10 with different $ZnCl_2$ loadings (0.5–2.0 mmol g^{-1}) under static or flowing air at 270 °C and also under N_2 flow at different temperatures (150–400 °C). Depending upon the $ZnCl_2$ loading and calcination temperatures, an appreciable amount of HCl is evolved in the thermal activation, indicating an occurrence of reaction between the $ZnCl_2$ and the surface hydroxyl groups of the clay ($-OH + ZnCl_2 \rightarrow -O-Zn-Cl + HCl$), leading to formation of new Lewis acid sites ($-O-Zn-Cl$). The Cl/Zn ratio, surface area and catalytic activity (in the benzene benzylation by benzyl chloride at 80 °C) of the clayzic formed in the thermal activation are influenced markedly by the $ZnCl_2$ loading and calcination conditions (temperature and gas atmosphere). The maximum catalytic activity for the clayzic is observed at the optimum $ZnCl_2$ loading (about 1.0 mmol g^{-1}) and calcination temperature (about 270 °C). The thermal activation at 270 °C under flowing N_2 led to a most active clayzic catalyst for the benzene benzylation. A temperature-programmed evolution of HCl in the calcination of $ZnCl_2$/Mont-K10 with different $ZnCl_2$ loadings from 25 to 400 °C at a linear heating rate of 2 °C min^{-1} has also been investigated.

KEY WORDS: clayzic; $ZnCl_2$/Mont-K10; thermal activation of $ZnCl_2$/Mont-K10; benzylation of benzene; temperature-programmed calcination of $ZnCl_2$/Mont-K10; HCl evolved in calcination of $ZnCl_2$/Mont-K10.

1. Introduction

Clayzic [1,2] is an important commercial solid catalyst useful for Friedel–Crafts-type liquid-phase benzylation and acylation reactions. It was first reported as a benzylation catalyst, as a substitute for homogeneous acid catalysts (such as $AlCl_3$, BF_3, H_2SO_4, etc.), which are not environmentally friendly, for the Friedel–Crafts reactions [3]. This catalyst is prepared by impregnating anhydrous $ZnCl_2$ from its acetonitrile solution on montmorillonite K10 clay and the impregnated clay is calcined in air at 280 °C [1,2]. A large increase in the activity of the catalyst in benzene benzylation by benzyl chloride is observed after its thermal activation at the optimum temperature (280 °C). The $ZnCl_2$ loading on the clay was also found to have an optimum value (1 mmol g^{-1}).

A few studies have been reported, attempting to explain the observed high activity of the clayzic catalyst. According to Cornelis *et al.* [4], the high activity of thermally activated clayzic catalyst is because of the ability of Zn ions to enhance the Brønsted acidity of the catalysts by polarization of their solvating water molecules. However, this hypothesis was found to be wrong in the diffuse reflectance FTIR studies of pyridine adsorbed on the clayzic catalyst [3]. These studies also showed that some Brønsted acid sites from the clay are destroyed during the formation of clayzic, and the resulting catalyst contains mainly Lewis acid sites. Rhodes *et al.* [5] have observed an increase in the surface area of the clayzic catalyst with increase of its calcination temperature but no correlation between the catalytic activity and surface area of the catalyst. In their further studies, Rhodes and Brown [6] concluded that the activity of clayzic is attributed to the presence of mesopores in the support. A high local concentration of zinc cations in structural mesopores is mostly responsible for the high activity of the catalyst [3]. However, this does not explain the optimum loading of $ZnCl_2$ for the clayzic catalyst to be most active. It is therefore of both practical and scientific interest to investigate in detail the thermal activation of the clayzic catalyst for understanding the catalytically active sites created in the catalyst during different thermal treatments to $ZnCl_2$/Mont-K10 (with different $ZnCl_2$ loadings).

