

Temperature-programmed surface reaction (TPSR) of pre-adsorbed carbon CO and CO/H₂ synthesis over Ru–Cs/Al₂O₃ catalysts

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Abstract

A series of silica supported ruthenium–caesium catalysts were prepared by sequential impregnation method, and characterized by total surface area determination, and temperature-programmed surface reaction (TPSR) of pre-adsorbed CO with H₂ to form mainly methane. The catalytic behaviour of the catalysts prepared was then studied using CO/H₂ synthesis performed in a continuous flow system operating under differential conditions at atmospheric pressure. TPSR experiments revealed that the amount of CO adsorbed estimated from methane formed, decreased with the addition of Cs. This was attributed mainly to site blockage, a purely geometric effect. The main product of the hydrogenation of the pre-adsorbed CO was methane. Peak temperature of methane shifted to higher temperatures with Cs doping indicating that methanation proceeds faster on Ru/Al₂O₃ catalyst than on the Cs doped ones. It is suggested that the addition of Cs lead to a decrease in the rate of CO dissociation which is thought to be an essential step in the methanation reaction. Catalytic activity data obtained for the CO/H₂ synthesis indicated that the role of Cs as a catalytic modifier is to limit the methanation reaction in preference to hydrocarbon chain growth. It was found that the order of reactivity of pre-adsorbed CO towards hydrogenation to methane in TPSR experiments (transient technique) with respect to Cs loading agreed well with the methanation activity observed in CO/H₂ reaction using the continuous flow system ('steady state' activity). This good correlation of relative activities obtained by the two sets of experiments demonstrates the validity of comparing TPSR results with those from reaction studies. © 1997 Elsevier Science B.V.

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1. Introduction

Supported catalysts based on Ru are of interest for CO hydrogenation reaction studies and have been the subject of numerous investigations [1–5]. The use of alkali species with transition metal catalysts for modification of the

catalytic behaviour has been common in ammonia synthesis and in Fischer–Tropsch synthesis [6–9].

A number of investigators [10–20] have used temperature-programmed surface reaction (TPSR) on supported metal catalysts to study the kinetics of methanation. The TPSR experiment is essentially a temperature-programmed desorption experiment carried out under reactive

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conditions using a mass spectrometer or a GC fitted with thermal conductivity detector (TCD) or flame ionization detector (FID) to detect the species evolving as a function of temperature. In a TPSR measurements, apart from simple desorption process, the evolution of product of a surface reaction may also be observed. Temperature-programmed methanation experiments is usually carried out by adsorbing carbon monoxide at room temperature followed by heating the catalyst in hydrogen at atmospheric pressure while detecting the methane produced as a function of temperature. This approach has proven to be successful for a number of metals on a variety of supports because CO adsorbs more strongly than hydrogen, and the methanation rate is faster than the rate of CO desorption. In general the methane profiles obtained from TPSR experiments are relatively narrow. This is mainly due to the fact that methane does not readily adsorb on the metal or the support. The methane peak temperature is usually taken as a good measure of the specific activity of the catalyst.

The present investigation was undertaken with the aim of (a) identifying the effects of Cs on CO adsorption and its subsequent hydrogenation using TPSR technique on silica-supported ruthenium catalysts and (b) its effect on the catalytic behaviour in CO/H₂ synthesis and (c) to test the validity of comparing the relative activities obtained from the TPSR results with those from reaction studies.

2. Experimental

2.1. Catalyst preparation

The Ru/Al₂O₃ catalyst was prepared by impregnating a high surface area γ -Alumina support with aqueous solution of RuCl₃ to give a Ru loading of 1% w/w. After impregnation, the catalysts were dried at 323 K for about 15 h and then reduced in a flow of hydrogen at 923 K overnight. The temperature of the catalyst was

raised from room temperature to the reduction temperature at a rate of 1 K/min.

