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CATALYTIC REACTION MECHANISMS

Physico-Chemical and Catalytic Study of the Co/SiO$_2$ Catalysts[1]

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Abstract—This paper is focused on the physico-chemical and catalytic properties of Co/SiO$_2$ catalysts. Silica-supported cobalt catalysts were prepared by sol-gel and impregnation methods and characterized by BET measurements, temperature programmed reduction (TPR$_{H2}$), X-ray diffraction (XRD), and thermogravimetry-mass spectroscopy (TG-DTA-MS). The sol-gel method of preparation leads to metal/support catalyst precursor with a homogenous distribution of metal ions into bulk silica network or on its surface. After drying the catalysts were calcined at 500, 700, and 900°C. The reducibility of the supported metal oxide phases in hydrogen was determined by TPR measurements. The influence of high temperature—atmosphere treatment on the phase composition of Co/SiO$_2$ catalysts was investigated by XRD and TG-DTA-MS methods. At least five crystallographic cobalt phases may exist on silica: metallic Co, CoO, Co$_3$O$_4$, and two different forms of Co$_2$SiO$_4$ cobalt silicate. Those catalysts in which cobalt was chemically bonded with silica show worse reducibility as a result of strongly bonded Co-O-Si species formed during high-temperature oxidation. The TPR measurements show that a gradual increase in the oxidation temperature (500–900°C) leads to a decrease in low-temperature hydrogen reduction effects (<600°C). The decrease of cobalt oxide reduction degree is caused by cobalt silicate formation during the oxidation at high temperature ($T \leq 1000$°C). The catalysts were tested by the reforming of methane by carbon dioxide and methanation of CO$_2$ reactions.

1. INTRODUCTION

Cobalt supported catalysts have found widespread applications in industrial processes such as hydrogenation and hydrotreating. The most common application is Fischer-Tropsch synthesis (long chair hydrocarbon production) [1, 2]. They are also active in the following reactions: hydrogenation of aromatic compounds [3, 4], cobalt monoxide [5], hydroxylation of hydrocarbons [6], the reductive amination of alcohols using ammonia [2, 7] hydrosulranization [8], dehydrogenation of alkanes in oxidative atmosphere [9, 10], convertion of methane to syngas [11], to higher hydrocarbons [12, 13], and the isomerization of hydrocarbons [14].

The selectivity and activity depend on the support [15, 16], methods of preparation, pretreatment conditions, extent of cobalt reduction [17, 18], the reaction conditions, the oxide promoter (TiO$_2$, rare earth oxides etc.) and the metal promoter (Cu, Ru etc.) [19], and also the interaction between metal or metal oxide and support [18, 20]. For example, the activity and selectivity of Co/SiO$_2$ catalysts obtained by reacting Co$_2$(CO)$_8$ with silica differ considerably from those of solids prepared from cobalt (II) nitrate impregnation [21, 22].

The interaction of cobalt particles with support has been the subject of many studies [1, 5, 20, 23–26]. The reducibility of cobalt catalysts depends on the kind of support (eg., SiO$_2$, Al$_2$O$_3$). Especially at low cobalt concentrations the reducibility of Co/SiO$_2$ catalysts is higher than Co/Al$_2$O$_3$ catalysts [2, 15, 16]. Cobalt is known to combine chemically with alumina forming compounds resistant to the reduction of cobalt aluminates [17, 18]. Although, silica is considered to be more inert than alumina the formation of cobalt silicates has been recently reported [24, 27, 28]. The main factors conditioning the formation of silicates on Co/SiO$_2$ catalyst are cobalt content and surface area of silica [9], the kind of cobalt precursor (CoCl$_2$, Co(NO$_3$)$_2$, Co-acetate) [21, 29], and conditions of catalyst preparation and calcination [16, 17, 29, 30].

The sol-gel process is a useful method for preparation of organically and simultaneously coordinatively modified catalysts. The use of the ≡Si–C≡ bond is a reasonable way to combine chemically organic and inorganic components of catalyst precursor [28, 31]. In this way there exists a possibility to lead in any functional group (in our case—(CH$_2$)$_3$NH$_2$ group) into an inorganic network [21, 29]. The cobalt ion creates coordination crosslinking points with amino groups in the organically modified silicate xerogels. The sol-gel method of preparation leads to metal/support catalyst precursor with a homogenous distribution of metal ions into bulk silica network or on its surface.

In this study the influence of preparation methods on the physico-chemical and catalytic properties of cobalt supported catalysts was investigated. The catalysts were prepared by two methods: sol-gel and impregnation of silica in water. This work describes temperature programmed reduction (TPR) of cobalt oxide/silica cat-

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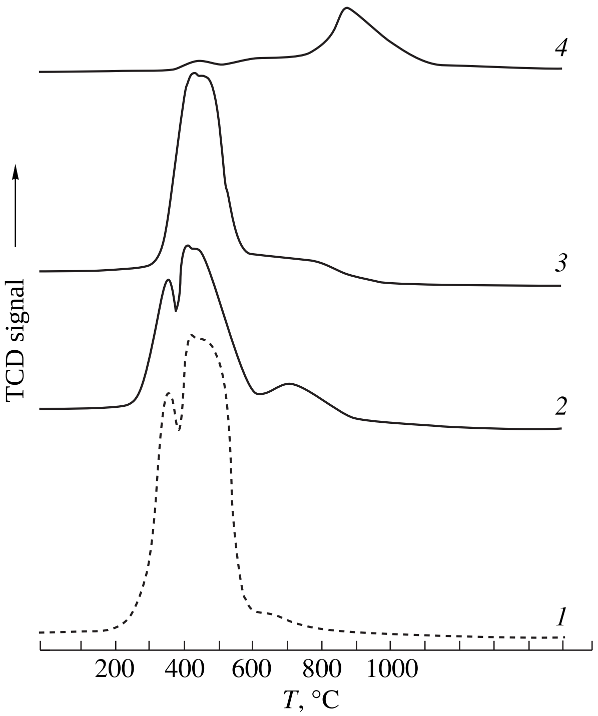

Fig. 1. TPR_{H_2} profiles for Co_3O_4 and 3%Co/SiO_2 impregnated catalyst oxidized at: 500°C, 1 h (curves *1*, *2*); 700°C, 0.5 h (curve *3*); and 900°C, 0.5 h (curve *4*), respectively.

alysts in hydrogen atmosphere and X-ray powder diffraction (XRD) investigations of phase composition. The examined catalysts were also tested in dry reforming of CH_4 and methanation of CO_2 reactions.

