Non-oxidative methane coupling over Co–Pt/NaY bimetallic catalysts

L. Guczi, K.V. Sarma and L. Borkó

Department of Surface Chemistry and Catalysis, Institute of Isotopes of the Hungarian Academy of Sciences,
PO Box 77, Budapest H-1525, Hungary

Received 27 October 1995; accepted 14 February 1996

Methane activation and coupling of the CH_x species formed from methane into higher hydrocarbons over NaY, Pt/NaY, Co/NaY, Co–Pt/NaY and Co–Pt/Al_2O_3 have been compared. Co–Pt/NaY and Co–Pt/Al_2O_3 showed exceptionally high yields (100%) referred to the adsorbed CH_x species and high selectivity in the formation of C_{2+} hydrocarbons (83.6 and 92.6%, respectively) in the two-step reaction using 523 K for chemisorption and 523 K for hydrogenation. However, the amount of CH_x is fourfold higher on Co–Pt/NaY than Co–Pt/Al_2O_3. The synergistic effect can be interpreted by insertion of Co into Pt inside the zeolite cages which causes a preferential coupling of CH_x species vs. its hydrogenation into methane. Separate experiments carried out on the removal of CH_x species with deuterium show that deep dissociation of methane does not occur on bimetallic catalyst and the weakly bonded CH_x species can easily participate in chain building reaction on the surface.

Keywords: Pt–Co in NaY; methane chemisorption; hydrocarbon formation

1. Introduction

Profound research has been carried out to study methane activation over metals, particularly over ruthenium and cobalt supported on silica, to form active CH_x species which could form higher hydrocarbons in the subsequent hydrogenation reaction [1–4]. This serves an alternative for oxidative coupling of methane (OCM) in which a significant amount of methane is oxidized into CO_2 [5–8].

The main problems in non-oxidative coupling are the low efficiency calculated for methane and the large gap between the temperature applied to activate methane and that at which the CH_x fragments can be hydrogenated [2]. Later, precious metals, like Pt, Pd, Ir and Rh supported over silica, were applied possessing a higher yield in ethane, but still low efficiency [9,10].

Recently, a series of experiments were carried out using NaY zeolite supported platinum catalyst which, in comparison with EUROPt 1, gave a better yield in higher hydrocarbons, and, more importantly, the temperature at which methane activation took place was 523 K [11–15]. The yield calculated on the fraction of the methane chemisorbed, became quite high.

The reason why we started methane coupling over Co–Pt/NaY catalysts is the following. First, methane can obviously be activated with high efficiency over well reduced cobalt catalysts, but the carbon deposited on the surface can easily be transformed into graphite or non-reactive carbon due to high temperature. As a result, a part of carbon is lost for further reaction and the catalyst is deactivated. Second, over Pt/NaY the temperature of methane decomposition is considerably lowered which might be due to the small metal particles confined in the supercage of NaY zeolite. Third, we have proven in a series of experiments that Pt–Co/NaY exhibits a superior behaviour in CO hydrogenation [16–20]. Furthermore, this family of catalysts has been well characterized and the presence of bimetallic particles has been identified.

In the present work we correlate the dissociative chemisorption of methane with the production of higher hydrocarbons over well characterized Pt/NaY, Co/NaY and Co–Pt/NaY catalysts. In methane chemisorption we determine the x values in the CH_x species after chemisorption using the deuterium exchange method elaborated in our laboratory [21,22]. The CH_x hydrogenation experiments are studied in a flow system developed by Belgued et al. [13].

2. Experimental

2.1. Sample preparation

The Pt/NaY, Co/NaY and Co–Pt/NaY catalysts were prepared by ion-exchange of NaY zeolite (Strem Chemicals, Lot No. 031112104). In order to prepare ion-exchanged samples the zeolite support was first stirred with carefully deionized water (200 $cm^3/g_{zeolite}$) at 343 K for 1 h. Dilute aqueous solution of $Pt(NH_3)_4(NO_3)_2$ or $Co(NO_3)_2$ (2×10^{-2} mol/cm^3) was added dropwise to the zeolite slurry under stirring at 343 K. The pH of the slurry was set to a final value of 6.5. After 24 h ion-exchange at the same temperature, the samples were filtered and thoroughly washed with deionized water. For preparation of Co–Pt/NaY bimetallic material, Pt^{2+} ions were introduced first; after filtering, the Pt/NaY was further exchanged with Co^{2+} ion solution. Co–Pt/Al_2O_3 was prepared by the incipient wetness method by co-impregnation using $Pt(NH_3)_4(NO_3)_2$ and $Co(NO_3)_2$ solution. All materials were dried in air first at room temperature and then at 383 K for 2 h. Calcination in oxygen was carried out in a stream of O_2 (40 cm^3/min) with a temperature ramp of 0.5 K/min from room temperature to 573 K, then holding the temperature here for 2 h. Reduction of the samples was carried out in a stream of H_2 (40 cm^3/min) raising the temperature to 723 K, holding the sample at this temperature for 1 h and then cooling down to room temperature.

