Novel Bimetallic Cobalt Catalysts for the Direct Amination of Alcohols

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Abstract:
Noble metal promotion was studied on a Co/γ-Al_2O_3 catalyst for the direct amination of *n*-octanol. The nature of the noble metal, the impregnation protocol and its loading were considered, obtaining an optimal formulation based on sequentially impregnated 5wt.%Ag_3-Co_{97}/γ-Al_2O_3. An increase in activity and selectivity suggested a co-catalytic effect of Ag. The deconvolved H_2-TPR profiles exhibited a decrease of the Co-support interaction, probably caused by the selective location of Ag nanoparticles in the Co-Al_2O_3 interphase, as evidenced from STEM-EDS microscopy. An unprecedented 90% conversion and 87% selectivity towards *n*-octylamine could be achieved at optimal conditions.

Keywords: Direct Amination, Cobalt, Noble Metal Promotion.

1. Introduction

The production of amines from alcohols and ammonia stands out as an atom-economic and eco-efficient pathway, producing water as the sole byproduct. Nevertheless some technological breakthrough is required in order to overcome the existing limitations, mainly related to the selective synthesis of primary amines.[1] Herein, we present a sequential optimization strategy studying the effect of noble metal (NM) promoters (*e.g.*, Au, Pd, Pt, Ru and Ag) on the catalytic properties of Co/γ-Al_2O_3. The influence of the nature of the promoter, the impregnation sequence and its loading will be considered, as they are generally reported to impact the catalytic performance[2–4]. The catalytic trends will be analyzed as a tool to understand the promotion mechanism, decoupling the reducibility increase from co-catalytic effects. Further characterization by H_2-TPR and STEM-EDS microscopy will allow to provide details on the Co reducibility, Co-support interaction and the Co-promoter relative distribution over the support.

2. Experimental

The 5wt.%Co/Al_2O_3 catalyst was prepared by incipient wetness impregnation of an aqueous solution of $Co(NO_3)_2\cdot 6H_2O$ over γ-Al_2O_3. The bimetallic formulations (5wt.%Co basis) were synthesized over γ-Al_2O_3 using aqueous solutions of the corresponding NM nitrate precursors following three different protocols: (i) sequential impregnation starting from the NM precursor (NM_y-Co_x), (ii) sequential impregnation starting from the Co precursor (Co_x-NM_y), and (iii) co-impregnation of both the NM and Co precursors $Co_x(NM)_y$, where x and y represent the Co and NM atomic composition (%). After impregnation, the catalysts were dried at 120 ºC for 12 h, calcined at 400 ºC for 2 h, and *in situ* reduced at 500 ºC under a 20% v/v H_2-N_2 mixture. The catalysts were characterized by H_2-TPR, ICP-OES, XRD and STEM-EDS, and tested in the amination reaction of *n*-octanol with NH_3 on a fixed bed reactor at varying conditions: 160-220 ºC, 100-1500 kPa, a weight-hourly-space-velocity (WHSV) of 0.66-2.9 h^{-1}, 3-21 equiv. NH_3 and 2.5-15 equiv. H_2 with respect to *n*-octanol and balance N_2.

3. Results and discussion

The different bimetallic formulations consisting in sequentially impregnated $Co_{98.5}$-$NM_{1.5}$ were first screened for the amination reaction of *n*-octanol with NH_3. Except Au, the different bimetallic catalysts exhibited an increase of the *n*-octanol conversion, being Pt the most efficient. Pt and Pd promoted the formation of the secondary amine *via* parasite disproportionation reactions, whereas Ru and Ag offered an excellent selectivity and were selected for the remainder of the study. With regards to the impregnation protocol, coimpregnated Co(Ru) and sequentially impregnated Ag-Co offered the best results. For such formulations, the promoter loading was optimized, obtaining in both cases volcano-type relations for the catalytic activity. The optimal formulations were $Co_{99.7}(Ru_{0.3})$ and Ag_3-Co_{97} (Table 1), affording >40% increase in activity relative to the parent Co catalyst. Interestingly, the analysis of the catalytic trends evidenced a superior activity at low H_2 pressures and an enhanced selectivity for the Ag_3-Co_{97} catalyst (Figure 1a), supporting a co-catalytic effect of Ag. This catalyst afforded 90% conversion and 87% selectivity towards *n*-octylamine at optimized conditions (100 kPa, 200 ºC, 21 equiv. NH_3, 6 equiv. H_2).

