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Effect of the basicity created by La_2O_3 addition on the catalytic properties of $Co(O)/SiO_2$ in $CH_4 + CO_2$ reaction

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Abstract

A series of $Co(O)/SiO_2$ catalysts modified by various amounts of La_2O_3 (5, 10 or 50 wt.%) were synthesized and studied in the reaction of reforming of methane by carbon dioxide to syngas at the temperature of 873 K. The catalysts were prepared by successive incipient wetness impregnation: La_2O_3–SiO_2 supports were first prepared by impregnating silica with $La(NO_3)_3$ solutions. After drying and calcining under airflow, samples were then submitted to a second impregnation with $Co(NO_3)_2$.

The purpose of this work is to study the acid–base property of these catalysts by CO_2 adsorption calorimetry at 353 K and to look at their impact on the catalytic property. The amounts of chemisorbed CO_2 and the site strength distribution of the basic sites, i.e., the basicity, were shown to be strongly dependent on La_2O_3 content. The following order of basicity was observed: $Co(O)/5\,wt.\%La_2O_3–SiO_2 < Co(O)/10\,wt.\%La_2O_3–SiO_2 \ll Co(O)/50\,wt.\%La_2O_3–SiO_2$.

The addition of La_2O_3 to the $Co(O)/SiO_2$ reference sample revealed a very positive effect on the catalytic stability of catalysts. La_2O_3 prevented cobalt phase sintering by avoiding particle coalescence.

Keywords: Methane dry reforming; Co/silica catalyst; La_2O_3 additive

1. Introduction

A wide range of catalysts containing cobalt have been tested in the reforming of methane by carbon dioxide to syngas [1–7]:

$$CH_4 + CO_2 = 2CO + 2H_2 \quad (\Delta H_r^\circ = +247.04\,\text{kJ/mol}) \tag{1}$$

This process is of industrial interest. One of the reasons is that this reaction gives a suitable CO/H_2 ratio for the Fischer–Tropsch [8] and methanol syntheses. The possibility to convert CO_2 sources to the products with a higher added value because of their purity also remains a non-negligible advantage. However, deactivation by carbon deposition remains one of the drawbacks of this reaction via methane cracking reaction (2) or by sintering of the active phase [9]:

$$CH_4 \rightarrow C_{(s)} + 2H_2 \tag{2}$$

Zhang and Verykios [10] studied deactivation of supported nickel catalysts during dry reforming of methane. They found that CH_4 mainly cracks on the metal crystallites to form H_2 and surface carbon species, while CO_2 preferably adsorbs on La_2O_3 support in the form of $La_2O_2CO_3$.

The reinforcing of the active phase by a co-metal addition, in its oxidized form like La_2O_3, limits this deactivation by modifying the structural properties and adjusting the acid–base function of the catalyst. Direct correlation has been established between the acid–base and catalytic properties of

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the catalysts [3,11]. By adding magnesia to Co/SiO_2 catalyst, it was demonstrated that very positive effects on catalyst stability arise from the formation of Mg_2SiO_4 [3]. A bifunctional mechanism was proposed which combines the accumulation of carbonates and hydrogeno-carbonate species on the catalyst support due to a medium basicity of Mg_2SiO_4 and the reactivity of small cobalt particles for methane activation. In this work, we present the effect of the basicity created by La_2O_3 addition on the catalytic properties of Co(O)/SiO_2.

2. Experimental

2.1. Catalyst preparation

Lanthanum cobalt silica-supported catalysts were prepared by successive incipient wetness impregnation of silica (Aerosil from Degussa, BET surface area = 196 m^2/g). The support materials $x$$La_2O_3$–$SiO_2$ with x = 0, 5, 10 or 50 wt.% were prepared by impregnating silica with a solution of lanthanum nitrate salts $La(NO_3)_3 \cdot 6H_2O$. Then the samples were dried at 353 K and calcined under airflow at 773 K for 4 h prior to impregnation with a given amount of an aqueous solution of cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ (Rhone-Poulenc) leading to 5 wt.% cobalt catalysts. These solids were again dried and calcined under air at 773 K for 4 h before being ground, crushed and sieved into 100–200 μm particles. The catalysts obtained are: Co(O)/SiO_2, Co(O)/5 wt.%La_2O_3–SiO_2, Co(O)/10 wt.%La_2O_3–SiO_2 and Co(O)/50 wt.%La_2O_3–SiO_2.