Metal content of the Pt and Co samples was determined by X-ray fluorescence (XRF) and the metal loading along with the symbols of the samples, is given in table 1. The bulk atomic ratio of the pure NaY zeolite was Na/Al/Si = 0.38/0.38/1.00.

2.2. Measurements of methane chemisorption

Chemisorption of methane was studied in an all-glass circulating system connected to a mass spectrometer type Kratos MS 20 via a capillary leak to ensure a viscous flow for the gas components into the mass spectrometer. 1.3 kPa of methane was admitted to the catalyst sample reduced in situ in a stream of hydrogen followed by evacuation down to 10^{-5} Pa, and circulated typically for 3 min. During methane chemisorption hydrogen was generated and monitored in the mass spectrometer at $m/e = 2$. After chemisorption the catalyst was evacuated and 13 kPa of deuterium gas was added to the system. Typically at 373 K the adsorbed CH_x species were removed in the form of CH_xD_y, where y is indicative of the number of deuterium atoms to form deuterated methane. In separate experiments we have given evidence [22] that additional hydrogen–deuterium exchange occurs neither between deuterium and methane, nor between deuterium and the protons in the surface hydroxyl groups. Thus, the deuterium content in the methane formed after hydrogenation may reflect the hydrogen content of the adsorbed CH_x species.

In separate experiments the amount of CH_x was determined by oxidation at 573 K in a stream of oxygen. The amount of CO_2 trapped at liquid nitrogen temperature, was determined by means of a mass spectrometer.

2.3. Measurements of methane coupling

A flow apparatus was constructed of stainless steel, except for the reactor (quartz), to measure the formation of higher hydrocarbons. All gases were purified to remove oxygen and moisture. High purity methane (Messer Griesheim T45, purity > 99.995) was applied for methane chemisorption. After having been reduced in a stream of hydrogen at 623 K, typically 100 mg of catalyst was flushed with helium and then methane at atmospheric pressure was introduced at 523 K. In order to determine the amount of methane chemisorbed on the surface, the carbon fragments were oxidized with oxygen at 523 K for 10 min. For this, the system was carefully flushed with He to remove the trace amount of methane, then after oxidation the forming CO_2 was frozen in a loop of a sampling valve at liquid nitrogen temperature. The amount of CO_2 collected was then determined by GC with TCD.

For methane coupling the following procedure was applied. After the methane was chemisorbed at 523 K for 10 min, the system was carefully flushed with helium, then after setting the temperature to 523 K, the hydrogenation started and the products were trapped in a loop of 3 cm^3 at liquid nitrogen temperature. Finally, the loop was closed, allowed to warm up to ambient temperature and its content was introduced into the gas chromatograph and the products were separated over a phenylisocyanate/Porasil C column 1/8 inch i.d. and 1 m long, and measured by FID. The carbon balance was determined by calibration.

Table 1
Metal loading of the NaY supported samples measured by XRF method. In parentheses the atomic compositions of the metals are shown

Catalyst	Co (wt%)	Pt (wt%)
Co/NaY	1.5 (1.0)	–
Pt/NaY	–	10 (1.0)
Co–Pt/NaY	0.93 (0.23)	10.4 (0.77)
Co–Pt/Al_2O_3	2.25 (0.5)	7.75 (0.5)

2.4. Catalyst characterization

The samples were characterized by temperature programmed reduction (TPR) and chemisorption [15], by X-ray photoelectron spectroscopy [19] and EXAFS measurements [23]. The results will be quoted throughout the paper.

3. Results and discussion

The data on dissociative chemisorption of methane and the amount of hydrogen evolved during 3 min circulation of 1.3 kPa methane, along with the CH_xD_y formation after the removal of carbonaceous species from the surface using 13 kPa of deuterium at 373 K, are presented in table 2.

