

# Performance of Co/MgO catalyst for CO<sub>2</sub> reforming of toluene as a model compound of tar derived from biomass gasification

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## Abstract

Catalytic performances of the CO<sub>2</sub> reforming of toluene on Co/MgO catalysts with different cobalt loadings were evaluated in a fluidized-bed reactor. The results showed that the conversion of toluene and the stability of Co/MgO increased, but the apparent reaction rate decreased at the initial stage with increasing the amount of metallic Co formed from the reduction of Co/MgO catalysts at 700 °C. The deactivation of Co/MgO catalysts was mainly resulted from that a part of the metallic Co was oxidized by CO<sub>2</sub> and could not be re-reduced by H<sub>2</sub> at reaction temperature. Therefore, the excess metallic Co on the higher Co loading catalysts was beneficial to the catalyst stability.

## Key words

cobalt catalyst; magnesia; carbon dioxide reforming; toluene; biomass; tar

## 1. Introduction

It is well known that biomass is one of the important primary and renewable energy sources, and its gasification to produce syngas has been regarded as one of the most promising options for biomass utilization [1,2]. Generally, syngas can be used in gas turbine for power generation, and converted into methanol, dimethyl ether, Fischer-Tropsch oils or other chemical products. However, the syngas produced from biomass cannot be directly used in these downstream applications due to the presence of tar, which is recognized as a byproduct from biomass gasification [3]. Such a kind of tar, being comprised of a large amount of aromatic compounds, will cause many severe problems, such as blocking transportation systems and equipments, as well as heavy coking of catalysts [2,4]. And moreover, tar is very dangerous because of its carcinogenic character [2].

To eliminate and/or transform tar in fuel gas, many research works have been done and the steam reforming of tar to produce H<sub>2</sub>-rich syngas over Ni-based catalysts has received much attention around the world [5]. Since steam has been widely used as the gasification agent [6] and Ni-based catalysts are commercially available for the reforming of naphtha, it is expected that the steam reforming over Ni-based catalysts may be effective for the reforming of tar and/or its

corresponding model compounds [7,8]. Besides the Ni-based catalysts, supported Co catalysts have been utilized for the steam reforming of tar. Furusawa et al. [9,10] found that 12 wt% Co/MgO catalyst calcined at 600 °C demonstrated the best performance (conv. 23%, 3 h) for the steam reforming of naphthalene. Wang et al. [11] found that 12 wt% Co/Al<sub>2</sub>O<sub>3</sub> showed higher activity and higher resistance to coke deposition than 12 wt% Ni/Al<sub>2</sub>O<sub>3</sub> in the steam reforming of toluene.

Actually, the concentration of CO<sub>2</sub> in the raw syngas produced from biomass gasification is in the range between 10 to 30 vol%, depending on the gasification conditions [12,13]. Therefore, the carbon dioxide reforming of tar would be a better choice than the steam reforming of tar for improving the effective conversion of carbon, the reduction of carbon dioxide emission, as well as the avoidance of extra energy consumption for introducing steam. In our previous work [14], the catalytic performance of Ni/MgO catalyst was compared with those of Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/ZrO<sub>2</sub> and Ni/SiO<sub>2</sub> catalysts for the CO<sub>2</sub> reforming of toluene, and it was found that Ni/MgO was the best one among the tested catalysts with the toluene conversion of 85% at 600 °C and much better stability.

In this work, Co/MgO catalysts with different amounts of Co loading were prepared and used to evaluate their catalytic performances for the carbon dioxide reforming of toluene which was taken as a model compound of tar. The catalysts

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were characterized by XRD and TPR to study the effect of different Co loading amounts on the catalytic performances. To our knowledge, Co-based catalysts have never been studied in regard to the catalytic performance for the carbon dioxide reforming of tar.

