Scientific goals

This work is currently focused on development of new generation of solid catalysts that can be used to increase the petrol quality and particularly its octane number.

Objectives

In order to replace existing technologically unfavourable and environmentally harmful liquid catalysts for alkylation of short paraffin's (petrol product) new generation of solid catalysts with superacidic properties should be developed. For this **metal oxides** with **covalently bonded** over flexible chain **acidic groups will be obtained**. This type of catalysts will be based on oxides with deferent acidity (zirconia, silica with monolayer of zirconia, zeolites, mesoporous silicates, zeolites ets.) that will be control and regulate by additional hydrophobisation of support surface. Acidic properties of covalently bonded groups will be also varied. Sulphonic, phosphonic and carboxylic acids will be attached to surface. This will allow to change distribution and impact of different nature acidic sites (Lewis/ Bronsted) and optimise catalytic properties of the materials. From flexibility of distant acidic centres bonded with surface over alkyl chain and hydrophobisity of surface superacidity of bonded layer can be expected. It can promote consequent decreasing of catalytic reaction temperature.

All mentioned above can provide new generation of superasidic catalysts for low-temperature isomerisation of petrols with next advantades:

1. **Better environmental protection (no leaching of strong acids)**
2. **technological improvements (no aggressive, highly corrosive liquids)**
3. **energy efficiency (increasing acidity of solid acids allowed low temperature isomerization)**

Proposed catalysts based on metal oxides and silicates with covalently bonded over flexible chain acidic groups (sulphonic, phosphonic and carboxylic). Due to combination of strong acid properties, hydrophobisity and insolubility these catalysts offer several advantages if use in petrol chemistry:

1. environmental protection (no leaching of strong acids)
2. technological improvements (no aggressive, highly corrosive liquids energy efficiency (increasing acidity of solid acids allowed low temperature isomerization)

Main results

- Optimal scheme for covalent immobilization of alkylsulphonic acid on silica surface was developed. It was demonstrated that two types of sulphonic acids is formed in the procedure proposed: α- and β-ethanesulphonic but the last one predominates and is much more stable then α- and decomposes only at 375ºC.
- Special scheme leading to statistical distribution of bonded groups was developed for protonic and ionic immobilization of heteropolyacids. TEM of immobilized HPA demonstrated homogenous distribution of HPA anions with no clustering.
- High stability in water and ethanol against leaching was demonstrated for these materials.
- New synthetic routes leading to the nanocomposite of silica-HPA and silica-Nafion were developed.
- The project samples were shown to be active in NH_3 adsorption only after pre-treatment at 250-300°C. Repeating adsorption – desorption cycles up to 350°C did not influence the number of active acid sites or their strength.
- It was demonstrated that low-temperature fluorination of silica with NH_4F can be used to replace low-acid silanoles on a silica surface.
- Catalytic activity of immobilized alkylsulphonic acid reaches its maximum at 120-140ºC which is higher than for commercially available catalysts. Specific activity of experimental catalysts is much higher than for commercial one. Selectivity of proposed catalysts also higher then for known ones.
- Immobilised HPA catalysts with high activity to ETBE synthesys were obtained.
- Superacidity solids with immobilised fluoroalkylsulphonic acid is high enough to be used for reaction of isomerisation of linear alkanes.
- The project developed superacid solids are more stable for negative influence of water vapour.