The present work was undertaken to find explanations for the high activity of the thermally-activated clayzic catalyst and for the requirement of optimum $ZnCl_2$ concentration and calcination temperature for its formation from the $ZnCl_2$-impregnated Mont-K10. We have shown here that, during the formation of clayzic

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1011-372X/02/0800-0163/0 © 2002 Plenum Publishing Corporation

catalyst from $ZnCl_2$/Mont-K10 by its thermal activation, a part of the zinc chloride is grafted to the clay by its reaction with the surface hydroxyl groups with an evolution of HCl gas, creating new active sites. A detailed investigation on the HCl evolved in the calcination of $ZnCl_2$/Mont-K10 (loading of $ZnCl_2$: 0.5–2.0 mmol g^{-1}) at different temperatures (150–400 °C) has been carried out. The resulting clayzic catalysts were evaluated for their performance in the benzylation of benzene by benzyl chloride.

2. Experimental

2.1. Preparation of $ZnCl_2$/Mont-K10

$ZnCl_2$-impregnated Mont-K10 ($ZnCl_2$ loading = 0.5–2.0 mmol g^{-1}) samples were prepared by impregnating $ZnCl_2$ on Mont-K10 as follows: A mixture of 10 g Mont-K10 and 75 ml dry acetonitrile was refluxed in a magnetically-stirred conical flask (250 ml capacity) while bubbling moisture-free N_2 (30 cm^3 min^{-1}) through the mixture to remove traces of moisture. Then anhydrous $ZnCl_2$ (Lancaster) (5, 10 or 20 mmol) was added to the mixture and the resulting mixture was refluxed under the N_2 flow for 30 min. The solvent from the mixture was then evaporated under vigorous stirring in the flow of N_2 and the $ZnCl_2$/Mont-K10 samples were stored in a desiccator.

2.2. Thermal activation of $ZnCl_2$/Mont-K10 and measurement of HCl evolved in the temperature-programmed calcination

The thermal treatment to the $ZnCl_2$/Mont-K10 catalyst was carried out in a U-type quartz reactor (kept in a temperature-programmable tubular furnace), while passing a moisture-free N_2 or air (space velocity: 2000 cm^3 g^{-1} h^{-1}) over the catalyst at different temperatures (150–400 °C) for a period of 5 h. The temperature of the catalyst was increased at a linear heating rate of 2 °C min^{-1}. After reaching the desired temperature, the catalyst temperature was maintained at that temperature for a period of 5 h. The amount of HCl evolved in the thermal treatment was measured quantitatively as a function of time by an acid–base titration (*i.e.* by absorbing the HCl from the effluent gas stream in a stirred aqueous NaOH solution). After the thermal treatment, the catalyst was cooled to room temperature under the moisture-free gas atmosphere and then stored in a desiccator.

The thermal treatment to the $ZnCl_2$/Mont-K10 ($ZnCl_2$ loading = 1 mmol) catalyst was also carried out under static air in a muffle furnace at 270 °C for 5 h. In this case also the temperature was reached at a heating rate of 2–3 °C min^{-1}. After the thermal treatment the catalyst was also removed from the furnace while hot (about 120 °C) and it was cooled in a desiccator.

2.3. Benzene benzylation reaction

Catalytic performance of the clayzic catalysts obtained by the different thermal treatments was measured for their activity in the liquid-phase benzene benzylation (by benzyl chloride) reaction at the following reaction conditions: reaction mixture = 1 ml benzyl chloride + 13 ml dry benzene + 0.1 g catalyst and temperature = 80 °C. The reaction was carried out in a magnetically stirred glass reactor (capacity: 25 cm^3) in a flow of moisture-free N_2 (30 cm^3 min^{-1}) bubbled through the reaction mixture. The conversion of benzyl chloride in the reaction

$$C_6H_6 + C_6H_5CH_2Cl \rightarrow C_6H_5CH_2C_6H_5 + HCl \quad (1)$$

was measured as a function of time as described earlier [7]. In the benzylation reaction, only mono-benzylated product (biphenyl methane) was formed.

