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The impact of ruthenium, lanthanum and activation conditions on the methanation activity of alumina-supported cobalt catalysts

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ABSTRACT

The influence of catalyst activation conditions and the presence of promoters (La, Ru) on the performance of γ-alumina-supported Co catalysts for the methanation reaction has been investigated. Physicochemical properties, Co crystallite size and the extent of Co_3O_4 reduction to metallic Co for both the monometallic and promoted catalysts were evaluated. Combined La and Ru addition produced the greatest activity improvement for converting carbon monoxide (CO) and hydrogen (H_2) to methane. Reduction conditions used to activate the catalyst were also found to have a direct influence on methanation activity. Maintaining the catalyst at 400 °C for 10 h during reduction enhanced catalyst activity, as well as increasing the H_2 concentration in the reducing gas stream. Characterisation of the reduced catalysts demonstrated that the extent of Co-oxide reduction to Co metal was the key to the improved methanation activity.

1. Introduction

Catalytic methanation has received considerable attention since Sabatier and Senderens first discovered the reaction of carbon monoxide and hydrogen over a nickel catalyst in 1902 [1]. Methanation is widely used both to produce methane and to remove traces of CO from inlet feed streams e.g. in ammonia synthesis plants where the CO is a catalyst poison. Many studies and extended reviews have been published on the Ni-based alumina supported system which is the traditional catalyst for methanation [2–7]. Numerous supported catalysts of group VIII metals (such as Co, Ru, Fe and Rh) have also been studied [8–14]. Co-based catalysts are known to be more active than the Ni catalysts although they are also more expensive. Consequently they have not received as much attention. Studies have shown that Co in its reduced state is more active and enhances methanation activity: this has been explained in terms of the presence of cobalt monocrystals and polycrystalline cobalt [10–12]. The addition of different promoters such as rare earth oxide metals and noble metals are believed to enhance the dispersion of Co metal as well as the reducibility of Co_3O_4 to metallic cobalt. It has been reported that La^{3+} promotes the formation of new active sites and enhances cobalt dispersion [15,16] while Ru has been suggested to increase the degree of Co reduction and thus to improve catalytic activity [17–19].

This work investigates the influence of promoters (La and Ru) on the methanation activity of γ-alumina-supported Co catalysts. The importance of conditions used during catalyst activation (reduction) was also studied with the aim of improving catalyst performance.

2. Experimental

2.1. Catalyst preparation

γ-Alumina (Norton type SA6176, 60–71 μm diameter, surface area = 234 m^2/g) was used as the catalyst support and coated with cobalt and lanthanum and/or ruthenium salts using conventional incipient wetness impregnation. Cobalt (20 wt%) was loaded onto γ-alumina using an aqueous solution of cobalt nitrate (Sigma Aldrich, 98+%). Promotion with lanthanum (1 wt%) and/or ruthenium (0.43 wt%) was performed either by co-impregnation of all components or by sequential addition of solutions of lanthanum nitrate (Aldrich, 99.99%) and ruthenium nitrosyl nitrate (Aldrich, 1.5% Ru) precursors. During the sequential addition process the catalyst was calcined at 400 °C for 8 h between each stage. Catalyst impregnation was performed at a constant pH of 2 via the addition of 3 M nitric acid under constant stirring. After the required components had been loaded onto the γ-alumina the slurry was dried for 12 h in an oven at 120 °C. The resulting solid was calcined at 400 °C for 8 h.

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2.2. Catalyst characterisation

2.2.1. Surface area and pore size distribution

BET surface area, pore volume and average pore diameter of the catalysts were evaluated by N_2 adsorption at 77 K using a Micromeritics Tristar 3000 instrument. The catalysts were outgassed at 150 °C for 6 h prior to analysis.

