



# Supercritical-phase-assisted highly selective and active catalytic hydrodechlorination of the ozone-depleting refrigerant $\text{CHClF}_2$

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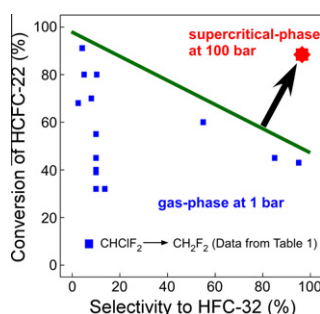
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## HIGHLIGHTS

- The supercritical-phase conversion of ozone-depleting HCFC-22 to valuable HFC-32.
- The highest HFC-32 yield (85.0%) ever reported.
- Increased catalytic activity by high  $\text{H}_2$  pressure and negligible mass transfer barrier.
- Suppressed catalyst poisoning by less carbide formation and better F/Cl removal.
- Increased catalytic selectivity by improved desorption of HFC-32.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 12 July 2012

Received in revised form 18 October 2012

Accepted 22 October 2012

Available online 26 October 2012

### Keywords:

Supercritical fluid

Catalysis

Hydrodechlorination

HCFC-22

HFC-32

## ABSTRACT

Catalysis in the supercritical fluids has been interested because of its high activity, high selectivity along with an easy purification of its products. Not using frequently-used supercritical inert solvents such as carbon dioxide and light hydrocarbons but using a supercritical mixture of reactants, we demonstrate highly active and highly selective catalytic hydrodechlorination of the ozone-depleting refrigerant  $\text{CHClF}_2$  (HCFC-22) to the ozone-inert  $\text{CH}_2\text{F}_2$  (HFC-32). Performing catalysis using a continuous-flow reactor with 66 wt.% Ni on silica–alumina, 5 wt.% Pd on  $\gamma$ -alumina and 5 wt.% Pd on activated carbon catalysts, we observe 95.9% conversion of HCFC-22 and 88.6% selectivity to hydrodechlorinated HFC-32 (which corresponds to 85.0% HFC-32 yield) over fully hydrogenated methane at 400 °C and 100 bar, which is the highest HFC-32 yield ever reported. The effects of the supercritical fluid on the improved catalytic activity and selectivity are discussed by characterizing spent catalysts using transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Because of the beneficial properties of the supercritical fluid in catalysis, the deactivation of the Pd on activated carbon catalyst by the existence of catalyst-poisoning palladium carbide ( $\text{PdC}_x$ ) and F/Cl compounds is minimized, which can increase the catalytic activity. In addition, the faster desorption of HFC-32 by the negligible mass transfer barrier may increase the selectivity to HFC-32 and inhibit the further conversion to the fully hydrogenated methane. The highly active and highly selective catalytic hydrodechlorination in supercritical condition can benefit new chemical processes that reduce the unwanted byproducts, resulting in high productivity of the desired chemicals.

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