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CATALYSIS

Nanostructured Hydrotalcite-Supported RuBaK Catalyst for Direct Conversion of Ethylene to Propylene[1]

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Abstract—A novel nanostructured hydrotalcite-supported alkali-doped ruthenium-based catalyst is introduced for the direct gas-phase conversion of ethylene to propylene at 70°C and 1 atm. The maximum conversion of ca. 87% was obtained at the initial time on stream with a 65% selectivity to propylene and a 6% selectivity to butenes via consecutive reactions. Both conversion and selectivity to olefinic products decreased after 24 min of operation, however.

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INTRODUCTION

Ethylene and propylene, the most important building blocks in the petrochemical industry, have long been obtained from steam pyrolysis of hydrocarbons [1–7]. Nonetheless, the reduced availability of propylene and butenes from the conventional sources has urged on-purpose technologies, that are planned to provide 30% of global propylene supply in 2025 [8]. A promising option to bridge this gap is the direct conversion of the relatively abundant ethylene to propylene through metathesis, catalyzed most effectively by Re, Mo, W, and Ni catalysts [9–12]. The reaction is more preferably carried out in heterogeneous systems rather than homogeneous ones, owing due to the simpler separation of the reaction mixture from the catalyst, rather facile regeneration of the catalyst, and decreased product contamination [13]. Although different inorganic supports can be envisaged [14], zeolites are not ideal choices for this purpose due to their too small apertures (below 1 nm) to allow both the grafting of active species and their accessibility to the reactants; the ordered mesoporous materials would then be more suitable [15]. The present contribution reports on the preparation of a ruthenium-based catalyst supported on a mesoporous clay material for the direct conversion of ethylene to propylene. The MgO and Al_2O_3 phases in the layered double hydroxide material were intended to facilitate the in situ dimerization and isomerization steps prior to the metathesis reaction.

EXPERIMENTAL

Materials. $RuCl_3 \cdot xH_2O$ (x = 1–3, 37% Ru content), KOH (98.0%), $Ba(NO_3)_2$ (99.0%), $Mg(NO_3)_2 \cdot 6H_2O$ (98.0%), $Al(NO_3)_3 \cdot 9H_2O$ (98.0%), NaOH (98.0%), and Na_2CO_3 (99.0%) were used as the starting materials. High-purity C_2H_4 (99.99%), H_2 (99.99%) and N_2 (99.99%) were used as reactants.

Catalyst preparation. The hydrotalcite (HT) support was synthesized using the co-precipitation method explained previously [16]. The as-synthesized support (5 g) was successively impregnated with 4.3 mL of 0.34 M $Ba(NO_3)_2$, 2.5 mL of 0.8 M $RuCl_3 \cdot xH_2O$ and 2.5 mL of 6.2 M KOH solutions using the incipient wetness impregnation method. At each impregnation step, the sample was dried at 110°C overnight. The final catalyst powders were calcined at 500°C for 5 h.

Catalyst and product characterization. The prepared support and catalyst were characterized using SEM, EDX, XRD, and N_2-adsorption techniques. The structure and morphology were analyzed on a Tescan instrument. The XRD patterns were recorded on a Siemens, D5000X-ray powder diffractometer (CuK_α radiation) with a step size of 0.02° and an exposure time of 2 s per step. The BET surface areas were measured with a Quantachrome

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[1] The text was submitted by the authors in English.

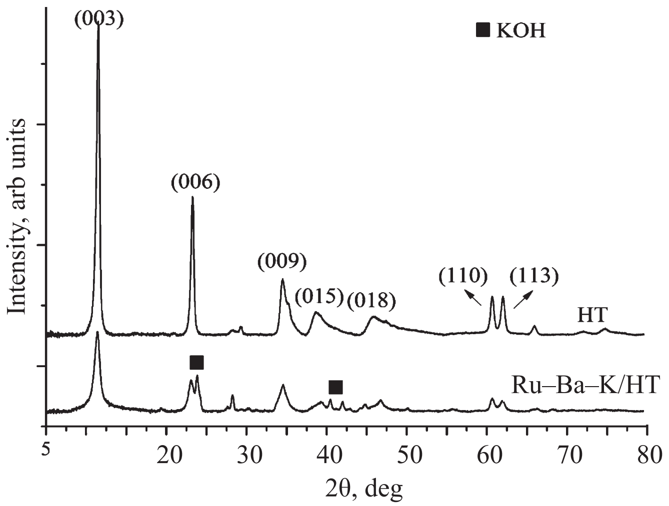

Fig. 1. XRD patterns of the HT support and RuBaK/HT catalyst.

