

SPR16 Application Note

Hydrogenolysis of Butyl Acetate to Butanol over Naphtha Reforming Catalysts in Conventional and High Throughput Slurry Reactors

Adapted from: Göbölös et al, *Catalysis of Organic Reactions*, Ed. J.R. Sowa Jr., CRC Press **2005**

The catalytic hydrogenolysis of esters to two alcohols is conventionally carried out using a copper chromite catalyst at 10 MPa H₂ pressure and 250°C. It was assumed that bimetallic naphtha reforming catalysts containing Pt and Re or Sn promoters could also be applied for the hydrogenation of carbonyl compounds. It has been proved that in the reforming catalysts at least part of the Sn or Re is in ionic form. Therefore, one might expect that ionic Sn or Re species as Lewis acid sites in naphtha reforming catalysts can also activate the C=O group of carbonyl compounds.

Butyl Acetate was hydrogenolysed to butanol over different RePt/Al₂O₃ and Re modified SnPt/Al₂O₃ naphtha reforming type catalysts in the SPR16 reactor and a conventional autoclave. Tests in the single autoclave revealed that Re is a crucial ingredient for high conversion and selectivity at 235°C and 6 MPa. The reaction order and apparent activation energy were measured in a single activity test using the SPR16.

Prior to the activity test 100 mg of 1Re1Pt/Al₂O₃ catalyst was reduced *in situ* in H₂ at 250°C and 1.0 MPa for 1h. The reaction order for AcOBu and apparent activation energy were determined in the 16 SPR16 reactors operated simultaneously. Reaction conditions were as follows: AcOBu concentration (solvent heptane); 0.38, 0.57, 0.76, 0.97 mol/l, P(H₂) = 6.0 MPa, reaction temperatures = 215, 220, 225 and 230°C, reaction time 3.6 h, stirrer speed 1000 rpm.

In the activity tests performed in the SPR16 the AcOBu conversion increased linearly up to around 50% with reaction time. Initial reaction rates were calculated from AcOBu conversion vs. reaction time dependence.

Results on AcOBu conversion and reaction rates obtained on the 1Re1Pt catalyst are listed in the tables 1 and 2.

The reaction order in AcOBu was slightly negative but close to zero. The activation energy only slightly depended on the concentration of AcOBu. Both reaction order and activation energy obtained were in good agreement with those reported in the literature for gas phase hydrogenolysis of methyl- and ethyl acetate.

The results clearly indicated that both Sn and Re probably in their ionic form (see TPR results) significantly improved the activity of platinum for the hydrogenolysis of AcOBu. Therefore, it is suggested that atomic closeness of positively charged Re or Sn species and metal nanoclusters, i.e. the formation of "M₁ⁿ⁺-M₂⁰" ensembles (M₁ = Re, Sn; M₂ = Pt, Re, RePt or SnPt alloy) is required to achieve high catalytic activity in the hydrogenolysis of esters.

Table 1 Hydrogenolysis of AcOBu on 1Re1Pt catalyst in SPR16 reactor. Effect of temperature and concentration on conversion and reaction rate.

T, °C	C = 0.38M X, % & r ₀	C = 0.57M X, % & r ₀	C = 0.76M X, % & r ₀	C = 0.97M X, % & r ₀
215	20.8, 1.968	15.4, 1.954	11.5, 1.941	8.7, 1.834
220	31.9, 2.691	21.0, 2.661	15.7, 2.655	12.8, 2.699
225	44.5, 3.758	28.3, 3.589	20.5, 3.467	16.4, 3.458
230	54.4, 4.594	35.3, 4.467	26.0, 4.385	20.5, 4.315

Abbreviations: c = initial concentration of AcOBu in mole/L; X = conversion of AcOBu at t=3.6 h, r₀ = initial reaction rate in mmole/g_{catalyst} h

Table 2 Hydrogenolysis of AcOBu on 1Re1Pt catalyst in SPR16 reactor. Reaction order for AcOBu and apparent activation energy.

T, °C	N	c, M	E _A , kJ/mol
215	-0.067	0.38	118.0
220	-0.001	0.57	114.0
225	-0.096	0.76	113.5
230	-0.068	0.97	113.5

Abbreviations: c = initial concentration of AcOBu in mol/l; n = reaction order for AcOBu; E_A = apparent activation energy in kJ/mol

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