2.2.2. Powder X-ray diffraction measurements

XRD measurements were carried out on a Philips X'Pert MPD diffractometer fitted with a Cu Kα source and operated with a scan rate of 0.01° per minute and a step size of 0.0262°. The average size of the Co_3O_4 crystallites in the calcined catalysts was estimated from the line width using the Scherrer equation. To identify the presence of Co metal after reduction using XRD, the reduced catalysts were passivated. Passivation involved passing a stream of 0.5% O_2/He at 10 ml/min at room temperature over the reduced catalyst surface for 10 h.

2.2.3. Hydrogen – temperature programmed reduction (TPR)

Catalyst reducibility over the temperature range 298–1173 K was determined by TPR experiments performed on a Micromeritics Autochem II 2920. The catalyst was pretreated by passing Ar gas through the catalyst bed for 30 min at 300 °C before cooling to room temperature. A 5% H_2/He gas stream (50 ml/min) was then passed over the catalyst while increasing the temperature at 5 °C/min to temperature up to 400 °C (unless otherwise stated).

2.2.4. Catalytic activity test

Activity tests were performed on 0.2 g samples (63–71 μm) mounted in a glass tube (6 mm I.D) fixed bed flow reactor operating at 200 °C and ambient pressure. H_2 and CO were supplied to the reactor using mass flow controllers. Prior to activity testing, the sample was activated in a flow of 50% H_2/He (50 ml/min) from room temperature to 400 °C where it was held for 10 h. The bed was then cooled to 200 °C under He after which the reactant gases (H_2/CO = 10) diluted with He were introduced at flow rate of 50 ml/min. Online gas chromatography analysis, using a Shimadzu GC8A gas chromatograph fitted with a Porapak Q column and a thermal conductivity detector, was used to determine CO and methane levels. Water produced by the reaction was removed by a cold trap located between the reactor and the chromatograph. The reported activities were obtained after 480 min and are expressed in terms of conversion of CO (%ppm).

3. Results and discussion

3.1. Physicochemical properties and crystallite size of cobalt species in oxidised catalysts

The pore size distributions of all catalysts indicated a predominantly mesoporous structure with variations in BET surface area as shown in Table 1. Impregnation with cobalt species led to a 13–22% reduction in surface area relative to that of the γ-alumina. The decrease in surface area could be due to plugging of the alumina pores by cobalt oxide crystallites. Lanthanum addition resulted in an increase in surface area (Table 1) suggesting it may be dispersed as a monolayer [20]. This effect was negated upon subsequent addition of Co whereby the surface area decreased from 270 m^2/g to 202 m^2/g. The addition of Ru, present in only small amounts, promoted little change to the surface area for the cobalt-containing catalysts of the original γ-alumina.

X-ray diffraction patterns of all samples (Fig. 1) exhibited Co_3O_4 reflections but no other peaks beyond those of the base alumina. Peaks due to lanthanum and ruthenium oxides were absent, in all probability due their much lower concentrations. However, the width of the Co_3O_4 peaks of the calcined samples differed and was influenced by the presence of the promoters. Average Co_3O_4 crystallite size was calculated using the Scherrer equation for the peaks located at $2\theta = 56°$ and 59.5° (4 2 2 and 5 1 1) and gave the values provided in Table 1. There was a decrease in the Co_3O_4 crystallite size following promotion with both La and Ru. Pre-impregnation by La produced a considerable decrease in Co crystallite size with Girardon et al. [21] suggesting that such a decrease could be related to a higher concentration of cobalt oxide crystallization sites formed during decomposition of cobalt nitrate complexes. Co-impregnation with Ru (Table 1) also served to reduce Co crystallite size although not to the same extent as La.

Table 1
Physical properties of non-reduced monometallic and promoted cobalt-based catalysts.

Catalysts	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)	XRD Co_3O_4 crystallite size (nm)
γ-Alumina	234	0.80	11.4	–
La/Al_2O_3	270	0.84	10.5	–
Ru/Al_2O_3	222	0.80	10.5	–
Co/Al_2O_3	189	0.55	10.1	10.3
[a] $Co/La/Al_2O_3$	202	0.57	9.6	6.5
[b] $RuCo/Al_2O_3$	182	0.55	9.8	9.4
[c] $RuCo/La/Al_2O_3$	195	0.56	9.6	8.3

[a] Two step impregnation: lanthanum impregnated on γ-alumina, dried and calcined, followed by addition of cobalt.
[b] Co-deposition of cobalt and ruthenium on γ-alumina.
[c] Two step impregnation: lanthanum impregnated on γ-alumina, dried and calcined, followed by co-deposition of cobalt and ruthenium.