Chem-BET 3000 analyzer at 77 K. The reaction products were analyzed on a GC equipped with capillary and packed columns as well as FID and TCD.

Catalytic activity. The reaction was carried out in a tubular reactor of 12 mm internal diameter in a setup similar to that explained previously [17–20]. A guard bed consisting of 4A molecular sieve, KOH, and silica gel particles was employed upstream to the reactor to remove unwanted impurities. A 0.15 g of catalyst powders dispersed in 0.90 g of quartz beads was placed between two plugs of quartz wool and activated in a reducing environment (with an H_2/N_2 molar ratio of 4) at the WHSV of 4 h^{-1} and 703 K for 3 h. The catalyst bed was cooled down to the reaction temperature in pure nitrogen (32 mL min^{-1}) and kept at this temperature for 3 h. Subsequently, the ethylene feedstock (2 mL min^{-1}) was introduced.

RESULTS AND DISCUSSION

The XRD patterns (Fig. 1) show the hydrotalcite structure (JCPDS no. 70-2151) as the only crystalline phase with an Mg/Al molar ratio of 2. In the case of the

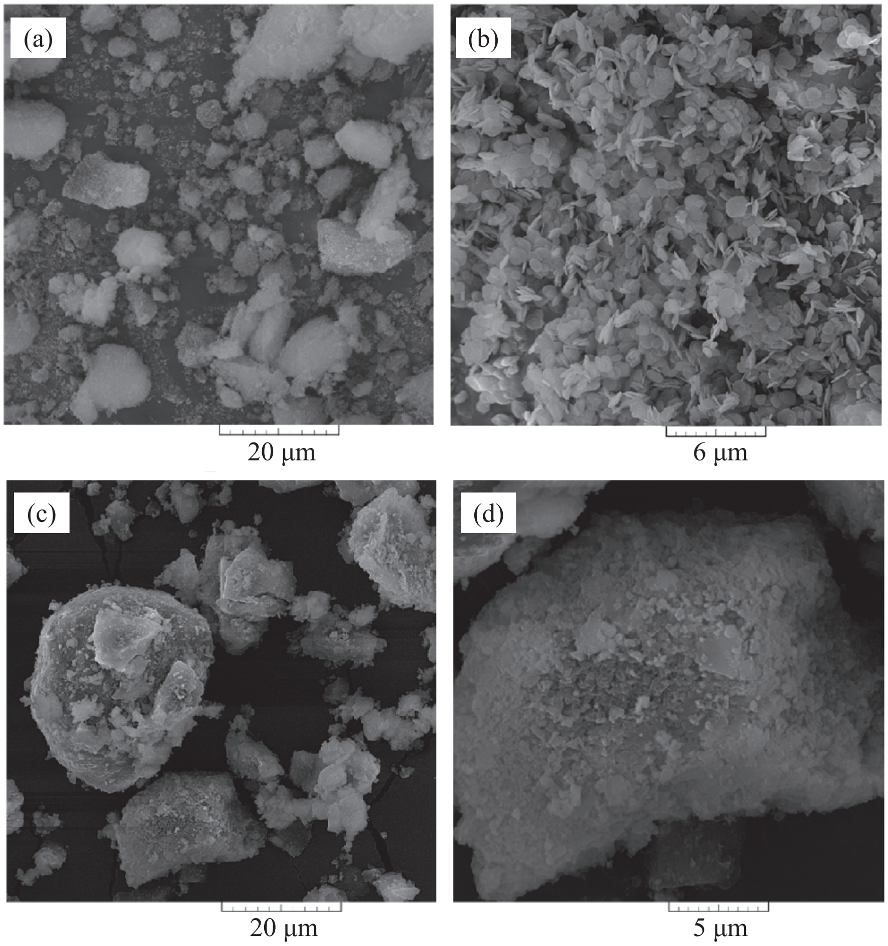

Fig. 2. SEM images of the HT (a–b) and RuBaK/HT (c–d) samples.

