

Roles of Al Sites of Zeolites in Anchoring $cis\text{-Ru}(\text{acac})_2(\text{C}_2\text{H}_4)_2$ and in the Genesis of Catalytically Active Species for Ethylene Dimerization

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Introduction

Supported metal complex catalysts—provided they are uniform in structure—offer all the advantages of molecular catalysts in solution, including high selectivity. Zeolites are attractive supports for such catalysts because they are crystalline and thus nearly uniform, offering well-defined bonding sites (Al sites) for metals in cationic complexes [1]. We have now prepared supported mononuclear metal complexes bonded to a zeolite by using a precursor with bidentate acac (acetylacetonate) ligands and reactive ethylene ligands; acac ligands can be easily replaced by the zeolite support acting as a bidentate ligand, with reactive ethylene ligands remaining bonded to the metal. We used IR and EXAFS spectroscopies to characterize the formation of a catalyst from this supported species, showing how zeolite Al sites aid both in the creation of the anchored complex and in removing additional acac ligands and thereby activating the complex as a catalyst for ethylene dimerization.

Materials and Methods

The supported catalysts were prepared by the reaction of $cis\text{-Ru}(\text{acac})_2(\text{C}_2\text{H}_4)_2$ with dealuminated zeolite Y (Si/Al = 15, 30 or 40 [atomic]) or zeolite beta (Si/Al = 19) in *n*-pentane at room temperature. Ru K-edge EXAFS spectra were recorded at liquid-N₂ temperature to characterize the initially prepared samples and at room temperature with a reacting mixture of C₂H₄/H₂ (25 kPa each) flowing over the catalyst to provide evidence of structural changes of the supported Ru complexes and of the active species. IR spectra were recorded with the samples in vacuum and in flowing reactants, with one goal being to characterize the acac ligands on Ru and on Al sites. Quantitative catalyst performance and kinetics data were determined with a flow reactor operated at room temperature fed with a mixture of C₂H₄/H₂ in He at atmospheric pressure.

Results and Discussion

EXAFS spectra characterizing a family of supported samples with varying Ru loadings show that Ru was bonded to the zeolite via 2 Ru–O bonds and that a fraction of the acac ligands originally bonded to Ru were removed and became bonded to Al sites of the zeolite; the latter species were identified by IR spectra characterizing acac bonded to Ru (1521 cm^{−1}) and acac bonded to Al (1537 cm^{−1}). Deconvolution of the IR spectra determined the fraction of acac ligands on Al sites; Figure 1 shows Al–acac% as a function of the Al/Ru ratio; the fraction of acac ligands removed from the Ru was independent of the Al content of the zeolite and structure of the zeolite (Y vs. beta), showing the generality of the synthesis chemistry. Thus, the results show that the Al sites acted as uniform set of Lewis acid sites that removed acac ligands from the Ru and thereby facilitated bonding of the Ru to the zeolite. Furthermore, when the supported ruthenium complexes were brought into contact with a mixture of ethylene + H₂, catalytic dimerization of the alkene began, and the spectra of the

working catalyst show that the Al sites of the zeolite facilitated the reaction by removing additional acac ligands from the Ru, thereby generating coordinatively unsaturated Ru complexes. Further still, H₂ increased the rate of the catalytic reaction, and this observation shows that it also reacted with the ruthenium in concert with the ethylene, forming reaction intermediates—presumably hydrides—that were in the catalytic cycle of ethylene dimerization. Thus, the Al sites played the role of a scavenger, both in the formation of the supported ruthenium complex and in the subsequent genesis of the catalytically active species that reacted (a) with ethylene to initiate ethylene dimerization and (b) with H₂ to facilitate (promote) the catalytic reaction (Scheme 1).

Scheme 1. Schematic of anchoring $cis\text{-Ru}(\text{acac})_2(\text{C}_2\text{H}_4)_2$ and activation of catalyst

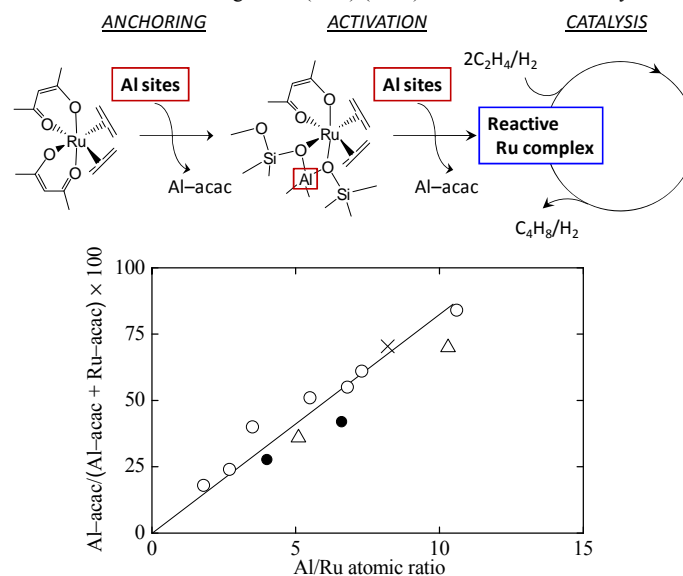


Figure 2. IR band area ratio of Al–acac/(Al–acac + Ru–acac) as a function of Al/Ru ratio. Zeolite and Si/Al ratio: (○) Y, 30; (△) Y, 15; (●) Y, 40; (×) beta, 19.

Significance

The roles of Al sites of zeolites shown here demonstrate how they play a key role in multiple steps of the preparation and operation of the supported ruthenium complex catalyst; the generality of the synthesis chemistry opens the way to preparing a potentially large class of zeolite-supported metal complex catalysts from precursors containing acac ligands.

Reference

1. Ehresmann, J. O.; Kletnieks, P. W.; Liang, A.; Bhirud, V. A.; Bagatchenko, O. P.; Lee, E. J.; Klaric, M.; Gates, B. C.; Haw, J. F. *Angew. Chem., Int. Ed.* 45, 574 (2006).