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ACTION OF HETEROPOLY ACID AND RELATED OXIDES IN ACYLATION OF CHLOROBENZENE WITH o-CHLOROBENZOYL CHLORIDE

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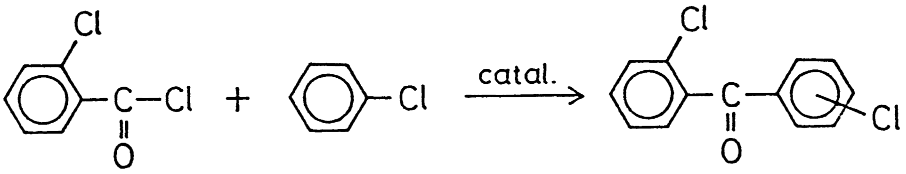
Heteropoly acids, MoO_3, and calcined $FeSO_4$ have been found to catalyze the acylation of chlorobenzene with o-chlorobenzoyl chloride. A kinetic study revealed that those catalysts are not active in their original forms, but the metal chlorides or metal complexes formed by reacting with chlorine are active for the acylation reaction.

Friedel-Crafts reactions using reagents such as $AlCl_3$, BF_3, $TiCl_4$, $ZnCl_2$ etc. are still important in industrial processes. Those processes, however, have several disadvantages; wasting a lot of reagents like $AlCl_3$, because of the reaction being mostly equimolar and of the difficulty of recycling them after use, and corrosion of containers by evolved acidic gases. In order to overcome these difficulties, several articles suggested a potential use of heteropoly acid (HPA)1), iron oxide,2) or activated iron sulfate3) as an alternative catalyst, which enables us to use it as a "catalyst" and to recover it after use. HPA is a fairly strong acid and its acidic property is owing to its structure. This acidic property is supposed to be responsible to the activity in the Friedel-Crafts reactions. This paper reports a synthesis of benzophenone derivatives and deals with the action of HPA in the following acylation reaction.



12-Molybdophosphoric acid (PMo_{12}), 12-molybdosilicic acid ($SiMo_{12}$), 12-tungstophosphoric acid (PW_{12}), and 12-tungstosilicic acid (SiW_{12}) were purchased from Nippon Inorganic Chemicals. 6-Molybdo-6-tungsto-phosphoric acid (PMo_6W_6) and 9-molybdo-3-vanadophosphoric acid (PMo_9V_3) were prepared following the literature.[4)] Those catalysts were calcined in air at the desired temperatures. The reaction was carried out at 130 or 135°C under N_2 atmosphere using 12.5g (0.071 mole) of o-chlorobenzoyl chloride, 23.2g (0.206 mole) of chlorobenzene, and 3g of catalyst. Products were analyzed by gas chromatography. Reaction products consisted of 2,4'-dichlorobenzophenone (over 90%), and 2,2'-and 4,4'-dichlorobenzophenone (less than 10%) in most cases.

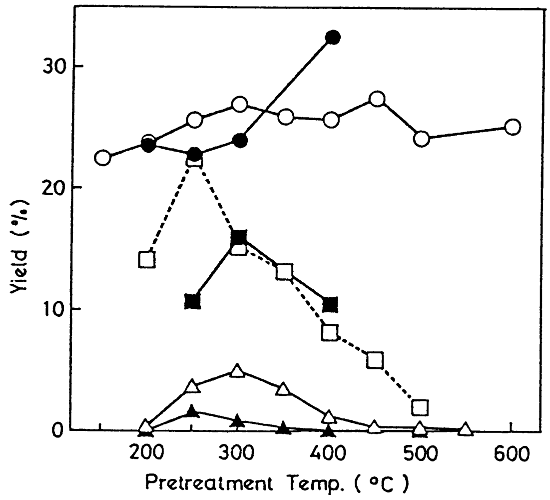


Fig 1. Effect of pretreatment temperature

react. temp.: 135°C
react. time : 180 min.

○ : PMo_{12}, △: PW_{12}, □: PMo_6W_6
● : $SiMo_{12}$, ▲: SiW_{12}, ■: PMo_9V_3

A typical result is shown in Fig. 1. PMo_{12} and $SiMo_{12}$ exhibited high activities, while PW_{12} and SiW_{12} showed low activities. The catalytic activities of PMo_6W_6 and PMo_9V_3 were intermediate.

Curious behaviors in both PMo_{12} and $SiMo_{12}$ series have been found, that is, even those catalysts calcined at such a high temperature that their structures are destroyed thermally (determined by DTA, PMo_{12}:440°C; $SiMo_{12}$:360°C) are still active. These results suggest that THE MATERIALS obtained after the thermal decomposition are also active for the acylation reaction: phosphoric acid, SiO_2, and MoO_3 are the possible canditates for active species. However, considering the facts that PW_{12} and SiW_{12} showed low activities and that Mo is a common element in PMo_{12} and $SiMo_{12}$, it seems likely to conclude that MoO_3 is the most probable active species.