2. MATERIALS AND METHODS

All the chemicals used were of guaranteed-reagent grade. Cobalt (II) nitrate $Co(NO_3)_2 \cdot 6H_2O$ (Fluka A.G.) and alkoxysilanes as tetramethoxysilane $Si(OCH_3)_4$ (abb. B) and 3-aimnopropylotrimethoxysilane $H_2N(CH_2)_3Si(OCH_3)_3$ (abb. A) (Aldrich Co), were used to prepare the animated xerogel surfaces coordinately modified with cobalt (II) nitrate. Commercial silica gel from the Merck (BET surface 364 m^2 g^{-1}, pore volume 2.3 cm^3 g^{-1}) was used to prepare the impregnated catalysts.

The cobalt catalysts were prepared by the sol-gel and impregnation methods. In the case of the sol-gel procedure the cobalt was introduced both in the bulk and on the surface of silica xerogels. In the surface case the aminated silica xerogels were first prepared by sol-gel method. In the next stage Co^{2+} ions from aqueous solution were chemisorbed by aminated xerogels. In this way cobalt (II) complexes with amino groups on silica surface were generated. In the bulk case Co^{2+} ions are introduced at the sol stage of preparation. Hydrolysis and polycondensation reactions produce a bulk organic-inorganic xerogel containing a metal complex. The impregnated Co/silica catalysts were also prepared by the conventional impregnation of SiO_2, using appropriate water solutions of cobalt (II) nitrate. Cobalt content in the catalysts was 3% in both cases. Details of the preparation procedure were described in paper [32].

Themogravimetric measurements were carried out in an oxidative atmosphere using TG-DTA-MS method. Thermobalance SETSYS-1600 (SETERAM) and a quadrupole mass spectrometer Thennostar (Balzers) were used. A linear heating rate of 10°C min^{-1} in the temperature range 20–1000°C was used. The surface area of the samples was determined by Sorptomatic 1900 (Carlo Erba) using low-temperature nitrogen adsorption. Temperature programmed reduction (TPR) investigation was carried out using AMI-1 Altamira Instrument. The samples of the fresh catalyst (0.2 g), prior to the TPR measurements were calcined at 500°C for 1 h, 700 and 900°C for 0.5 h in 10% O_2 90% Ar gas stream. The oxidized samples were reduced in a 10% H_2–90% Ar gas flowing stream (50 cm^3 min^{-1}). Katharometer was used as a detector. X-ray diffraction (XRD) measurements were performed with a porycrystalline D 5000 Siemens X-ray difractometer. It was operating with a scanning speed of 0.03° per 10 s. Diffraction patterns were recorded in the range of $2\theta = 0°–80°$, using nickel—filtered CuK_α radiation.

The cobalt/silica catalysts were tested in the reactions of the dry reforming of methane and methanation of carbon dioxide. The catalytic reactions were carried out under atmospheric pressure in a flow system, using a vertical quartz tube (8 mm diameter) as a reactor. The molar ratio of the reactant gases in the dry reforming of methane reaction was $CH_4/CO_2 = 1 : 1$ and the flow rate of gas mixture was 70 ccm/min. In the case of the methanation reaction the molar ratio of reactant gases was $H_2/CO_2 = 5 : 1$ and the flow rate of the gas mixture was 50 cm^3/min. Co/SiO_2 catalyst samples (0.1 g) were tested in the temperature range 300–900°C. At given temperature the sample was stabilized 30 min in the stream of reactants prior to activity measurements.

3. RESULTS AND DISCUSSION

3.1. TPR Measurements

The influence of oxidation temperature on TPR profiles for Co/SiO_2 catalysts prepared by various methods is presented in Figs. 1–3. The processes of reduction take place in a wide temperature range from 200 up to 1100°C. TPR profiles differ considerably depending on the method of preparation and the oxidation temperature.

One common feature of TPR profiles of sol-gel catalysts after oxidation at 500°C for 1 h is the desorption effect usually observed in the temperature range 500–700°C (Figs. 2, 3). This desorption effect was attributed to the evolution of carbon dioxide and was experimentally confirmed by using a mass spectrometer as a

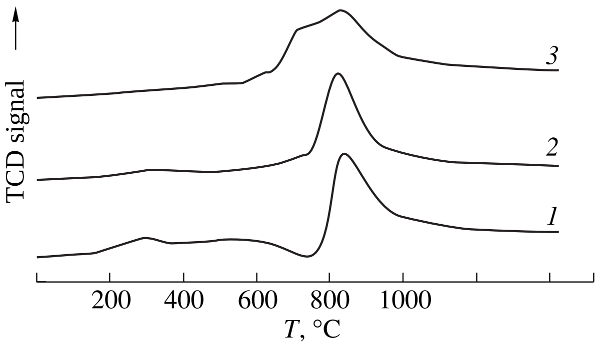

Fig. 2. TPR_{H_2} profiles for $3\%Co/SiO_2$ catalyst (sol-gel "in bulk"), oxidized at: 500 (*1*), 700 (*2*), 900°C (*3*), respectively (1 h).

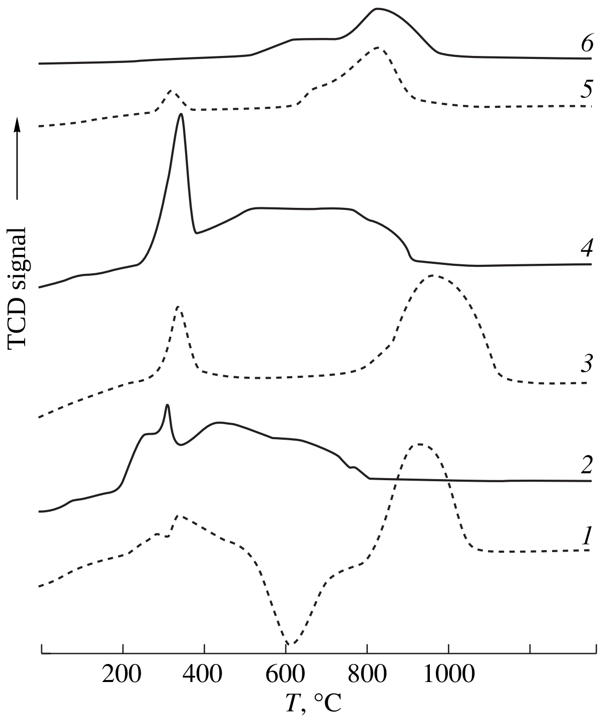

Fig. 3. TPR_{H2} profiles for $2\%Co/SiO_2$ catalyst (sol-gel "on surface") oxidized and reoxidized at: 500, 700, 900°C (1 h); curves *1*, *3*, *5* and *2*, *4*, *6*, respectively.