The Cs-promoted Ru/Al₂O₃ samples were prepared by adding the proper amount of aqueous caesium nitrate solution to reduced, unused Ru/Al₂O₃ samples. The resulting mixtures were dried, and the dried powders were then heated at 923 K in a flow of hydrogen overnight using a similar procedure as before.

2.2. Surface area determination

Specific surface areas of the catalysts used were determined by adsorption of nitrogen at liquid nitrogen temperature in a flow system similar to that suggested by Nelson et al. [21].

2.3. CO adsorption and TPSR

Chemisorption of CO was carried out in a conventional pulse system operating at room temperature. Prior to the chemisorption run, the catalyst sample (0.5 g) was reduced in flowing hydrogen at 723 for 2 h followed by flushing for 30 min in a He stream at the same temperature. The catalyst bed was subsequently cooled in the flowing He to room temperature. Calibrated pulses of CO were injected by means of a sample loop (0.1 ml) into the He carrier gas (25 ml/min) and detected by a thermal conductivity detector. CO injections were continued until no significant difference could be seen in the heights or areas of CO peaks eluted. By comparing the amount of CO reaching the detector and the amount of CO injected into the system, the quantity of CO adsorbed on the catalyst could be determined.

The reactivity of CO adsorbed on the catalysts studied was investigated by TPSR of the pre-adsorbed CO with H₂. Directly after the CO adsorption the He stream was replaced by H₂ (40 ml/min) and the catalyst bed was heated from 300 K to 723 K at a rate of 20 K/min. The amount of methane produced was recorded as a function of temperature. Before entering the detector, water and other condensibles were

frozen out of the gas in a liquid nitrogen cold trap.

2.4. Kinetic measurements for CO/H₂ synthesis

The catalytic experiments were carried out using a conventional flow system operating under differential conditions at atmospheric pressure. The reactor was constructed from Pyrex glass tubing of 12 mm internal diameter. The catalyst was held in place by means of quartz wool. The reactor was externally heated using a furnace connected to a temperature controller. For typical experiments, the reactor contained 1 g of catalyst.

Before each experiment, the catalyst was pre-treated in situ with H₂ flow at 723 K for nearly 16 h, then cooled to the reaction temperature before switching pure H₂ to the reactant feed. The reactant feed was a premixed mixture of H₂-CO-Ar, with a volumetric composition of 42:10:48 supplied by B.O.C. Specialist Gases. The total gas flow rate above the catalyst was close to 40 ml/min. The reaction was allowed to proceed for 60 min at 523 K before analysis. The effluent gas was analyzed by gas chromatography using flame ionization detector (Pye Unicam 4500). Porapak Q (80–100 mesh) packed column of 2 m length, 1/8" diameter, was used to affect the separation of the produced hydrocarbons (C1–C5). Traces of methanol and ethanol were detected in the effluent. Calibration of the detector response was carried out by injecting gas mixtures of known composition supplied by Phase Separation.

3. Results and discussion

3.1. CO adsorption

Table 1 lists the various catalysts, their Cs loading, amount of CO adsorbed, dispersion values defined as CO:Ru i.e., the ratio of total CO molecules adsorbed with respect to the total ruthenium atoms, and metal surface area. The dispersion was calculated from the amount of CO adsorbed assuming that one CO molecule is chemisorbed by one surface Ru atom. Surface area (S) per gram Ru was calculated according to the following equation:

$$S = N\sigma/M \times R$$

where *N* is Avogadro's number, σ is the cross-sectional area of one Ru atom, taken as 8.17 Å², *M* is the molecular weight of Ru, *R* is the ratio of CO molecules adsorbed per Ru atom i.e. CO/Ru.

As can be seen from Table 1 the amount of CO adsorbed onto the surface of the catalyst is reduced with the addition of Cs. This could be attributed to site blockage due to Cs adspecies situated on the surface of the Ru particles. This seems to agree with the findings of other authors who have reported a decrease in the amount of CO adsorbed and in the ruthenium dispersion upon the addition of an alkali to ruthenium supported catalysts [22,23].

