

Structure-Reactivity Relationship for Alumina Supported Nickel Oxide Catalysts

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Introduction

Development of catalysts on a scientific basis is the challenge for catalysis science. Oxidative dehydrogenation (ODH) of alkanes is an energetically attractive route for the production of alkenes. Among the different catalysts proposed in the literature for this process, only a few of them focused on nickel oxide containing catalysts. Because of their ability to adsorb oxygen easily and to generate highly active surface oxygen species, nickel oxide was generally considered as a catalyst for total oxidation and inappropriate for selective oxidation or oxydehydrogenation [1,2]. In previous works [3-6], we demonstrated that just this capability of generating electrophilic oxygen species can be used for the oxidative dissociation of strong C-H bonds in hydrocarbons. Analysis of the factors which determine the catalytic properties of nickel oxide and the possibility of their control led to the conclusion that they essentially depended on the type of the NiO species formed on the carrier and their distribution on the catalyst surface.

The present research focuses on the spectroscopic investigation of NiO species formed on different kinds of alumina and their structure-activity/selectivity relationship in the selective oxydehydrogenation of cyclohexane to cyclohexene.

Materials and Methods

A series of catalysts were prepared by ionic exchange method using four different alumina supports and a freshly prepared solution of nickel hexaamine. After washing and filtering, the nickel-loaded samples were dried and calcined for 6 h at 600°C. In order to modify the structure of nickel oxide species by keeping the nickel loading, samples were also calcined by different programs. For characterization of catalysts BET, TPR/TPO/TPD, XRD, FTIR, and Raman spectroscopy investigations were performed. Because of its high commercial interest, cyclohexane oxydehydrogenation was used as test reaction.

Results and Discussion

Systematic investigations of the catalytic system, NiO/ γ -Al₂O₃, revealed a connection between the catalytic performances (activity, selectivity) and the structure of the NiO species formed on the catalyst surface. On the basis of the TPR, XRD, FTIR and Laser-Raman spectroscopy, a new model was developed for the formation and structure of the NiO species on NiO/ γ -Al₂O₃ catalysts, which allowed the understanding of their role in the cyclohexane oxidation. The proposed model includes the following possible NiO species: (i) *bulk-NiO* crystallites, (ii) *isolated NiO units* (oxidized single Ni atoms) on the surface of the carrier, (iii) *bi-dimensional NiO monolayer* developed on top of the alumina carrier, (iv) *surface nickel oxide species* incorporated in the surface of the carrier and having NiAl₂O₄ character, and (v) *bulk-NiAl₂O₄* consisting of nickel cations which migrated deeply under the surface of the alumina carrier.

Correlation of the catalytic properties and the structural characteristics of the catalysts show that the bi-dimensional NiO monolayer is responsible for both the activity and the selective formation of cyclohexene (Figure 1). In contrast, the bulk NiAl₂O₄ species cause a low activity and also a small selectivity to dehydrogenation products. Bulk NiO species lead to complete oxidation.

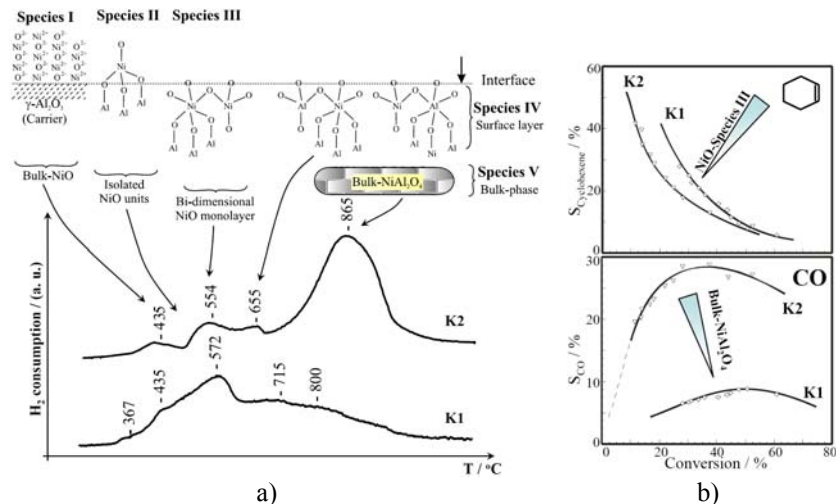


Figure 1: Structure of NiO species on NiO/ γ -Al₂O₃ and TPR pattern (a), and the selectivity vs. conversion in the oxydehydrogenation of cyclohexane (b).

Significance

The fundamental study presented here allows a better understanding of the formation of nickel oxide species on alumina supported catalysts and can be considered as a basis for a scientific design of catalysts with tailor-made properties. In addition to this, the study can also be a good example for reconsidering the role of electrophilic oxygen species in the partial oxidation of hydrocarbons.

References

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