detector. Only in the case of impregnated catalyst does the oxidation at 500°C lead to a carbon free cobalt oxide/silica catalyst. In this case, sol-gel methods much longer than 1 h oxidation at 500°C or a higher temperature of catalyst calcination is required to completely remove any carbon residues. The reoxidation at 500°C removes this effect entirely (compare curves *1* and *2* in Fig. 3). Contrary to our results, Ernst *et al.* [33] reported that a temperature of 550°C is sufficient for the entire decomposition of cobalt supported catalyst precursors prepared by sol-gel method.

The TPR measurements show that a gradual increase in the oxidation temperature (500–900°C) leads to a decrease in the low-temperature hydrogen reduction effects. Calcination at 500°C leads to the formation of Co_3O_4 phase [17, 34, 35]. Ernst *et al.* [36] suggest that two types of structures could be present on the surface, Co_3O_4 as well as Co_2SiO_4. Their suggestions are based on the similarity with the Co/Al_2O_3 system, where the $CoAl_2O_4$ spinel can be readily formed [17, 18]. Potoczna-Petru *et al.* [4] confirmed the presence of small crystallites of Co_3O_4 on the surface of the catalyst calcined in air at 550°C.

The reduction profile of unsupported Co_3O_4 shows two heavily overlapped peaks with their maxima located at about 350 and 450°C, respectively (curve *1* in Fig. 1). The deconvolution procedure of this profile strongly suggests that hydrogen reduction of Co_3O_4 takes place as a two stage process in the temperature range 200–600°C according to equations:

$$Co_3O_4 + H_2 \longrightarrow 3CoO + H_2O, \quad \text{(I)}$$

$$CoO + H_2 \longrightarrow Co + H_2O. \quad \text{(II)}$$

The TPR profiles for 3% Co/SiO_2 impregnated catalyst after its oxidation at 500°C is similar to that representing bulk Co_3O_4 (compare curves *1* and *2* in Fig. 1). The alternative explanation based on a bimodal distribution of small and large cobalt oxide crystallites on silica surface was postulated [26]. The first peak would correspond to the reduction of large particles and the second one to those small particles. In order to verify such an interpretation, the independent TG-DTA-MS method of bulk Co_3O_4 reduction in 5% H_2–95% Ar stream was applied and appropriate results are presented in Fig. 4. Both the TG and DTG curves confirm a two step reduction of Co_3O_4 phase. The first TG mass drop of 6.7% and the second one of 20.1% are in good accordance with theoretical values predicted by Eqs. (I) 6.6, (II) 19.9%, respectively. Also, DTA curve and MS profiles representing hydrogen uptake (m/z = 2) and water evolution (m/z = 18) confirm the reduction pathway $Co_3O_4 \longrightarrow CoO \longrightarrow Co$ [25, 34, 37].

As can be seen from Fig. 1 (curve *1*) and Fig. 4, the reduction of bulk Co_3O_4 to metallic Co is accomplished up to 600°C but in the case of sol-gel catalysts the high temperature reduction effects were also observed in the temperature range 600–1000°C. The TPR peak ca. 800°C would be ascribed to the reduction of strongly interacting CoO_x–SiO_2 species, whereas the low temperature reduction is characteristic only of cobalt oxide phase weakly bonded to silica surface. Because the high temperature reduction effects (above 500°C) dominate, one can anticipate that only a small part of Co_3O_4 phase is not involved in strong interactions with the silica support.

This weakly bonded Co_3O_4 phase almost disappears after the oxidation at 900°C (Figs. 1–3). The major part of cobalt oxide phase is reduced in the temperature range above 600°C and is attributed to strongly interacting with the silica surface CoO_x–SiO_2 phase (600–

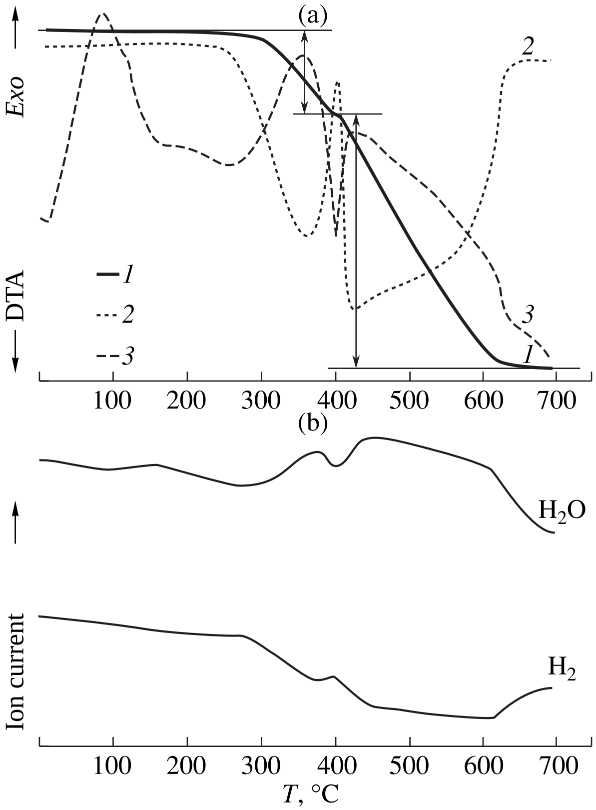

Fig. 4. Thermogravimetric TG-DTA-MS reduction of bulk Co_3O_4 in the 5%H_2 –95% Ar stream: (a) TG (*1*), DTG (*2*), and DTA (*3*); (b) changes in the amounts of H_2O and H_2 according to mass spectrometry.