Table 1 also indicates that the La- and Ru-promoted Co crystallites were smaller than the γ-alumina pore diameter. This suggests that the cobalt oxide may be present in the γ-alumina pores compared with the un-promoted catalyst where crystallite sizes are larger.

3.2. Cobalt catalyst reduction

The influence of the promoting metals, La and Ru, on the reducibility of the supported cobalt catalysts was studied by temperature programmed reduction (TPR). The TPR profiles of monometallic and promoted cobalt catalysts are shown in Fig. 2. The hydrogen consumption profiles showed distinct peak regimes

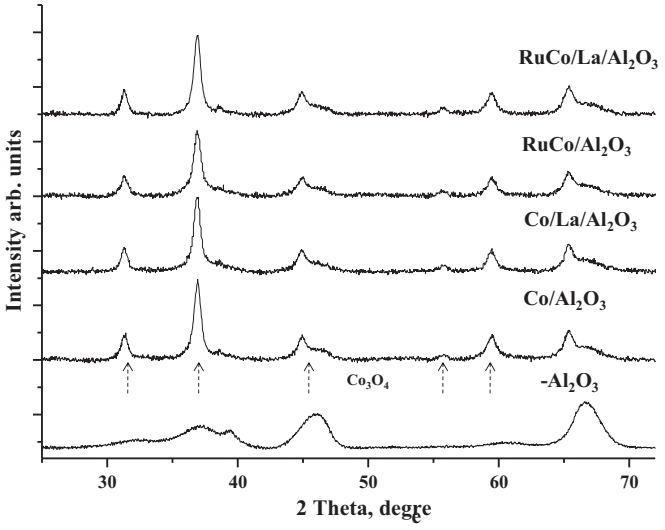

Fig. 1. X-ray diffraction patterns of calcined monometallic and La- and/or Ru-promoted γ-alumina supported cobalt catalysts.

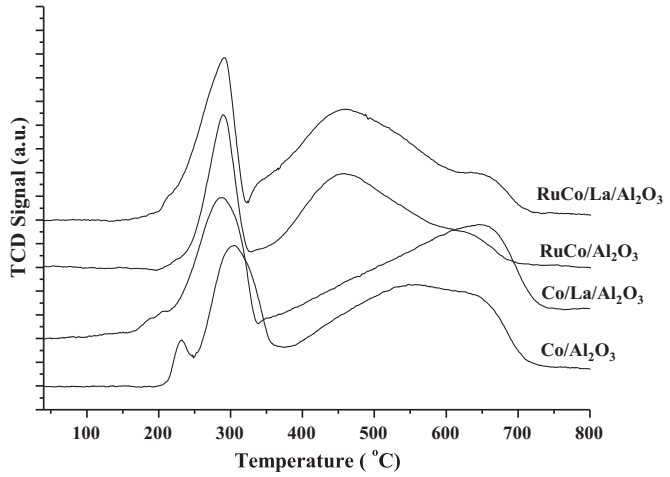

Fig. 2. TPR profiles of monometallic and La- and/or Ru-promoted cobalt alumina-supported catalysts.