3. Results and discussion

Results showing the amount of HCl gas evolved in the calcination of $ZnCl_2$/Mont-K10 (with different loadings of $ZnCl_2$) at the different temperatures and under the different gas atmospheres (N_2 and air) are presented in table 1. Results in figures 1 and 2 show a strong influence of $ZnCl_2$ loading and calcination temperature, respectively, of the $ZnCl_2$/Mont-K10, on the Cl/Zn ratio, surface area and turnover rate (TOR) in the benzene benzylation at 80 °C for half the reaction (*i.e.* 50% conversion of benzyl chloride) of the resulting thermally activated clayzic catalyst.

From the results, the following important observations can be made.

Table 1

Effect of $ZnCl_2$ loading and calcination conditions on the amount of HCl evolved in the calcination of the $ZnCl_2$/Mont-K10 (period of calcination = 5 h)

$ZnCl_2$ loading (mmol g^{-1})	Calcination condition		Amount of HCl evolved (mmol g^{-1})
	Temperature (°C)	Gas atmosphere	
1.0	270	Static air	–
1.0	270	Air flow	0.43
1.0	270	N_2 flow	0.36
1.0	150	N_2 flow	0.01
1.0	180	N_2 flow	0.05
1.0	300	N_2 flow	0.40
1.0	400	N_2 flow	0.95
2.0	270	N_2 flow	0.53
0.5	270	N_2 flow	0.27

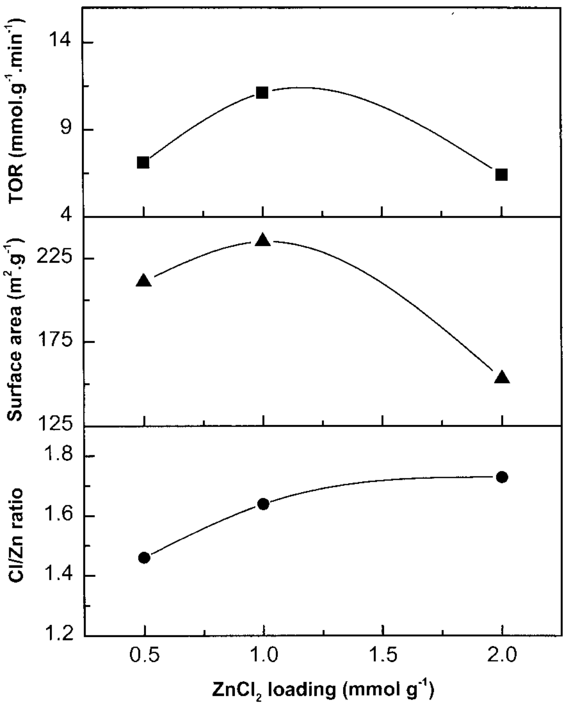

Figure 1. Effect of the $ZnCl_2$ loading in $ZnCl_2$/Mont-K10 on the Cl/Zn ratio, surface area and catalytic activity (in terms of the TOR at half the benzene benzylation reaction at 80 °C) of the thermally activated catalyst (at 270 °C for 5 h under flowing N_2).

1. In all the cases, HCl gas is evolved in the calcination of $ZnCl_2$/Mont-K10. The amount of HCl evolved shows a strong dependence upon both the $ZnCl_2$ loading and calcination temperature; the higher the temperature or $ZnCl_2$ loading, the larger the amount of HCl evolved (table 1).
2. The Cl/Zn ratio is higher for the higher $ZnCl_2$ loading (figure 1). It is, however, decreased with increase of the calcination temperature (figure 2). Both the surface area and benzene benzylation activity TOR of the clayzic catalyst is passed through a maximum (at the $ZnCl_2$ loading of about 1.0 mmol g^{-1}) with increase of the $ZnCl_2$ loading (figure 1). These two are also passed through a maximum (at the calcination temperature of about 270 °C) with increase of the calcination temperature (figure 2). The observed maximum for the catalytic activity in both cases is very much consistent with that observed earlier [1,2].