800°C), or it forms a cobalt silicate phase reducible in the temperature range 800–1000°C. The considerable decrease in reduction effects after oxidation at 900°C strongly suggests that a significant part of the cobalt oxide phase does not participate in redox cycling forming nonreducible cobalt silicate $2CoO + SiO_2 \longrightarrow Co_2SiO_4$ [20, 29, 38]. Kogelbauer *et al.* [28] reported that silicates were formed from metal and silica. Many factors (the nature of SiO_2, the cobalt content, preparation method, and precursor salt) can influence the strength of the interaction between the cobalt oxide phase and the silica. Thus several types of cobalt silicates with a spinel structure like $Co_2^{2+}SiO_4$ and $Co_{1-x}^{2+}Co_2^{3+}Si_{x/2}O_4$ (Co^{3+} in an octahedral site) have been postulated [26]. Puskas *et al.* [27] observed the formation of the cobalt species, which can be reduced above 700°C. Rosynek and Polansky [30] reported the influence of the SiO_2 support on the reducibility of supported cobalt oxide phases. They also observed that the reduction of cobalt oxide to metallic cobalt occurs in several steps and it is not complete at 900°C, and the XPS study confirmed the formation of various oxidation states of cobalt.

Table 1. Degree of Co_3O_4 reduction versus oxidation temperature

Catalysts	Oxidation temperature [°C]	Degree of reduction [%]
3% Co/SiO_2 (nitrate) impregnated	500	80
	700	75
	900	30
2% Co/SiO_2 (sol-gel “on surface”)	500	–
	700	64
	900	38
2% Co/SiO_2 (sol-gel “in bulk”)	500	–
	700	25
	900	30

These studies clearly showed the influence of preparation methods on the reducibility of cobalt catalysts with the same cobalt content (ca. 3.0%). The sol-gel method leads to the formation of cobalt oxide phase strongly interacting with silica support after the oxidation of catalyst precursor at 500°C and such interactions would be explained taking into account the homogenous initial distribution of cobalt ions in the silica network or on its surface. For the impregnated catalyst, the highly resistant or non-reducible cobalt oxide phases are formed during high temperature oxidation (700–900°C).

The influence of oxidation temperature on the degree of cobalt oxide phase reduction is shown in Table 1. The degree of reduction was calculated by integration of the surface area under TPR profiles presented in Figs. 1–3 and compared to the area of known volume of hydrogen pulse and the stoichiometry of the reduction was based according to the following reaction:

$$Co_3O_4 + 4H_2 \longrightarrow 3Co + 4H_2O. \qquad \text{(III)}$$

The reducibility of the impregnated Co/SiO_2 catalyst (30–80%) was relatively high in comparison with other catalysts. The increase of oxidation temperature leads to the considerable lower reducibility of Co/SiO_2 catalysts. Such behavior seems to confirm the formation of non-reducible cobalt silicate phase during the catalyst oxidation at 900°C. More than 70% of supported cobalt was inevitably incorporated into the silica network.

The influence of Co/SiO_2 catalyst oxidation and reoxidation on TPR profiles is presented in Fig. 3. The surface complexation of cobalt ions on animated silica surface should lead to atomically dispersed cobalt species on the silica surface. After oxidation at 500°C the formation of surface CoO_x–SiO_2 species could be anticipated. As can be seen in Fig. 3 the bimodal cobalt oxide distribution is evident. The relatively small reduction effect (200–600°C) can be assigned to $Co_3O_4 \longrightarrow$ Co reduction. Whereas the major reduction takes place in the temperature range 600–1000°C and it represents the reduction of CoO_x–SiO_2 surface species (curve *3* in Fig. 3). The reoxidation of this sample at the same temperature (curve *4* in Fig. 3) results in a considerable change in the distribution of the cobalt oxide phase. The enhancement of the low temperature reduction peak and considerable shift to lower temperatures for the high temperature reduction effect clearly indicates that the redistribution of cobalt oxide phase takes place during the first TPR run. The sintering in hydrogen at 1000°C seems to be responsible for the change in cobalt oxide distribution leading to cobalt oxide, which is not as strongly stabilized by the silica surface as it was in the course of the first oxidation step. Because such behavior is not observed for oxidation and reoxidation at 900°C, the significant incorporation of Co^{2+} ions into silica bulk seems evident at this temperature (compare Table 1).

The influence of pretreatment conditions on TPR profiles for impregnated 3% Co/SiO_2 catalyst is presented in Fig. 5. Temperature programmed decomposition in argon stream is represented by curve *1* and reflects the reduction effects taking place above 600°C for CoO phase strongly bonded to silica surface and cobalt silicate surface phase reduction. Curves *2* and *3* represent TPR profiles after the oxidative temperature programmed decomposition in O_2–Ar stream up to 900°C. Cooling the sample in an argon stream leads to the reduction effect assigned only to cobalt silicate surface phase reduction. Whereas cooling in an O_2–Ar stream results in additional reoxidation of cobalt leading to CoO phase formation. The low temperature oxidation of Co/SiO_2 sample precursor at 500°C is represented by TPR profile as curve *4* in Fig. 5. Both weakly bonded Co_3O_4 and strongly bonded CoO and Co_2SiO_4 phases reduction effects are clearly visible in this figure.

3.2. The XRD Studies

The influence of sample pretreatment conditions on XRD profiles for Co_3O_4 alone and 3.0 wt % Co/SiO_2 catalyst (prepared by impregnation method) is presented in Fig. 6. The XRD spectrum of bulk Co_3O_4 after 2 h oxidation at 600°C in oxygen stream and subsequent TPR run up to 900°C is represented by curve *1* which is almost entirely consistent with the literature pattern characteristic of fcc Co metal crystalline phase. The appearance of CoO phase traces is caused by cobalt metal reoxidation during cooling of the reduced sample in an argon atmosphere. XRD profiles of Co/SiO_2 samples are characterized by a broad diffraction band with maximum intensity at $2\theta = 22°$ and with a considerable tailing towards higher diffraction angle characteristic of amorphous silica.

