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The chemical heterogeneity of active surface of solid catalysts

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The chemical adsorption behaviors of three adsorbates on the Ni-W/F-Al_2O_3-SiO_2 and the supported Ni catalysts have been investigated. On the basis of fractal geometry, the roughness fractal dimension (D_r) and the chemisorption fractal dimension (D_c) of the catalysts are estimated. We use the difference between D_c and D_r to characterize the chemical heterogeneity of active sites on the catalytic surface. It is found that the chemical heterogeneity of the acid sites of the Ni-W/F-Al_2O_3-SiO_2 catalyst is very large, while it decrease with increasing of impregnating operation times in preparation of the supported Ni catalyst. After 4 times impregnation, the chemical heterogeneity of its active surface for the supported Ni catalyst is eliminated.

1. Introduction

It is well established that the catalysis of solid catalyst is determined not only by the geometric parameters such as particle size, specific surface area, pore-size distribution, and the surface morphology of solid catalyst, but also by the distribution of active sites on the surface of solid catalyst and the variation of surface bonded ability [1]. The latter are defined as the *chemical heterogeneity of active surface of solid catalyst*. Although the geometric parameters and the chemical components of solid catalyst can be characterized by many techniques such as SEM, TEM, XPS, UPS, and LEED, a determination of the chemical heterogeneity of active surface is still challenged. In the early 1980's, with the recognition of Chaos theory and fractal geometry theory [2], it became possible to establish a new method for studying surface phenomena and complicated catalytic problems. It has been shown that fractal geometry is common in nature on both microscopic and macroscopic length scales [3, 4]. Materials used as catalysts or catalyst supports often have a fractal-like structure [5]. The fractal dimension, D, has successfully been used to characterize the surface properties of solid catalyst.

Based on the concept of fractal geometry, Pfiefer and Avnir [6] suggested a relationship between the monolayer adsorption quantity on the solid particle surface, N, and particle size, $R : N \propto S_g \propto R^{D_r - 3}$, where S_g is the specific surface area and D_r is the *surface roughness fractal dimension*, $2 \leq D_r \leq 3$. This parameter is only attributed to the geometric accessibility. They further proposed that selectivity of adsorption is attributed to both the geometric accessibility and the chemical heterogeneity of the active surface if chemical interactions occur in the molecule/surface complex. This is especially true for metal catalysts dispersed on porous supports. There exists a following relation between the chemical adsorption quantity, N_c, and particle size, $R : N_c \propto R^{D_c - 3}$, in which D_c is the *chemisorption fractal dimension*. This parameter is attributed to both the geometric accessibility and the chemical heterogeneity. By comparing D_c with D_r, the chemical heterogeneity of active surface might be investigated.

In this paper, the monolayer adsorption and the chemical adsorption quantities on the Ni-W/F-Al_2O_3-SiO_2 catalyst and the supported Ni catalysts are determined using BET and chromatographic methods, respectively. On the basis of fractal geometry, the roughness fractal dimension (D_r) and the chemisorption fractal dimension (D_c) of the catalysts are estimated. Furthermore, the chemical heterogeneities of active surface for the two catalysts are analyzed from the difference between D_r and D_c.

2. Experimental

A Ni-W/F-Al_2O_3-SiO_2 catalyst is prepared by coprecipitation method, which is then crushed and labeled as NiW1, NiW2, NiW3, NiW4, and NiW5 with respect to five different particle sizes. A supported Ni catalyst is prepared by impregnation method. Diatomite with a specific surface area ($S_g = 43.95$ m^2/g) is used as a support and impregnated in the aqueous solution of $Ni(NO_3)_2$ for 8 hours and the dried at 120 °C. The above procedure is repeated several times, *n*, until the fixed quantity of $Ni(NO_3)_2$ is supported fully. The supported Ni catalyst is then calcined at 400 °C for 2 hours, crushed, sieved and labeled as Ni1, Ni2, Ni3, Ni4, and Ni5 with respect to five different particle sizes.

The monolayer adsorption quantities of methanol on the catalysts are estimated by static adsorption BET method. The adsorption quantities are proportional to extensibility of quartz springs after adsorbed. The vacuum of system is better than 1×10^{-3} Pa, and the sensitivity range of quartz springs used is 68–70 mm/100 mg.

