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Highly Active and Low Moisture Sensitive Supported Thallium Oxide Catalysts for Friedel–Crafts-Type Benzylation and Acylation Reactions: Strong Thallium Oxide–Support Interactions

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Liquid-phase benzylation of benzene by benzyl chloride (at 80°C) over basic TlO_x (without support) and supported TlO_x prepared using different low and high surface area commonly used catalyst carriers has been investigated. The catalysts have been characterized by their surface area and also by XRD, FTIR, and XPS. Strong TlO_x–support interactions (which are chemical in nature) have been observed for the catalysts prepared using high surface area (HS), supports, such as Si–MCM-41, silica gel (HS), silica–alumina (HS), alumina (HS), and zirconia (HS), which have surface hydroxyl groups. These catalysts are found to be inactive for benzene benzylation or benzoylation reaction. However, the TlO_x supported on sintered low surface area (LS) macroporous catalyst carriers [viz. zirconia (LS), silica (LS), and silica–alumina (LS)], which have no surface hydroxyl groups, showed high benzene benzylation activity. TlO_x/zirconia (LS) is a highly promising catalyst for both the benzylation and acylation of benzene and other aromatic compounds and it shows high activity, even in the presence of moisture. The activity of this catalyst for the benzylation of benzene and substituted benzenes is in the following order: benzene > toluene > *p*-xylene > anisole. The induction period for the benzylation and acylation reactions over the catalyst, however, depends strongly on the moisture present in the catalyst and/or in the reaction mixture. The induction period is drastically reduced by the HCl gas pretreatment of the catalyst before the benzylation or acylation reaction. Only the catalyst that contains Tl_2O_3 shows activity for the benzylation and acylation reactions. A redox mechanism for these reactions over the supported TlO_x catalysts has been proposed. © 2001 Academic Press

Key Words: **benzylation of benzene; benzylation of aromatic compounds; benzoylation of aromatic compounds; TlO_x/zirconia (LS).**

INTRODUCTION

Friedel–Crafts-type reactions catalyzed by homogeneous acid catalysts are commonly used in organic synthesis (1). However, the commonly used homogeneous acid catalysts (viz., $AlCl_3$, BF_3, and H_2SO_4) pose several problems, such as difficulty in separation and recovery, disposal of spent catalyst, corrosion, high toxicity, etc. Development of reusable solid acid catalysts having high activity in the Friedel–Crafts reaction is, therefore, of great practical importance. Hence, efforts are made to replace the homogeneous acid catalysts by solid acid catalysts, such as heteropolyacids salts (2, 3), sulfated ZrO_2 or Fe_2O_3 (4–6), sulfated Al_2O_3–ZrO_2 (or TiO_2) (7), acid-treated clays (8), Fe/MCM-41 (9), cation-exchanged clays (10, 11), $ZnCl_2$, $CuCl_2$, $MgCl_2$, or $FeCl_3$ supported on montmorillonite K-10 (12, 13), HY, H-beta, and H–ZSM-5 zeolites (14–17), and Ga- or Fe-substituted H–ZSM-5 (18), for benzylation (2–4, 9–12, 18) and benzoylation (2, 3, 5–8, 13, 15–17) of aromatic compounds.

Acidic catalysts are, in general, moisture sensitive and hence demand a moisture-free reaction mixture for these reactions. It is, therefore, of great practical interest to have a solid catalyst having high activity but little or no moisture sensitivity for the Friedel–Crafts-type reactions. Recently, we (19) reported on montmorillonite K-10 or Si–MCM-41 supported $GaCl_3$ and $InCl_3$ catalysts, showing high activity and only little moisture sensitivity in the benzylation of benzene, which is otherwise relatively difficult to accomplish because of the absence of any electron-donating group in the aromatic substrate. Very recently, we (20) observed that Si–MCM-41 supported Ga_2O_3 and In_2O_3 catalysts also show very high activity in the benzylation of benzene with benzyl chloride; these catalysts were also found to be highly active in the benzoylation of benzene and other aromatic compounds. The supported In_2O_3 and $InCl_3$ catalysts showed higher benzene benzylation activity than that showed by supported Ga_2O_3 and $GaCl_3$ catalysts. Since Tl is the next group IIIA element, it is interesting to study the activity of the supported TlO_x and TlCl catalysts in the Friedel–Crafts-type reactions.

Our preliminary investigation indicated that TlCl deposited on Si–MCM-41 or montmorillonite K-10 is almost inactive for the benzene benzylation with benzyl chloride and the benzylation activity of supported TlO_x (which is basic in nature) varies drastically depending upon the nature and/or surface area of the support used. The present investigation was, therefore, undertaken to study TlO_x

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(catalyst)–support interactions, which strongly influence the catalytic activity of supported TlO_x (viz., TlO_x deposited on different supports with or without surface hydroxyls) in the Friedel–Crafts-type benzylation and acylation reactions.

EXPERIMENTAL

The supported TlO_x catalysts, loading of metal oxide (based on Tl_2O) = 2–40 wt% (Table 1), were prepared by impregnation of different supports [viz., sintered low surface area macroporous silica (LS) (SS-5231 having pore volume (pv) = 0.25 cm^3 g^{-1}), silica–alumina (LS) (SA-5205 having pv = 0.35 cm^3 g^{-1}), and zirconia (LS) (SZ-5564 having pv = 0.15 cm^3 g^{-1}), obtained from Norton Co., USA, and high surface area silica gel (HS), silica–alumina (HS), Si–MCM-41 (HS), alumina (HS), and zirconia (HS)] in the form of fine particles with thallous nitrate from its aqueous solution by the incipient wetness technique, drying, and calcination in air at 450°C for 4.5 h. The TlO_x (without support) was obtained by calcination of powdered thallous acetate at 450°C for 4.5 h. All low surface area supports are highly sintered macroporous materials, having no surface hydroxyl groups.

The catalysts were characterized by their surface area using a surface area analyzer (Quantachrome, USA) and the crystalline phases by XRD using a Phillips diffractometer (1730 series) and Cu$K\alpha$ radiation and also by FTIR (in Nujol medium) using a Perkin–Elmer FTIR (1600 series) and XPS using a VG-Scientific ESCA-3 MK II electron spectrometer.

The liquid-phase benzylation and benzoylation reactions over the catalysts were carried out in a magnetically stirred glass reactor (capacity: 25 cm^3) fitted with a reflux condenser, having low dead volume, mercury thermometer, and arrangement for continuously bubbling moisture-free N_2 (30 cm^3 min^{-1}) through the liquid reaction mixture at the following reaction conditions by the procedure given earlier (19, 20): reaction mixture = 13 ml of moisture-free aromatic substrate and 1.0 ml of benzyl or benzoyl chloride, amount of catalyst = 0.1 g (for benzylation) or 0.4 g (for benzoylation), and temperature = 80 or 110°C. In all the cases, the product formed was mainly mono-benzylated or acylated one, and there was no formation of polybenzyl or polyacyl chloride. The amount of benzylated or acylated product formed was equivalent (within 2–5% error) to the amount of benzylating or acylating agent consumed in the reaction.

