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Detection of Carbon in Hydrocarbon Conversion $\text{Ni}_{1-x}\text{Cu}_x\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ Catalysts Using a Thermogravimetric Technique

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Abstract: Thermal behavior of hydrocarbon conversion $\text{Ni}_{1-x}\text{Cu}_x\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ catalysts have been investigated under oxidizing and reducing atmospheres. A method based on a thermogravimetric technique of deposited carbon evaluation has been developed. Carbon deposited on the catalytic surface during methane cracking can be removed from the catalysts by gasification in air at temperatures $<650^\circ\text{C}$.

Keywords: carbon gasification, hydrocarbon, Ni(Cu)-based catalyst, TGA analysis

INTRODUCTION

Catalytic conversion of hydrocarbons such as steam reforming, electrochemical oxidation, etc., has been investigated intensively for many years (Trimm, 1980; Zhang et al., 2002; McIntosh and Gorte, 2004). One of the main problems in these catalytic processes is carbon (coke) formation, which is generally considered to poison the catalyst (Trimm, 1983). An accumulation of significant amounts of carbon can create some operational problems in the reactors. The accumulation of carbon can be minimized but usually cannot be eliminated. As a result, it is necessary to stop operations from time to time in order to remove carbon from the catalyst, for example, by gasification with air. Regeneration should be performed at the lowest possible temperature in order to avoid catalyst deactivation by sintering. Therefore, keeping the carbon deposition on the surface of catalysts under control is very important. In general, catalytic coke may be produced on acidic oxides or on metals (Trimm, 1984).

This article describes a thermal behavior and thermogravimetric method for estimating the amount of carbon deposited on a broad range of Ni-

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Cu catalysts supported on $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (known as SDC) during methane cracking.

EXPERIMENTAL

The catalysts $\text{Ni}_{1-x}\text{Cu}_x\text{-Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC), where $0 \leq x \leq 1$ were prepared by decomposition of nitrate solutions of Cu and Ni in the presence of SDC followed by reduction in forming gas (8% H_2 –92% Ar) at 900°C for 5 hr. All the catalysts contained ~50 wt% of metallic phase. The samples containing different amounts of carbon were obtained by methane cracking on $\text{Ni}_{1-x}\text{Cu}_x$ –SDC catalysts. For this purpose, 300 mg samples were placed in the tube reactor and pre-treated at 800°C for 1 hr in flowing (40 cm^3/min) forming gas. After the pre-reduction stage the reactor was cooled to 200°C and the system flushed with pure Ar. Then the reactor was heated at a rate of 5°C/min up to 800°C in a flowing (40 cm^3/min) gas mixture of 5% CH_4 and 95% Ar. To estimate the amount of carbon deposition, the mixture of CH_4/Ar was allowed to flow through the reactor for a period of 2 hr. Then the reactor was cooled rapidly (20°C/min) to room temperature and the catalysts analyzed. The reference samples were prepared by solid state mixing SDC and CuO in a proper ratio to get a composition containing 50 wt% of Cu after reduction in forming gas.

Thermogravimetric analysis of the catalysts before and after testing was performed in the range from 25°C to 900°C using a Setaram SETSYS-evolution apparatus (SETARAM Instrumentation, Caluire, France). About 15–35 mg of a sample was subjected to a controlled temperature program (heating/cooling rate 5°C/min) in an air or forming gas flow rate of 40 cm^3/min . The instrument was calibrated in accordance with the procedure recommended in the operation manual.

X-ray powder diffraction measurements were carried out on a Bruker D8 (Bruker AXS GmbH, Karlsruhe, Germany) diffractometer using $\text{CuK}\alpha$ radiation.