The formation of appreciable amounts of HCl gas reveals a reaction between the surface hydroxyl groups of the clay and the $ZnCl_2$ in the calcination of $ZnCl_2$/Mont-K10, as follows:

$$-OH + ZnCl_2 \rightarrow -O-Zn-Cl + HCl \qquad (2)$$

A large decrease in the intensity of the IR peak at about 3605 cm^{-1} corresponding to the presence of hydroxyl groups, after the calcination of $ZnCl_2$/Mont-K10, is

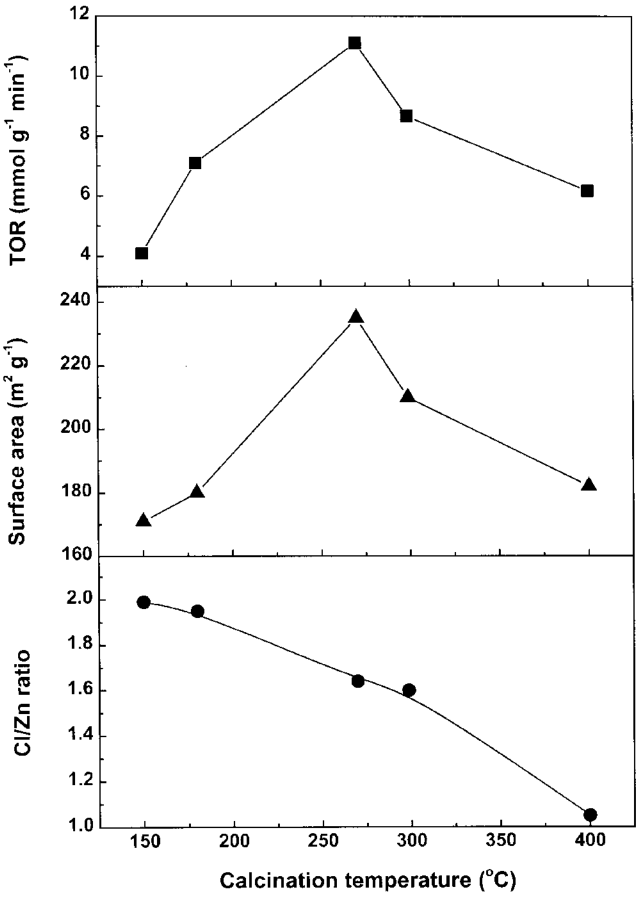

Figure 2. Effect of the temperature of calcination (under flowing N_2 for 5 h) of $ZnCl_2$/Mont-K10 ($ZnCl_2$ loading = 1.0 mmol g^{-1}) on the Cl/Zn ratio, surface area and catalytic activity (in terms of the TOR at half the benzene benzylation reaction at 80 °C) of the thermally activated catalyst (at 270 °C for 5 h under flowing N_2).

observed. This strongly supports the grafting of $ZnCl_2$ on the clay according to the above reaction, forming Lewis acidic –O–Zn–Cl species. The formation of these species at their optimum concentration seems to be responsible for the observed high activity of the clayzic catalyst. The earlier observed destruction of most of the Brønsted acid sites (*i.e.* acidic hydroxyl groups) from the clay during the formation of clayzic containing mainly Lewis acid sites [3], also supports the formation of HCl and Lewis acidic –O–Zn–Cl species by the above reaction in the thermal activation.