To study the effect of moisture present in the catalyst and in the reaction mixture, the catalyst stored over water at 30°C for 12 h and the benzene saturated with water at 30°C, respectively, were used for the reaction.

TABLE 1

Results of the Benzylation of Benzene with Benzyl Chloride over TlO_x and Supported TlO_x (Loading of TlO_x = 20 wt%) Catalysts at 80°C

Catalyst	Colour of the catalyst	Surface area (m^2 g^{-1})		Substrate	Time for 50 and 90% conversion of benzyl chloride (min)		Induction period (min)	TON for half reaction (min^{-1})	Apparent reaction rate constant, $k_a \times 10^3$ (min^{-1})
		Support	TlO_x or supported TlO_x		50%	90%			
TlO_x (without support)	Dark grey	—	0.5	Dry benzene	29.3	40.7	24.8	3.2	153.6
TlO_x/silica–alumina (HS)	Light grey	255	207	Dry benzene	No reaction for 2.5 h		—	—	—
TlO_x/silica–alumina (LS)	Dark grey	<0.05	0.2	Dry benzene	3.3	10.0	0.3	28.0	248.0
TlO_x/silica gel (HS)	Light grey	280	51	Dry benzene	No reaction for 2.5 h		—	—	—
TlO_x/Si–MCM-41 (HS)	Very light grey	1180	49	Dry benzene	No reaction for 2.5 h		—	—	—
TlO_x/silica (LS)	Grey	0.2	0.3	Dry benzene	9.0	19.0	4.0	10.3	163.3
TlO_x/alumina (HS)	Off white	151	116	Dry benzene	No reaction for 2.5 h		—	—	—
TlO_x/zirconia (HS)	Grey	51	29	Dry benzene	No reaction for 2.5 h		—	—	—
TlO_x/zirconia (LS)	Dark grey	0.1	0.3	Dry benzene	2.4	8.2	0.1	38.5	291.5
TlO_x/zirconia (LS)	Dark grey	0.1	0.3	Moist benzene[b]	3.5	9.8	0.4	26.4	267.8
TlO_x/zirconia (LS) (moist)[a]	Dark grey	0.1	0.3	Moist benzene[b]	3.8	10.0	0.6	24.3	274.2
TlO_x/zirconia (LS)[c]	Very light grey	0.1	0.2	Dry benzene	No reaction for 1.5 h		—	—	—

Note. Reaction conditions: reaction mixture = 13 ml of moisture-free substrate and 1.0 ml of benzyl chloride; amount of catalyst = 0.1 g of supported TlO_x and 0.02 g of TlO_x.

[a] Catalyst was stored over water in desicator at 30°C for 12 h.

[b] Benzene saturated with water at 30°C (0.37 mol% water in benzene).

[c] Catalyst was prepared by decomposing thallous nitrate deposited on zirconia (LS) under a N_2 atmosphere at 450°C for 4.5 h.

To study the effect of HCl gas pretreatment to the catalyst on its performance in the benzylation or benzoylation reaction, a HCl(gas)–N_2 mixture (20 mol% HCl) was bubbled through a mixture of the aromatic substrate (which is to be benzylated or benzoylated) and catalyst under stirring at the reaction temperature for a period of 5 min. The substrate–catalyst mixture was flushed with pure N_2 (30 cm^3 min^{-1}) for 30 min to remove physically adsorbed or absorbed HCl in the reaction mixture and then the reaction was started by injecting benzyl chloride or benzoyl chloride in the reaction mixture.

RESULTS

Catalyst Characterization

Color and surface area of catalysts. Data on the color and surface area of the TlO$_x$ catalysts with and without catalyst support are given in Table 1.

The color of catalysts varies from off white/light grey to dark grey depending upon the catalyst support, more particularly its surface area. In general, the color of catalyst supported on the high surface area support was lighter than that on the low surface area support. The catalyst color is changed from grey to dark grey with increasing loading of TlO$_x$ from 20 to 40 wt% on zirconia (HS).

It is interesting to note that the surface area of supported TlO$_x$ is lower than that of the support itself for the high surface area supports, but it is higher for the low surface area supports (Table 1). There is a reduction in the surface area after deposition of TlO$_x$ on the high surface area supports. The reduction is, however, drastic for the silica gel and it is more drastic for the Si–MCM-41.

XRD. XRD spectra of the TlO$_x$ catalysts with and without the different supports are presented in Figs. 1 and 2.

The XRD spectra (Fig. 1) show that there is no presence of Tl_2O_3 phase in the TlO$_x$ (20 wt%)/zirconia (HS) but the Tl_2O_3 phase appears when the TlO$_x$ loading on the support is increased from 20 to 40 wt% (Figs. 1b, c). However, even at 20 wt% loading of TlO$_x$, the presence of Tl_2O_3 phase at a larger concentration is observed for the TlO$_x$ (20 wt%)/zirconia (LS) catalyst (Fig. 1d).

The XRD spectra in Fig. 2 show that, for the same loading of TlO$_x$, there is little or no presence of the Tl_2O_3 phase in TlO$_x$ (20 wt%)/Si–MCM-41 (Fig. 2a) and TlO$_x$ (20 wt%)/silica–alumina (HS) (Fig. 2c). However, for the catalyst supported on the low surface area supports [TlO$_x$ (20 wt%)/silica (LS) (Fig. 2b) or silica–alumina (LS) (Fig. 2d)], the Tl_2O_3 phase is observed distinctly.

For the TlO$_x$ (20 wt%)/Si–MCM-41, no characteristic XRD peak (at $2\theta = 1°–2°$) is observed, indicating a structural collapse of the Si–MCM-41.

FTIR. FTIR spectra of the Si–MCM-41, silica gel (HS), and silica-alumina (HS) with or without TlO$_x$ deposited on them are shown in Fig. 3.

