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Selective deactivation of metal catalysts for amination of alcohols to primary amines

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PURPOSE OF THE ABSTRACT

Introduction

Although catalyst deactivation is undesired, intentional poisoning of fresh catalysts is sometimes performed to selectively block some active surface sites, in an effort to either moderate the activity and / or to improve the selectivity of reactions [1]. Deposition of carbonaceous species on the surface of the catalyst appears to be one of the main reasons of catalyst deactivation. Here, to the best of our knowledge, we show for the first time the beneficial effect of selectively deactivating a Co/Al₂O₃ catalyst for the direct amination of primary aliphatic alcohols with ammonia.

Key Results

Selective deposition of carbon over Co/Al₂O₃ (15 wt%) was performed by reduction of the catalyst in a flow of H₂ at 400 °C, with subsequent cooling down to 250 °C and treatment of the catalyst in inert atmosphere with the vapors of 1-butanol. The characterization of the catalyst by TEM, TG and FTIR shows the presence of aliphatic carbon species on the surface of the metal (Figure 1). We propose that the polymer is formed by dehydrogenation and condensation of formed aldehyde. The high reactivity of aldehyde results in condensation close to dehydrogenating metal sites with direct deposition of carbon species on the surface of metallic Co.

The effect of alcohol pretreatment was studied in the direct amination reaction of alcohols with NH₃ in both gas and liquid phases, over unmodified and purposely deactivated Co/Al₂O₃ catalysts. The parent Co/Al₂O₃ catalyst shows high catalytic activity in the high range of GHSV or reaction times. However, the selectivity to primary 1-butylamine is low, and it decreases strongly with increasing 1-butanol conversion: for instance, at 30 % 1-butanol conversion, the selectivity to butylamine is 55 % and it drops to 20 % at 90 % conversion (Figure 2). The same effect is observed during amination of 1-octanol in the liquid phase.

The effect of catalyst deactivation by pretreatment with 1-butanol was studied for Co/Al₂O₃ catalysts, containing from 2.5 to 5.5 wt. % C. The so-prepared catalysts show gradual decrease of the catalytic activity in gas and liquid phase by a factor of 2-3 at the highest carbon amount. Comparison of the selectivities to primary amines at the same conversions of alcohols shows that in the gas phase amination it increases to 60 % and 80 % after 0.25 h and 0.5 h. The same effect of increase of the selectivities has been observed in the liquid phase. The selectivity increases almost twice to 90 % in comparison with the parent catalyst.

Mechanism

According to our earlier studies, the main reason for low selectivity towards primary amines is their self-coupling, leading to secondary and tertiary amines [2]. We have performed model reaction of 1-octylamine conversion at the same reaction conditions before and after carbon deposition. Our results show significant increase of the contribution of secondary imine after carbon deposition and suppressed hydrogenation to secondary amine in comparison with the parent catalyst where secondary amine was the main product of the reaction.

The possible explanation of this effect here could be in lower accessibility to metal surface after carbon deposition on the surface of Co nanoparticles. In order to prove it we have conducted model experiment of hydrogenation of long chain bulky ketone (tricosan-12-one) in comparison with octanal to alcohols over parent and treated catalysts

to mimic hydrogenation of primary and secondary imines. Our results show that both catalysts demonstrate comparable catalytic activity in hydrogenation of octanal. However, carbon deposition leads to almost full suppression of hydrogenation of tricosane-12-one in comparison with high activity over parent Co/Al₂O₃. Thus, the effect can be explained by low accessibility of bulky secondary imines to the metallic surface.

FIGURES

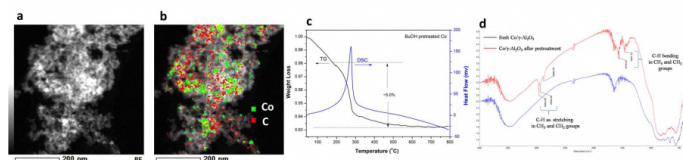


FIGURE 1

TEM image (a), STEM-EDX (b), TG analysis (c) and FTIR (d) of Co/Al₂O₃ catalyst treated by butanol

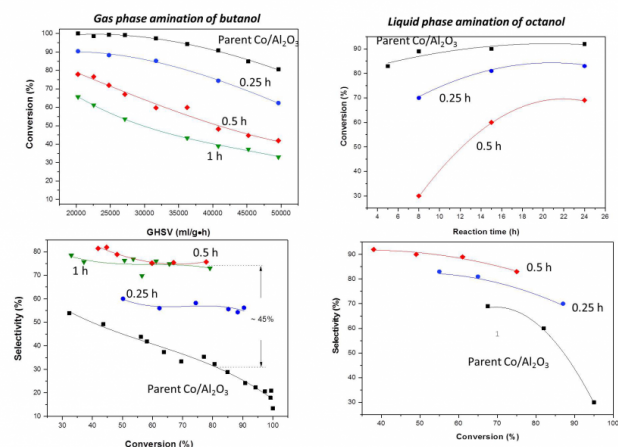


FIGURE 2

The effect of pretreatment of Co/Al₂O₃ catalyst in butanol vapors for different time on conversion of alcohol and selectivity in amination of butanol in gas phase in fixed bed reactor (NH₃/alcohol = 7; alcohol flow: 0.08-1.1 ml/min, catalyst: 30 mg; 140 o

KEYWORDS

amination | primary amines | selective deactivation | carbonaceous species

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