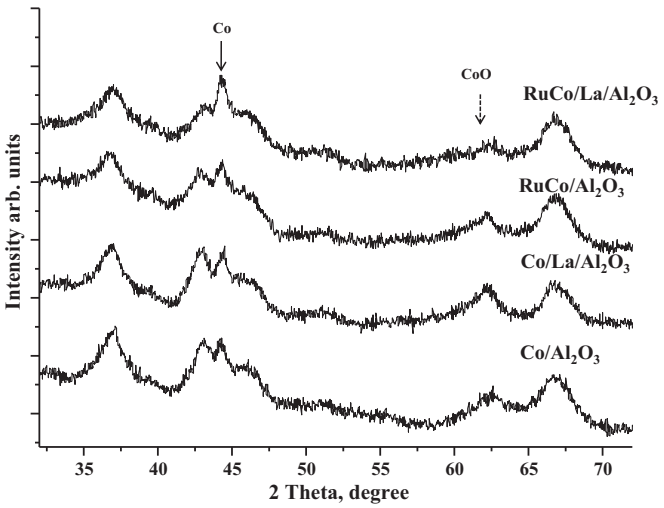

Fig. 3. X-ray diffraction patterns of monometallic and La- and/or Ru-promoted cobalt alumina-supported catalysts following reduction in 5% H_2/He at 400 °C and passivation in 0.5% O_2/He under room temperature for 10 h.

for all catalysts. The peak between 200 and 250 °C could be due to the reductive decomposition of residual cobalt nitrate [22]. The low temperature peak (250–400 °C) results from the reduction of Co_3O_4 to CoO. The moderate temperature peak (400–600 °C) is attributed to the reduction of CoO to Co metallic phase while the peak at temperatures higher than 600 °C arises through reduction of more difficult to reduce mixed Co oxides [23,24]. The TPR profiles indicate catalysts promoted with Ru underwent reduction from Co_3O_4 to CoO at slightly lower temperatures than those without Ru. The moderate temperature peak was also more pronounced for the Ru-promoted catalysts compared with the neat Co-alumina. This infers reducibility of the Co was enhanced by Ru addition. The presence of La also shifted the Co_3O_4 to CoO reduction peak to a slightly lower temperature but appeared to suppress the reduction of CoO to Co metal, perhaps due to the formation of mixed Co oxides which were harder to reduce.

The TPR profiles in Fig. 2 were performed in 5% H_2/He mixtures, ramped directly from room temperature to 850 °C at 5 °C/min. The measurements were repeated but with a 10 h holding period at 400 °C (mimicking the conditions closer to those used to activate the catalyst prior to methanation) within the ramping pattern. These findings are presented in Table 2 where H_2 consumption for the moderate temperature peak (CoO reduction to metallic Co) with and without the holding period are compared. Table 2 shows all catalysts held at 400 °C for 10 h experience a significant decrease in H_2 consumption for the second peak. Since the Co loadings are similar, this demonstrates the 10 h holding period promotes reduction of CoO to Co compared to when the temperature is not maintained for any length of time. The effect was amplified when Ru was present.

These TPR experiments were conducted in 5%H_2/He mixtures (due to the limitations of the TPR system) but reduction prior to methanation involved 50% H_2/He mixtures. Chernavskii et al. [25] have shown that hydrogen partial pressure can affect the extent of cobalt reduction. Therefore, the findings from these TPR experiments can provide only qualitative information on Co reducibility and are not suitable for quantitatively evaluating the actual fraction of CoO reduced.

Further information on the reducibility of the Co species in monometallic and promoted Co catalysts was obtained through comparison of X-ray diffraction measurements conducted on catalysts reduced in both 5% H_2/He and 50% H_2/He mixtures at 5 °C/min ramp and then maintained at 400 °C for 10 h followed by passivation under 0.5% O_2/He at room temperature. The patterns for catalysts treated under these conditions are given in Figs. 3 and 4, respectively. Within these diffraction patterns, the peak located at a 2θ of 44.3° (1 1 1) is due to Co metal in the cubic form (rather than the hexagonal close packed which is more stable at room temperature) [26], while peaks at 2θ of 42.8° and 45.8° represent CoO and Co_3O_4, respectively [27,28]. In Fig. 3, it is apparent that the addition of Ru increases the reduction of CoO while the addition of both La and Ru exacerbates this effect and intensifies the Co metal peak.

Table 2
The effect of holding the temperature at 400 °C for 10 h during ramping to 850 °C on the reduction of CoO to Co.