2.2. Fresh catalysts characterization

The chemical analysis was performed by ICP spectrometry and the amount of lanthanum oxide is given in Table 1.

The phase analysis of fresh catalysts was determined by X-ray powder diffraction on Philips PW 1 050/81 diffractometer using Cu Kα radiation ($\lambda = 1.54184$ Å) with a voltage of 45,000 V and tube current of 35 mA over a 2θ range of 5–80°.

2.3. CO_2 adsorption microcalorimetry

The differential and integral heats of carbon dioxide adsorption were measured at 353 K in a high-temperature Tian-Calvet-type microcalorimeter (Setaram HT) linked to a volumetric adsorption system. Each sample (0.1 g) was placed in a calorimetric cell and first reduced in H_2 at 873 K overnight before being evacuated for 2 h at the same temperature and then successive small doses of CO_2 were sent onto the sample. For each dose, calorimetric peak and residual pressure are collected as a function of time. From calorimetric and volumetric data, the differential heats of adsorption versus coverage and the corresponding isotherms can be plotted [3].

2.4. Catalysts testing

The $CH_4 + CO_2$ reaction was carried out at atmospheric pressure in a 6 mm i.d. fixed-bed quartz U-tube reactor. After reduction in situ for 2 h at 873 K under hydrogen, a mixture of methane (Air Liquide, N45), carbon dioxide (Air Liquide, N48) and helium (Air Liquide) was passed through the catalyst (0.1 g). The water produced in the reaction was condensed out and the reacting gases and products were analyzed with a TCD chromatograph Intersmat using a Porapack Q column.

2.5. Carbon deposition determination

After catalytic testing, the used samples were submitted to carbon analysis and regeneration under oxygen flow.

The combustion of deposited carbon was studied using thermogravimetry coupled to differential scanning calorimetry (Setaram TG-DSC 111). The used catalyst was held in quartz cell hanged by a quartz suspension in the calorimeter. Samples were heated from room temperature to 973 K with a flow rate of 5 K/min in a mixture of 65% O_2 in helium using a flow of 23 ml/min. The weight loss and heat flow were collected and processed by microcomputer.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. XRD phase analysis of fresh catalysts

The X-rays diffraction spectra of the four samples freshly calcined are presented in Table 1 and Fig. 1. Only Co_3O_4 cubic crystalline phase is detected in unpromoted Co(O)/SiO_2 sample and Co(O)/5 and 10 wt.% La_2O_3–SiO_2 catalysts. After adding cobalt oxide to 50 wt.% La_2O_3–SiO_2, shown by curve 4, it can be seen that the 23° 2θ band, characteristic of SiO_2, disappears and the catalyst display diffraction peaks of

Table 1
Physicochemical properties of freshly catalysts

Catalyst	La_2O_3 loading (wt.%)	S_{BET} (m^2/g)	XRD phases	CO_2[a] adsorption (μmol/m^2 catalyst)
Co(O)/SiO_2	–	185	Co_3O_4, SiO_2	0
Co/5 wt.%La_2O_3–SiO_2	4.0	103	Co_3O_4, SiO_2	~0.01
Co/10 wt.%La_2O_3–SiO_2	8.7	129	Co_3O_4, SiO_2	0.04
Co/50 wt.%La_2O_3–SiO_2	44.0	49	Co_3O_4, La_2O_3	0.48

[a] Amount of adsorbed CO_2 under an equilibrium pressure of 65.8 Pa as measured by adsorption microcalorimetry.