The observed trend showing a maximum in the variation with the $ZnCl_2$ loading and/or calcination temperature of the surface area is same as that of the TOR (figures 1 and 2). This indicates a correlation between the surface area and catalytic activity of the clayzic catalyst. When the TOR is plotted against the effective concentration of –O–Zn–Cl per unit area of the clayzic catalysts prepared under different conditions (table 1), a maximum is observed at the –O–Zn–Cl concentration of about 1.5 μmol m^{-2} (figure 3). This

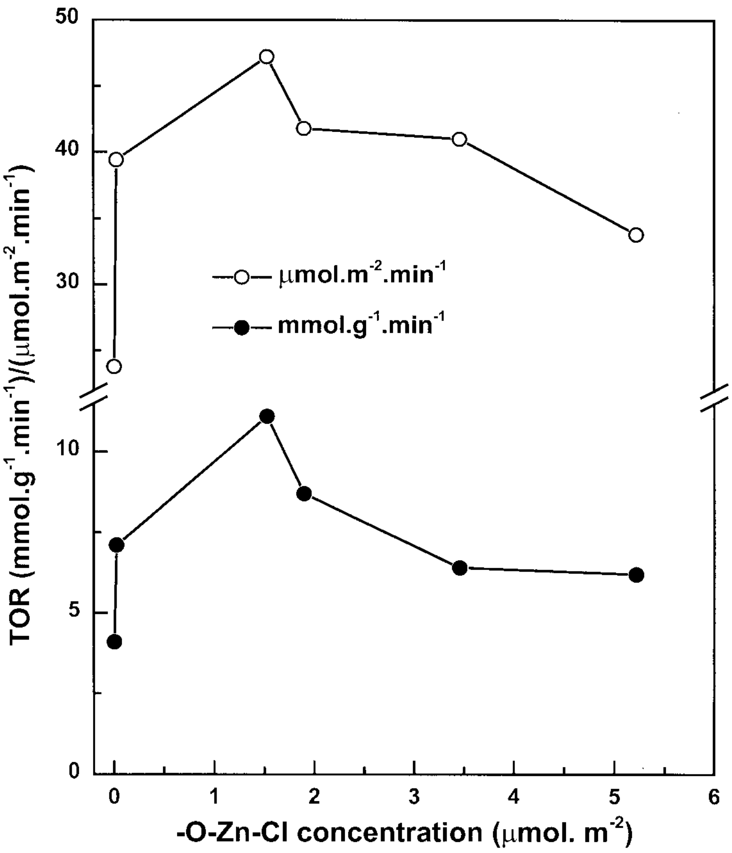

Figure 3. Variation of the TOR with the effective $-O-Zn-Cl$ concentration per unit area of clayzic catalyst.

reveals that there is an optimum concentration of $-O-Zn-Cl$ per unit area for the clayzic catalyst to be highly active in the benzylation reaction. It may be noted that the observed optimum $-O-Zn-Cl$ concentration corresponds to the catalyst prepared under the optimum conditions ($ZnCl_2$ loading = 1.0 mmol g^{-1} and calcination temperature = 270 °C) (figures 1 and 2).

Results in table 2 show that the gas atmosphere used in the thermal activation plays a significant role in deciding the catalytic activity of the resulting clayzic. The clayzic formed in the presence of flowing N_2 shows the highest catalytic activity. The use of flowing air in the thermal activation results in clayzic with a slightly lower Cl/Zn ratio and catalytic activity. The use of static air in the thermal activation, however, provides clayzic with a much lower catalytic activity.

Table 2

Effect of the gas atmosphere used in the thermal activation of $ZnCl_2$/Mont-K10 ($ZnCl_2$ loading = 1.0 mmol g^{-1}) on the Cl/Zn ratio, surface area and TOR (for half the benzene benzylation at 80 °C) of the thermally activated catalyst at 270 °C for 5 h

Gas atmosphere	Cl/Zn ratio	Surface area ($m^2 g^{-1}$)	TOR (mmol g^{-1} min^{-1})
Flowing N_2	1.64	235	11.1
Flowing air	1.57	230	10.8
Static air	–	224	7.0

The HCl evolved in the temperature-programmed calcination (TPC) from 50 to 400 °C and at 400 °C for 5 h of the $ZnCl_2$/Mont-K10 with the different $ZnCl_2$ loadings has been measured as a function of temperature and time. The results are presented in figure 4. The data on the total amount of HCl evolved, Cl/Zn ratio and surface area of the clayzic catalyst obtained after the TPC and also on the peak maximum temperature are given in table 3. The TPC curves (dX/dt *versus* T) are broad and show two peaks; the second peak in the case of $ZnCl_2$ loadings of 1.0 mmol g^{-1} is not resolved (figure 4). The peak maximum temperature for both the TPC peaks is increased with increasing the $ZnCl_2$ loading (table 3).