## 2. Experimental

### 2.1. Catalyst preparation

Co/MgO catalysts with different Co loadings were prepared by impregnation method. MgO powders (Shanghai Chemicals, AR,  $S_{\text{BET}} = 34 \text{ m}^2/\text{g}$ ) were impregnated with an aqueous solution of  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Shanghai Chemicals, AR) at room temperature for 12 h, then dried at  $120^\circ\text{C}$  for 6 h, finally calcined at  $700^\circ\text{C}$  in air for 6 h. Co/MgO catalysts with different Co loading amounts were denoted as  $\text{Co}(x)/\text{MgO}$ , where  $x$  is the weight percentage (wt%) of Co loading.

### 2.2. Characterization

The crystalline phases of the catalyst were examined by powder X-ray diffraction system (Rigaku, D/MAX 2500/PC) using  $\text{Cu } K_\alpha$  radiation operated at 45 kV and 40 mA. Diffraction data were recorded using continuous scanning with a step of  $0.05^\circ/\text{s}$ .

The reducibility of the catalyst was characterized by temperature-programmed reduction with  $\text{H}_2$  ( $\text{H}_2$ -TPR). Catalyst (100 mg, 0.3–0.45 mm) was pretreated at  $500^\circ\text{C}$  in  $\text{N}_2$  flow (40 mL/min) for 30 min in a straight quartz reactor, cooled to  $100^\circ\text{C}$  and then shifted to 5%  $\text{H}_2/\text{N}_2$  flow (30 mL/min). The  $\text{H}_2$  consumption was recorded continuously as a function of the reduction temperature by a thermal conductivity detector (TCD). The amount of  $\text{H}_2$  consumption was calibrated by reducing a precisely weighed CuO sample. In all  $\text{H}_2$ -TPR experiments, the temperature was programmed up to 570, 700 or  $800^\circ\text{C}$ , respectively, with a heating rate of  $10^\circ\text{C}/\text{min}$  and maintained at the desired temperature until no  $\text{H}_2$  consumption could be detected.

$\text{H}_2$  chemisorption for quantification of metallic Co sites was measured with a Micromeritics AutoChem 2920 instrument. The catalyst (500 mg) was reduced at  $700^\circ\text{C}$  for 1 h under 10%  $\text{H}_2/\text{Ar}$  stream. After the reduction, the reduced catalyst was purged at  $700^\circ\text{C}$  for 20 min and cooled to  $40^\circ\text{C}$  with Ar (99.995%), then 10%  $\text{H}_2/\text{Ar}$  was pulsed (0.275 mL per pulse) over the catalyst until no further adsorption of  $\text{H}_2$  was detected.

The amount of carbon deposited on the used catalyst was measured by thermogravimetric analysis (TGA) with a controller of Perkin-Elmer, TAC 7/DX. The used catalyst was pretreated at  $500^\circ\text{C}$  under Ar flow (40 mL/min) for 30 min to remove adsorbed species, cooled to  $100^\circ\text{C}$  and then heated from  $100^\circ\text{C}$  to  $800^\circ\text{C}$  under 20%  $\text{O}_2/\text{Ar}$  flow (50 mL/min) with a heating rate of  $10^\circ\text{C}/\text{min}$ .

### 2.3. Evaluation of catalytic activity

The carbon dioxide reforming of toluene was carried out in a quartz fluidized-bed reactor (i.d. = 9.8 mm) at atmospheric pressure. Catalyst (0.5 mL, 0.3–0.45 mm) was initially reduced in  $\text{H}_2$  flow at  $700^\circ\text{C}$  for 1 h and then cooled to  $570^\circ\text{C}$  for the reforming reaction. During the reaction, liquid toluene was supplied with a rate of 0.3 mL/h by an HPLC pump (ASI, 501) to a constant temperature evaporator ( $120^\circ\text{C}$ ), where the gas mixture of 285 mL/min argon (balance gas) and 14.5 mL/min  $\text{CO}_2$  controlled by mass flowmeters (Brooks, 5850E) was also supplied.

