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ΘΕΜΑ:

- 1. Hydroconversion of paraffins over bifunctional Ni-zeolites**
- 2. Redox and catalytic behavior of mesoporous silicates containing transition metals**

ΤΟΠΟΣ: Αίθουσα Σεμιναρίων ΙΤΕ/ΕΙΧΗΜΥΘ

ΗΜΕΡΟΜΗΝΙΑ: Παρασκευή, 16 Σεπτεμβρίου 2005

ΩΡΑ: 12:00

ΠΕΡΙΛΗΨΗ

- In the petrochemical industry the catalytic dewaxing processes improve the cold properties of diesel oils and lubricating base oils (low pour point, high viscosity index). The ideal oil should consist of slightly branched paraffins. In the process the long-chain linear paraffin content of the feed wax is removed by cracking or/and transformed into slightly branched paraffins via hydroisomerization. Dewaxing by hydroisomerization is more economical than dewaxing by hydrocracking because the yield is higher. Typical dewaxing catalysts are bifunctional catalysts which consist of highly dispersed metals (Pt, Pd, Ni) supported on acid zeolites (ZSM-5 (Mobil), mordenite (BP)), SAPO-11(Chevron)).

The balance of the hydrogenation-dehydrogenation function and the acidity of the zeolite is crucial as it determines activity, stability, and the product selectivity. The conventional reaction mechanism of alkane isomerization and hydrocracking on bifunctional zeolites are monomolecular. According to this mechanism, alkanes are dehydrogenated on the metal phase, and alkenes formed are protonated at the Brønsted acid sites yielding alkylcarbenium ions. After C-C bond rearrangement and eventually scission, isomeric or fragmented alkylcarbenium ions desorb as product alkenes that are hydrogenated at the metal phase to yield the product alkanes.

Our aim was the preparation and characterization of bifunctional dewaxing Ni catalysts possessing high selectivity to feed isomers at high conversion. The effects of the preparation method of the Ni-catalysts, metal to acid sites ratio and the structure of the zeolite on the activity and product selectivity were studied in n-decane and n-hexane hydroconversion.

2. The development of new, more active and selective catalysts is a real challenge for catalytic science. At the beginning of the 90's the discovery of a new family of mesoporous molecular sieves called M41S, opened new possibilities to prepare catalysts for reactions of relatively large molecules. The most important member of the family, known as MCM-41, possesses regular, hexagonal array of pores with pore diameter in the 1.5-5 nm range, however the silicate wall of the pores is amorphous. At the beginning scientific interest focused on the investigation of the alumina containing MCM-41 varieties, but soon they were proved to be inferior to zeolites in their acid strength and did not show higher activity than zeolites, e.g. in cracking reactions of large hydrocarbon molecules. Therefore research had a preference for MCM-41, modified with transition metals, in order to prepare catalysts with redox properties. The formation of catalytically active metal species in these materials can be achieved by different preparation methods, e.g. by direct synthesis or post synthesis procedures (impregnation, grafting).

In order to develop new materials having different redox catalytic properties than zeolites, we prepared iron, nickel, copper and cobalt containing MCM-41 materials by direct synthesis methods or by impregnation. We studied the nature and the chemical environment of these transition metals, the possibility of isomorphous substitution. We investigated also the type and strength of the formed acidic centers and the reducibility of the metal species. Independently of the preparation methods the reduction of divalent metals (Cu or Ni) in MCM-41 structure resulted in formation of finely dispersed metallic nanoclusters in the channels or at the external surface of the samples. Ni-MCM-41 materials proved to be active catalyst in toluene hydrogenation to methyl cyclohexane.

In contrast, iron can be stabilized in MCM-41 structure by linkages to the silicate framework through oxygen. By reduction only Fe(III)→Fe(II) transformation occurred up to 973 K and the existence of redox cycle by the consecutive reductions and oxidation was also evidenced. Fe-MCM-41 materials showed high activity in CO oxidation at low temperature (<325 K).