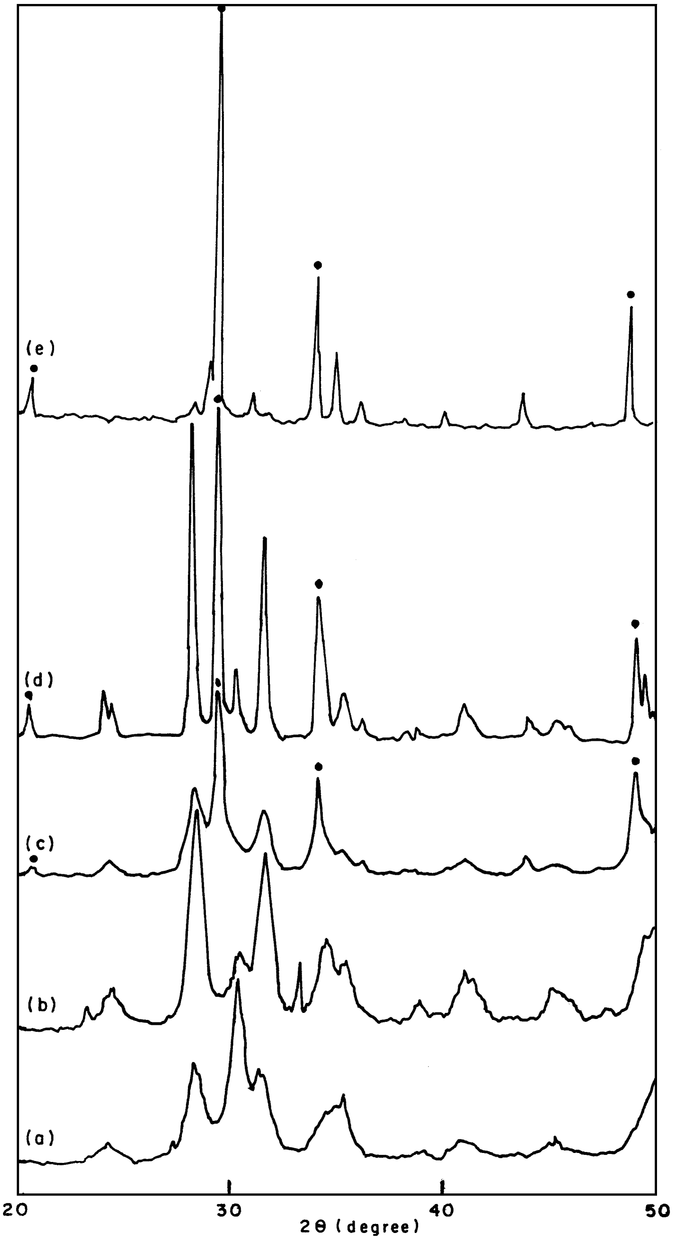

FIG. 1. XRD spectra of (a) zirconia (HS), (b) TlO$_x$ (20%)/zirconia (HS), (c) TlO$_x$ (40%)/zirconia (HS), (d) TlO$_x$ (20%)/zirconia (LS), and (e) TlO$_x$ obtained from Tl (I) acetate by decomposition in air [Tl_2O_3 phase (●)].

Because of the deposition of TlO$_x$ on the above supports, the IR spectra are influenced as follows:

—There is a significant decrease in the intensity of IR peak at around 960 cm^{-1}, which is assigned for terminal Si–OH (21).

—There is a shift in the IR peaks [assigned for Si–O–Si (21)] at around 450 and 1080 cm^{-1} and also a change in the IR band at 700–900 cm^{-1}, which is also assigned for Si–O–Si (21).

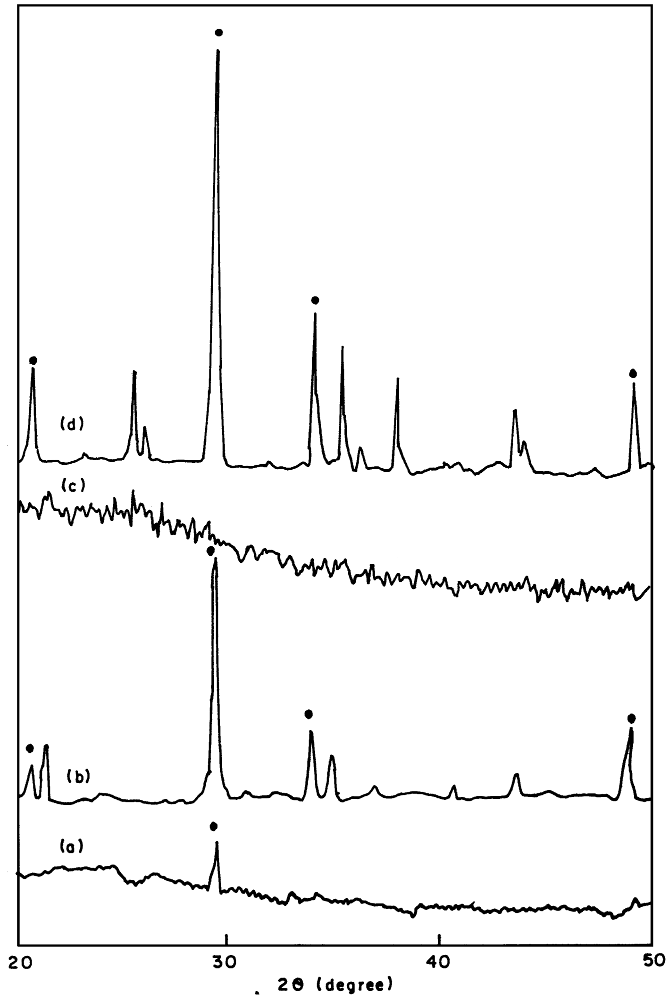

FIG. 2. XRD spectra of (a) TlO$_x$ (20%)/Si–MCM-41, (b) TlO$_x$ (20%)/silica (LS), (c) TlO$_x$ (20%)/silica–alumina (HS), and (d) TlO$_x$ (20%)/silica–alumina (LS) [Tl$_2$O$_3$ phase (●)].

XPS. XPS data for the zirconia-supported TlO$_x$ catalysts are presented in Table 2.

The surface Tl/Zr ratio is increased by five- to six fold with increasing TlO$_x$ loading on the high surface zirconia from 20 to 40 wt%. However, even for the lower loading, the Tl/Zr ratio is much higher when TlO$_x$ is deposited on the low surface area zirconia (Table 2).

Benzylation Reactions

The TlO$_x$ catalysts with and without different commonly used high and low surface area supports are compared in Table 1 for their performance in the benzylation of benzene (at 80°C). The catalysts that showed little or no benzene benzylation activity also did not show any activity for the benzoylation of benzene (at 80°C) or toluene (at 110°C) for a long period (3 h). Turnover number (TON) for half the benzene benzylation reaction (i.e., at 50% conversion of benzyl chloride) was estimated as the moles of benzyl chloride converted per mole of TlO$_x$ per unit time. The apparent reaction rate constant (k_a) for the benzylation of benzene by benzyl chloride (with excess of benzene) was estimated from the linear plots (Fig. 4) according to the first-order rate expression,

