CATALYTIC HYDROGEN TRANSFER OVER MAGNESIA,
PART XVIII. CHEMOSELECTIVE REDUCTION OF FORMYL AND ACETYL DERIVATIVES OF FURAN AND THIOPHENE

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Abstract
Chemoselective reduction of formyl and acetyl derivatives of furan (F) and thiophene (T) to the corresponding carbinols by 2-propanol has been performed in vapour phase over MgO as a catalyst. Formyl derivatives of (F) and (T) have been reduced to the corresponding carbinols with selectivity 96 and 71%, respectively. Above 573 K the reduction of (T)-CHO was accompanied by the formation of thiophene whose yield increased with temperature (36% at 723 K). Acetyl derivatives of (F) and (T) have been reduced to the corresponding carbinols which at higher temperatures underwent dehydration to vinyl derivatives and were further reduced to ethyl derivatives.

Keywords: Reduction of formyl and acetyl derivatives of furan and thiophene, chemoselectivity, hydrogen transfer, 2-propanol, magnesia

INTRODUCTION

Chemoselective reduction of α,β-unsaturated carbonyl compounds is an important step in the manufacture of various fine chemicals. The hydrogenation of such compounds over monometallic catalysts leads to saturated carbonyl products since the C=C bond is attacked preferentially. Many attempts have been
made to design a catalytic system with high inverse chemoselectivity. The usage of polymetallic catalysts [1], strong metal support interaction (SMSI) effect [2,3], introduction of promoters [4] and the metal particle size control [5] are the partial solutions of this problem. Catalytic transfer reduction over metal oxide catalysts is known to be a very selective method for the reduction of carbonyl group in various ketones and aldehydes [6-9]. In this method the reduction of conjugated, unsaturated carbonyl compounds into unsaturated alcohols occurs with high chemoselectivity with alcohols as hydrogen donors [10-12]. Hydrocarbons cannot be used instead of alcohols as a source of hydrogen due to their low donor activity as it was shown very recently [13]. The heteroaromatic ring in the carbonyl derivatives of furan and thiophene as well as the carbonyl group is susceptible to hydrogen attack. Moreover, the presence of this ring is the source of high reactivity, which is rather troublesome.

We decided therefore to study the transformations of simple carbonyl derivatives of furan and thiophene, in the presence of 2-propanol acting as hydrogen donor, with the aim of recognizing the activity, selectivity and chemoselectivity of magnesium oxide catalyst in the reaction. The present work is a part of our studies concerning the applicability of the hydrogen transfer reaction in the reduction of carbonyl groups in various organic compounds catalysed by magnesium oxide.

**EXPERIMENTAL**

**Catalyst**

Magnesium oxide was prepared by thermal decomposition of Mg(OH)$_2$. The details of the catalyst preparation were given before [14]. The sieved fraction of 0.5-1.0 mm grains diameter was calcined at 873 K for 1 h in a stream of dry air and for 5 h in a stream of dry deoxygenated nitrogen. Specific surface area of MgO was 52 m$^2$/g, pore volume 1.6 cm$^3$/g.

**Reagents**

2-Acetylfuran (F)-COCH$_3$, 2-acetylthiophene (T)-COCH$_3$, 2-formylfuran (F)-CHO and 2-formylthiophene (T)-CHO were all Aldrich products of 98-99\% purity. They were purified by distillation under reduced pressure in nitrogen atmosphere and kept in Schlenk type tubes covered with metallic foil to prevent sunlight. (F)-COCH$_3$, $n^{20\text{D}} = 1.5068$ (exp); (T)-COCH$_3$, $n^{20\text{D}} = 1.5650$ (exp);