Although cobalt could be an active catalyst for methane dissociative chemisorption, reduction of Co^{2+} ions into metallic particles encaged in NaY zeolite is difficult because of the migration of Co^{2+} ions into small cages. Due to the difficult reducibility of Co^{2+} in NaY zeolite, methane uptake from the gas phase (methane initially present 102.5 μmol) was very small on Co/NaY (2 $\mu mol/g_{cat}$) compared to NaY supported Pt catalyst (8.2 $\mu mol/g_{cat}$).

In order to increase the reducibility of Co in NaY a second metal is added. In our laboratory the greatly

Table 2
Amount of methane chemisorbed, the amount of hydrogen evolved (in $\mu mol/g_{cat}$) and the initial distribution of the deuterated species in methane

Catalyst	$(CH_4)_{ads}$ $(\mu mol/g_{cat})$	$(H_2)_{evolved}$ $(\mu mol/g_{cat})$	Initial % of CH_xD_y				
			d_0	d_1	d_2	d_3	d_4
Co/NaY	2	0	67	0	15	14	3
Co/Al_2O_3	4	0.43	12	0	12	29	47
Pt/NaY	8.2	1.8	19	0	37	30	13
Co–Pt/NaY	14.9	15	11	0	0	65	24

enhanced reducibility of cobalt ions in the presence of platinum in NaY zeolite was proven by the superior performance of Co–Pt/NaY in the CO hydrogenation [16–20]. It is, therefore, interesting to use this system in the low temperature non-oxidative methane coupling reactions. Clearly, methane uptake was higher on Co–Pt/NaY at 523 K (14.9 $\mu mol/g_{cat}$), than on both Pt/NaY (8.2 $\mu mol/g_{cat}$) and Co/NaY (2 $\mu mol/g_{cat}$). This is the result of the increase in reducibility of Co ions in the presence of platinum, consequently, of the increase in the number of metal atoms exposed to the surface.

The higher adsorbability of methane on Co–Pt/NaY catalysts is supported both by the proportion of CD_4 formed and the amount of hydrogen evolved during methane chemisorption. The amount of hydrogen recorded in the gas phase is significantly higher (15 $\mu mol/g_{cat}$) than those measured over Pt/NaY (1.8 $\mu mol/g_{cat}$), Co/NaY (near to nil) and Co/Al_2O_3 (0.43 $\mu mol/g_{cat}$) [22]. Co/Al_2O_3 is applied only as a reference sample on which cobalt ions are reduced to a higher extent, than on Co/NaY. As shown in fig. 1, with increasing temperature both methane chemisorption and hydrogen generation rise.

Initial distributions of the various deuterated products in methane need further interpretation. On the Co/NaY sample methane is hardly chemisorbed, dissociation of hydrogen from the C–H bond does not occur as indicated by the amount of hydrogen evolved (practically nil) and the predominant fraction of methane-d_0. Since metallic cobalt is normally active in C–H rupture, when Co^0 is present (e.g. on the Co/Al_2O_3 sample [22]), the prevailing species in the deuterated methane is methane-d_4. On the other hand, on Pt/NaY the amount of methane-d_0 significantly decreases and maximum at methane-d_2, methane-d_3 species is observed. On the Co–Pt/NaY sample a significant drop in methane-d_0 is observed and the deuterium content in methane is shifted towards the value characteristic of Co, but still the extent of methane dissociation is reduced by the presence of Pt, thus methane-d_3 becomes predominant.

Methane coupling was carried out in two steps: in the first step, the methane passed over the catalyst sample for 10 min at 523 K and at atmospheric pressure. Then the system was flushed with helium for 1 h followed by the second step when the chemisorbed species were hydrogenated at 523 K in a stream of hydrogen. Results are presented in tables 3 and 4. As can be seen methane chemisorption takes place also on pure NaY, but the amount is low and only very small amount of higher hydrocarbons is formed. Although a large amount of methane is adsorbed on Pt/NaY the yield is low, but the selectivity is high in formation of higher hydrocarbons in agreement with the results of Belgued et al. [12,13]. Co/NaY shows higher yield and high selectivity in higher hydrocarbon production. Nevertheless, methane chemisorption is low on Co/NaY, presumably because of the low degree of reduction of the cobalt ions into metallic particles in the zeolite cage [16].