3.2. Temperature-programmed surface reaction of pre-adsorbed CO

The methane profiles resulting from TPSR experiments for all the catalysts investigated are

Table 1
Characterization of Ru-Cs/alumina samples

Cs w/w%	Surface area (m ² /g)	CO adsorbed (μmol/g cat)	CO/Ru	metal area (m ² /g Ru)
0.00	166	25	0.255	123
0.10	163	20	0.204	99
0.25	186	19	0.193	93
0.50	204	17	0.170	83

shown in Fig. 1. The intensities of the TPSR profiles are expressed in arbitrary units and are not directly comparable since the attenuation of the recorder and the TCD current may be different. As can be observed in Fig. 1 the hydrogenation of the adsorbed CO lead to the formation of one single CH₄ peak. The shape of the CH₄ peaks appears somewhat distorted, on the lower temperature side. Doping of the Ru/Al₂O₃ with Cs, results in alterations of the position of the CH₄ peak, which shifts to higher temperatures with Cs doping. The peak temperature, T_{\max} , for the different catalysts investigated is summarized in Table 2. The TPSR experiments show that upon doping Ru/Al₂O₃, the activity for the hydrogenation of adsorbed CO is reduced. It must be emphasized here that, whether molecularly adsorbed CO reacts via direct hydrogenation or via dissociation followed by hydrogenation of the carbon formed cannot be answered by the present experiments. However recent studies clearly show that the dominant mechanism involves the dissociation of CO followed by the hydrogenation of the surface carbon atoms to methane [20]. If this is the case, then it is reasonable to assume that the reduction in the hydrogenation activity of adsorbed CO upon doping with Cs, could be attributed to the reduction of the CO dissociation rate on these doped

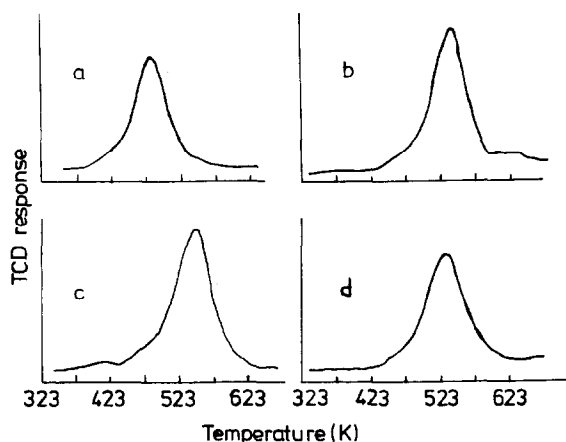


Fig. 1. Methane profiles during H₂ TPSR of CO adsorbed on the Ru-Cs/Al₂O₃ catalysts ($\beta = 20^\circ\text{C}/\text{min}$), Cs 0.0% (a), Cs 0.10% (b), Cs 0.25% (c) and Cs 0.50% (d).

Table 2

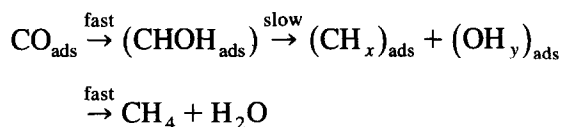
TPSR data of adsorbed CO for Ru-Cs/alumina catalysts

Cs w/w%	T_{\max}/K	FWHM/K	E_a (kJ mol ⁻¹)	
			A	B
0.00	481	52	85 ± 5	84
0.10	539	56	101 ± 4	100
0.25	546	60	92 ± 3	95
0.50	533	62	88 ± 3	88

A – activation energies calculated from Arrhenius plots.