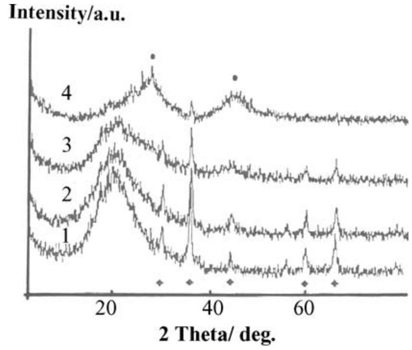

Fig. 1. XRD patterns of (1) Co(O)/SiO_2, (2) Co(O)/5 wt.%La_2O_3–SiO_2, (3) Co(O)/10 wt.%La_2O_3–SiO_2 and (4) Co(O)/50 wt.%La_2O_3–SiO_2 samples. (♦) Co_3O_4 and (●) La_2O_3.

La_2O_3 [12]. From Fig. 1, it also appears that the intensity of Co_3O_4 crystalline peaks decreases with an increase in La_2O_3 loading (5 and 10–50 wt.%). This regression results from a decrease of Co_3O_4 particle size. Therefore, the cobalt oxide is better dispersed in the presence of La_2O_3.

3.1.2. *Acid–base properties*

Surface basicity of our catalysts was studied by carbon dioxide adsorption at 353 K. The differential heats of CO_2 adsorption versus coverage are illustrated with the corresponding isotherms in Fig. 2. As can be seen, the adsorbed amount of carbon dioxide (Table 1) and the corresponding basicity are strongly dependent on La_2O_3 concentration. Co(O)/50 wt.%La_2O_3–SiO_2 sample presents a much large amount of strong strength basic sites ($70\ \text{kJ/mol} < Q < 120\ \text{kJ/mol}$) with an initial heat of adsorption of 120 kJ/mol as pointed out in Fig. 2(A) by dark triangle symbols and a total amount of adsorbed CO_2 of 0.48 μmol/m^2 (Table 1). This higher loading sample (50 wt.% La_2O_3) exhibits a second population of medium strength basic sites ($Q = 70$ kJ/mol) then a continual decrease of the strength of basic sites.

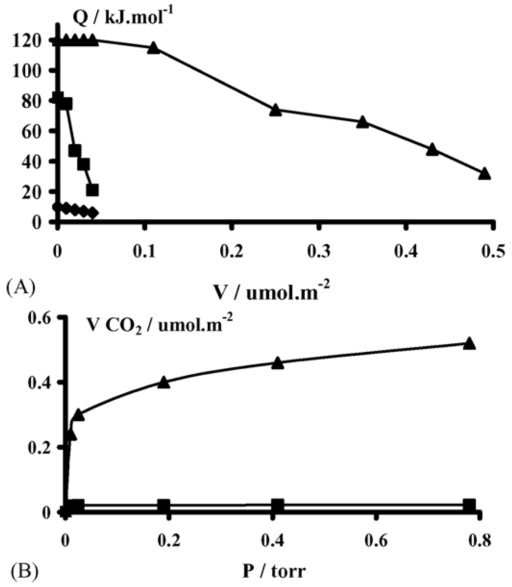

Fig. 2. Differential heats (A) and isotherms (B) of CO_2 adsorption at 353 K vs. (▲) Co/50 wt.%La_2O_3–SiO_2, (■) Co(O)/10 wt.%La_2O_3–SiO_2 and (♦) Co(O)/SiO_2.

At medium La_2O_3 content (10 wt.%, Fig. 2(A), square symbols), the basicity decreased to vanish on Co(O)/SiO_2 sample. In other words, addition of La_2O_3 tends to neutralize the weak acidity of Co/silica catalyst and modifies the distribution of the basic sites on the surface at very high La_2O_3 content. Thus, the basicity measured by CO_2 adsorption increased regularly over the range of La_2O_3 addition. It is clear from Fig. 2(B) that the number of basic sites depends mainly on the concentration of La_2O_3.