The chemical adsorption quantities of n-butyamine on the acid surface of the Ni-W/F-Al_2O_3-SiO_2 catalyst are determined by temperature-programmed desorption (TPD) using highly-purified N_2 as a carrier at an adsorption temperature of 120 ± 1°C. The sample (approximately 100 mg) was pretreated at 400 °C for longer than 6 hours in N_2 atmosphere. The concentration of *n*-butyamine in tail-gas is monitored by gas chromatograph. The chemical adsorption quantities of H_2 on active surface of the supported Ni catalyst are determined at 120 ± 1°C using highly-purified argon as a carrier by H_2-O_2 titration [7]. The samples are reduced at 400 °C for 4 hours in H_2 atmosphere before determined.

3. Results and discussion

The monolayer adsorption quantities of methanol on the catalysts with different particle size at 30 °C are determined and the results are listed in Tables I and II. The value of D_r is estimated by least-square fitting $\log N$ vs $\log R$. The values of correlation coefficients, close to one, listed in Tables I and II, confirm a linear relationship between $\log N$ and $\log R$, indicating the validity of fractal geometry in the two catalysts. From Table II, it was found that D_r continuously decreases with increasing the impregnation time, which may result from the reduction of surface roughness of the catalyst during impregnation processes. This infers that during the impregnation, the irregular parts of catalyst surface might have a high priority to adsorbing $Ni(NO_3)_2$.

The chemical adsorption quantities of *n*-butyamine on acid surface of the Ni-W/F-Al_2O_3-SiO_2 catalysts with different particle sizes are shown in Fig. 1. The consumption of H_2 on the supported Ni catalyst is determined by H_2-O_2 titration. Though many parameters, such as pre-treatment and surface structure of catalyst, affect the stoichiometric relation of H_2-O_2 titration on Ni surface [7], the adsorption quantity of H_2 is still proportional to the H_2 consumption. The H_2 consumption, therefore, is used to estimate the D_c. It is found that the adsorption quantities of *n*-butyamine molecule and H_2 consumption, log N_c, linearly depend on the particle size, $\log R$, as shown in Figs 1 and 2, suggesting that the active surfaces of the two catalysts are fractal.

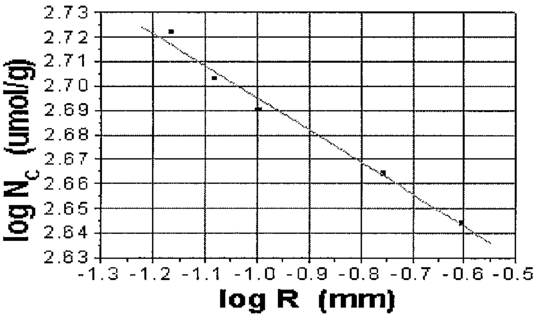

Figure 1 The chemical adsorption quantities of *n*-butyamine on Ni-W/F-Al_2O_3-SiO_2 as a function of particle size.

TABLE I The monolayer adsorption quantities of methanol on the Ni-W/F-Al_2O_3-SiO_2 catalysts with different particle sizes at 30 °C

Catalyst	NiW1	NiW2	NiW3	NiW4	NiW5		
Average diameter (mm)	0.675	0.250	0.180	0.101	0.0685	D_r	Correlation Coefficient
N (μ mol/g)	438.8	597.3	780.3	903.6	922.4	2.429 ± 0.057	0.9855

TABLE II The monolayer adsorption quantities of methanol on the supported Ni catalysts with different particle sizes at 30 °C

Catalyst		Ni1	Ni2	Ni3	Ni4	Ni5		
Average diameter (mm)		0.250	0.175	0.135	0.115	0.101	D_r	Correlation Coefficient
	Support	260.7	320.2	365.6	400.6	433.3	2.440 ± 0.008	0.9956
Monolayer	Catalyst impregnated for 1 time	271.0	345.3	403.1	458.2	498.2	2.329 ± 0.013	0.9964
Adsorption	Catalyst impregnated for 2 times	293.0	378.4	452.4	513.9	562.8	2.279 ± 0.007	0.9971
Quantities	Catalyst impregnated for 3 times	305.4	397.4	472.5	540.7	595.5	2.264 ± 0.012	0.9936
	Catalyst impregnated for 4 times	334.7	444.2	534.7	609.3	676.8	2.224 ± 0.009	0.9984
N (μ mol/g)	Catalyst impregnated for 5 times	359.2	489.3	598.4	684.0	762.7	2.175 ± 0.009	0.9970

