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Microcalorimetric study of the acidity and basicity of Ni/SiO$_2$ catalysts modified by metallic additives Fe, Co, Zr and Ce

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Abstract

The acidity and basicity of silica-supported nickel catalysts modified by metallic additives such as Fe, Co, Zr and Ce have been determined by adsorption microcalorimetry. These catalysts have been tested in the catalytic reforming of methane with carbon dioxide. The results indicate that the metallic additives modify noticeably the acidity of the Ni/SiO$_2$ catalysts, the acidity increasing in the order: Ni–Ce < Ni < Ni–Co < Ni–Fe < Ni–Zr. Moreover, it was demonstrated that the most active catalyst in the CH$_4$ + CO$_2$ reaction is the least acidic, namely, Ni–Ce/SiO$_2$. © 1997 Elsevier Science B.V.

Keywords: Ni/SiO$_2$ catalysts; Acidity; Microcalorimetry; Adsorption; Reforming of methane

1. Introduction

The reforming of methane by carbon dioxide on catalysts containing supported nickel or noble metals [1–4] is a reaction of great industrial importance. The literature data show the importance of the nickel-supported interaction in the determination of the performance of the catalysts [1–8]. The primary purpose of this study was to elucidate the role of some additives on catalyst activity and coking resistivity of supported nickel catalysts and the relationship with their acid–base properties.

For this aim, we have determined the acidic and basic properties of Ni/SiO$_2$ catalysts modified by metallic additives (Fe, Co, Zr and Ce) using adsorption microcalorimetry of probe molecules NH$_3$ for acidity, CO$_2$ and SO$_2$ for basicity. We have tried to correlate these acidic properties with the activity of these catalysts in the CH$_4$ + CO$_2$ reaction.

2. Experimental

2.1. Preparation of the catalysts

The catalysts (Table 1) were prepared by the incipient wetness impregnation method. The silica (aerosil) was impregnated by a solution of nickel nitrate and stirred for 30 min. The precursor was then dried at 110°C overnight and finally calcined at 700°C for 6 h (under air, $d = 1.2$ dm^3 h^{-1}, 5°C min^{-1}). The Ni–M/SiO$_2$ catalysts (M = Fe, Co, Zr, Ce) were obtained by a double impregnation of the Ni/SiO$_2$ catalyst by the corresponding metal nitrate. The other steps in the preparation (drying, calcination) were identical to those performed on Ni/SiO$_2$. The catalysts, omitting

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Table 1
Physicochemical characteristics of different catalysts

Catalyst	SiO_2 support	Ni	Ni–Ce	Ni–Co	Ni–Fe	Ni–Zr
Composition (wt%)	—	1.52	1.39/1.12	1.40/0.93	1.21/0.98	1.34/1.01
Surface area (m^2/g)	200	189	203	197	250	220

the support, have been named as follows: Ni/SiO_2 = Ni, Ni–Ce/SiO_2 = Ni–Ce, etc.

2.2. Characterization

The specific surface area was determined by the BET method using a Coultronics apparatus. The metallic additives increase the specific surface area of the reference catalyst Ni (189 m^2/g), mainly in the case of iron (250 m^2/g) (Table 1).

X-ray diffraction patterns were obtained using a Phillips PW 3710 apparatus. They showed the formation of a well-dispersed NiO phase. Analyses by infrared spectrometry (performed on a Brücker IFS 80 apparatus) showed identical spectra corresponding to that of SiO_2, because of the low metallic loadings of the catalysts.

2.3. Microcalorimetry

The adsorption microcalorimetry measurements have been performed in a heat-flow microcalorimeter of the Tian-Calvet type (Setaram C80) coupled to a volumetric line equipped with a Barocel gauge for the pressure measurements [9,10]. The outgassing of the samples under vacuum overnight was performed at 450°C on an independent line with a furnace. The adsorption temperature was maintained at 80°C in order to limit physisorption. The adsorption of basic (NH_3) or acidic (CO_2, SO_2) probe molecules was performed by sending successive small doses of the gases into the calorimetric cell, until a final equilibrium pressure of about 0.6 torr was reached. Both the calorimetric and the volumetric data were stored and analyzed by microcomputer processing.