3.2. *Catalytic activity of Co(O)/x wt.%La_2O_3–SiO_2 catalysts*

The catalytic reaction behaviors for methane reforming over Co(O)/SiO_2 and modified catalysts are compared in Fig. 3 at 873 K. The catalytic activity is given, as percentage, in terms of CO_2 and CH_4 conversions. The conversions of methane and carbon dioxide are expressed as the ratio of the number of moles converted to the number of moles present initially in the feed. The proportions of the various gases in the reactant feed being $CH_4/CO_2/He = 10/10/80\%$. In all cases, 100 mg of catalyst was introduced in a quartz tube, and the reactant mixture flow was fixed at 22 ml/min. Fig. 3 indicates that associating La_2O_3 to Co(O)/SiO_2 ostensibly modifies its activity and stability. The activity of the Co(O)/SiO_2 catalyst is completely lost after 3 h of reaction time. Co(O)/5 wt.%La_2O_3–SiO_2 and Co/10 wt.%La_2O_3–SiO_2 display rather close initial activities, but after 5 h of reaction time, a higher deactivation rate is observed for Co/5 wt.%La_2O_3–SiO_2. On the contrary, the initial conversion of CH_4 (△ symbol in Fig. 3) and CO_2 (▲ symbol in Fig. 3) of the catalyst with high La_2O_3 loading are preserved over time under these conditions. While the reference

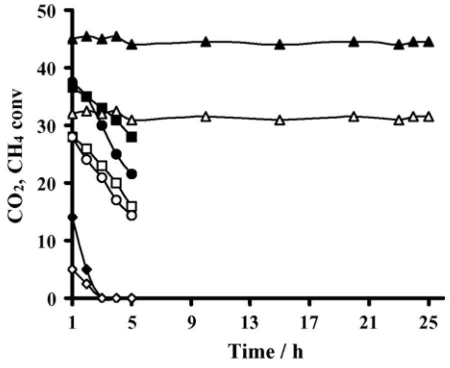

Fig. 3. Influence of time of reaction on CO_2 and CH_4 conversions: filled symbols – CO_2. (▲, △) Co(O)/50 wt.%La_2O_3–SiO_2; (■, □) Co(O)/10 wt.%La_2O_3–SiO_2; (●, ○) Co(O)/5 wt.%La_2O_3–SiO_2 and (♦, ◊) Co(O)/SiO_2 catalysts. Reaction conditions: $T = 873$ K, $P = 1$ atmosphere and $CH_4/CO_2/He = 10/10/80\%$.