The best result is obtained on Co–Pt/NaY bimetallic catalyst. Formation of bimetallic clusters in NaY supercage has been confirmed by TPR and XPS results [16,19]. The amount of methane chemisorbed is the highest among the samples studied and the CH_x species are converted to hydrocarbons in 100%. The selectivity for

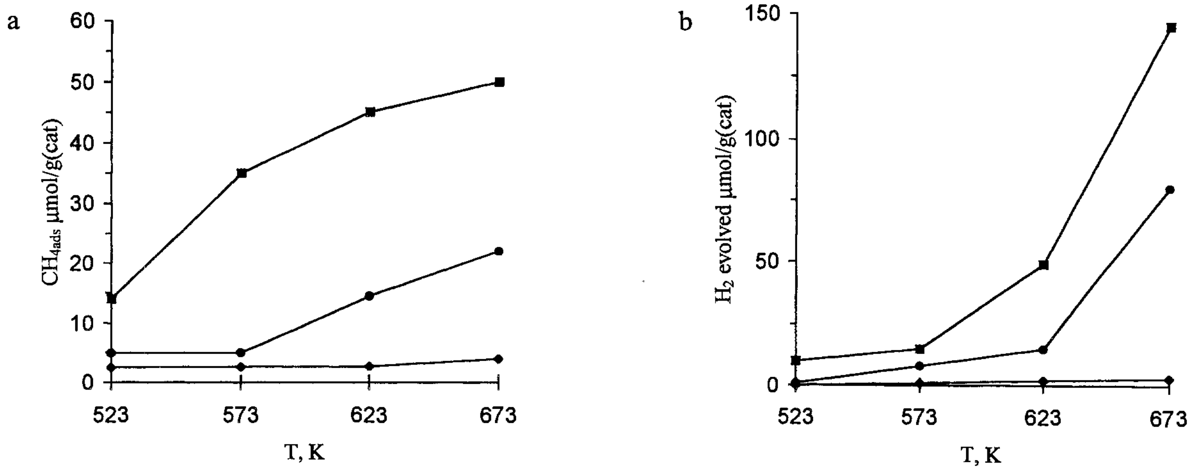

Fig. 1. Chemisorption of methane over Co/NaY (◆), Co/Al_2O_3 (●) and Co–Pt/NaY (■) samples as a function of temperature. (a) CH_x formed and measured by oxidation ($\mu mol/g_{cat}$) and (b) hydrogen evolved during chemisorption ($\mu mol/g_{cat}$).

Table 3
Yield, conversion and selectivities of methane coupling over NaY, Pt/NaY, Co/NaY, Co–Pt/NaY and Co–Pt/Al_2O_3 catalysts

Catalyst	$(CH_4)_{ads}$ [a] (μmol/g_{cat})	$(CH_4)_{conv}$ [b] (μmol/g_{cat})	Yield [c] (%)	S_{C_1} [d] (%)	$S_{C_{2+}}$ [e] (%)
NaY	6.8	0.5	8.0	77.3	22.7
Pt/NaY	32.0	2.5	7.8	23.7	76.3
Co/NaY	8.9	2.1	23.9	19.3	80.7
Co–Pt/NaY	37.5	39.8	~ 100	16.4	83.6
Co–Pt/Al_2O_3	9.8	10.5	~ 100	7.4	92.6

[a] Amount of CH_4 adsorbed in form of CH_x.
[b] Amount of CH_x converted into C_{2+} hydrocarbons.
[c] $(CH_4)_{conv}/(CH_4)_{ads}$ in percent.
[d] Selectivity of methane among the hydrocarbons formed.
[e] Selectivity of C_{2+} among the hydrocarbons formed.

higher hydrocarbons is 83.6%, which is nearly as high as was reported in the open literature. A yield of 88% was reported by Jiang et al. using a trap for ethylene evolved in the catalytic loop [24]. The Co–Pt/Al_2O_3 sample also shows high yield and high value in C_{2+} selectivity ($S_{C_{2+}}$ is about 92%), but its adsorbability is fourfold less than on zeolite supported Co–Pt bimetallic sample.

In order to understand the mechanism of the process we have to consider the catalyst structure in respect of both particle size and reducibility. As shown in table 3 the blank sample (without metal component) has negligible activity compared to metal containing samples because the metal component used for activation of methane chemisorbed, is missing. Pt is easily reduced in NaY zeolite, whereas cobalt is practically irreducible. Methane is easily activated on platinum indicated by methane/deuterium exchange. According to earlier studies carried out over Pt films step-wise exchange is predominant for methane/deuterium [25,26]. Due to the small particle size and zeolite environment, CH_x species are formed with significant hydrogen content, the x value being between 1 and 2 as indicated by the low proportion of CD_4 species shown in the experiments using deuterium (see table 2).