$$\log[1/(1-x)] = (k_a/2.303)\cdot(t-t_0), \qquad [1]$$

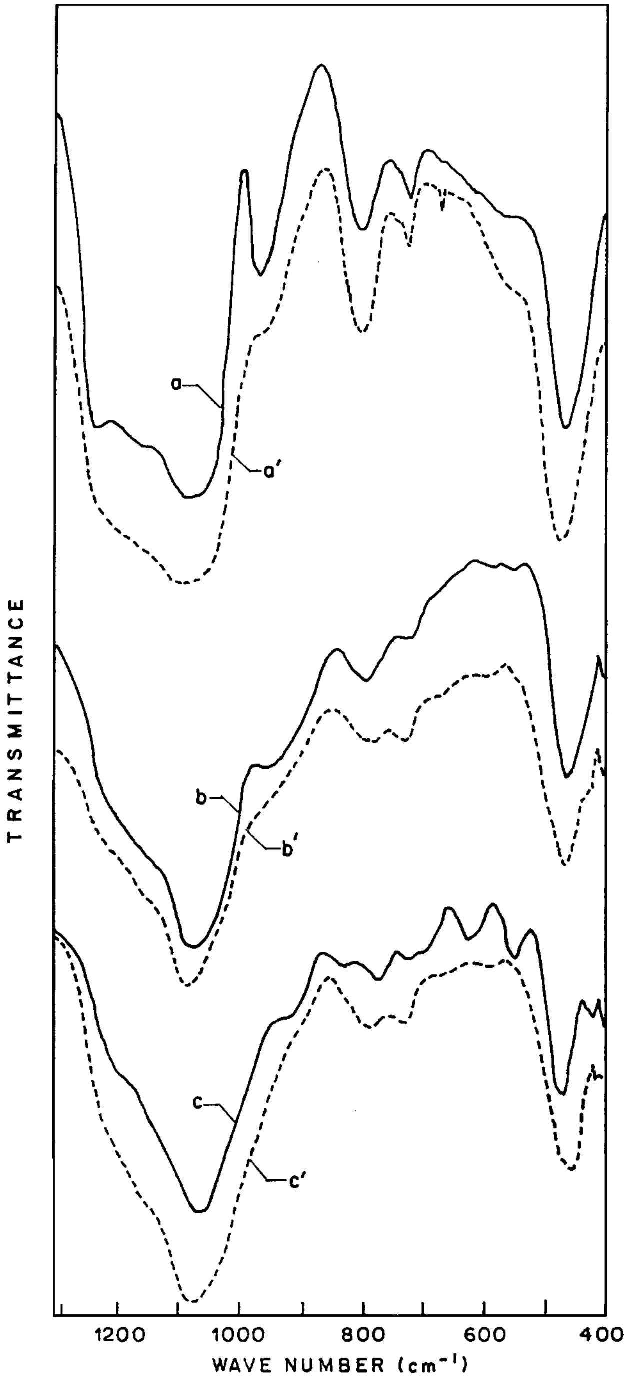

FIG. 3. IR spectra of Si–MCM-41 (a), TlO$_x$/Si–MCM-41 (a′), silica gel (b), TlO$_x$/silica gel (b′), silica–alumina (HS) (c), and TlO$_x$/silica–alumina (c′).

TABLE 2

XPS Data for Zirconia-Supported TlO_x Catalysts

	Binding energy (BE) (eV)						
Catalyst	Tl ($4f_{7/2}$)	BE [Tl ($4f_{7/2}$)]– BE [Tl ($4f_{5/2}$)]	Zr ($3d_{5/2}$)	BE [Zr ($3d_{5/2}$)]– BE [Zr($3d_{3/2}$)]	O (1s)	Surface Tl/Zr ratio
TlO_x (20)/zirconia (HS)	119.1	4.4	182.8	2.0	531.1	0.04
TlO_x (40)/zirconia (HS)	119.1	4.5	182.2	2.0	530.9	0.22
TlO_x (20)/zirconia (LS)	119.4	4.1	183.0	2.5	531.8	0.43

where x is the fractional conversion of benzyl chloride and t and t_0 are the time and induction period, respectively, of the reaction.

From the comparison in Table 1, the following important observations can be made:

—The chemically similar supports with low surface area provided a much more active supported TlO_x catalyst for the benzene benzylation reaction. TlO_x when supported on the high surface area catalyst carriers showed almost no catalytic activity in the reaction.

—The TlO_x without support also shows high catalytic activity but the reaction induction period for this catalyst is much larger.

—Among the TlO_x catalysts supported on the low surface area catalyst carriers, the TlO_x/zirconia (LS) showed the best performance (lowest induction period and highest catalytic activity, TON).

—The TlO_x/zirconia (LS) shows high benzene benzylation activity, even when moisture at the level of its saturation is present in the substrate and/or in the catalyst. However, because of the presence of moisture in the reaction mixture, the reaction induction period is increased from 0.1 to 0.6 min.

—When the TlO_x/zirconia (LS) catalyst was prepared by calcination under N_2 instead of air, it showed no activity for the benzene benzylation.

Results showing the influence of TlO_x loading on the reaction rate constant (k_a) for the zirconia (LS), zirconia (HS), and silica gel (HS) supported TlO_x catalysts are presented in Fig. 5.

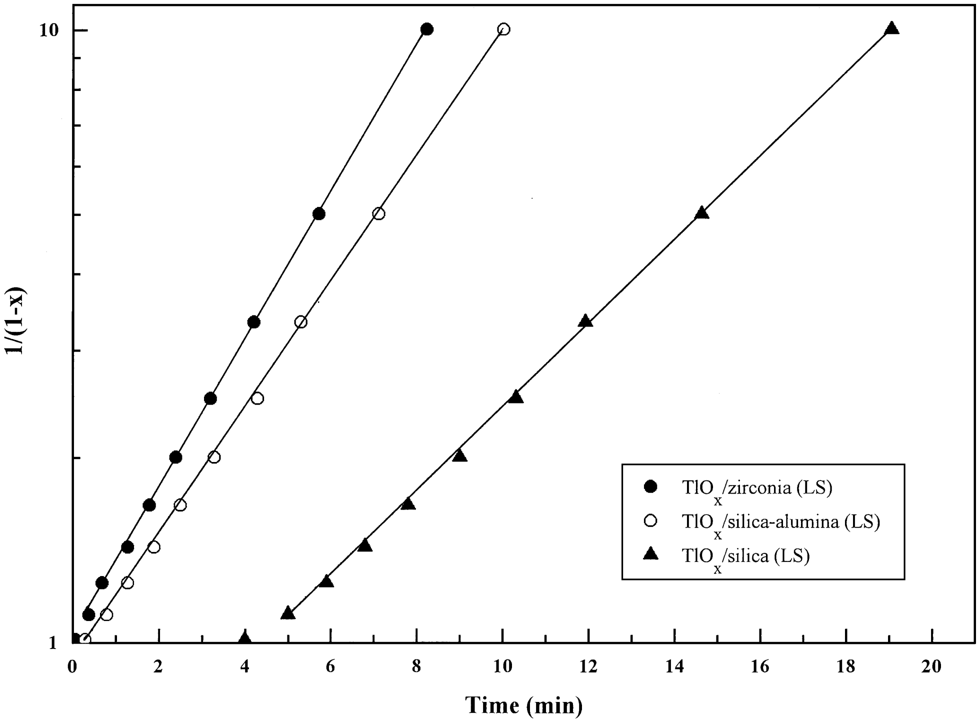

FIG. 4. First-order reaction plots (according to Eq. [1]) for the benzylation of benzene (at 80°C) over different supported TlO_x catalysts.