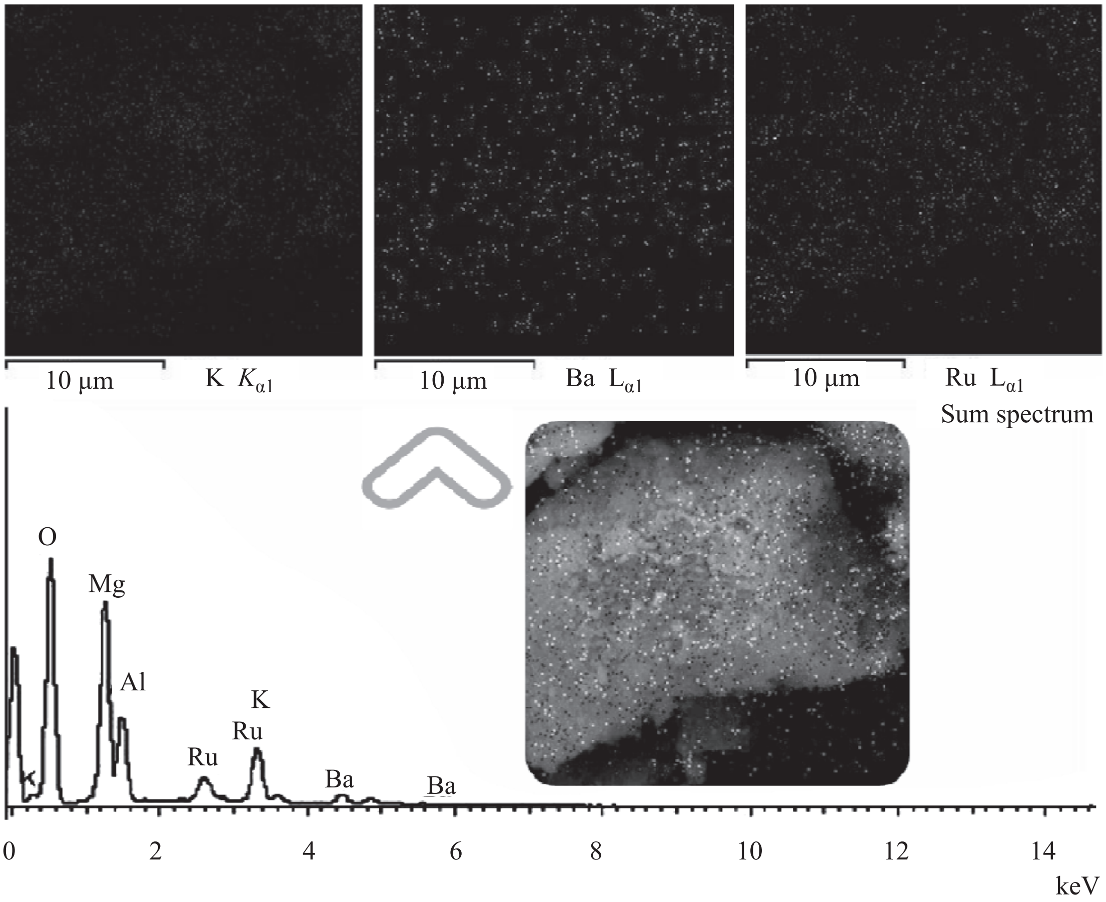

Fig. 3. EDX results and elemental maps of the RuBaK/HT catalyst.