TABLE III The D_c values of the catalysts

Catalysts	Ni-W/F-Al_2O_3-SiO_2 catalysts	Supported Ni catalysts				
		$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$
D_c	2.861 ± 0.013	2.691 ± 0.014	2.502 ± 0.021	2.325 ± 0.013	2.232 ± 0.009	2.180 ± 0.027
Correlation Coefficient	0.9962	0.9970	0.9931	0.9960	0.9981	0.9912

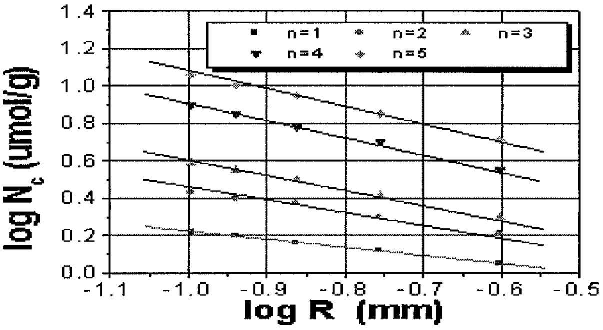

Figure 2 The H_2 consumption on the supported Ni vs the particle size.

The values of D_c listed in Table III are estimated by least-square fitting $\log N_c$ vs $\log R$.

The D_r is purely resulted from the effect of geometric factor on the adsorption, while the D_c measures the irregularity of the active surface including both the geometric and chemical factors. The quantitative difference between D_c and D_r may be used to characterize the extent of chemical heterogeneity of the active surface of solid catalyst. For Ni-W/F-Al_2O_3-SiO_2 catalyst, the difference, $\Delta D = D_C - D_r = 0.432$, suggests that the catalyst acid surface might have rather strong chemical heterogeneity, i.e. the heterogeneity in the distribution of acid sites and the activation energy of chemical adsorption.

The influences of impregnation times on D_c and D_r of the supported Ni catalyst are shown in Fig. 3. It is found that both D_c, D_r and the difference, $\Delta D = D_C - D_r$, decrease with increasing the impregnation time, n. After $n > 3$, the difference tents to zero, which implies elimination of the chemical heterogeneity of catalyst surface. When $n \geq 4$, the dependence of N_c on R relies almost totally on the geometric accessibility of the catalyst surface.

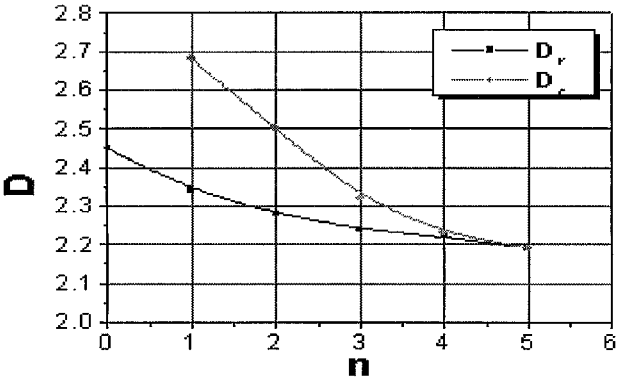

Figure 3 The influence of impregnation times on D_r and D_c.

4. Conclusions

1) The surfaces of the Ni-W/F-Al_2O_3-SiO_2 catalyst and the supported Ni catalyst and their active surfaces are obviously fractal.

2) During the process of impregnation, the “filling up effect” makes a reduction in the irregularity of the supported Ni catalyst surface.

3) The acid surface of the Ni-W/F-Al_2O_3-SiO_2 catalyst prepared by the co-precipitation method is rather heterogeneous. The active surface of the supported Ni catalyst becomes gradually homogenous with increasing the impregnation time while the chemical heterogeneity is eliminated basically when $n > 3$.

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