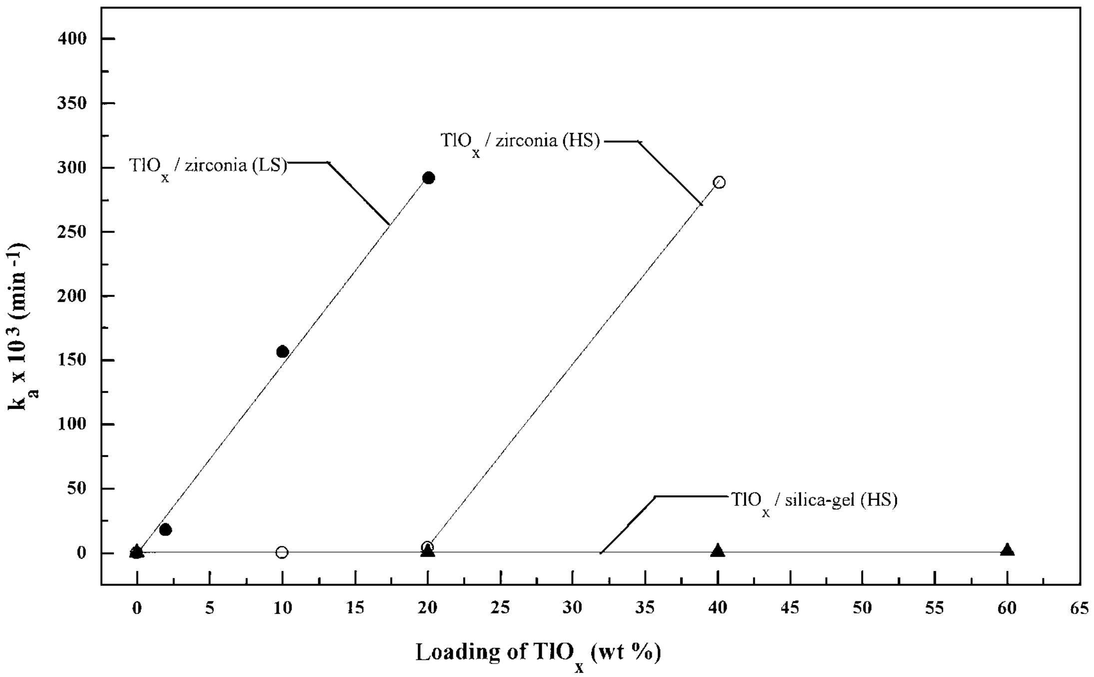

FIG. 5. Variation of apparent reaction rate constant (k_a) for the benzylation of benzene (at 80°C) over TlO_x/zirconia (LS), TlO_x/zirconia (HS), and TlO_x/silica gel (HS) with the loading of TlO_x on the different supports.

For the zirconia (LS) supported TlO_x catalyst, the reaction rate constant is increased almost linearly with the TlO_x loading. However, the zirconia (HS) supported TlO_x catalyst shows catalytic activity only above the TlO_x loading of 20 wt% but the silica gel (HS) supported TlO_x does not show any catalytic activity, even at the TlO_x loading as high as 60 wt%.

Figure 6 shows the effect of the time of reflux of the unsupported TlO_x catalyst (with dry benzene) and also of the HCl (gas) pretreatment to the catalyst, before starting

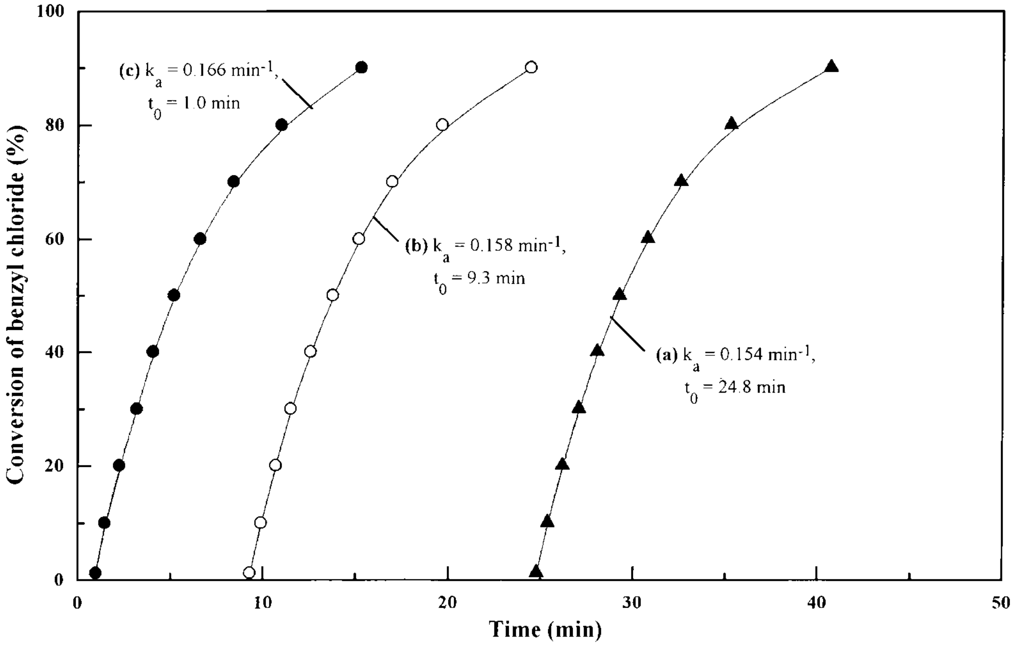

FIG. 6. Effect of time of reflux with benzene and HCl pretreatment of the catalyst, before starting the reaction, on the induction period (t_0) and conversion of benzyl chloride in the benzylation of benzene (at 80°C) over TlO_x obtained from Tl (I) acatate [reflux time: (a) 0.5 h and (b) 4 h; (c) HCl pretreated catalyst].