impregnated catalyst, the diffractogram with well-defined peaks at 11.5°, 23°, 34°, 61°, and 62° was again typical of a hydrotalcite material, indicating that the RuBaK/HT catalyst was successfully prepared with acceptable dispersions of Al, Ru, and Ba in the crystalline hydroxide layers [21]. The XRD patterns also indicated the KOH signals on the catalyst. The intensities of (003), (006), (009), (110), and (113) planes being explicitly related to the crystallinity of the material were observed to decrease upon impregnation, however, due most probably to the increase in the number of cations of higher ionic radii in the brucite sheet [22]. The surface areas (and pore volumes) of HT and RuBaK/HT were, respectively, 45.6 and 54.4 $m^2 g^{-1}$ (and 0.81 and 0.96 $cm^3 g^{-1}$), indicating that the impregnation and final calcination steps increased the initial surface area without changing the interlayer spacing in the clay structure.

The surface morphologies are shown in Fig. 2, which indicates the existence of lamellar nano-particles shaping HT aggregates. On the contrary, the impregnated catalyst exhibited agglomerated micro-clusters on the surface. The elemental composition and the dispersion of species on the surface of the samples are shown in Fig. 3, which proved the satisfactory distributions of the active moieties. The positive influence of barium oxide on the dispersion of ruthenium on the surface has been demonstrated previously [23]. The amounts of active elements on the surface were close to the nominal values in the precursor solution. It is worth mentioning, however, that the Mg/Al ratios on the surface of HT and RuBaK/HT were higher than the corresponding theoretical values owing to the effect of pH during HT preparation as the molar ratio of Mg/Al in a hydrotalcite prepared under the pH of 11–14 is anticipated to be around 3.1–3.2 [24]. The EDX data pointed to an Ru content of 4% on the surface.

The table demonstrates the catalytic performance of RuBaK/HT for the gas-phase conversion of ethylene. As evident, the initial conversion of ethylene was ~87% with a propylene selectivity of 65 wt %, a selectivity of ~6 wt % to butenes, and a ca. 2 wt% C_{5+} selectivity.

A three-step reaction can be contemplated [25–28] as the main events occurring during this process. First, Performance of the RuBaK/HT catalyst

Reaction conditions and performance data		
Reaction temperature, °C	70	70
Pressure, atm	1	1
Time-on-stream, min	1	24
Ethylene conversion, %	86.8	22.2
Product selectivities, wt%		
Propylene	65.0	0.5
Propane	22.7	0.5
Butenes	5.9	31.5
Butane	4.6	56.8
C_{5+} Products	1.8	10.8
Propylene + Butenes	70.9	32.0

ethylene is conceived to dimerize on MgO and Ru centers to produce 1-butene. Then, 1-butene is isomerized to 2-butene on $MgO/MgAlO_x$ or acidic Al_2O_3 sites and, finally, the Ru centers catalyze the cross-metathesis between ethylene and 2- butene. Meanwhile, the presence of Ba and K modifiers could attenuate and suite the strength of acidic sites on the surface [29]. After about 24 min, the conversion decreased to ca. 22 wt % and the predominant olefinic product was butene rather than propylene. The total selectivity to olefins (propylene and butenes) also decreased to 32 wt %.

The investigated process can be combined with an ethane-to-ethylene technology to produce propylene from ethane as a cost-effective feedstock. Assuming an 80% conversion for the ethane dehydrogenation in an olefin plant, an integrated two-step ethane-to-olefins process with the catalyst introduced in this study would convert 49% of ethane to propylene and butenes. The decrease in the activity of the catalyst entails the use of reaction–regeneration cycles, however.

CONCLUSIONS

A nanostructured RuBaK/HT catalyst (Mg/Al = 2) with a satisfactory dispersion of ruthenium was successfully synthesized using a constant-pH coprecipitation method and applied to the direct conversion of ethylene to propylene in the gas phase. The results demonstrated a maximum conversion of about 87% to propylene and butenes, respectively, with selectivities of 65 and 6 wt % under the mild conditions of 70°C and 1 atm. The overall selectivity to propylene and butenes decreased to 32% after 24 min of operation, however, necessitating a reaction–regeneration cycle in a possible industrial practice.

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