2.4. Catalytic test

The catalytic tests have been performed at 600°C in a tubular quartz reactor [11], with a 0.1 g sample of the catalyst, using a reactant CO_2/CH_4 mixture (Air Liquide) in a proportion of 4/1 ($P = 1$ atm, $d = 1.3\ dm^3\ h^{-1}$).

The catalysts were prereduced under H_2 (16 h, $d = 1.3\ dm^3\ h^{-1}$) at 600°C. The reactants and products were analyzed by gas-phase chromatography using a catharometric detector and a Carbosieve B column.

3. Results and discussion

3.1. Adsorption microcalorimetry

3.1.1. NH_3 adsorption:

The differential enthalpy of ammonia adsorption was plotted as a function of coverage for various catalysts, Fig. 1. In this figure, we can see that the silica used as support displays a very weak acidity both in number and strength, but that this latter was modified in all cases by the metal additives.

In the case of Ni and Ni–Ce, the differential heats are within the same range and the curves have the same general features. The initial heat of adsorption

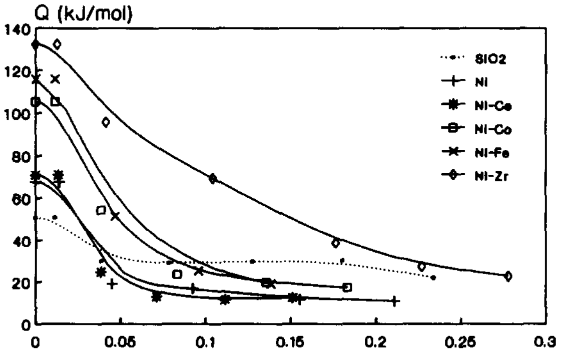

Fig. 1. Differential heats of NH_3 adsorption as a function of the adsorbed volume.

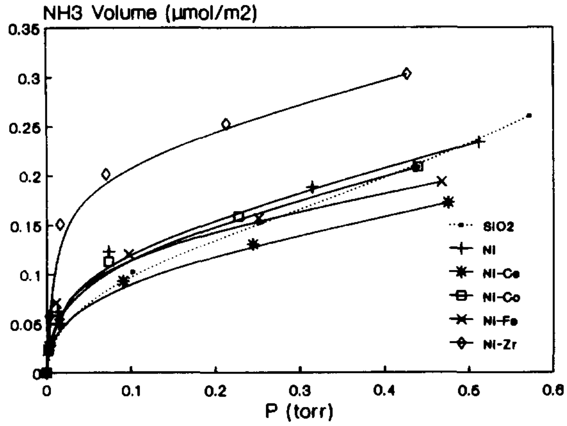

Fig. 2. Isotherms of ammonia adsorption on various catalysts.

rises from 50 to 67 kJ mol^{-1}. In the case of other samples, these initial heats are much higher: 105, 116 and 132 kJ mol^{-1} for Ni–Co, Ni–Fe and Ni–Zr, respectively. The Co, Fe and Zr additives have thus strongly modified the acidity of the Ni/SiO$_2$ catalyst. The Co and Fe additives cause similar increase in number and strength of the acid sites.

The ammonia adsorption isotherms corresponding to various catalysts are shown in Fig. 2. This figure evidences the modification in number of the acidic sites of silica caused by the additives. The addition of nickel slightly reinforces this weak acidity. The Fe or Co additives have the same effect, while the Ni–Zr catalyst displays a much higher number of acidic sites, and the Ni–Ce catalyst is undoubtedly the least acidic of all.

Table 2 presents the initial heat of adsorption (Q_{init}), the total adsorbed volume of ammonia per unit surface area under an equilibrium pressure of 0.2 torr (V_{NH_3}) and the corresponding integral heat (Q_{int}). This table shows that the total volume of adsorbed ammonia is close to that of the SiO$_2$ support in the case of Ni, Ni–Ce, Ni–Co and Ni–Fe catalysts (~0.15 µmol/m^2). In the case of Ni–Zr, this volume is much higher (0.248 µmol/m^2), and the number of strong acidic sites ($Q > 80$ kJ/mol) is strongly increased. However, the Ni–Ce sample indeed appears as the least acidic of all the studied catalysts.