RESULTS AND DISCUSSIONS

Figure 1 shows three consecutive TG runs under different atmospheres for the reference mixture of 14.94 mg SDC and 18.70 mg CuO. It is clear that CuO can be quantitatively reduced and then metallic Cu can be oxidized at temperatures below 500°C. The oxidation-reduction process is complete and reproducible. The reversible mass change observed above 600°C is attributed to oxygen content variation in $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9-\delta}$ as δ depends on oxygen partial pressure (Tuller and Norwick, 1975). TG curves for the SDC-CuO(Cu) samples prepared from SDC and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ are presented on Figure 2. For the SDC-CuO in forming gas (curve a), three distinctive ranges are

Figure 1. Thermocycling profile for SDC-CuO reference sample under different atmospheres (heating and cooling rate 5°/min).

observed. In zone 1 (<180°C) the mixture loses absorbed water. A steep weight loss at about 200°C (zone 2) is due to reduction of CuO and formation of Cu. The reduction of SDC is negligible and can be observed at temperatures above 500°C (see zone 3). A TG curve in air (curve b) shows just oxidation of metallic Cu at the temperatures above 200°C. The constant mass was obtained at 550°C. The amount of oxygen uptake during oxidation of Cu in air and mass loss during CuO reduction in forming gas determined from each of the thermal curves are in good agreement indicating the reaction is complete and reversible.

The results of thermogravimetric analyses in FG of some representative SDC-Ni_{1-x}Cu_xO are given in Figure 3. It can be seen that Ni_{1-x}Cu_xO, where $0 \leq x \leq 1$, can be reduced in the temperature range from 200°C to 400°C. The reduction temperature increases with increase in NiO concentration. In all cases, very little reduction of SDC is observed at >500°C. TG curves of SDC-Ni_{1-x}Cu_x catalysts in air are presented in Figure 4. Doping Ni with Cu decreases the resistance of Ni_{1-x}Cu_x alloys towards oxidation. It can be seen that Ni-rich alloys ($x \leq 0.48$) have very similar reduction behaviors. The samples are oxidized in the range from 250°C to 550°C. The value of oxygen uptake, which is determined from the difference of the initial and final mass taken once the plateau has been reached at 550°C match well

Figure 2. TGA curves (heating and cooling rate 5°/min) for SDC-Ni_{1-x}Cu_xO in forming gas (a) and for SDC-Ni_{1-x}Cu_x in air (b).

with the data obtained during reduction experiments and those calculated for SDC-Ni_{1-x}Cu_x mixtures. Therefore, these experiments showed that the composition of SDC-Ni_{1-x}Cu_x catalysts can be easily controlled by applying the TGA method.

The oxidation behavior of SDC-Ni_{1-x}Cu_x catalysts containing deposited carbon is more complex. In general, the oxidation process will include two parallel chemical reactions:

The reduction of the Ni_{1-x}Cu_xO samples in forming gas will regenerate the catalysts:

Subtracting reaction (3) from (1) and (2) gives:

Figure 3. Mass loss curves for SDC-Ni_{1-x}Cu_xO samples at the heating rate of 5°/min in forming gas.

Therefore, a TGA run of carbon containing SDC-Ni_{1-x}Cu_x samples in air followed by a run in forming gas provide not only practical information on catalyst regeneration temperature but also on amount of carbon deposited on the catalyst during catalytic processes.

It is well known that Ni catalysts supported on oxides are very effective in methane decomposition (Chen et al., 1997; Rostrup-Nielsen and Trimm, 1977). In contrast, Cu shows very low activity toward hydrocarbons and does not catalyze the formation of carbon (Li et al., 1985). Therefore, it may be expected that the activity of binary Ni_{1-x}Cu_x system will depend on copper concentration. The x-ray patterns of some representative catalysts measured after the catalytic test are presented on Figure 5. The samples consist of three phases, namely, SDC, Ni_{1-x}Cu_x, and carbon. A broad peak ($2\theta = 26.5^\circ$, $d = 3.3605 \text{ \AA}$) can be assigned to carbon. This is the most intense peak in the carbon x-ray pattern (ICDD file 75-0444). It can be seen that the amount of carbon deposited on catalysts, in general, decreases with increase in Cu content in the Ni_{1-x}Cu_x phase.