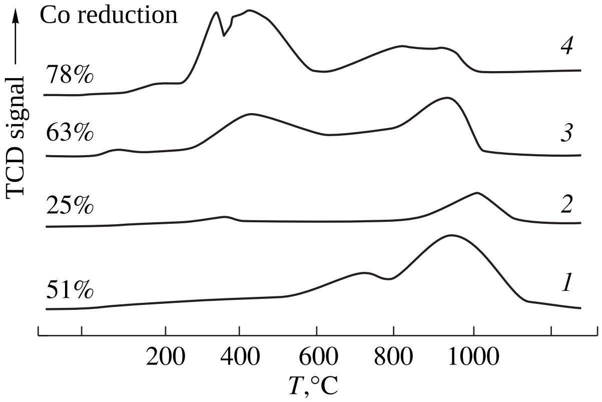

Fig. 5. The influence of pretreatment conditions on TPR profiles for 3% Co/SiO_2 catalyst samples. (*1*) After TPDec in Ar stream up to 900°C; (*2*, *3*) after TPDec in O_2–Ar stream up to 900°C and cooling in Ar and O_2–Ar stream, respectively; (*4*) after TPDec in O_2–Ar stream up to 500°C and cooling in O_2–Ar stream.

Additionally, depending on the pretreatment conditions sharp diffraction reflections characteristic of crystalline CoO, Co_3O_4, Co_2SiO_4, and Co metal phases are observed (curves *2*–*4* in Fig. 6). The oxidation of Co/SiO_2 sample at 600°C leads to crystalline Co_3O_4 phase dispersed on silica surface (curve *2*). Oxidation at a still higher temperature of 900°C results in Co_3O_4 phase decomposition and transformation into CoO and cobalt silicates crystalline phase (curve *3*). The oxidation at 600°C and subsequent reduction up to 900°C leads to metallic phase and another non-reducible cobalt silicate crystalline structure (curve *4*). The existence of non-reducible cobalt silicate phase in the dispersed Co/SiO_2 system may serve as an independent XRD experimental explanation of the observed considerable decrease in dispersed cobalt oxide reducibility on silica surface (compare Table 1). The calculated decrease in Co_3O_4 reduction degree after high temperature oxidation cannot be entirely explained on the following scheme of phase transformation: $Co_3O_4 \longrightarrow CoO \longrightarrow$ reducible Co_2SiO_4. Such an approach would lead to 25% lower reducibility. At over 70% lower, the calculation of values of reduction degree strongly suggest the non-reducible Co_2SiO_4 cobalt silicate formation. One can infer that more than 50% of the cobalt may form this kind of silicate. Despite the numerous data referring to Co/SiO_2 system some problems still remain unresolved. According to Jablonski *et al.* [38] total reduction of cobalt can be achieved at 900°C. Our catalyst containing 3 wt % Co after oxidation at 900°C shows the coexistence of cobalt silicate and CoO phases (curve *3* in Fig. 6) and TPR profiles for these phases are represented as curve *4* in Fig. 1 and curve *5* in Fig. 3. In this case the degree of cobalt reduction is about 30% of total reduction (Table 1) and can be assigned to transformation of CoO into non-reducible Co_2SiO_4. This process is rather common during high

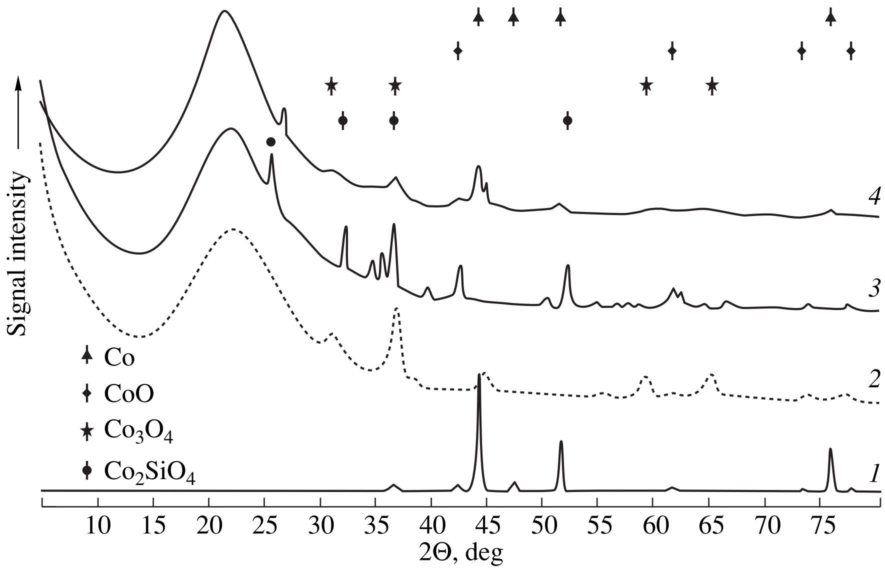

Fig. 6. The influence of pretreatment conditions on XRD profiles for bulk Co_3O_4 and supported 3% Co/SiO_2 samples: (*1*) Co_3O_4 after 2 h O_2 at 600°C and TPR run up to 900°C; (*2*, *3*) 3% Co/SiO_2 after 2 h O_2 at 600 and 900°C, respectively; (*4*) 3% Co/SiO_2 after 2 h O_2 at 600°C and TPR run up to 900°C.

temperature oxidation of Co/SiO_2 system and seems to be confirmed by Ernst *et al.* [36] and others [24, 27, 28].

3.3. Reforming of Methane by Carbon Dioxide

The effect of the method of cobalt catalysts preparation on the activity in dry reforming of methane as a function of reaction temperature is presented in Fig. 7. The 2–3% Co/SiO_2 catalysts show rather poor activity after calcination and reduction at 500°C (Fig. 7a). This fact, reflecting the existence of non-reducible phase of cobalt strongly interacting with the support is responsible for small concentration of metallic cobalt sites on the silica surface. The activity of these catalysts increases significantly after hydrogen reduction at 700°C (Fig. 7b).

The impregnated catalyst appeared the most active one, while the catalysts obtained by the sol-gel process exhibit lower activity. A reduction temperature of 900°C (Fig. 7c) practically does not change the activity of the impregnated catalyst, but sol-gel catalysts activity decreased about 50%. The conversion of CH_4 and CO_2 and activity of cobalt catalysts in reaction of dry reforming of methane at 800°C is shown in Table 2. Higher conversion of CH_4 is equal to 23% for the impregnated catalyst. Similar results were obtained by Rodriguez and coworkers [39, 40]. They provided comparative studies of various catalysts in the same reaction. The conversion of CO_2 is higher than the conversion of CH_4. This phenomena is probably caused by the reverse WGS reaction:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O, \qquad \text{(IV)}$$

taking place simultaneously with the dry reforming reaction. This reaction causes consumption of CO_2 and increases the efficiency of reaction to carbon monoxide formation.