The H_2-TPR profiles revealed interesting differences between Co(Ru) and Ag-Co. Ru was found to efficiently decrease the reduction temperature of Co driven by a H_2 spillover mechanism.[5] In contrast, Ag only slightly decreased the overall reduction temperatures, but markedly diminished the interaction between the support and Co^{2+} crystallites. Further characterization of the $Co_{99.7}(Ru_{0.3})$ and Ag_3-Co_{97} catalysts by STEM-EDS microscopy revealed a homogeneous distribution for Ru within the Co particles, while Ag was found in the form of segregated nanoparticles selectively surrounding Co (Figure 1b). Ag-inclusion in the Co-Al_2O_3 interphase could be related to the observed decrease in the Co-Al_2O_3 interaction.

Table 1. Reaction results for the best performing catalysts (Al_2O_3-supported)

Catalyst	Co (wt.%)[(a)]	NM (wt.%)[(a)]	%Co reduction[(b)]	Co° crystallite size (nm)[(c)]	Yield n-Octylamine[(d)]
Co	4.9%	-	28%	8.2	28.5%
$Co_{99.7}(Ru_{0.3})$	4.9%	0.02%	86%	6.6	40.0%
Ag_3-Co_{97}	5.0%	0.25%	83%	10.1	42.0%

(a) ICP; (b) H_2 consumption below 500 ºC during H_2-TPR; (c) XRD (Scherrer equation); (d) Conditions: 180 ºC, 101 kPa, WHSV = 1.9 h^{-1}, 9 equiv. NH_3, 3.4 equiv. H_2, balance N_2

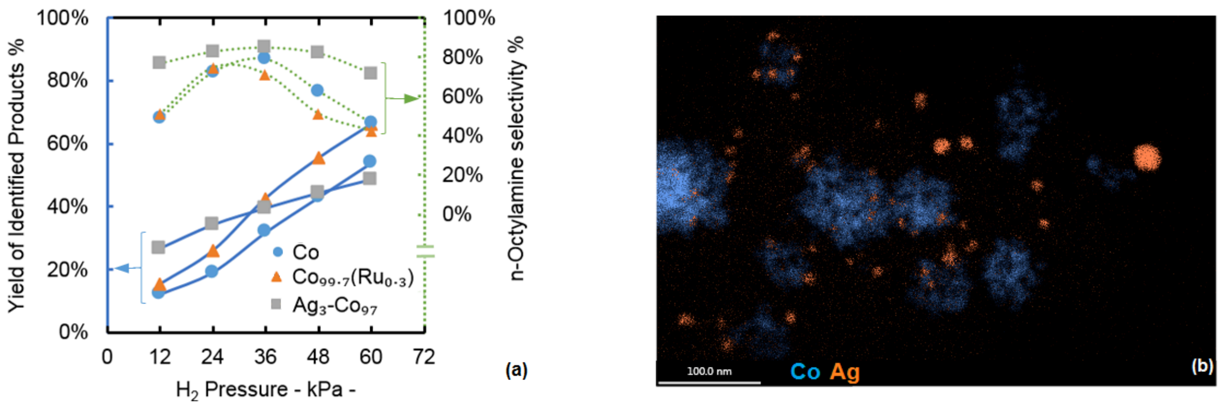

Figure 1. (a) Effect of the H_2 pressure on the yield to identified products (*n*-octylamine, dioctylamine and octanentrile) and *n*-octylamine selectivity to Co, $Co_{99.7}(Ru_{0.3})$ and Ag_3-Co_{97}. Reaction conditions: 180 ºC, 100 kPa, WHSV = 6.6 h^{-1}, 6 eq. NH_3 and balance N_2. Carbon balance > 95% **(b)** STEM-EDS elemental mapping of the Ag_3-Co_{97} catalyst.

4. Conclusions

The effect of the noble metal nature, the impregnation sequence and the loading were studied on bimetallic Co-NM catalysts supported over γ-Al_2O_3. Two optimized formulations were obtained based on $Co_{99.7}(Ru_{0.3})$ and Ag_3-Co_{97}. The analysis of the catalytic trends at varying reaction conditions indicated a co-catalytic effect for Ag_3-Co_{97} with a superior selectivity towards the primary amine. A 90% *n*-octanol conversion and 87% selectivity towards *n*-octylamine could be achieved at optimal conditions. This formulation shows various advantages compared to reported formulations, exploiting an inexpensive catalyst, using mild conditions and not requiring the use of additives and/or organic solvents.

References

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