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"Touching" chemistry-selective amination of alcohols to primary amines by ammonia

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PURPOSE OF THE ABSTRACT

Boudart classified heterogeneous catalytic reactions in two groups depending on the sensitivity of the catalytic activity on the particle size. On the one hand, for structure-sensitive reactions, the turnover frequency (TOF), or reaction rate normalized per surface atom, changes with the particle size [1]. On the other hand, for structure-insensitive reactions, the TOF remains directly proportional to the number of surface sites in a broad particle size range. Herein, we present a systematic study of the influence of the Ru particle size on the catalytic activity and selectivity for direct amination reactions. We have synthesized and characterized a series of Ru nanoparticles (NPs) with uniform size, shape and structure and tested them in direct amination of 1-octanol (OL) with NH₃ targeting the synthesis of 1-octylamine (OA) [2].

Water-in-oil microemulsion with water droplets formed by reverse micelles dispersed in a continuous hexanol phase were prepared for the synthesis of Ru NPs with variable sizes according to ref [3].

The TEM images and histograms (Figure 1) indicate a uniform size distribution for all the synthesized Ru NPs. For comparison, a reference Ru/Al₂O₃ catalyst prepared by conventional impregnation of a Ru salt precursor exhibited a broader particle size distribution with an average size of Ru NPs of 5 nm.

The catalytic performance of Ru NPs was studied in the liquid-phase amination reaction of OL with NH₃ in a batch reactor.

The conversion-selectivity curves measured for different Ru NPs and Ru/Al₂O₃ were shown in Figure 2. Interestingly, a very high OA selectivity at high OL conversion can only be achieved for smaller Ru NP-2 nm. For Ru NPs with larger sizes (i.e. 3, 5 and 9 nm), the OA selectivity declines gradually with the OL conversion, matching the pattern obtained on Ru/Al₂O₃. Octylnitrile and secondary imine were obtained as the main products over Ru NP-2 nm and dioctylamine was the main product over large Ru NPs and Ru/Al₂O₃. Note that the secondary imine did not undergo subsequent hydrogenation to secondary amine over Ru NP-2 nm. Similar structural sensitivity of the selectivity to primary amine on the Ru NP size was also observed for a wide range of other alcohols (furfuryl alcohol, benzyl alcohol and 2-butanol).

Conclusion

The primary octanol amination is found to be a structure insensitive reaction, while, the self-coupling of octylamine was sensitive to the size of Ru NPs. Lower rate of amine self-coupling was observed over smaller non-supported Ru NPs. The structural sensitivity of Ru NPs to octylamine self-coupling was attributed to the structural and electronic effects during hydrogenation of secondary imine.

FIGURES

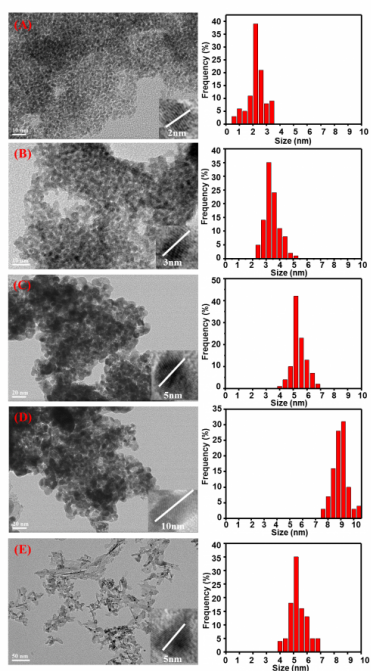


FIGURE 1

Figure 1

TEM images and histograms of ruthenium particle size in Ru NP-2 nm (a), -3 nm (b), -5 nm (c), -9 nm (d), and Ru/Al₂O₃(e)

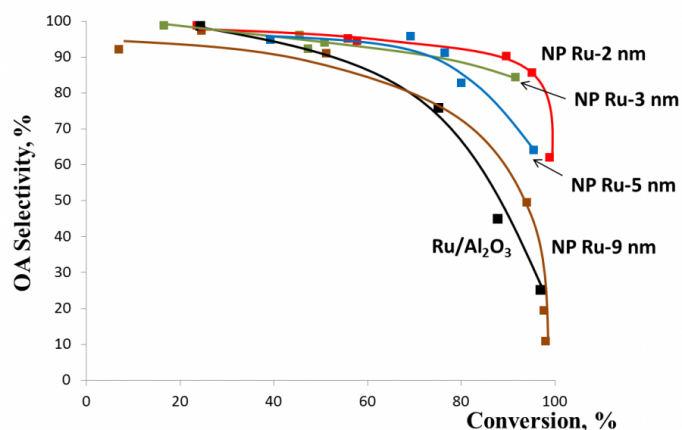


FIGURE 2

Figure 2

Conversion-selectivity curves for Ru NPs and Ru/Al₂O₃ in amination

KEYWORDS

amination | primary amines | structure sensitivity | alcohols

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