Although cobalt is reduced to a small extent, it still manifests itself to be the best catalyst and the small amount of methane chemisorbed can be ascribed to the small number of metal atoms exposed to the surface. This is supported by methane chemisorption over Co/Al_2O_3 [22] on which, in the subsequent deuteration of the surface CH_x species, the proportion of highly deuterated molecules increased.

Table 4
Selectivities (%) of the various products over NaY, Pt/NaY, Co/NaY, Co–Pt/NaY and Co–Pt/Al_2O_3 catalysts

Catalyst	C_1	C_2		C_3	C_4	C_5	C_6	C_{7+}
		ethane	ethylene					
NaY	77.3	–	16.2	0.7	5.8	–	–	–
Pt/NaY	23.7	17.0	36.3	9.9	13.1	–	–	–
Co/NaY	19.3	64.6	5.6	0.7	0.7	3.3	5.4	3.1
Co–Pt/NaY	16.4	58.2	0.2	1.1	0.6	17.9	5.0	0.6
Co–Pt/Al_2O_3	7.4	3.7	13.9	2.3	2.0	20.7	16.8	33.2

The best catalyst appears to be when cobalt and platinum are combined inside the zeolite cage. Platinum facilitates reduction of cobalt whose particle size is still small (X-ray amorphous [17]) and a large number of metal atoms are exposed to the surface. Thus, methane chemisorption increases on bimetallic particles (see fig. 1), but the extent of its hydrogen dissociation during chemisorption is not as high as on pure cobalt [27] which is also supported by deuterium experiments (table 2). In addition, due to the enhanced hydrogen activation on the bimetallic particles, the conversion of CH_x species into hydrocarbons occurs with 100% yield with a selectivity of C_{2+} close to 84%.

The effect is explained in the following way. A combination of Co with Pt matrix (Pt is in excess compared to Co) causes a synergistic effect on the secondary process, i.e., on the C–C bond formation. It must be noted that Co alone is an excellent Fischer–Tropsch catalyst to form higher hydrocarbons [27], consequently, probability of the chain propagation vs. hydrogenation is high. On the other hand, on cobalt the hydrogen chemisorption is activated, therefore hydrogen is provided by dissociation mainly on Pt atoms. Hence, C–C bond formation from CH_x vs. its hydrogenation to methane is favoured on cobalt promoted by platinum. The 100% yield is likely due to the diminished C–Co bond strength as a result of the presence of cobalt in Pt neighbourhood, thereby surface chain propagation is also facilitated.

The "goodness" of Co–Pt/NaY catalyst in methane coupling could be predicted also from the results obtained in the experiments of dissociative methane chemisorption and the number of deuterium atoms in methane after deuteration. On the bimetallic catalyst the enhanced reactivity to form higher hydrocarbons is closely related to the comparatively large fraction of the methane-d_2 and methane-d_3 indicating the presence of a non-completely dissociated form of methane. That is, for high reactivity a value of $1 < x < 2$ for hydrogen content in CH_x is required. If the value of x is too high, dissociative chemisorption of methane is hampered, if $x = 0$ the carbon is easily transformed into non-reactive carbon species.

It is worth mentioning that in the distribution of higher hydrocarbons Co–Pt/NaY catalyst has a sharp maximum at C_5 and C_6. It might be a result of the zeolite matrix in which these hydrocarbons could preferably be produced. However, Co–Pt/Al_2O_3 also has high selectivity to these hydrocarbons but chain growth continues further as indicated by the high C_{7+} values. It is believed that on alumina supported Co–Pt bimetallic catalyst no geometrical constraint exists thus higher hydrocarbons can also be produced, while in NaY the zeolite geometry prevents the formation of long chains. The advantage of zeolite supported Co–Pt bimetallic catalyst is the preferred dissociative adsorption of methane indicated by the high amount of CH_x formation

4. Conclusions

A synergistic effect has been observed in the two-step methane coupling to form higher hydrocarbons over Pt/NaY, Co/NaY, Co–Pt/NaY and Co–Pt/Al_2O_3 catalysts.

Co–Pt/NaY and Co–Pt/Al_2O_3 showed an exceptionally high yield (100%) referred to the adsorbed CH_x species and high selectivity in formation of C_{2+} hydrocarbons (83.6 and 92.6%, respectively) at 523 K for chemisorption and 523 K for hydrogenation. The synergistic effect can be interpreted by insertion of Co into Pt inside the zeolite cages which causes a preferential coupling of CH_x species vs. its hydrogenation into methane. Experiments with deuterium show that on bimetallic catalyst deep dissociation of methane does not occur (small amount of CD_4) and the weakly bond CH_x species can easily participate in chain building reaction on the surface.

