

Characterization of Supported Nickel Catalysts Derived from RF Non-thermal Plasma Technology

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Introduction

Non-thermal plasma based techniques have attracted significant attention for catalyst design and development lately. [1-5] Catalysts with unusual and highly advantageous catalytic properties including room temperature reduction, unusual metal particle structure and metal-support interactions, and enhanced selectivity and stability have been reported.[2-5] For example, plasma derived Ni/Al₂O₃ and Pd/Al₂O₃ have been reported to show enhanced stability and selectivity for benzene hydrogenation and for selective hydrogenation of acetylene, respectively. [2,3] This study focuses on the characterization of supported Ni catalysts derived from the RF non-thermal plasma technique to relate to the enhanced activity and stability of Ni catalysts for benzene hydrogenation. The goal is to demonstrate the unique capability of the RF plasma technique to modify the interaction between metals/metal precursors and supports and to control the structure, size and shape of metal particles. The plasma process can be applied to various supported metal catalysts for various industrial catalytic processes.

Experimental

Supported nickel catalysts were prepared by the incipient wetness technique with rf non-thermal plasma modifications before and/or after impregnation. Plasma treatments were carried out in a custom-designed 360° rotating RF plasma system. The details of the system are described in a previous publication. [2] The catalysts with plasma treatments before and after impregnation are designated as (B) and (A), respectively. For example, H₂(A) denotes a catalyst with H₂ plasma treatment after nickel nitrate impregnation. The catalyst that is first modified by the air plasma then impregnated with nickel precursor followed by hydrogen plasma treatments is designated as air(B)H₂(A). A catalyst which was not plasma-treated, designated "uncalcined," is used as a reference. Benzene hydrogenation studies were carried out at space velocity of ~63,000 cc/h-g at 150°C with H₂/benzene =18/1 reduced at 450°C or 600°C for activity or stability test, respectively.

In-situ XRD analysis was performed in 5%H₂/He under a temperature program with a 5°C/min ramping rate from room temperature and with 10 minutes holds at 300°C, 400°C, 450°C, 475°C, 500°C, 525°C, 550°C, and 575°C, followed by a four hour hold at 600°C. XRD scans were made during each of the holds and multiple scans were made during the hold at 600°C. Metal particle size was estimated based on the Ni (111) peaks.

Results and Discussion

The activity and stability of various 5%Ni/Al₂O₃ catalysts for benzene hydrogenation are summarized in Table 1. As shown in Table 1, both RF non-thermal plasma treatments before and after the impregnation of precursors can enhance the catalytic activity and stability. Above all, the combination plasma treatment, air(B)H₂(A), show the most significant improvement,

with 21.5% increase in activity and 62.7% in stability than the un-calcined one. It demonstrates that plasma process can potentially take the advantages of modifying both supports and metal precursors to produce novel catalytic materials.

In-situ XRD was used to characterize the effect of plasma treatments and the results are summarized in Table 2. Compared to the reaction results, it can be summarized:

1. Catalysts with plasma treatments before the impregnation of precursors show similar particle growing trend with temperature below 600°C. But, the treatments stabilize the nickel particle size at 600°C as compared to the un-calcined one.
2. Plasma treatments after the impregnation of precursors, on the other hand, tend to delay the growth of nickel particles below 575°C, but with a sudden increase in particle size at the first measurable temperature. It suggests that the metal-support interaction has been significantly altered by the plasma treatments.
3. The combination plasma treatment, air(B)H₂(A), limited the nickel particle size to be smaller than other catalysts after extended reduction at 600°C, matching with the catalytic stability result.

Table 1. Activity and stability of various 5%Ni/Al₂O₃ catalysts

Catalyst	% Conversion, reduced at 450°C	Activity Enhancement	% Conversion, reduced at 600°C	Relative Stability
Un-calcined	46.9	NA	29.5	NA
Air(B)	55.8	+19.0%	36.9	+25.1%
H ₂ (B)	52.1	+11.1%	35.2	+19.3%
Air(A)	51.2	+9.2%	44.2	+50.0%
H ₂ (A)	46.3	-1.3%	43.0	+45.8%
Air(B)H ₂ (A)	57.0	+21.5%	48.0	+62.7%

Table 2. In-situ XRD Analyses: Nickel particle size, in nm, estimated at different temperatures

Catalyst	475°C	500°C	525°C	550°C	575°C	600°C	600°C (1h)	600°C (2h)	600°C (3h)	600°C (4h)
Air(B)	NP*	<2.0*	2.9	3.2	3.5	3.5	4.3	4.1	4.3	-
H ₂ (B)	NP	NP	<2.0	2.6	3.5	3.3	4.5	3.7	4.3	3.9
Uncal	NP	<2.0	<2.0	2.4	3.1	3.3	3.9	4.2	4.5	4.6
Air(A)	NP	NP	NP	<2.0	<2.0	3.6	4.3	4.4	4.4	4.3
H ₂ (A)	NP	NP	<2.0	<2.0	<2.0	3.8	4.0	4.5	4.7	4.7
Air(B)H ₂ (A)	NP	NP	<2.0	<2.0	3.3	3.3	3.9	4.4	3.9	3.6

*NP: No peak detected; <2.0: Peak detected but particle size cannot be estimated

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