B – activation energies calculated from the peak temperatures and the half-widths of methane profiles.

samples, which is reflected in the increase in the CH₄ peak temperature in the TPSR experiments. This finding looks strange and is different from what is known about the effect of alkali additives which show that in the absence of H₂ leads to an increase in the rate of CO dissociation [24–26]. However it is in agreement with that reported by Mori et al. [27] who investigated the effect of the alkalis on the dissociation of the C–O bond in the methanation over Ru supported catalyst using a transient method (PSRA). To resolve the discrepancy the authors suggested that the mechanism for the C–O bond dissociation in the CO hydrogenation is different from that in the absence of H₂ [27–31]. It was concluded that the dissociation of the C–O bond in the CO hydrogenation is not a simple unimolecular process in which an adsorbed CO decomposes to C_{ads} and O_{ads} and that hydrogen atoms play an important role in the C–O bond dissociation process. It was suggested [28–31] that CO dissociates to surface carbon (CH_x)_{ads} and oxygen (OH_y)_{ads} species via the formation of an intermediate of a partially hydrogenated CO species (CHOH)_{ads} which is in equilibrium with adsorbed CO as shown below:



Based on this mechanism the authors argued that the suppressing effect of alkalis on the C–O

bond dissociation comes as a result of decrease in the equilibrium concentration of $(\text{CHOH})_{\text{ads}}$ which lead to a decrease in the rate constant for CO dissociation.

An attempt was made to deduce E_a from the TPSR profiles produced using lineshape analysis. The rate expression for the TPSR is

$$d\text{CH}_4/dt = k[\text{H}_2]^n \theta_{\text{CO}}^m \quad (1)$$

where k is the rate constant $= Ae^{-E_a/RT}$, θ_{CO} is the carbon monoxide surface coverage, n and m are the orders of the reaction with respect to hydrogen and CO respectively.

Eq. (1) can be approximated as [19]

$$d\text{CH}_4/dt = Ae^{-E_a/RT} \theta_{\text{CO}} \quad (2)$$

because (i) hydrogen is present in large excess as to be considered essentially constant over the whole TPSR profile, and (ii) previous studies has confirmed a first-order dependence of the methanation reaction on CO coverage, under experimental condition of low CO pressures and excess hydrogen [32,33]. Now the rate of methane production at any temperature is proportional to the TPSR profile amplitude at that temperature, while the area under the portion of each TPSR profile to the right of that temperature is proportional to the surface coverage of CO at that temperature. Hence a plot of $\ln[h/\text{Area}]$ vs. $1/T$ would give a straight line and the activation energy is obtained from its slope. Activation energies for methanation calculated from the resulting Arrhenius plots for the different specimens investigated are compiled in Table 2. Table 2 also reports activation energies estimated from the peak temperatures and the halfwidths (full width at half height) of each methane TPSR profile [34]. Both methods of calculations gave comparable values for the activation energies. E_a values reported here agree very well with those reported by Sen et al. [13] who reported a methanation activation energy of 84 kJ/mol estimated from half width maximum for a first order process for Ru/ Al_2O_3 sample.

3.3. Kinetic measurements

Fig. 2 depicts the variation of the catalytic activity for the production of methane, higher hydrocarbons (C2–C5) and total hydrocarbons at 523 K as a function of Cs loading. The plot reveals that the rate of production of methane decreased more steeply with the initial addition of Cs (0.1% w/w) when compared to that of higher hydrocarbons production (Fig. 2). Because the Fischer–Tropsch reaction (production of higher hydrocarbons) is inhibited to a lesser extent than that of the methanation reaction in this region, it is apparent that the role of Cs as a catalytic modifier here is to limit the production of methane in preference to hydrocarbon chain growth. It is more likely that with the presence of Cs species most of the surface Ru^0 cannot adsorb hydrogen and that this is the reason why the selectivity to higher hydrocarbons increases with the Cs presence. Further addition of Cs do not have any significant effect on the rate of production of methane or higher hydrocarbons. The general decline in the activity of the catalysts investigated here with the alkali addition is in agreement with the findings of some other authors [22,35–38]. The initial drop in activity could be explained by the blocking of some Ru active sites by some of the added Cs species. It seems that at higher Cs loadings Cs species tend to agglomerate into large particles and hence do not spread out efficiently to cover more Ru sites

