

BENZYL CHLORIDE TRANSFORMATION AS A PROBE FOR
ELECTRON TRANSFER ON Rh/TiO₂ UNDER SMSI STATE

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Benzyl chloride transformation has been studied over Rh/TiO₂ under SMSI state to give evidence for the transfer of electrons from support to metal.

Реакция превращения бензилового хлорида была исследована на катализаторе Rh/TiO₂, для которого характерно сильное взаимодействие металла с носителем. Получены доказательства перехода электронов от носителя на металл.

INTRODUCTION

The phenomenon of strong metal support interaction (SMSI) in systems of Group VIII metals supported on reducible metal oxides has attracted attention in recent years. Several mechanism based on geometric and electronic factors have been proposed to explain the origin of the so-called SMSI effect and its influence on catalytic activity [1]. The concept of electronic interaction was first proposed by Solymosi et al. [2]. Subsequently the mechanism of transfer of electrons from support to metal was postulated [3]. The geometric effect is understood from the structural elucidation of catalysts. Measurements of binding energy (eV) by XPS [4] and electrical conductivity [2] give clues to the electron transfer from support to metal.

Though catalytic reactions can be used as a diagnostic tool for this study, to the best of our knowledge, no reaction has so far been studied for understanding the electronic factors operating in the SMSI state. In the present work, benzyl chloride transformation is studied as a model reaction on Rh/TiO₂, which supports the concept of electron transfer from support to metal.

EXPERIMENTAL

Rh/TiO₂ (ca. 1 wt.% Rh) was prepared by impregnating TiO₂ (Anatase, Tioxide International, UK, pore volume=0.3 cm³ g⁻¹; surface area=70 m² g⁻¹) with an aqueous solution of RhCl₃·3H₂O. It was dried overnight at 423 K and then calcined in air at 623 K for 3 h. The catalyst is reduced both at low temperature (LTR, 573 K) and at high temperature (HTR, 773 K) and tested for SMSI behavior. About 0.5 g of the fresh catalyst is loaded in a glass microreactor. The reactant benzyl chloride is fed at the rate of 0.052 mol h⁻¹ with the help of a motor-driven syringe, using nitrogen as a carrier gas. The reaction is carried out under two different activation conditions (Scheme 1). In one experiment, the catalyst is reduced at HTR for 3 h and the reaction is carried out at 573 K. In the other experiment, the catalyst is subjected only to high temperature calcination (HTC) in nitrogen at 773 K for 3 h before reaction. The above experiments are repeated on Rh/γ-Al₂O₃, at 573 K after reduction at 773 K. The products are analyzed with a HP 5890 gas chromatograph, using an SE-30 column.

RESULTS AND DISCUSSION

Under HTR conditions, the main products formed are dibenzyl and toluene while under HTC conditions, only dibenzyl is formed. Although the conversion is 10-15% in both cases, the selectivity for dibenzyl is about 90% in HTC and 40% in HTR. Dibenzyl may have been formed through benzyl radical dimerization both on HTR and HTC catalysts. The formation of toluene on HTR cata-

lyst may be explained by the transformation of benzyl radical through the participation of adsorbed hydrogen species. On HTC catalyst, the absence of toluene could, therefore, be attributed to the absence of hydrogen species. Both dibenzyl and toluene are not formed on Rh/ γ -Al₂O₃ catalyst. This can be explained due to the not so easily reducible nature of Al₂O₃ compared to TiO₂(A), thereby not helping the formation of dibenzyl or toluene.

The probable mechanism of the formation of benzyl radical is shown in Fig. 1. In the SMSI state the boundary atoms of the metal clusters near the reduced Ti³⁺ cations are expected

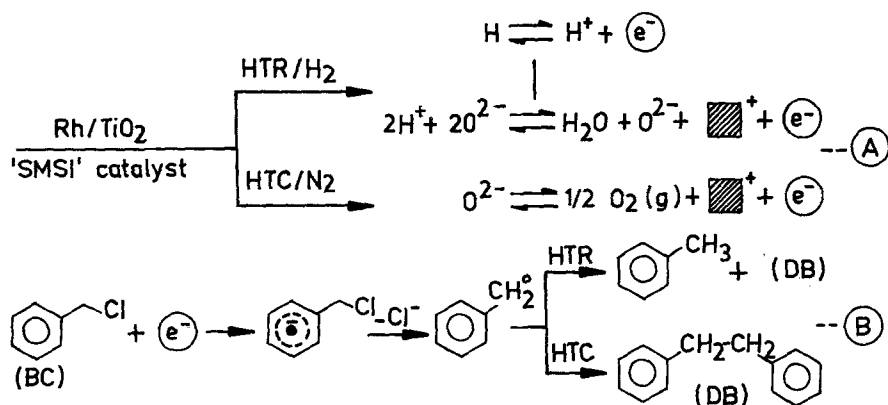


Fig. 1. Schematic representation of (A) generation of SMSI electrons (ϵ); and (B) formation of dibenzyl and toluene over Rh/TiO₂

to acquire increased charge density by virtue of the close proximity of energy levels of the cluster and the reduced support. The metal cluster as a whole interacts with the nucleophilic benzyl chloride. This in turn acquires extra charge density from the peripheral atoms of the cluster to give rise to the

adsorbed state of the benzyl chloride anion radical. This eventually loses Cl^- ion to form benzyl radical. The chloride ion reacts with hydrogen on the surface to form HCl under HTR conditions. In the absence of surface hydrogen species, i.e. under HTC conditions, the chloride ion may be retained by the catalyst surface. The surface transformations of adsorbed benzyl chloride can give rise to either toluene (if hydrogen species is present on the surface) or dibenzyl (by radical combination reaction).

It is interesting to note that even on TiO_2 , dibenzyl is formed though in small quantities compared to Rh/TiO_2 . This is not surprising since titania is a reducible oxide and charge transfer on the surface is reported [5]. When Rh/TiO_2 is subjected to SMSI conditions of treatment, there is a tunneling of electrons from the oxide to metal [3] because of its electron withdrawing capacity leading to an enrichment of electrons on the metal crystallites which helps benzyl radical formation.

Benzyl radical formation as an intermediate over Rh/TiO_2 both under HTR and HTC conditions thus suggests the presence of an excess charge density on metal crystallites of the catalyst. It is also interesting to observe benzyl radical formation on HTC catalyst. This lends support to the origin of SMSI due to lattice oxygen deficiency [6] of TiO_2 and the electron transfer from the support. This concept of creating anion radicals on SMSI catalyst can be efficiently applied for the catalytic synthesis of linear biaryls. This study thus supports the concept of electron transfer from support to metal in SMSI catalyst.

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