Novel Bimetallic Cobalt Catalysts for the Direct Amination of Alcohols

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Abstract:
Noble metal promotion was studied on a Co/γ-Al₂O₃ 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.%Agₓ-Coᵧ/γ-Al₂O₃. An increase in activity and selectivity suggested a co-catalytic effect of Ag. The deconvoluted H₂-TPR profiles exhibited a decrease of the Co-support interaction, probably caused by the selective location of Ag nanoparticles in the Co-Al₂O₃ 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. 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-Al₂O₃. 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. 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 H₂-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/Al₂O₃ catalyst was prepared by incipient wetness impregnation of an aqueous solution of Co(NO₃)₂·6H₂O over γ-Al₂O₃. The bimetallic formulations (5wt.%Co basis) were synthesized over γ-Al₂O₃ using aqueous solutions of the corresponding NM nitrate precursors following three different protocols: (i) sequential impregnation starting from the NM precursor (NMₓ-Coₓ), (ii) sequential impregnation starting from the Co precursor (Coₓ-NMᵧ), and (iii) co-impregnation of both the NM and Co precursors Coₓ(NMᵧ), where x and y represent the Co and NM atomic composition (%). After impregnation, the catalysts were dried at 120 °C for 12 h, calcined at 400 °C for 2 h, and in situ reduced at 500 °C under a 20% v/v H₂-N₂ mixture. The catalysts were characterized by H₂-TPR, ICP-OES, XRD and STEM-EDS, and tested in the amination reaction of n-octanol with NH₃ on a fixed bed reactor at varying conditions: 160-220 °C, 100-1500 kPa, a weight-hourly-space-velocity (WHSV) of 0.66-2.9 h⁻¹, 3-21 equiv. NH₃ and 2.5-15 equiv. H₂ with respect to n-octanol and balance N₂.

3. Results and discussion
The different bimetallic formulations consisting in sequentially impregnated Co₉₈.₅-NM₁.₅ were first screened for the amination reaction of n-octanol with NH₃. 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 °C, 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$_2$O$_3$ interphase could be related to the observed decrease in the Co-Al$_2$O$_3$ interaction.

**Table 1. Reaction results for the best performing catalysts (Al$_2$O$_3$-supported)**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co (wt.%)$^{(a)}$</th>
<th>NM (wt.%)$^{(a)}$</th>
<th>%Co reduction$^{(b)}$</th>
<th>Coº crystallite size (nm)$^{(c)}$</th>
<th>Yield n-Octylamine$^{(d)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>4.9%</td>
<td>-</td>
<td>28%</td>
<td>8.2</td>
<td>28.5%</td>
</tr>
<tr>
<td>Co$<em>{99.7}$(Ru$</em>{0.3}$)</td>
<td>4.9%</td>
<td>0.02%</td>
<td>86%</td>
<td>6.6</td>
<td>40.0%</td>
</tr>
<tr>
<td>Ag$<em>3$-Co$</em>{97}$</td>
<td>5.0%</td>
<td>0.25%</td>
<td>83%</td>
<td>10.1</td>
<td>42.0%</td>
</tr>
</tbody>
</table>

(a) ICP; (b) H$_2$ consumption below 500 °C during H$_2$-TPR; (c) XRD (Scherrer equation); (d) Conditions: 180 °C, 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 °C, 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$_2$O$_3$. 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**