The effluent gases from the reactor were analyzed using an on-line gas chromatograph (Agilent, GC-6820) equipped with a TDX-101 column and a thermal conductivity detector (TCD) to analyze  $\text{H}_2$ , CO,  $\text{CH}_4$  and  $\text{CO}_2$ . Simultaneously, toluene and other aromatic products were determined by a flame ionization detector (FID) with a HP-5 capillary column. The conversion of toluene ( $X_t$ ) and the content ( $P_i$ ) of CO,  $\text{CO}_2$  and  $\text{H}_2$  were calculated as follows:

$$X_t (\%) = (C_{t,\text{in}} - C_{t,\text{out}}) \times 100\% / C_{t,\text{in}} \quad (1)$$

$$P_i (\%) = C_{i,\text{out}} \times 100\% / C_{p,\text{out}} \quad (2)$$

where  $C_{t,\text{in}}$  and  $C_{t,\text{out}}$  are toluene mole of the inlet and outlet gases, respectively.  $C_{i,\text{out}}$  is the mole of gas out of reactor ( $i = \text{CO}, \text{H}_2$  or  $\text{CO}_2$ ), and  $C_{p,\text{out}}$  is the total mole of products out of reactor in which Ar was not included.

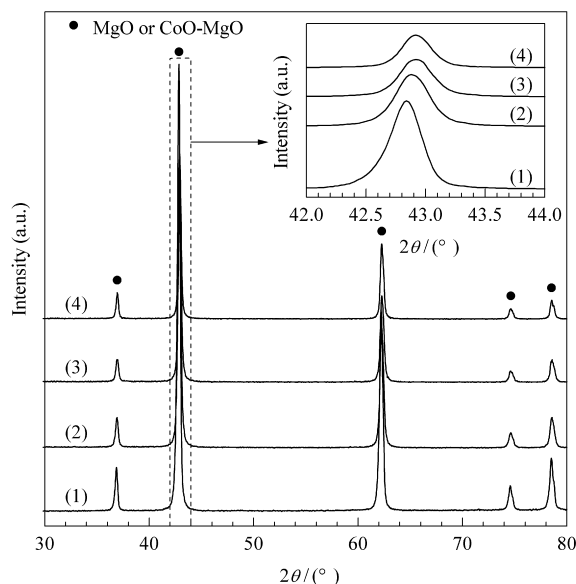
## 3. Results and discussion

### 3.1. The characterization of Co/MgO catalysts

Figure 1 shows the XRD patterns of Co/MgO catalysts with different Co loadings. For pure MgO support, five major peaks at  $2\theta = 36.9^\circ, 42.8^\circ, 62.3^\circ, 74.6^\circ$  and  $78.5^\circ$  were identified as the typical face-centered cubic crystallography of MgO. As Co was supported on MgO, no diffraction peaks corresponding to cobalt oxides could be detected by XRD, but the diffraction peaks corresponding to MgO shifted to higher angles on Co/MgO catalysts. The magnified XRD patterns for the (2 0 0) plane of MgO as a demonstration (as inserted in Figure 1) clearly showed that the deviation increased with increasing the Co loadings, and the lattice parameters ( $a$ ) of the (2 0 0) plane changed from 0.4211 nm in pure MgO to 0.4209 nm in Co(5)/MgO and 0.4208 nm in Co(9)/MgO, implying that the interaction between cobalt and MgO formed new cobalt-containing compounds, such as  $\text{MgCo}_2\text{O}_4$  and CoO-MgO solid solution [15]. It is difficult to differentiate  $\text{MgCo}_2\text{O}_4$  and CoO-MgO solid solution by XRD due to the fact that the diffraction peaks of them are very close to each other [16], but these two compounds and cobalt oxides could be characterized by TPR.