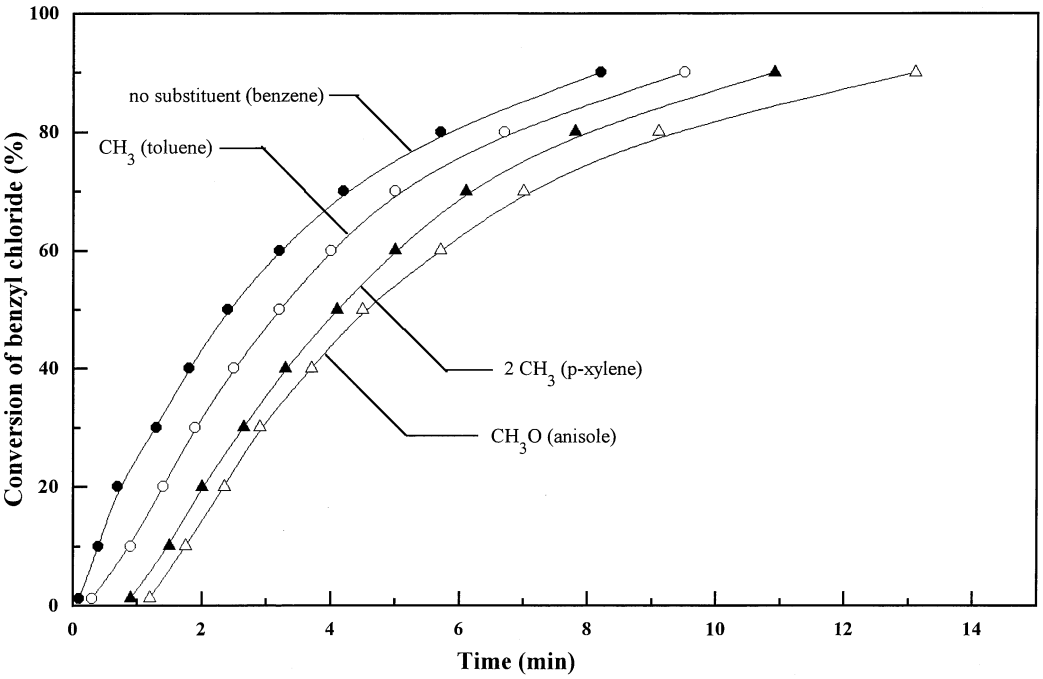

FIG. 7. Effect of the presence of different substituent groups in the aromatic (benzene) nucleus on its benzylation with benzyl chloride over the TlO$_x$ (20%)/zirconia (LS) at 80°C (reaction mixture = 13 ml of benzene or substituted benzene + 1 ml of benzyl chloride + 0.1 g catalyst).

the benzylation reaction, on the induction period in the benzene benzylation reaction.

The induction period is decreased markedly (from 24.8 to 9.3 min) with increasing reflux time (from 0.5 to 4 h) (Fig. 6a, b). It is also decreased drastically due to the pretreatment by HCl gas of the catalyst (Fig. 6a, c). It is interesting to note here that although the induction period is strongly influenced by the reflux period and the HCl pretreatment of the catalyst, there is only a very small change in the reaction rate constant. Thus, in all the cases, after the induction period, the reaction proceeds at almost the same rate.

Results showing the influence of different substituent groups attached to an aromatic benzene nucleus on the conversion of benzyl chloride in the benzylation of corresponding substituted benzenes (at 80°C) over the TlO$_x$ (20 wt%)/zirconia (LS) catalyst are presented in Fig. 7. The first-order rate constants (k_a) and induction period for the benzylation reactions are as follows:

Substrate:	Benzene	Toluene	*p*-Xylene	Anisole
$k_a \times 10^3$ (min^{-1}):	291.5	267.8	253.0	203.8
Induction period (min):	0.1	0.3	0.9	1.2

The results indicate that, unlike the conventional acid catalyst (1), the benzylation activity of the catalyst is decreased due to the presence of electron-donating groups, such as methyl and methoxy groups, in the aromatic compound.

Acylation Reactions

The high and low surface area zirconia-supported TlO$_x$ catalysts are compared for their performance in benzene benzoylation (at 80°C) and toluene benzoylation (at 110°C) reactions in Table 3.

Like the benzylation reaction, the TlO$_x$ (20 wt%)/zirconia (LS) showed much higher benzene or toluene benzoylation activity than that of the TlO$_x$ (40 wt%)/zirconia (HS). The reaction induction period for the former is also smaller. The TlO$_x$ (20 wt%)/zirconia (HS) showed no activity in both the benzene and toluene benzoylation reactions.

Like the benzene benzylation, the induction period in the benzene benzoylation reaction over TlO$_x$/zirconia (LS) catalyst is decreased very markedly due to the HCl pretreatment of the catalyst before the reaction (Fig. 8). The rate of benzoylation after the induction period for both cases (i.e., with and without the HCl pretreatment) remained almost the same.

The TlO$_x$ (20 wt%)/zirconia (LS) and TlO$_x$ (20 wt%)/Si–MCM-41 catalysts are compared with the earlier reported catalysts for their performance in the benzene benzylation, benzene benzoylation, and toluene benzoylation reactions under similar conditions in Table 4.

TABLE 3

Results of the Benzoylation with Benzoyl Chloride of Benzene and Toluene over Supported TlO_x Catalysts

Catalyst	Induction period (min)	Time (min) required for 50 and 80% conversion of acylating agent: 50%	80%	TON for half reaction (min^{-1})
		Benzoylation of benzene at 80°C		
TlO_x (20)/zirconia (LS)	9.2	158.0	—	0.15
TlO_x (20)/zirconia (HS)	—	No reaction for 2.5 h		—
TlO_x (40)/zirconia (HS)	11.5	196.0	—	0.06
		Benzoylation of toluene at 110°C		
TlO_x (20)/zirconia (LS)	2.3	17.4	96.5	1.32
TlO_x (20)/zirconia (HS)	—	No reaction for 2.5 h		—
TlO_x (40)/zirconia (HS)	4.5	32.0	165.0	0.36

Note. Reaction mixture = 13 ml of benzene or toluene and 1.0 ml of benzoyl chloride; amount of catalyst = 0.4 g.

DISCUSSION

Influence of Catalyst Support: Strong TlO_x–Support Interactions

A comparison of the supported TlO_x catalysts for their performance in the benzene benzylation (Table 1) shows that TlO_x deposited on the low surface area supports has high catalytic activity in the reaction but that deposited on the high surface area supports has almost no activity for the reaction. In contrast, the Ga_2O_3 and In_2O_3 catalysts deposited on high surface area supports, such as Si–MCM-41 and silica gel (Table 4), showed very high benzene benzylation activity (20). The observed strong influence of the catalyst support on the activity of the supported TlO_x catalysts clearly shows strong TlO_x–support interactions. Strong metal–support interactions are well known and are observed for many supported metals (22, 23). However, the information on the strong metal oxide–support interactions, which are mainly chemical in nature, is scarce; these have been observed for a few supported metal oxide (Li–MgO, La–MgO, and La–CaO) catalysts (24–26). In the present case, since TlO_x is basic, it can interact chemically