The results (figure 4 and table 3) show that the HCl evolved in the TPC is increased and consequently the Cl/Zn ratio of the clayzic obtained in the TPC is decreased with increase of the $ZnCl_2$ loading. The surface area of the resulting clayzic is also decreased with increase of the $ZnCl_2$ loading. This trend for the surface area of the clayzic obtained in the thermal activation at 400 °C is, however, different from that observed for the clayzic obtained in the thermal activation at 270 °C (figure 1). The observed increase in the peak maximum temperature is expected because of the availability of a

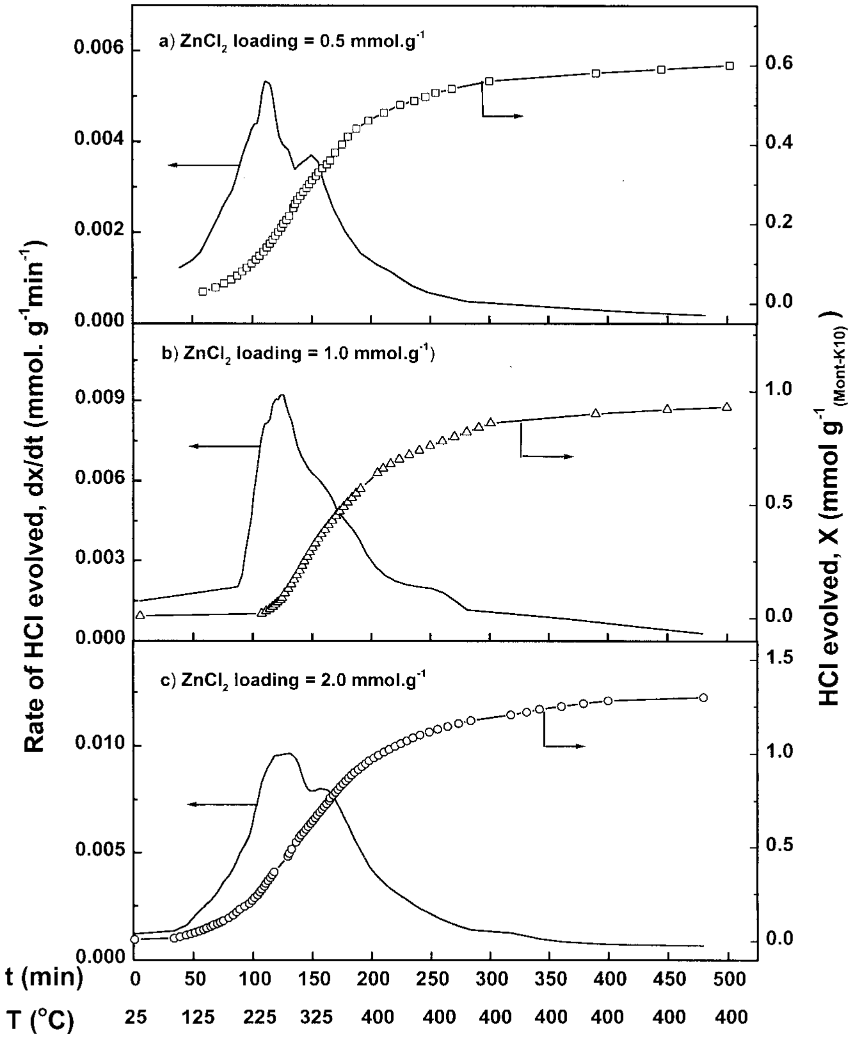

Figure 4. HCl evolved in the TPC of $ZnCl_2$/Mont-K10 catalysts with different $ZnCl_2$ loadings in a flow of N_2 (linear heating rate: 2 °C min^{-1}).

limited number of reactive surface hydroxyl groups for reaction 2 with increasing the $ZnCl_2$ loading.