Catalysts	H_2 consumption from TPR profiles (mmol of H_2/g)		
	No holding	After holding for 10 h	% Additional reduction[a]
Co/Al_2O_3	2.43	1.532	37
$Co/La/Al_2O_3$	2.433	1.46	40
$RuCo/Al_2O_3$	2.389	0.753	68
$RuCo/La/Al_2O_3$	2.378	0.619	74

[a] The effect was measured by the difference in area of the TPR peaks over the 400–600 °C temperature range. Reduction was performed under 5% H_2 in Ar gas stream.

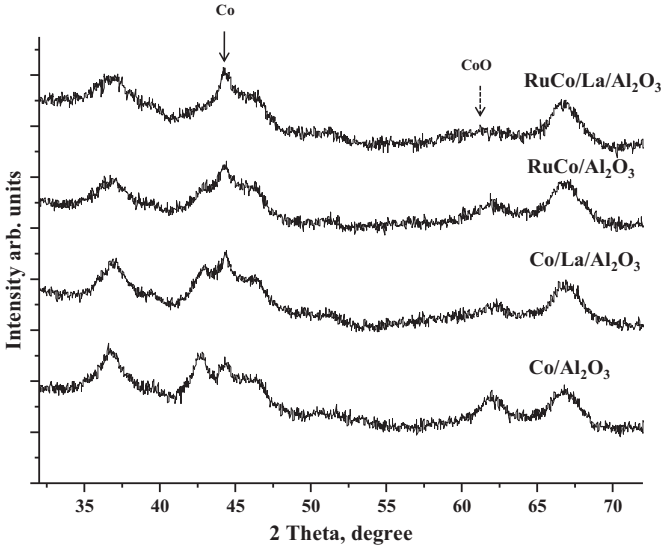

Fig. 4. X-ray diffraction patterns of monometallic and La- and/or Ru-promoted cobalt alumina-supported catalysts following reduction in 50% H_2/He at 400 °C and passivation in 0.5% O_2/He under room temperature for 10 h.

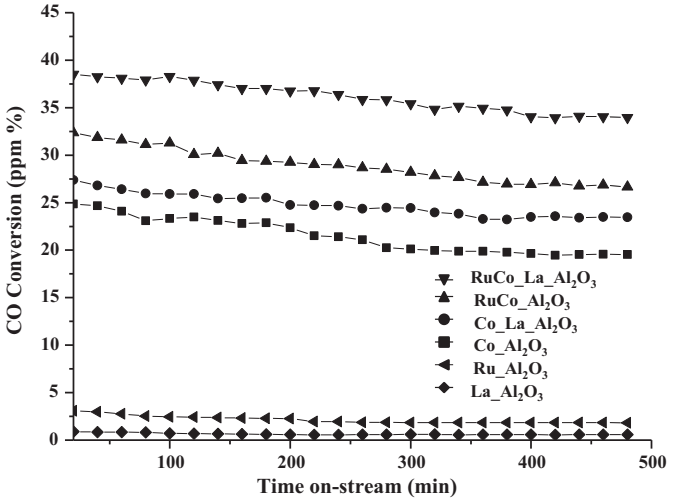

Fig. 5. Conversion of CO with time on stream (min) for monometallic and La- and/or Ru-promoted γ-alumina supported cobalt catalysts. Included are La-promoted γ-alumina and Ru-promoted γ-alumina catalysts as controls. Reduction in 50% H_2/He at 400 °C for 10 h followed by methanation with reactant gases ratio, H_2/CO = 10 at 200 °C for 480 min.

Comparing the CoO peaks in Fig. 4 with Fig. 3 indicates that greater reduction results from the higher H_2 concentration in the reducing gas stream.