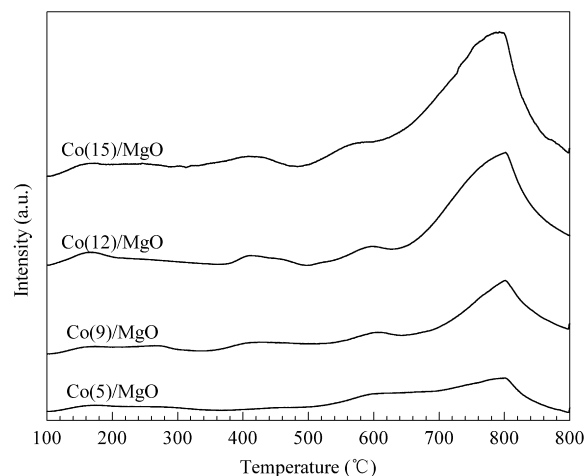
$\text{H}_2$ -TPR profiles of the Co/MgO catalysts with different Co loadings are presented in Figure 2. As far as Co/MgO catalysts are concerned, many literatures reported that  $\text{Co}_3\text{O}_4$  can

be reduced below 500 °C, while  $\text{MgCo}_2\text{O}_4$  can be reduced below 700 °C. However, the reduction of  $\text{CoO-MgO}$  solid solution requires a temperature higher than 800 °C [16–20]. Therefore, the peak ranging from 350 °C to 500 °C corresponded to the reduction of  $\text{Co}_3\text{O}_4$ , and the peak ranging from 500 °C to 650 °C could be assigned to the reduction of  $\text{MgCo}_2\text{O}_4$ . The peak ranging from 650 °C to 800 °C, which was formed by maintaining the temperature at 800 °C, was related to the incomplete reduction of  $\text{CoO-MgO}$  solid solution.



**Figure 1.** XRD patterns of Co/MgO catalysts with different Co loadings. (1) MgO, (2) Co(5)/MgO, (3) Co(9)/MgO, (4) Co(15)/MgO

The reduction degrees of the different catalysts reduced at 570 °C (note that it is the reaction temperature) and 700 °C (note that it is the pre-reduction temperature before the reforming reaction), respectively, were calculated. Table 1 lists that the reduction degrees of Co species over all Co/MgO catalysts were below 3% and 5% at 570 °C and 700 °C, respectively, indicating that most of cobalt in Co/MgO catalysts was present in the form of  $\text{CoO-MgO}$  solid solution, while less of cobalt existed as the cobalt oxides and  $\text{MgCo}_2\text{O}_4$ . The amount of these Co species increased with increasing the Co loadings from TPR results, but the cobalt oxides and  $\text{MgCo}_2\text{O}_4$  phases were not detected by XRD due to their high dispersion.



**Figure 2.** TPR profiles of calcined Co/MgO catalysts with different Co loadings

**Table 1.** Data calculated from TPR profiles of calcined Co/MgO catalysts with different Co loadings

Co loading (wt%)	The amount of reduced Co <sup>a</sup> ( $\mu\text{mol/g}_{\text{cat}}$ )		Reduction degree <sup>a</sup> (%)		Dispersion of metallic Co <sup>b</sup> (%)
	570 °C	700 °C	570 °C	700 °C	
5	11.8	32.7	1.4	3.9	23.7
9	21.7	56.2	1.4	3.7	20.1
12	35.2	84.9	1.7	4.2	17.6
15	56.7	115.7	2.3	4.6	16.2

<sup>a</sup> Ratio of the metallic Co amount estimated from TPR results to the Co loadings;

<sup>b</sup> The ratio of the amount of the metallic Co from  $\text{H}_2$  chemisorption results to the amount of the metallic Co from TPR results over the catalyst reduced at 700 °C

### 3.2. Catalytic performance of Co/MgO catalysts

Catalytic performances of Co/MgO catalysts reduced at 700 °C for the  $\text{CO}_2$  reforming of toluene are listed in Table 2.

The reaction products obtained were  $\text{H}_2$  and CO, and hydrocarbons such as alkane, benzene and so on, were not detected within the detection limit. Table 2 shows that the toluene conversion of Co(5)/MgO catalyst was about 90% at the initial stage (0.5 h), and it increased with the amount of Co loading.