Acknowledgement

The authors are indebted to the COST program of the European Commission (project No. COST D5/0001/93) and the National Science and Research Grant.

References

[1] T. Koerts and R.A. van Santen, J. Mol. Catal. 70 (1991) 119; 74 (1992) 185;
A. de Koster and R.A. van Santen, J. Catal. 127 (1991) 141.

[2] T. Koerts and R.A. van Santen, J. Chem. Soc. Chem. Commun. (1991) 1281.

[3] T. Koerts, M.J.A.G. Deelen and R.A. van Santen, J. Catal. 138 (1992) 101.

[4] T. Koerts, P.A. Leclercq and R.A. van Santen, J. Am. Chem. Soc. 114 (1992) 7272.

[5] J.R. Rostrup-Nielsen, Catal. Today 21 (1994) 257.

[6] M. Baerns, K. van der Wiele and J.R.H. Ross, Catal. Today 4 (1989) 471.

[7] J.H. Lunsford, in: *Studies in Surf. Sci. and Catal.*, Vol. 61, eds. A. Holmen, K.-I. Jens and S. Kolboe (Elsevier, Amsterdam, 1991) p. 3; in: *Proc. 10th Int. Congr. on Catalysis*, Vol. A, eds. L. Guczi, F. Solymosi and P. Tétényi (Akadémiai Kiadó, Budapest, 1993) p. 103; in: *Studies in Surf. Sci. and Catal.*, Vol. 81, eds. H.E. Curry-Hyde and R.F. Howe (Elsevier, Amsterdam, 1994) p. 1.

[8] J.L.G. Fierro, Catal. Lett. 22 (1993) 67.

[9] F. Solymosi, A. Erdôhelyi and J. Cserényi, Catal. Lett. 16 (1992) 399.

[10] F. Solymosi, Gy. Kutsán and A. Erdôhelyi, Catal. Lett. 11 (1991) 149.

[11] F. Solymosi, I. Kovács and K. Révész, Catal. Lett. 27 (1994) 53.

[12] M. Belgued, P. Pareja, A. Amariglio and H. Amariglio, Nature 352 (1991) 789.

[13] M. Belgued, H. Amariglio, P. Pareja, A. Amariglio and J. Saint-Just, Catal. Today 13 (1992) 437.

[14] E. Mielczarski, S. Monteverdi, A. Amariglio and H. Amariglio, Appl. Catal. 104 (1993) 215.

[15] P. Pareja, A. Amariglio, M. Belgued and H. Amariglio, Catal. Today 21 (1994) 423.

[16] G. Lu, T. Hoffer and L. Guczi, Catal. Lett. 14 (1992) 207.

[17] G. Lu, T. Hoffer and L. Guczi, Appl. Catal. 93 (1992) 61.

[18] G. Lu, Z. Zsoldos, Zs. Koppány and L. Guczi, Catal. Lett. 24 (1994) 15.

[19] Z. Zsoldos G. Vass, G. Lu and L. Guczi, Appl. Surf. Sci. 78 (1994) 467.

[20] L. Guczi, A. Sárkány and Zs. Koppány, Appl. Catal. 120 (1994) L1.

[21] L. Guczi, V.K. Sarma, Zs. Koppány and A. Sárkány, paper at 14th Meeting of the North American Catalysis Society, Snowbird, 1995 June 10–16, USA.

[22] L. Guczi, V.K. Sarma, Zs. Koppány, R. Sundararajan and Z. Zsoldos, 4th Natural Gas Symposium, Kruger National Park, South Africa, 19–23 November 1995; in: *Studies in Surf. Sci. and Catal.* (Elsevier, Amsterdam, 1995), in press.

[23] D. Bazin, F. Maire, F. Garin, G. Lu and L. Guczi, to be published.

[24] Y. Jiang, I.V. Yentetakis and C.G. Vayenas, Science 264 (1994) 1563.

[25] C. Kemball, Adv. Catal. 11 (1959) 223.

[26] D.W. McKee and K. Norton, J. Phys. Chem. 68 (1964) 481.

[27] C.H. Bartholomew, in: *New Trends in CO Activation*, Studies in Surf. Sci and Catal., Vol. 64, ed. L. Guczi (Elsevier, Amsterdam, 1991) p. 158.