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Highly selective Ru/HBEA catalyst for the direct amination of fatty alcohols with ammonia

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PURPOSE OF THE ABSTRACT

Alkylamines are key intermediates in the chemical industry for preparing polymers, dyes, pharmaceuticals, agrochemicals and surfactants compounds.1 In particular, primary amines issued from the alkylation of ammonia with fatty alcohols are useful intermediates for further derivatization reactions. Ruthenium nanoparticles can afford high selectivity to primary amines in the reductive amination of aromatic, furanic and aliphatic aldehydes/ketones with NH3 and H2,2 and in the direct amination of alcohols.3

Herein we show how acid architecture around ruthenium nanoparticles can affect the catalytic activity in the direct amination of alcohols. To this aim, we prepared and deeply characterized a series of ruthenium catalysts supported over acid supports, including a variety of zeolites with variable topology and Si/Al ratios, and ?-alumina. The catalytic performance was assessed in the liquid-phase amination reaction of 1-octanol (OL) and ammonia NH3 both in batch and pre-pilot (2 L) continuous stirred-tank reactors (CSTR) with flash separation of 1-octylamine (OA).

The catalytic activity (TOFOA) over Ru black and Ru/C kept almost unchanged with the average size of Ru nanoparticles at 30 h-1 (Figure 1a). However, the TOFOA increased when the Ru particles were loaded on acid supports (~100 h-1), especially for Ru/HBEA(25). The OA selectivity decreased with the OL conversion in detriment of DOA. Ru/BEA(25)_4 (Ru size = 17 nm) (blue curve) exhibited only a slight decline of the OA selectivity to 90% at 90% OL conversion, resulting in a OA yield of 81% (Figure 1b).

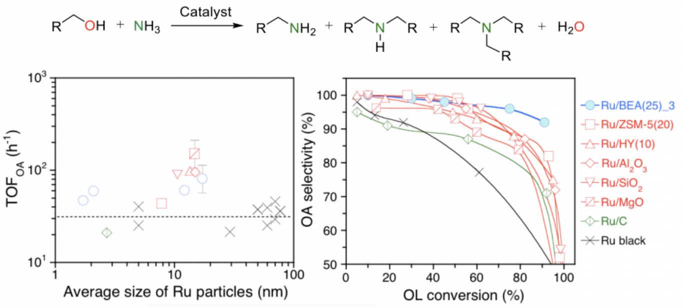
A catalytic test was carried out in a CSTR for assessing the stability of Ru/HBEA(25)_4 during 120 h continuous operation at a flowrate of 25 g/h with concomitant removal of OA out of the reactor (Figure 2). The reactor composition kept stable at steady state with 3.8 wt% OL, 2.7 wt% OA, 38 wt% DOA and 55 wt% TOA. Two liquid phases were recovered from the condenser, i.e. the organic and aqueous phases. The OA composition in the organic phase reached 80% with 87% OL conversion.

Given its promising performance, Ru/HBEA(25)_4 was studied in detail. The reduction of Ru/HBEA(25)_4 species in Ru/H-BEA(25)_4 is splitted into different bands in the range 90-200 °C, pointing out a strong interaction with the acid support. In situ XAS spectra revealed complete reduction of RuOx/HBEA(25) under H2 at 180 °C for 30 min. The coordination number of Ru (EXAFS) was 11 ± 0.8 corresponding to an average particle size in the range 3-20 nm in agreement with the PXRD and HR-TEM. These results point out that Ru nanoparticles are mainly located at the external surface of HBEA(25). XANES revealed that nitridated species on Ru can react with OL.

We measured the OA-TPD profiles for Ru/HBEA(25)_4. Four bands can be clearly visualized in the first region with an overall OA density of 362 ?mol.g-1. The second region also comprises four bands with an overall OA density of 677 ?mol.g-1, which compares well with the total acid density measured by NH3-TPD (740 ?mol.g-1). Unlike other zeolites, Ru/HBEA(25)_4 shows high ability for desorbing OA around 180 °C, which corresponds to

the temperature for OL amination with NH3. This property combined with the medium strength of the acid sites (inferred by NH3-TPD), affording pre-concentration near the Ru nanoparticles, are regarded as key drivers for selectivity towards OA in Ru/HBEA(25)_4. 27Al MAS NMR points out possible dealumination in HBEA(25) during Ru impregnation, resulting most likely in the generation of AlOx clusters on the external surface stabilizing the Ru nanoparticles. In this view, Ru@AlOx on the external surface of HBEA(25), with Lewis acidity, could behave as active sites for the reaction, where the internal Brønsted centers could behave as NH3 storage buffer. This surface architecture promotes pre-concentration and reactivity of NH3 near the metallic Ru nanoparticles, as well as fast desorption of OA at the reaction temperature.

FIGURES



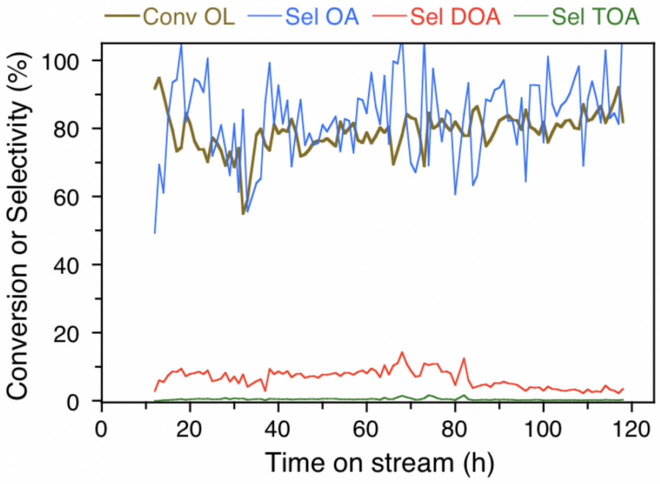


FIGURE 1

Figure 1.

(a) Evolution of TOFOA as a function of the average size of Ru NPs for supported Ru catalysts and Ru black; and (b) Selectivity-conversion curves for OL amination with NH3 over the different Ru catalysts at comparable Ru loading. Reaction conditions: OL-

FIGURE 2

Figure 2.

Time-evolution of the OL conversion and selectivity to the different amines during continuous OL amination with NH3 in CSTR. Reaction conditions: OL flowrate 25 g/h, NH3- 4.5 barg, H2- 1.0 barg, T- 180 °C, WHSV- 0.3 h-1. The catalysts were pre-reduced bef

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KEYWORDS

Animation | 1-Octanol | Ammonia | Ruthenium

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