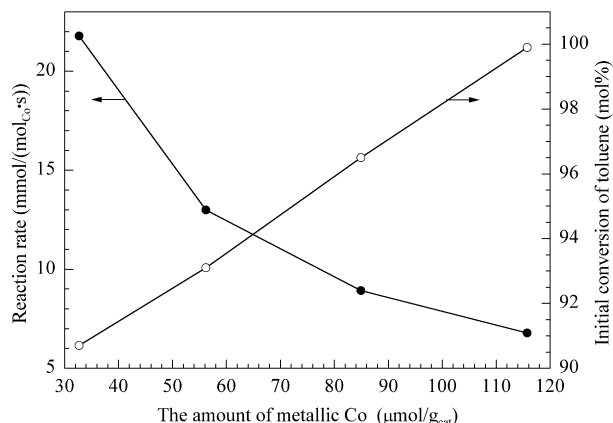
**Table 2.** Catalytic performance of Co/MgO catalysts with different Co loadings

Co loadings (wt%)	Conversion of toluene <sup>a</sup> (mol%)	Ratio of $\text{CO}/\text{H}_2$ in products <sup>a</sup> (mol)	Stability <sup>b</sup> (%)	Coke amount (wt%)
5	90.7	3.26	0	0.3
9	93.1	3.25	43.1	—
12	96.5	3.20	78.3	—
15	99.9	3.36	93.5	0.4

<sup>a</sup> The conversion of toluene and the ratio of  $\text{CO}/\text{H}_2$  in products at 0.5 h on stream;

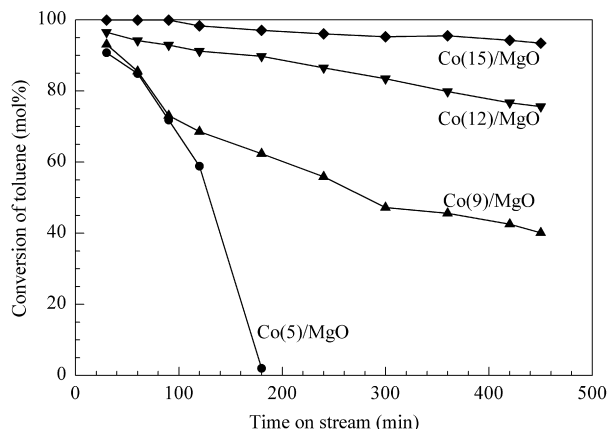
<sup>b</sup> The ratio between the toluene conversion at 7 h and that at 0.5 h on stream

Figure 3 shows a positive linear correlation between the initial conversion of toluene and the amount of metallic Co over the Co/MgO catalysts reduced at 700 °C, suggesting that the metallic Co species from the reduction of cobalt oxides and  $\text{MgCo}_2\text{O}_4$  under 700 °C were the active sites for the reforming reaction at the initial stage. However, a negative correlation between the initial reaction rate and the amount of metallic Co was also observed (Figure 3), implying that not all the metallic Co participated in the catalytic reaction at the initial stage over the Co/MgO catalysts with higher Co loading.



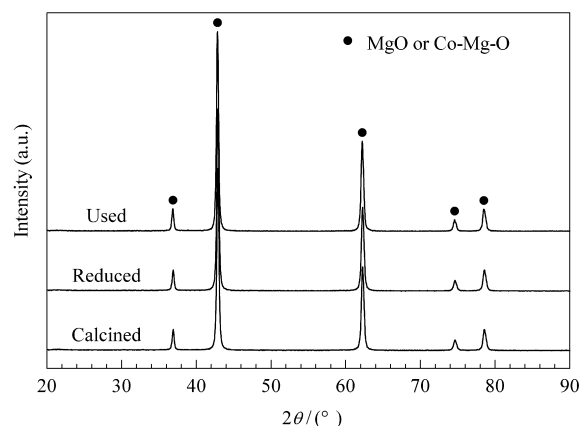
**Figure 3.** Dependences of reaction rate and the initial conversion of toluene on the amount of metallic Co over Co/MgO catalysts reduced by  $\text{H}_2$  at 700 °C for 1 h