Figure 2 shows the time course of the reaction which was carried out using PMo_{12} and MoO_3. The result clearly shows that MoO_3 was active as well as PMo_{12}. Taking the appearance of induction periods for both catalysts into consideration, the acylation reaction may take place when MoO_3 or PMo_{12} was tranformed to some other active species. The transformation causes the observed induction period. The Figure also contains the result when $MoCl_5$ was used. This time, the initial reaction rate was high and no induction period was found.

Since $MoCl_5$ was active in the acylation reaction and it completely dissolved into reaction mixture, a question arises whether the active species derived from PMo_{12}, $SiMo_{12}$, and MoO_3 are on the solid surface or in the liquid. After the reaction was started as usual using MoO_3 as a catalyst, the catalyst was separated from reaction mixture by filtration and the reaction was continued without solid catalyst. New reactants were added to the separated solid catalyst and the reaction was started. Results of those reactions are compared in Fig. 3, and it clearly shows that even in the homogeneous system the reaction took place continuously. In fact, about 40% of Mo ion was found in the liquid phase after 60 min reaction, which was revealed by a spectroscopic analysis using sodium thiocyanate. Figure 3 also indicates that the heterogeneous system, which was freshly prepared after the separation, still has an induction period. Thus, we conclude as follows. In the acylation reaction, which liberates hydrogen chloride during the reaction, true active species should be in liquid phase and the reaction proceeds homogeneously. Active species could be a halogenated Mo compound which may be formed by a reaction between PMo_{12}, $SiMo_{12}$ or MoO_3 and HCl evolved.

Situation was the same when the reaction was performed by an iron oxide which

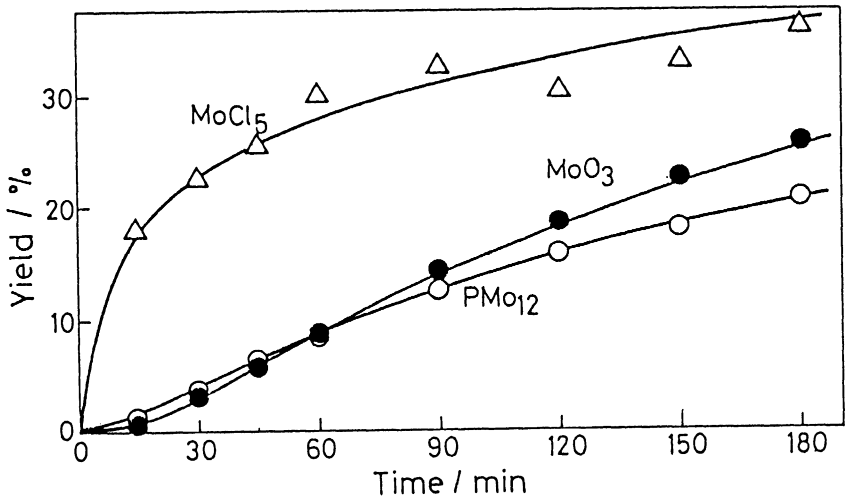


Fig. 2 Reaction time course

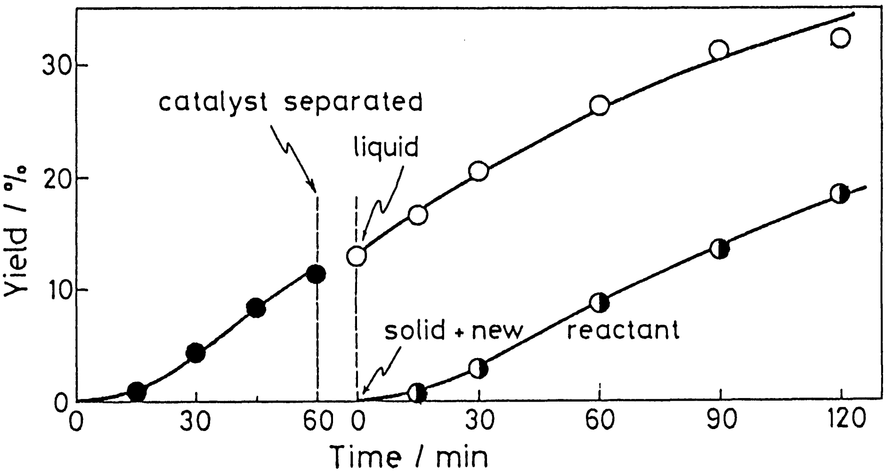


Fig. 3 Separation of solid catalyst
catalyst: MoO_3; reaction temp.: 135°C

was prepared by calcining $FeSO_4 \cdot 7H_2O$ at 600°C. The reaction was faster than those catalyzed by Mo compounds, and the catalyst separation experiments revealed that the reaction also took place homogeneously.

Thus, as far as the acylation reaction using an acyl halide concerns, the metal oxides which provide soluble halogenated species do act as neither their original forms nor heterogeneous catalysts. The transformation of an original oxide may be initiated by the reaction of the oxide with HCl or chloride ion which is formed by the hydrolysis of benzoyl chloride by a trace of water contained in the system.

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