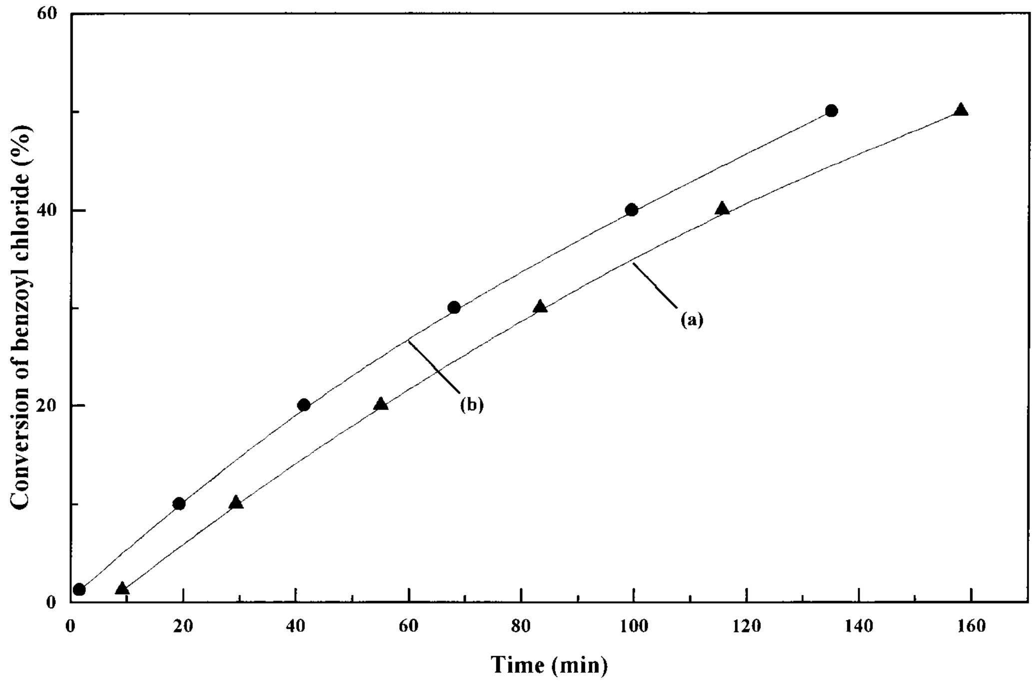

FIG. 8. Effect of HCl pretreatment of the catalyst, before starting the reaction, on the induction period (t_0) and conversion of benzoyl chloride in the benzoylation of benzene (at 80°C) over TlO_x/zirconia (LS) catalyst [(a) without HCl pretreatment and (b) with HCl pretreatment].

TABLE 4

Comparison of the Present Catalysts with the Earlier Ones for Their Activity in the Benzylation (with Benzyl Chloride) of Benzene (at 80°C) and Benzoylation (with Benzoyl Chloride) of Benzene (at 80°C) and Toluene (at 110°C)

Catalyst	Catalyst/($C_6H_5CH_2Cl$/or C_6H_5COCl) wt ratio	Conversion of benzyl or benzoyl chloride and reaction time required		Ref.
		Conversion (%)	Time (min)	
		Benzene benzylation (at 80°C)		
TlO$_x$/zirconia (LS)	0.1	50	2.4	Present work
TlO$_x$/Si–MCM-41	0.1	No reaction for 2.5 h		Present work
Ga_2O_3/zirconia (LS)	0.1	50	5.4	16
In_2O_3/zirconia (LS)	0.1	50	7.3	16
Ga_2O_3/Si–MCM-41	0.1	50	2.5	16
Ga_2O_3/silica gel	0.1	50	11	16
In_2O_3/Si–MCM-41	0.1	50	2.4	16
$GaCl_3$/Mont. K-10	0.1	50	4.7	15
$InCl_3$/Mont. K-10	0.1	50	2	15
H–FeMFI	0.1	50	6.7	14
H–GaAlMFI	0.1	50	22.8	14
Nafion-H	0.1	24	120	3
Sulfated ZrO_2	0.1	50	135	4
Sulfated Fe_2O_3–ZrO_2	0.1	50	33	4
		Benzene benzoylation (at 80°C)		
TlO$_x$/zirconia (LS)	0.33	50	165	Present work
TlO$_x$/Si–MCM-41	0.33	No reaction for 2.5 h		Present work
In_2O_3/Si–MCM-41	0.33	50	286	16
H-Beta	0.33	54	1080	11
		Toluene benzoylation (at 110°C)		
TlO$_x$/zirconia (LS)	0.33	83	103	Present work
TlO$_x$/Si–MCM-41	0.33	No reaction for 2.5 h		Present work
In_2O_3/Si–MCM-41	0.33	83	148	16
Ga_2O_3/Si–MCM-41	0.33	83	205	16
H-Beta	0.33	83	1083	12
Sulfated ZrO_2	0.5	50	192	5

with the weakly or strongly acidic surface hydroxyls of high surface area supports.

The low surface area supports (Table 1) are highly sintered macroporous materials and hence have no surface hydroxyl groups, whereas the high surface area supports (Table 1) are known to have appreciable amounts of surface hydroxyl groups. Even a highly crystalline material like mesoporous Si–MCM-41 has different types of surface hydroxyls, as terminal Si–OH groups (27, 28). The Si–MCM-41 sample used in the present study also has appreciable amounts of surface hydroxyl groups (29). The silica gel support also has large amounts of surface hydroxyl. The strong TlO$_x$–support interactions in the present case are mostly due to the presence of surface hydroxyl groups in the high surface area supports. This hypothesis is supported by the following observations:

—For the high surface area supports, the surface area of the supported TlO$_x$ catalysts is much lower than that of the corresponding support (Table 1). In the case of Si–MCM-41 support, its structure is collapsed with a drastic reduction in the surface area (from 1180 to 49 $m^2\ g^{-1}$) because of the deposition of TlO$_x$.

—The intensity of the IR peak at 960 cm^{-1} (assigned to terminal Si–OH) is reduced markedly due to the deposition of TlO$_x$ on the Si–MCM-41, silica gel, and high surface area silica–alumina (Fig. 3). This indicates the consumption of the surface hydroxyl groups in the chemical interactions with the deposited TlO$_x$.

—The XRD spectra of the TlO$_x$ (20 wt%) supported on Si–MCM-41, silica–alumina (HS), and zirconia (HS) show little or no presence of the Tl_2O_3 phase (Figs. 1b and 2a, c). A small Tl_2O_3 phase for the TlO$_x$/zirconia (HS) is seen only when the TlO$_x$ loading is increased from 20 to 40 wt% (Fig. 1b, c). In contrast, for the TlO$_x$/zirconia (LS), even for the TlO$_x$ loading of 20 wt%, a distinct Tl_2O_3 phase is observed (Fig. 1d). It may be noted that only those supported TlO$_x$ catalysts are active in the reaction for which distinct XRD peaks showing the presence of Tl_2O_3 phase are observed.

—The surface Tl/Zr ratio is an order of magnitude (10 times) larger when TlO_x is deposited on the low surface area zirconia than on the high surface area zirconia (Table 2). Also, there is a large increase in the surface Tl/Zr ratio (from 0.04 to 0.22) with doubling of the TlO_x loading on the high surface area zirconia.

The observations on the Tl_2O_3 phase and surface Tl/Zr ratio for the high surface area zirconia for the two TlO_x loadings (20 and 40 wt%) show that an appreciable fraction of the TlO_x loaded on the support is consumed in the TlO_x–support interactions.