Figure 4 shows the stability of the catalysts increased with the Co loadings. Co(5)/MgO catalyst showed rapid deactivation during 3 h on stream, and the conversion of toluene decreased from 90.7% in the initial stage to about zero. Co(15)/MgO catalyst exhibited the smallest decrement of toluene conversion during 7.5 h on stream. The stabilities of Co/MgO catalysts were in the following consequence, i.e., Co(15)/MgO > Co(12)/MgO > Co(9)/MgO > Co(5)/MgO, implying that the excess metallic Co over the higher Co loading catalysts was beneficial to the catalyst stability.



**Figure 4.** Dependence of toluene conversion on time on stream over Co/MgO catalysts. Reaction conditions: 570 °C, 0.005 mL/min toluene, 14.5 mL/min  $\text{CO}_2$ , GHSV =  $36000 \text{ h}^{-1}$ , Ar as the balance gas

Generally, the deactivation of the non-noble metal catalyst for the carbon dioxide reforming of hydrocarbon can be attributed to the carbon deposition, the sintering of metallic particles and the catalyst structure change. Table 2 shows the amount of carbon deposition on the used Co/MgO catalysts measured by  $\text{O}_2$ -TGA was so little to be neglected, suggesting that the carbon deposition was not the reason for their deactivation. Table 1 shows that the dispersion degree of the reduced Co/MgO catalysts decreased with the increasing of Co loadings, and the metallic Co phase could not be detected on all Co/MgO catalysts, even for the Co(15)/MgO catalyst after reduction and reaction by XRD (not shown here), implying that the metallic Co was in high dispersion state. On the other hand, if we supposed that the deactivation of Co(5)/MgO catalyst was caused by the sintering of metallic Co particles, the reduced Co(15)/MgO catalyst should be sintered rapidly due to that it had much more amount of metallic Co than the reduced Co(5)/MgO catalyst (Table 1). In fact, Co(15)/MgO catalyst was much more stable, implying that the deactivation of Co(5)/MgO catalyst was not caused by the sintering of metallic Co particles. Figure 5 shows that the XRD pattern of Co(5)/MgO catalyst after the  $\text{CO}_2$  reforming of toluene was almost the same as it was after reduction, and both MgO and CoO-MgO solid solution phases could be detected in the patterns.



**Figure 5.** XRD patterns of different Co(5)/MgO catalyst samples

The catalytic behavior of the deactivated Co(5)/MgO catalyst after re-reduction in situ by  $\text{H}_2$  at 700 °C for 30 min was tested again for the reforming reaction. Figure 6 shows that the activity was restored, but lost within 3 h on stream. Carrying out this process for several cycles, the similar phenomenon could be repeated and only about 4% of the initial conversion of toluene was lost from 92.7% to 89.1% during four cycles. It suggests that the basic structure of the used Co(5)/MgO catalyst was not changed distinctly during the reaction, and the sintering of metallic Co particles did not happen. We speculate that metallic Co over Co(5)/MgO catalyst might be oxidized by  $\text{CO}_2$ , and some oxidized Co species could not be re-reduced to the metallic Co by  $\text{H}_2$  and/or CO during the reforming process at the reaction temperature. Wang et al. [20] reported that the number of metallic sites was too small

and most of them were oxidized by  $\text{CO}_2$  for  $\text{CO}_2$  reforming of  $\text{CH}_4$  over Co/MgO catalysts, and thus, the system became catalytically less active.