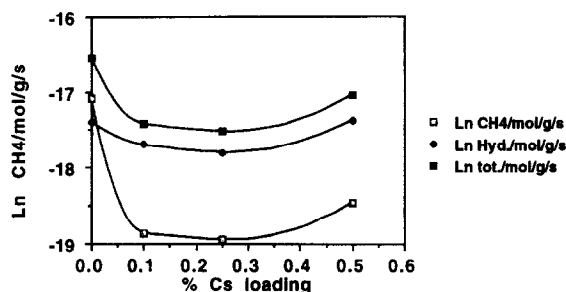


Fig. 2. Variation of the methane production, higher hydrocarbons and total hydrocarbons production as a function of Cs loading for the Ru–Cs/ Al_2O_3 catalysts investigated at 523 K.

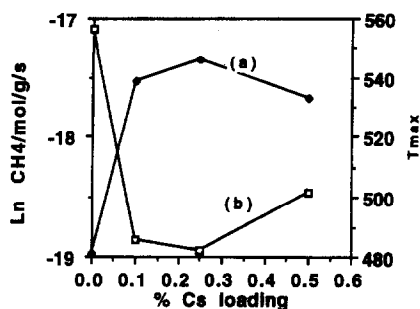


Fig. 3. (a) Methane peak temperature (T_{max}) during TPSR of adsorbed CO on Ru–Cs/ Al_2O_3 catalysts with H_2 . (b) Activity for methane production at 523 K in CO hydrogenation (flow system) over Ru–Cs/ Al_2O_3 catalysts.

as is the case in the sample with lower Cs loading. Another reason which could be envisaged for the observed variation in the activity, is that low loadings of Cs tend to preferentially block the most active Ru sites (presumably edges and corners) but much less abundant on the Ru surface. Once these low coordination sites are covered, no appreciable variation in the activity with composition is to be expected. While this is admittedly a mere speculation it is not without roots since similar sort of thing has been suggested by other authors for copper modified Ru/ SiO_2 system [39,40].

What is interesting to report here is the existence of a close correlation between peak temperatures of methane produced under TPSR conditions and the activities of methanation reaction obtained for the catalysts in CO hydrogenation using the flow system here. This is summarized in Fig. 3, where the methane peak temperature T_m obtained for TPSR experiments and the methanation activity of the catalysts investigated in the flow system at 523 K expressed as $\ln CH_4/mol/s/g$ are plotted as a function of Cs loading. The initial rise in T_{max} with the first addition of Cs (0.1% w/w) which indicates a decrease in the reactivity of pre-adsorbed CO (TPSR experiments) can be closely correlated with the initial decrease in methanation activity using the flow system. The addition of more Cs does not seem to have an appreciable effect on T_{max} . The same thing could be said

for the methanation activity i.e. the activity for methane production do not show any appreciable change with further addition of Cs within the loading range investigated. This close correlation of the relative activities obtained by the two sets of experiments could be taken as an indication of the validity of comparing TPSR results with those from reaction studies in this case.

4. Conclusions

(1) The peak temperature for methane produced from hydrogenation of pre-adsorbed CO in TPSR experiments on Ru–Cs/ Al_2O_3 catalysts indicates that methanation proceeds faster on Ru/ Al_2O_3 catalyst than on the Cs doped ones. It is suggested that Cs addition reduces the rate of CO dissociation.

(2) Activity data obtained from CO– H_2 synthesis seems to suggest that the role of Cs as a catalytic modifier is to limit the formation of methane in preference for hydrocarbon formation.

(3) It is found that the reactivities of pre-adsorbed CO on Ru–Cs/ Al_2O_3 catalysts with hydrogen to form methane correlate closely with their catalytic activities for the production of methane in CO– H_2 reaction in the flow system. This is a clear demonstration on the validity of comparing TPSR results with those from reaction studies.

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