3.4. Methanation of Carbon Dioxide

The strong influence of Co/SiO_2 catalyst precursor on the methanation activity is presented in Fig. 8. The samples were pretreated in an oxygen stream at 500°C for 1 h and subsequently reduced in a hydrogen stream for 1 h at the same temperature. The order of Co/SiO_2 catalyst methanation reactivity is $Co(NO_3)_2$ > Co (sol-gel, surface) > Co (sol-gel, bulk) and seems to reflect the reducibility of these catalysts. As can be deduced from Figs. 1–4, the formation of cobalt metallic phase in the course of hydrogen reduction at 500°C should follow an analogical pattern. Thus, one can infer that strong cobalt-silica (Co–O–Si) interaction does not enhance the activity of Co/silica methanation catalysts. The low methanation activity for 3 wt %Co/SiO_2 catalyst prepared by sol-gel method and cobalt surface complexation is caused by favorable formation of cobalt silicate phase, which is not active in this reaction.

The effect of pretreatment procedure on methanation activity for Co/SiO_2 catalyst is presented in Fig. 9. From three pretreatment procedures at 500°C: reduction, reduction following oxidation, and oxidation, the first procedure results in the most efficient catalyst, whereas the last one gives very poor catalyst. Such an approach reflects the different state of the catalyst surface. One can anticipate complete reduction of cobalt oxide phase leading to highly dispersed metallic crys-

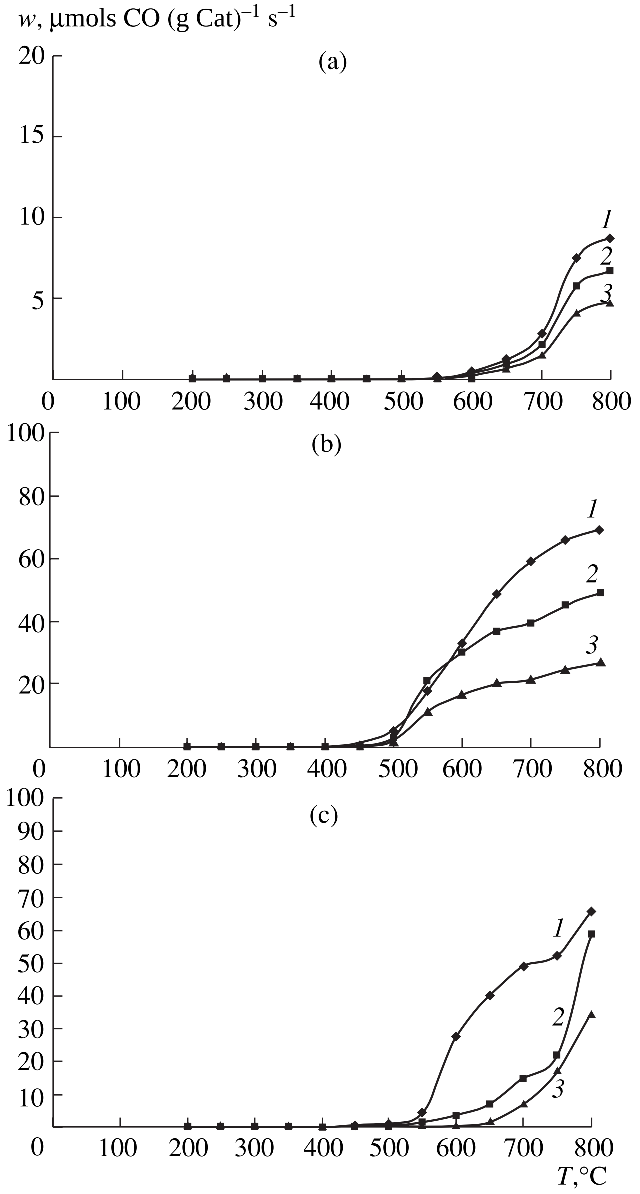

Fig. 7. The influence of Co/SiO_2 catalysts preparation on the dry reforming of CH_4 selectivity. The catalyst was pretreated in oxygen 2 h at 500°C and reduced in hydrogen 1 h: (a) at 500, (b) at 700, (c) at 900°C. (*1*) Supported 3% Co/SiO_2, (*2*) sol-gel 2% Co/SiO_2 (on the surface), (*3*) sol-gel 3% Co/SiO_2 (in the bulk).

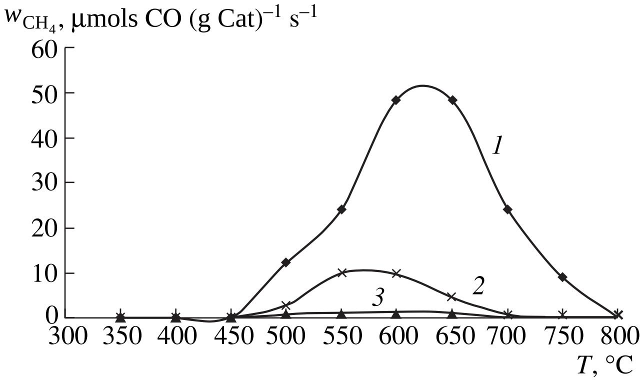

Fig. 8. Influence of Co/SiO_2 catalyst precursor on methanation selectivity. The catalyst was pretreated in oxygen 1 h at 500°C and reduced in hydrogen 1 h at 500°C. (*1*) 3% Co/SiO_2 (impregnation); (*2*) 2% Co/SiO_2 (sol-gel, on the surface), (*3*) 3% Co/SiO_2 (sol-gel, in the bulk).