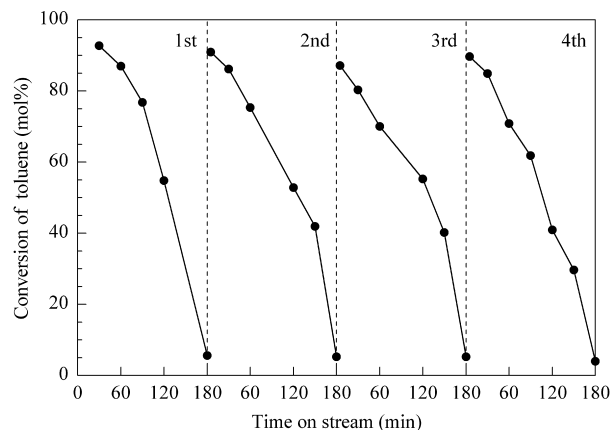
In order to prove the above speculation, the reduction behaviors of Co(5)/MgO and Co(15)/MgO catalysts after reduction at  $700^\circ\text{C}$  then oxidation by  $\text{CO}_2$  at  $570^\circ\text{C}$  for 0.5 h were examined. Figure 7 shows the cycle TPR profiles, where Figure 7(1) is the first cycle and Figure 7(2) is the second cycle. For Co(5)/MgO catalyst, the cycle TPR profile displayed the reduction of cobalt oxides at the temperature below  $500^\circ\text{C}$  and the reduction of  $\text{MgCo}_2\text{O}_4$  at the temperature from  $500^\circ\text{C}$  to  $650^\circ\text{C}$ , confirming that the metallic Co species were oxidized by  $\text{CO}_2$  under the reaction temperature of  $570^\circ\text{C}$ . The relative ratio of  $\text{H}_2$  consumption in the second cycle to that in the first cycle was 0.92, and the area of total reduction peak for the cobalt oxides decreased while for  $\text{MgCo}_2\text{O}_4$  increased, indicating that the amount of the reducible Co species decreased under the reaction temperature.

Comparing with the TPR result of the fresh Co(5)/MgO catalyst (Figure 2), the peaks at the temperature range from  $200^\circ\text{C}$  to  $500^\circ\text{C}$  associated to different particle sizes of  $\text{Co}_3\text{O}_4$  [19] were observed clearly in cycle TPR profile of Co(5)/MgO catalyst; and the relative ratio of  $\text{H}_2$  consumption from the first oxidized catalyst to that from the fresh catalyst was 1.83. It means that the metallic Co sites from a part of CoO-MgO solid solution as well as from the cobalt oxides and  $\text{MgCo}_2\text{O}_4$  were oxidized by  $\text{CO}_2$ , and the oxidized Co sites formed redistributed and/or diffused into the MgO support [21].

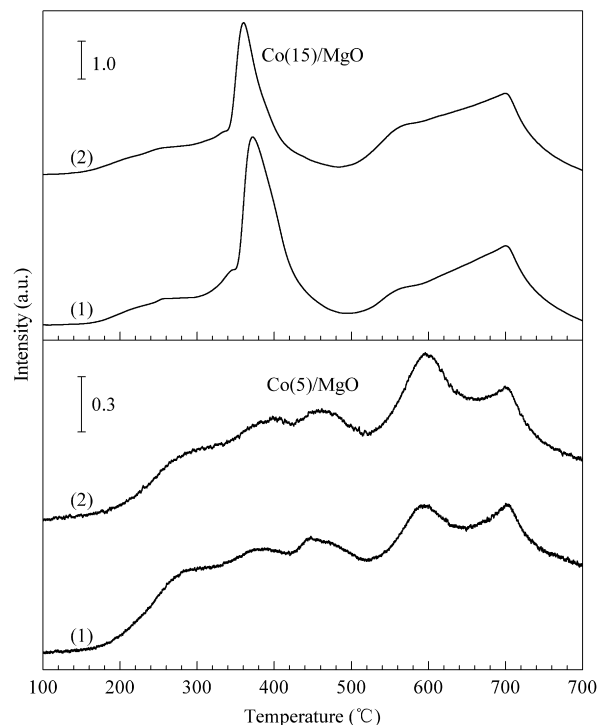
A similar phenomenon was also observed over Co(15)/MgO catalyst, but Co(15)/MgO catalyst was more stable in the activity. Perhaps, the amount of the excess metallic Co on the Co/MgO catalysts reduced at  $570^\circ\text{C}$  increased with the increase of Co loadings. It is partially supported by a sharp peak with more intensity for the reduction of cobalt oxides over Co(15)/MgO catalyst in the cycle TPR profiles.