3.3. Effect of ruthenium and lanthanum on methanation activity

The catalytic activities of the pre-reduced monometallic and promoted Co catalysts, in terms of CO consumption, are provided in Fig. 5. The Co/Al_2O_3 catalyst converted ~19% of the CO at a reaction time of 480 min. The inclusion of La alone increased the conversion by ~3% in absolute terms while the addition of Ru alone increased conversion by ~7%. These increases in conversion cannot be attributed to the methanation activity of the additives alone as the conversion of the La/Al_2O_3 and Ru/Al_2O_3 control catalysts are much lower (<1% and ~2%, respectively). Coupling the La and Ru additives with cobalt gave the greatest activity improvement, with the $RuCo/La/Al_2O_3$ catalyst exhibiting a CO consumption of 34% after 480 min of reaction. Again, this improvement is not merely an additive effect and indicates the Ru and La cooperate to enhance catalyst activity.

The improvements in activity upon La and Ru addition to the Co catalyst may be explained by the TPR and XRD results if the presence of Co metal is crucial for the methanation activity. The XRD results in Fig. 4 indicated the different additives promoted Co metal formation at the expense of CoO during H_2 reduction. The extent to which this occurred mimics the activity results with, for example, the co-promoted catalyst displaying both the highest activity and the greatest degree of CoO reduction. The production of Co metal is similarly demonstrated by the TPR results (Table 2) where holding the $RuCo/La/Al_2O_3$ sample at 400 °C for 10 h gave the largest increase in the extent of CoO reduction (74%) resulting in higher methanation activity (Fig. 5).

The role of Co metal on activity was then investigated. The neat Co/Al_2O_3 and Ru/La promoted Co/Al_2O_3 were reduced at 400 °C in 5% H_2/He with and without a holding time of 10 h and in 50% H_2/He with the 10 h holding time. The methanation activities (Table 3) confirm that both catalysts have poor activity in the absence of the holding time at 400 °C. As indicated by the TPR results (Fig. 2), this temperature represents the point at which all the Co_3O_4 has been converted to CoO with only a small amount of CoO to Co metal. X-ray diffraction patterns (not shown) of these samples showed only CoO (i.e. no Co metal peak was observed). The methanation activity

Table 3
CO conversion by monometallic and La/Ru-promoted Co/Al_2O_3 methanation catalysts after 480 min on-stream under varying reduction conditions.

Reduction conditions	CO consumption (% ppm)	
	Co/Al_2O_3	$RuCo/La/Al_2O_3$
5% H_2/He, 400 °C – no holding	1	5
5% H_2/He, 400 °C – holding for 10 h	7	15
50% H_2/He, 400 °C – holding for 10 h	19	34

improved when the catalysts had been held at 400 °C for 10 h under 5% H_2/He, which can be attributed to the increased reduction of CoO (Table 2) to metallic Co (Fig. 3). Increasing the H_2 concentration to 50% (and holding at 400 °C for 10 h) more than doubled catalyst activity, which can be attributed to further CoO reduction (Fig. 4) resulting from the higher H_2 concentration.

Small amounts of Ru enhance Co_3O_4 reduction and subsequently improve methanation activity [29,30]. This improvement is attributed to the dissociation of H_2 on Ru with spill over of the active hydrogen to cobalt oxide where it facilitates reduction of Co_3O_4 and CoO [17,23]. La addition does not have as marked an improvement in methanation activity as Ru [20]. In this instance the primary effect of La is to reduce the Co_3O_4 crystallite size. This may assist with Co dispersion on the γ-alumina surface, increasing the availability of the Co-oxide surface for reduction and catalysis.

4. Conclusion

The effect of La and Ru promoters in γ-alumina-supported Co catalysts has been investigated, together with the effect of reduction conditions during catalyst activation. Catalysts prepared with co-impregnated Co and Ru after impregnation by La gave the highest level of activity. The activity was governed by the degree of reduction to Co metal ($Co_3O_4 \rightarrow CoO \rightarrow$ metallic Co) which was strongly influenced by the presence of the promoters and the reduction conditions required to activate the catalyst. Reduction to Co metal was enhanced by holding the temperature of reduction at 400 °C for 10 h with up to 74% additional CoO reduction achieved compared with the situation where the temperature was not held. CoO reduction was further facilitated by using a greater H_2 concentration in the reducing gas stream.

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