The drastic reduction in the surface area of the Si–MCM-41 and silica gel after the deposition of TlO_x on them is due to their structural collapse resulting from the reaction between their surface hydroxyls and TlO_x. The reduction in the surface area for the silica–alumina (HS) is relatively smaller and this may be due to its smaller number of surface hydroxyls.

Thus, unlike Ga_2O_3 and In_2O_3, TlO_x interacts strongly with the high surface area supports, mostly through their surface hydroxyl groups. Further studies are necessary for understanding the nature of chemical interactions. Nevertheless, when compared to the low surface area supports, the supported TlO_x is more active than the supported Ga_2O_3 and In_2O_3 catalysts for the benzene benzylation (Table 4). Also, like the supported Ga_2O_3 and In_2O_3 catalysts (20), the activity of the TlO_x/zirconia (LS) catalyst is only little affected by the presence of moisture in the catalyst or in the reaction mixture (Table 1). However, because of its toxicity, the TlO_x catalyst should be handled much more carefully.

Effect of Moisture and HCl Pretreatment on the Reaction Induction Period

The induction period for the benzene benzylation is reduced markedly because of increasing of reflux period and consequently removal of the adsorbed moisture from the unsupported TlO_x catalysts (Fig. 6a, b). It is also interesting to note that the TlO_x catalysts supported on the low surface area support (which are sintered macroporous materials and hence do not contain significant amounts of adsorbed moisture) have a much lower induction period (Table 1). These observations indicate that the adsorbed moisture present in the catalyst is responsible for the high induction period for the unsupported TlO_x; the removal of adsorbed water from the catalyst results in a decrease in the induction period.

The induction period of the unsupported TlO_x catalyst is reduced drastically because of the HCl pretreatment to the catalyst before the benzene benzylation reaction (Fig. 6a, c). A similar observation is also made for the benzoylation of benzene over the TlO_x/zirconia (LS) (Fig. 8). These observations reveal that, during the induction period, the catalyst is activated by the HCl (which is a by-product) produced in both the benzylation and benzoylation reactions. The influence of moisture on the induction period is, therefore, attributed to a reduction due to the presence of moisture in the rate of catalyst activation by the HCl produced in the initial reaction.

Catalyst activation by HCl during the induction period may result from the removal of adsorbed water from the catalyst (TlO_x is basic in nature and hence adsorption of HCl on it is stronger than that of water) or from the chemisorption of HCl on the catalyst modifying its surface active sites or from both. After use in the reaction, the catalyst showed the presence of a significant amount of chlorine. A further detailed investigation is necessary for understanding catalyst activation during the induction period.

Effect of Electron-Donating Substituent Groups

According to the classical mechanism of the Friedel–Crafts-type acid-catalyzed benzylation or acylation reaction, the benzylation or acylation of an aromatic compound is easier if one or more electron-donating groups are present in the aromatic ring (1). Surprisingly, in the present case the activity of the TlO_x/zirconia (LS) catalyst for benzylation (under the same conditions) of the aromatic compounds with or without electron-donating groups (CH_3 and CH_3O) is opposite to that expected from the classical mechanism (Fig. 7). The first-order rate constant for the benzylation of benzene and substituted benzenes is in the following order: benzene > methyl benzene > *p*-dimethylbenzene > methoxy benzene. This shows that, for this catalyst, the reaction mechanism is different from that for the classical acid-catalyzed benzylation reactions.

Reaction Mechanism

The active supported TlO_x catalysts were found to contain Tl_2O_3, which is basic in nature. The standard reduction potential for $Tl^{3+} \rightarrow Tl^{1+}$ ($E^\circ_{Tl^{3+}/Tl^{1+}}$) is positive (+2.06 V), and hence the reduction of Tl^{3+} to Tl^{1+} is relatively easy. The benzylation and acylation reactions over these catalysts are, therefore, expected to follow a redox mechanism similar to that proposed earlier for the alkylation (10) and acylation reactions (30), as follows:

$$2C_6H_5CH_2(\text{or CO})Cl + Tl^{3+} \rightarrow 2C_6H_5CH_2(\text{or CO})Cl^+ + Tl^{1+} \quad [2]$$

$$C_6H_5CH_2(\text{or CO})Cl^+ \rightarrow C_6H_5CH_2^+(\text{or } CO^+) + Cl \quad [3]$$

$$C_6H_5CH_2{}^+(\text{or } CO^+) + ArH \rightarrow C_6H_5CH_2(\text{or CO})Ar + H^+ \quad [4]$$

$$2Cl + Tl^{1+} \rightarrow 2Cl^- + Tl^{3+} \quad [5]$$

$$H^+ + Cl^- \rightarrow HCl. \quad [6]$$

The TlO_x/zirconia (LS) obtained by calcination in a N_2 atmosphere contained Tl_2O and no Tl_2O_3. This catalyst showed no activity for the benzene benzylation (Table 1), which is consistent with the above mechanism.

CONCLUSIONS

The following important conclusions have been drawn from this investigation:

1. Because of its basic nature, TlO_x interacts strongly (chemically) with the surface hydroxyls (both weakly and strongly acidic ones) of high surface area catalyst supports such as Si–MCM-41, silica gel, alumina, silica–alumina, and zirconia, causing a large reduction in the surface area of the support; the structure of Si–MCM-41 is collapsed after the deposition of TlO_x on it. The supported TlO_x prepared using the high surface area supports are inactive in the benzylation of benzene. In contrast, the TlO_x supported on low surface area sintered macroporous zirconia, silica, or silica–alumina catalyst carriers shows high benzene benzylation activity. TlO_x/zirconia (LS) is a highly promising catalyst for both the benzylation and acylation of benzene and other aromatic hydrocarbons. It shows high benzene benzylation activity, even in the presence of moisture in the catalyst or in the reaction mixture. Only the catalyst that contains Tl_2O_3 shows activity for the benzylation and acylation reactions.

2. The TlO_x/zirconia (LS) catalyst shows the following trend for its activity in the benzylation of benzene and substituted benzenes containing electron-donating groups (viz. CH_3 and CH_3O): benzene > methyl benzene > *p*-dimethylbenzene > methoxy benzene, which is totally opposite to that observed for the acid-catalyzed Friedel–Crafts-type benzylation reactions. This trend and the basic nature of the catalyst indicate that the benzylation and acylation reactions follow a redox mechanism in the present case.

3. The induction period for the benzylation and acylation reactions depends strongly on the presence of moisture in the catalyst and/or in the reaction mixture; it is decreased with a decreasing amount of moisture. During the induction period, the catalyst is activated most probably by the modification of its surface by interaction with the HCl (a by-product) produced in the initial benzylation or acylation reaction. Pretreatment by HCl gas of the catalyst causes a drastic reduction in the induction period for both the benzylation and acylation reactions.

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