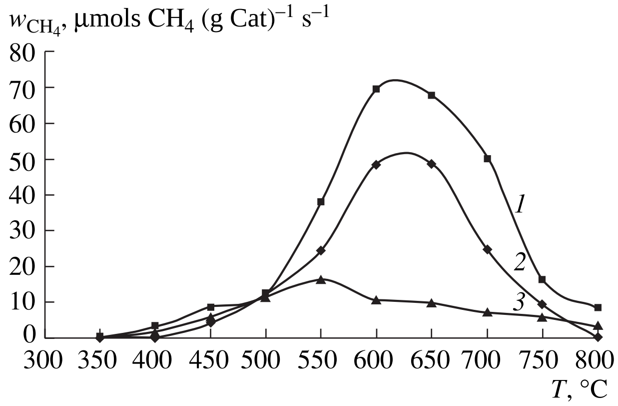

Fig. 9. Influence of the pretreatment of Co/SiO_2 impregnated catalyst on methanation selectivity. (*1*) Reduced in H_2 at 500°C for 1 h, (*2*) oxidized and then reduced, (*3*) oxidized in O_2 at 500°C for 2 h.

tallites on the silica surface after reduction. Lower degree of cobalt oxide reduction and lower dispersion of metal can be envisaged after oxidation and subsequent reduction. In the case of oxidation alone, poor reduction of the catalyst is being developed in reaction conditions. The applied Co/silica catalysts were not very selective for methane formation. They were much more selective in the partial reduction of CO_2 towards carbon monoxide. The influence of the catalyst precursors on the selectivity to carbon monoxide is presented in Fig. 10. The same trend was observed as for methanation activity (compare Fig. 8).

For Co/SiO_2 catalyst the selectivity of CO_2 hydrogenation to CH_4 is comparable to the selectivity towards CO at a temperature lower than 450°C (compare Figs. 8 and 10). At still higher temperature the formation of CO excessively predominates the formation of CH_4. Such temperature behavior of a Co/SiO_2 catalyst can be expected on the basis of thermodynamic equilibrium conditions [41]. The strongly exothermic methanation of CO_2 becomes unfavorable above 500°C whereas the slightly endothermic formation of CO becomes favorable above 600°C. Also, the reforming of CH_4 with CO_2 to synthesis gas, being strongly endothermic, may serve as a possible explanation of CH_4 disappearance and increasing CO evolution [42]. Many authors strongly suggest that CO_2 hydrogenation proceeds via CO hydrogenation [43–48]. The high temperature of CO formation seems to be little affected by carbon deposit

Table 2. Conversion of CH_4, CO_2 and activity of cobalt catalysts in reaction of dry reforming of CH_4 at 800°C

Catalysts	Pretreatment conditions T_{ox}/T_{red} [°C]	Conversion of [%]		Activity [µmoleCO/g cat s]
		CH_4	CO_2	
3% Co/SiO_2 (Impregnated)	500/500	0.3	1.0	8.75
	500/700	23.0	27.0	69.30
	500/900	22.0	25.5	65.75
3% Co/SiO_2 (sol-gel “in bulk”)	500/500	0.2	0.6	4.77
	500/700	9.0	10.5	27.12
	500/900	3.5	10.0	24.95
2% Co/SiO_2 (sol-gel “on surface”)	500/500	0.3	0.8	6.73
	500/700	17.0	19.0	49.30
	500/900	9.0	18.0	41.10

on Co/SiO_2 catalyst surface but the excessive carbon deposition leads to rapid deactivation of Co/SiO_2 catalyst in methanation of CO_2. Very significant fractions of CO are produced on Co/SiO_2, Ni/SiO_2 and especially on Fe/SiO_2 [49, 50]. The relatively low methanation activity of Co/SiO_2 catalysts is attributed to the low content of metallic cobalt on the silica surface, strong metal-support interaction induced during preparation, and/or pretreatment procedure.

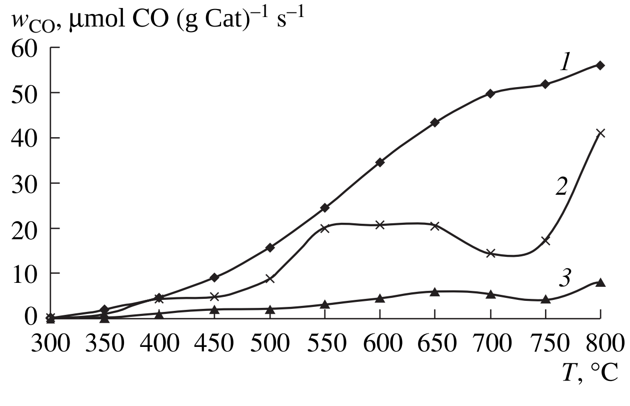

Fig. 10. Influence of Co/SiO_2 catalyst precursor on the carbon monoxide selectivity. The catalyst was pretreated in oxygen 1 h at 500°C and reduced in hydrogen 1 h at 500°C. (*1*) 3% Co/SiO_2 (impregnation); (*2*) 2% Co/SiO_2 (sol-gel, on the surface); (*3*) 3% Co/SiO_2 (sol-gel, in the bulk).

The dispersion degree of active phase, thermal stability as well as its reducibility strongly depends on the method of preparation, type of precursor and preliminary treatment. These factors have a great influence on the activity of examined catalysts in the hydrogenation of carbon dioxide to methane and carbon monoxide.

CONCLUSIONS

Despite the complexity of the TPR process one can conclude that cobalt oxide/silica system reducibility does depend on the method of catalyst preparation. Those catalysts in which cobalt is chemically bonded with silica show worse reducibility as a result of strongly bonded Co-O-Si species and cobalt silicate phase formed during the high-temperature oxidation. The TPR measurements show that a gradual increase in the oxidation temperature (500–900°C) leads to a decrease in the low-temperature hydrogen reduction effects. The decrease in cobalt oxide reduction degree is caused by non-reducible cobalt silicate formation during the high temperature treatment of Co/SiO_2 system. For low loaded Co/SiO_2 system, the cobalt oxide phase chemically interacting with the silica surface is responsible for its low activity. Both reactions: methanation of CO_2 and dry reforming of CH_4 with CO_2 are catalyzed by metallic Co phase. The catalyst activity and selectivity are strongly influenced by the catalyst pretreatment conditions and the method of its preparation.

