

# Real-time *in situ* FTIR analysis of liquid phase catalytic reactions

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When running a heterogeneous catalytic reaction in the liquid phase, one commonly extracts samples using an auto-sample such as GC and then analyzes them after the reaction is complete. There are two disadvantages to this technique: 1) reactor volume may be affected, which could in turn affect the kinetics of interest, and 2) process control is not possible because analysis takes place after the reaction is over.

A study was conducted to determine if interactions of the liquid with the solid catalyst could be seen using the online technique of ReactIR™. Could the heterogeneous catalyst be observed? And is there an effect of catalyst particle size on the spectra obtained? The applicability of ReactIR™ was illustrated by two reactions: 1) analysis of the catalytic esterification of 1-octanol and hexanoic acid over Nafion silica catalysts in an open reflux configuration at atmospheric pressure, and 2) the hydrogenation reaction of lactones over Cu/Zn-oxide catalysts at 50 Bar H<sub>2</sub> in an autoclave.

The first reaction was performed in decane. The acid conversion and rising of the ester bonds during the reaction could be clearly seen with ReactIR™ (Figure 1). Initial rates of the esterification agreed with those determined by conventional offline GC analysis. ReactIR™ also observed an additional strong and broad absorption band around 1100cm<sup>-1</sup>. It was assessed by variation of the reaction mixture that this band is a result of the formation of Si-O-R linkages by reaction of 1-octanol with the silica surface. This implies that in liquid-phase reactions, online analysis of intermediate species adsorbed on heterogeneous catalysts may be feasible.

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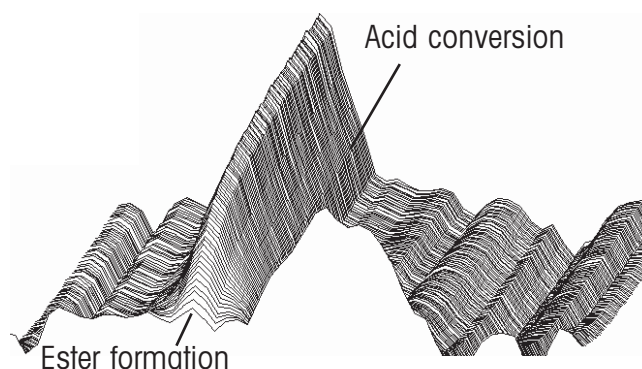


Figure 1:  
Results in decane,  
1780-1680 $\text{cm}^{-1}$   
region - ReactIR™  
shows acid  
conversion and  
rising of ester  
bonds

Next, Lasentec® FBRM® was applied to look for particle attrition. Figure 2 shows the start of the reaction in decane compared with the end of the reaction. FBRM® confirms that because the 1100 $\text{cm}^{-1}$  band was not observed in decane, particle size distribution is virtually unchanged. There is some change in the agglomeration size of the particles, but no dramatic effect. Lasentec® PVM® images affirm that particle size barely changes during the reaction.

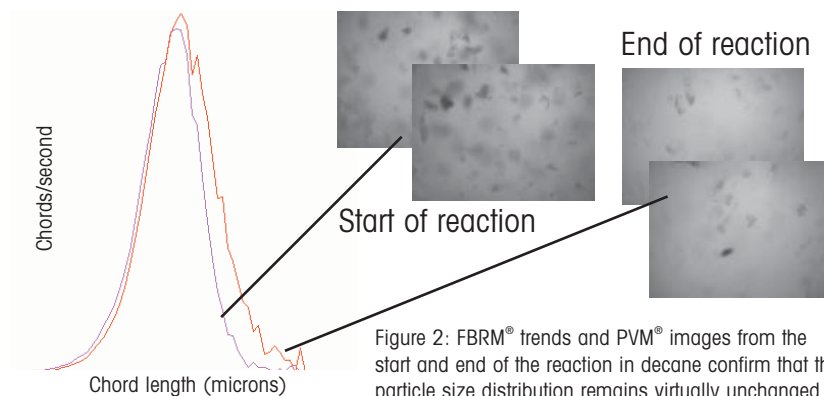


Figure 2: FBRM® trends and PVM® images from the start and end of the reaction in decane confirm that the particle size distribution remains virtually unchanged

The second reaction (i.e., hydrogenation of lactones) illustrated the use of ReactIR™ with a Sentinel™ probe at high pressures in an autoclave. Indications for leaching of copper from the catalyst composition into the liquid phase were observed. This very important information might have remained unnoticed if conventional GC analysis had been applied.

In conclusion, ReactIR™ was found to be a very useful technique for analyzing heterogeneous catalysis reactions in the liquid phase. The concentration profiles from GC and ReactIR™ were in good agreement and unexpected results were found with ReactIR™ that could not be observed in GC data.

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