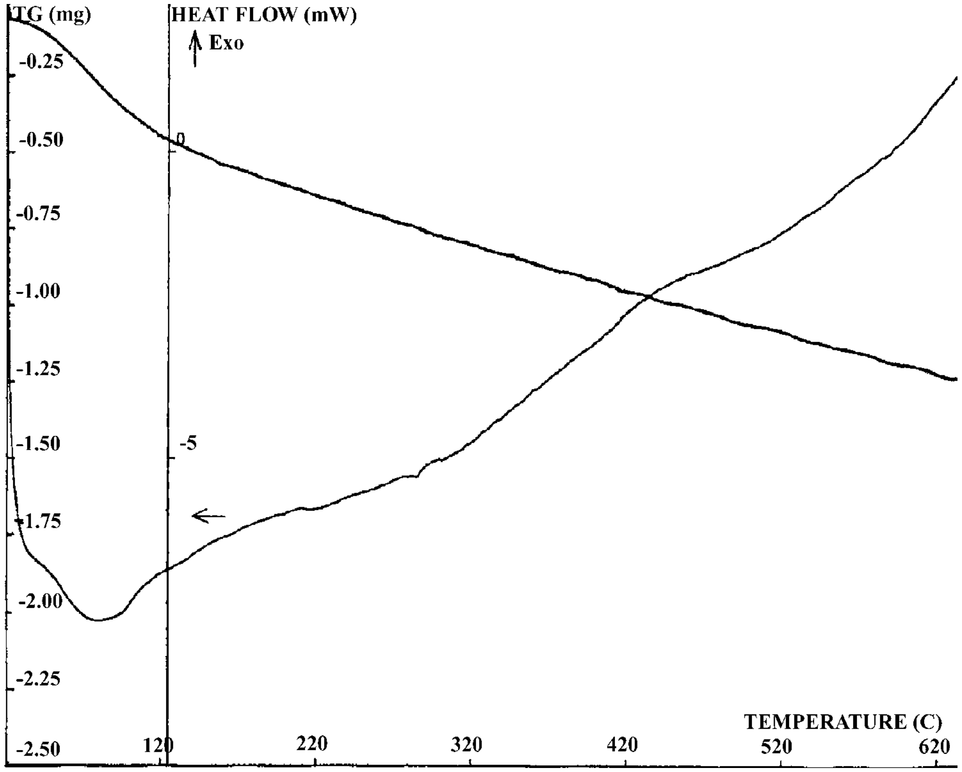

Fig. 4. TG and heat flow profiles of Co(O)/5 wt.%La_2O_3–SiO_2 sample after use for 25 h. Reaction conditions: $T = 873$ K, $P = 1$ atmosphere and $CH_4/CO_2/He = 10/10/80\%$.

cobalt catalyst showed slightly improved activity compared to the low and medium La_2O_3 contents (after 5 and 10 wt.% La_2O_3 addition), this catalyst exhibited poor resistance to carbon deposition. An important amount of carbon (0.41 wt.%) was detected by chemical analysis of carbon [3] while only traces of carbon were observed on the La_2O_3-doped samples.

So catalyst deactivation cannot be ascribed to coke deposition in the case of low to medium La_2O_3 contents, as confirmed by DSC–TG (differential scanning calorimetry coupled with thermogravimetry) study of the used catalysts (after 25 h reaction time), where no weight loss due to carbon combustion could be detected. The results of this experiment are given in Fig. 4 for the Co(O)/5 wt.%La_2O_3–SiO_2 used catalyst. The change in the weight as a function of temperature can be assigned only to a water loss. This resistance to coking has been obtained by adding MgO to cobalt catalysts [2,11] and also by adding La_2O_3 [13] or cerium oxide [14] to nickel catalysts. As a consequence, the aging of the catalysts is caused by the collapse of the metallic phase in the catalysts with low La_2O_3 loading.

From the above results, it can be deduced that there exists a direct relationship between basicity and activity since basicity was shown to increase regularly over the range of La_2O_3–Co/silica active samples. As a matter of fact, for high La_2O_3 concentration, a strong basicity was measured, which corresponded to the most active catalyst. So, lanthanum oxide addition adjusts the acid function of the unpromoted catalyst, which is the main responsible of carbon formation [3] and presents a beneficial effect on activity and catalytic stability by avoiding carbon deposition on the surface of catalyst.

On the other hand, in the case of the highly La_2O_3 loaded sample, Co(O)/50 wt.%La_2O_3–SiO_2, diffraction peaks of La_2O_3 were observed (Fig. 1, curve 4). This result indicates that for this tuned amount of La_2O_3 additive, the formation of La_2O_3 phase promotes the formation of well-dispersed cobalt particles and prevents their sintering under our reacting conditions.

4. Conclusion

The deactivation of cobalt-based catalysts deposited on silica and modified by La_2O_3 in the dry reforming of methane at 873 K is caused by sintering of the metallic cobalt particles. This phenomenon is compensated by the introduction of a high content of lanthanum oxide. By adding La_2O_3 to Co(O)/SiO_2 sample, it was observed that the very positive effects on catalytic stability of catalysts arise from the formation of La_2O_3 crystalline phase. This La_2O_3 phase prevents cobalt phase sintering by avoiding particle coalescence.

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