Quantitative characterization of the deposited carbon and its thermal behavior was determined by thermogravimetric analyses. Typical TG curves for

Figure 4. TGA curves for some SDC-Ni_{1-x}Cu_x catalysts in air (heating and cooling rate 5° min).

the carbon-containing SDC-Ni_{1-x}Cu_x catalysts recorded in air are presented on Figure 6. Actually, the mass change for each curve is a combination of two processes: carbon oxidation resulting in mass loss due to CO₂ removal and Ni_{1-x}Cu_x oxidation resulting in mass gain due to formation of Ni_{1-x}Cu_xO and Cu or Ni oxides. The curves for $x = 0.89$ and 1.0 show the highest mass gain because of low carbon content. They resemble that for pure SDC-Cu (see Figure 4). The oxidation process takes place at relatively low temperature and constant mass is obtained at $\sim 550^\circ\text{C}$. Ni-rich catalysts ($0 \leq x \leq 0.48$) contained more carbon and could be oxidized at high temperatures. The oxidation process seems to be completed at 650°C for all the samples investigated.

The data obtained from each of the thermal curves are presented in Table 1. The mass of the catalyst containing carbon (m_o) can be presented as:

$$m_0 = m_c + m_m + m_s \quad (5)$$

Figure 5. XRD patterns of SDC-Ni_{1-x}Cu_x catalysts containing deposited carbon; (*) represents the diffraction peaks of SDC.

where

m_c = mass of carbon

m_m = mass of deposited metal phase

m_s = mass of SDC support.

Metal loading can be determined from:

$$k = m_c / (m_m + m_s) \quad (6)$$

and the final (m_1) sample mass taken at 650°C can be expressed as follows:

$$m_1 = m_s + m_m / k_1 \quad (7)$$

Solving these three independent equations for m_c gives for the amount of carbon deposited, the following equation:

$$m_c = m_0 - m_1 / (1/k - 1 + 1/k_1) - m_1 k_1 / (k/1 - k) + k_1 \quad (8)$$

Figure 6. Mass loss curves in air at the heating rate 5°/min for SDC-Ni_{1-x}Cu_x catalysts containing carbon: (a) $x = 0.09$, (b) $x = 0.28$, (c) $x = 0$, (d) $x = 0.48$, (e) $x = 0.89$, (f) $x = 1$.

where

m_0 = initial mass of the catalyst containing carbon

m_1 = mass of sample taken at 650°C in air

k = metal loading, which is metal fraction in the mass of the catalyst

k_1 = ratio of molecular weights of Ni_{1-x}Cu_x and Ni_{1-x}Cu_xO

Table 1. Numerical data calculated for carbon containing SDC-Ni_{1-x}Cu_x from the TGA curves

x , mol	Metal loading, k	$M_{\text{WNiCu}}/M_{\text{WNiCuO}}$, k_1	m_0 , mg	m_1 , mg	Mass change at 650°C, %	Carbon mass, m_c , mg	Carbon content, %
0	0.52	0.7858	16.088	15.378	-4.4	2.619	16.3
0.09	0.50	0.7871	14.892	13.887	-6.8	2.660	17.9
0.28	0.52	0.7897	17.820	16.600	-6.9	3.239	18.2
0.48	0.52	0.7924	15.724	16.261	3.4	1.413	9.0
0.89	0.51	0.7977	15.360	17.021	10.8	0.288	1.9
1.0	0.51	0.7991	16.041	17.960	12.0	0.122	0.7

The metal loading can be determined from reduction curves for the completely oxidized SDC-Ni_{1-x}Cu_xO samples. Our calculation proved that carbon deposition is noticeable for Ni-rich catalysts. The TGA curves show a negative mass change in this case. The maximum amount (18.2%) of carbon is detected for SDC-Ni_{0.72}Cu_{0.28} catalyst.

CONCLUSIONS

The thermal behavior of methane cracking SDC-Ni_{1-x}Cu_x catalysts after catalytic testing was investigated by thermogravimetric analyses while heating in air and forming gas. The Ni_{1-x}Cu_xO can be reduced in the temperature range from 200°C to 550°C. The amount of carbon deposited during methane cracking was calculated for different samples from TGA curves. The deposited carbon can be removed by controlled heating in air up to 650°C. Thermogravimetry provides a rapid method for determining the amount of carbon in the catalysts and the required conditions for its gasification. This test method can be applied to evaluate catalyst behavior in catalytic reactions involving hydrocarbon conversions.

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