REFERENCES

1. *Stud. Surf. Sci. Catal.*, Guczi, L., Ed., 1991, vol. 64.
2. Sewell, G.S., O'Connor, C.T., and van Steen, E., *Appl. Catal. A*, 1995, vol. 125, p. 99.
3. Backman, L.B., Rautianed, A., and Lendlad, M., *Appl. Catal. A*, 2001, vol. 208, p. 223.
4. Potoczna-Petru, D., Jablonski, J.M., and Okal, J., *Appl. Catal. A*, 1998, vol. 175, p. 113.
5. Reuel, R. and Bartholomew, C., *J. Catal.*, 1984, vol. 85, p. 63.
6. Huang, L. and Xu Y., *Appl. Catal. A*, 2001, vol. 205, p. 183.
7. Kainulainen, T.A., Niemela, M.K., and Krause, A.O.I., *Catal. Lett.*, 1998, vol. 53, p. 97.
8. Minoto, Y., Aoki, K., and Shiroi, M., *Appl. Catal. A*, 2001, vol. 209, p. 79.
9. Schuurman, Y., Ducarme, V., and Chen, T., *Appl. Catal. A*, 1997, vol. 163, p. 227.
10. Tepesti, E., Kaddoun, A., and Mazzochia, C., *Appl. Catal. A*, 1998, vol. 166, p. 259.
11. Feneira-Aparicio, P., Rodrigez-Ramos, L., and Guerrero-Ruitz, A., *Appl. Catal. A*, 1997, vol. 148, p. 343.
12. Koerts, T. and van Santer, R.A., *J. Mol. Catal.*, 1990, vol. 70, p. 119.
13. Guczi, L., Sarma, K.V., and Borko, L., *J. Catal.*, 1997, vol. 167, p. 495.
14. Garin, F., Girard, P., Make, G., Lum, G., and Guczim, L., *Appl. Catal. A*, 1997, vol. 152, p. 237.
15. Bartholomew, C.H. and Reuel, R.C., *Ind., Eng. Chem Prod. Res. Dev.*, 1985, vol. 24, p. 56.
16. Backman, L.B., Rautiainen, A., Krause, A.O.I., *et al.*, *Catal. Today*, 1998, vol. 43, p. 11.
17. Chin, R. and Hercules, D., *J. Phys. Chem.*, 1982, vol. 86, p. 360.
18. Arnoldy, P. and Moulijn, J.A., *J. Catal.*, 1985, vol. 93, p. 38.
19. Guczi, L., Sarma, K.V., Koppany, Zs., and Sundarajan, R., *Stud. Surf. Sci. Catal.*, 1997, vol. 107, p. 333.
20. Paryjczak, T., Rynkowski, J., and Karski, S., *J. Chromatog.*, 1980, vol. 188, p. 254.
21. Matsuzaki, T., Takeuchi, K., Hoaka, T.A., Arakawa, H., and Sugi, Y., *Appl. Catal. A*, 1993, vol. 105, p. 159.
22. Matsuzaki, T., Takeuchi, K., Hoaka, T.A., Arakawa, H., and Sugi, Y., *Catal. Today*, 1996, vol. 28, p. 251.
23. Zowtiak, J.M. and Bartholomew, C.H., *J. Catal.*, 1983, vol. 83, p. 107.
24. Coulter, K. and Sault, A., *J. Catal.*, 1995, vol. 154, p. 56.
25. Ming, H. and Baker, B.G., *Appl. Catal. A*, 1995, vol. 123, p. 23.
26. Okamoto, Y., Nagata, K., Adachi, T., *et al.*, *J. Phys. Chem.*, 1991, vol. 95, p. 310.
27. Puskas, L., Fleisch, T.H., Hall, J.B., *et al.*, *J. Catal.*, 1992, vol. 134, p. 615.
28. Kogelbauer, A., Weber, J.C., and Goodwin, J.C., *Jr. Catal. Lett.*, 1995, vol. 34, p. 259.
29. Rosynek, M. and Polansky, C., *Appl. Catal.*, 1991, vol. 73, p. 97.
30. Ho, S.W., Houalla, M., and Hercules, D.M., *J. Phys. Chem.*, 1990, vol. 94, p. 6396.
31. Viswanathan, B. and Gopalkrishnan, R., *J. Catal.*, 1986, vol. 99, p. 342.
32. Jóźwiak, W.K., Szubiakiewicz, E., Góralski, J., and Kłonkowski, A., J. *Thermal. Anal.* (in press).
33. Ernst, B., Libs, S., and Chaumette, P., *Appl. Catal. A*, 1999, vol. 186, p. 145.
34. Van Steen, E., Sewell, G., Makhothe, R., *et al.*, *J. Catal.*, 1996, vol. 162, p. 220.
35. Riva, R., Miessner, H., Vitali, R., *et al.*, *App. Catal. A*, 2000, vol. 196, p. 111.
36. Ernst, B., Besaddik, A., Hilaire, L., *et al.*, *Catal. Today*, 1998, vol. 39, p. 329.
37. Brown, R., Copper, M., and Whan, D., *Appl. Catal.*, 1982, vol. 3, p. 177.
38. Jablonski, J., Wolcyiz, M., and Krajczyk, L., *J. Catal.*, 1998, vol. 173, p. 530.
39. Lewicki, A., Paiyjczak, T., Jozwiak, W.K., and Rynkows, M., *J. Wiad Chem.*, 2002, vol. 56, p. 281.
40. Satterfield, C.H., *Heterogeneous Catalysis in Industrial Practice, Me Graw-Hill*, New York, 1991.
41. Rostup-Nielsen, J.R., *Catal. Today*, 2000, vol. 63, p. 159.
42. Ferreira-Aparicio, P., Guerero-Ruitz, A., and Rodrigez-Ramos, I., *Appl. Catal. A*, 1998, vol. 107, p. 177.
43. Ferreira-Aparicio, P., Guerrero-Ruitz, A., and Rodrigez-Ramos, I., *Stud. Surf. Sci., Cat.*, 2000, vol. 130, p. 3675.
44. Chang, F.W., *J. Catal. A*, 1997, vol. 158, p. 225.
45. Ruckenstein, E. and Wang, H.Y., *Appl. Catal. A*, 2000, vol. 204, p. 257.
46. Dalton, J.A. and Martin, G.A., *J. Chem. Soc. Faraday Trans. I*, 1979, vol. 75, p. 1011.
47. Weatherbee, G.D. and Bartholomew, C.H., *J. Catal.*, 1982, vol. 68, p. 67.
48. Peebles, D.E., Goodman, D.W., and White, J.M., *J. Phys. Chem.*, 1983, vol. 87, p. 4378.
49. Agrawal, P.K., Katzer, J.R., and Manogue, W.H., *J. Catal.*, 1981, vol. 69, p. 312.
50. Bowman, R.M. and Bartholomew, C.H., *Appl. Catal. A*, 1983, vol. 7, p. 179.