In conclusion, adsorption microcalorimetry of the basic probe molecule NH$_3$ has demonstrated that all these catalysts present an acidic character, more or less pronounced. The acidity of the catalysts was found to increase in the order Ni–Ce < Ni < Ni–Co < Ni–Fe < Ni–Zr.

3.1.2. CO$_2$ and SO$_2$ adsorption

Under the experimental conditions described above ($T = 80°$C), no chemisorption of CO$_2$ or SO$_2$ was observed at the surface of various catalysts. However, a weak physisorption was observed on all samples.

3.2. Catalytic tests

Under our experimental conditions, only the Ni, Ni–Ce and Ni–Co catalysts are active (Table 3). The most active catalyst (30.2 and 61.9% conversion in CO$_2$ and CH$_4$, respectively) and the most selective ($\text{TT}_{\text{CO}} = 18.3\%$) is Ni–Ce. Cerium has thus an appreciable promoter effect. On the contrary, cobalt seems to act as inhibitor: 8.9 and 11.2% conversion for TTG(CO$_2$) and TTG(CH$_4$), respectively, in presence of Ni–Co instead of 8.6 and 16.2% with Ni only. Fe and Zr completely inhibit the reaction.

The carbon deposition, evaluated from the carbon balance, is quite low for all the studied catalysts. Table 3 indeed shows that the carbon balance is close to 100%.

Table 2
NH$_3$ adsorption microcalorimetry data at $T = 80°$C on various catalysts

Catalyst	Q_{init} (kJ/mol)	V_{NH_3} adsorbed (µmol/m^2)	Q_{int} (J/m^2 × 10^2)	N sites (µmol/m^2) $Q > 80$ kJ/mol
SiO$_2$	51	0.135	0.45	0
Ni	68	0.157	0.40	0
Ni–Ce	71	0.120	0.34	0
Ni–Co	105	0.151	0.62	0.03
Ni–Fe	116	0.145	0.68	0.04
Ni–Zr	132	0.248	1.62	0.09

Table 3
Rate of conversion in CO_2 and CH_4, amount of CO produced and carbon balance at $T = 600^\circ C$, $d = 1.3\ l\ h^{-1}$, $CO_2/CH_4 = 4$

Catalyst	Ni–Ce	Ni	Ni–Co	Ni–Fe	Ni–Zr
TTG/CO_2 (%)	30.2	8.6	8.9	0	0
TTG/CH_4 (%)	61.9	16.2	11.2	0	0
n CO × 10^2/TTCO (mol h^{-1} g^{-1}) (%)	12.1/18.3	6.8/11.5	2.6/4.7	0	0
Carbon balance X (%)	90	97	95	0	0

The global activity and CO selectivity in the $CH_4 + CO_2$ reaction have been shown to increase in the following order for our catalysts: Ni–Fe = Ni–Zr ≪ Ni–Co < Ni < Ni–Ce. It appears that the catalytic activity decreases when acidity increases. It is however difficult to ascribe the deactivation of the catalysts entirely to coke deposition.

4. Conclusion

The present work has demonstrated that metallic additives such as Fe, Co, Zr and Ce noticeably modify the acidic character of the Ni/SiO_2 catalyst as determined by ammonia adsorption microcalorimetry, the acidity increasing in the order:

$$\begin{aligned} &Ni-Ce/SiO_2 < Ni/SiO_2 < Ni-Co/SiO_2 \\ &\quad < Ni-Fe/SiO_2 < Ni-Zr/SiO_2. \end{aligned}$$

The basicity of these catalysts, measured by adsorption of CO_2 and SO_2 probe molecules, remains weak and mainly localized in the field of physisorption.

The most active catalyst in the $CH_4 + CO_2$ reaction is the least acidic sample, namely, Ni–Ce/SiO_2.

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