In addition, the catalyst is circulated continuously between the bottom zone and the upper zone in the fluidized bed from time by time. Actually, the bottom zone was an oxidative atmosphere region, since toluene and  $\text{CO}_2$  were supplied from the bottom of the reactor with a larger amount of  $\text{CO}_2$ . In this oxidative region, metallic Co catalyzed the reforming reaction; at the same time, some of them might be oxidized to cobalt oxides by  $\text{CO}_2$ . The upper zone was a reductive atmosphere region, where  $\text{H}_2$  and CO were produced at the expense of  $\text{CO}_2$  consumed. In this reductive region, some kinds of the oxidized metallic Co could be re-reduced by  $\text{H}_2$  and/or CO. If such oxidation-reduction cycle went successfully on at the reaction temperature, the catalyst could maintain its efficient activity. However, the used Co(5)/MgO re-reduced at  $570^\circ\text{C}$  had a poor activity, while re-reduced at  $700^\circ\text{C}$  restored its activity as shown in Figure 6, revealing that the oxidation-reduction cycle on the Co(5)/MgO was unsuccessfully at the reaction temperature. With the amount of Co loading increasing, Table 1 shows that the amount of metallic Co from the reduced catalysts at the reaction temperature increased. For example, the amount of metallic Co over Co(12)/MgO reduced

at  $570^\circ\text{C}$  ( $35.2 \mu\text{mol/g}_{\text{cat}}$ ) can match with that of Co(5)/MgO reduced under  $700^\circ\text{C}$  ( $32.7 \mu\text{mol/g}_{\text{cat}}$ ). The excess active Co species were responsible for a stable high catalytic performance. In addition, more  $\text{H}_2$  and CO produced with the increasing Co loading, which were beneficial to the reduction of cobalt species in the upper zone of the fluidized bed.



**Figure 6.** Cyclic activity of the Co(5)/MgO catalyst. In each cycle, the deactivation catalyst was reduced in situ by  $\text{H}_2$  at  $700^\circ\text{C}$  for 0.5 h, and then the reforming reaction was carried out at  $570^\circ\text{C}$ .



**Figure 7.** The cyclic TPR profiles of Co(5)/MgO and Co(15)/MgO catalysts. (1) The catalyst oxidized by  $\text{CO}_2$  at  $570^\circ\text{C}$  for 0.5 h after the fresh catalyst reduced at  $700^\circ\text{C}$ , (2) the catalyst re-oxidized by  $\text{CO}_2$  at  $570^\circ\text{C}$  for 0.5 h after process (1)

#### 4. Conclusions

The catalytic performances of Co/MgO catalysts for  $\text{CO}_2$

reforming of toluene were investigated. The activity and stability of Co/MgO catalysts increased with the amount of Co loading. The catalyst characterization results showed that the CoO-MgO solid solution could not be reduced and was inactive for the reforming reaction, while the metallic Co formed from the reduction of cobalt oxides and  $\text{MgCo}_2\text{O}_4$  was responsible for the initial catalyst activity of  $\text{CO}_2$  reforming of toluene.

Moreover, the initial activity was linearly related to the amount of metallic Co formed from the catalysts reduced at  $700^\circ\text{C}$ , while the stability was closely related with the amount of metallic Co formed from the catalysts reduced at the reaction temperature. The deactivation of Co/MgO catalysts was mainly caused by that a part of the metallic Co was oxidized by  $\text{CO}_2$  which could not be re-reduced by  $\text{H}_2$  and/or CO at the reaction temperature.

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