4. Conclusions

From the present studies on the thermal activation by calcination of $ZnCl_2$/Mont-K10 (with different $ZnCl_2$ loadings) at different temperatures (150–400 °C) and under different gas atmospheres, the following important conclusions can be drawn.

1. An appreciable amount of HCl gas is evolved in the thermal activation, depending upon the $ZnCl_2$ loading and the calcination conditions. The HCl evolved is increased with increase of the $ZnCl_2$

Table 3
Dependence on the $ZnCl_2$ loading of the total amount of HCl evolved in the TPC of $ZnCl_2$/Mont-K10 (from 25 to 400 °C and at 400 °C for 5 h), surface area and Cl/Zn ratio of resulting $ZnCl_x$-grafted Mont-K10 and the TPC peak maximum temperature (for the d*X*/d*t* *versus* *T* curves in figure 4)

$ZnCl_2$ loading (mmol g^{-1})	Amount of HCl evolved (mmol g^{-1})	Surface area (m^2 g^{-1})	Cl/Zn ratio in $ZnCl_x$-grafted Mont-K10	TPC peak maximum temp. (°C)	
				First peak	Second peak
0.5	0.58	201.4	0.84	250	330
1.0	0.95	182.0	1.05	272	345 (hump)
2.0	1.34	155.5	1.33	278	350

loading and/or calcination temperature. Thus the formation of clayzic in the thermal activation involves a reaction between $ZnCl_2$ with surface hydroxyl groups of the clay, leading to the creation of new Lewis acid active sites (–O–Zn–Cl) with the evolution of HCl.
2. The Cl/Zn ratio of the resulting clayzic is decreased with increase of the calcination temperature but is increased with increase of the $ZnCl_2$ loading.
3. Both the surface area and benzene benzylation activity of the resulting clayzic is passed through the maximum with increase of the $ZnCl_2$ loading or the calcination temperature, indicating a correlation between the surface area and the catalytic activity.
4. The clayzic catalyst with maximum activity can be obtained by calcining $ZnCl_2$/Mont-K10 with the optimum $ZnCl_2$ loading (about 1.0 mmol g^{-1}) at the optimum temperature (close to 270 °C) in a flow of inert gas.

Acknowledgment

One of the authors (K.M.) is grateful to the Council of Scientific and Industrial Research, New Delhi, India, for a research fellowship.

References

[1] J.H. Clark, A.P. Kybett, D.J. Macquarrie, S.J. Barlow and P. Landon, J. Chem. Soc., Chem. Commun. (1989) 1353.
[2] S.J. Barlow, T.W. Bastock, J.H. Clark and S.R. Cullen, J. Chem. Soc. Perkin Trans. 2 (1994) 411.
[3] J.H. Clark, S.R. Cullen, S.J. Barlow and T.W. Bastock, J. Chem. Soc. Perkin Trans. 2 (1994) 1117.
[4] A. Cornelis, P. Laszlo and S.F. Wang, Tetrahedron Lett. 34 (1993) 3849.
[5] C.N. Rhodes, M. Franks, G.M.B. Parkes and D.R. Brown, J. Chem. Soc., Chem. Commun. (1991) 804.
[6] C.N. Rhodes and D.R. Brown, J. Chem. Soc., Faraday Trans. 88 (1992) 2269.
[7] V.R. Choudhary, S.K. Jana and B.P. Kiran, J. Catal. 192 (2000) 257.